ROBERT D. PURRINGTON

THE HEROIC AGE

The Creation of Quantum Mechanics, 1925–1940

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ACKNOWLEDGMENTS

I learned my quantum mechanics from Bob Karplus, Mel Eisner, and John Gammel. Karplus introduced me to the subject with the help of David Bohm's classic book, Eisner's personal take on the subject allowed me to make it my own, and Gammel showed me how to apply it. Gammel, whose own contributions to two- and three-nucleon problems are well known, and who was a student of Bethe, completed my education in quantum mechanics and specifically the quantum theory of scattering, which occupied my attention for over a quarter-century after he guided my PhD research in the late 1960s. But from Mel Eisner I really *learned* quantum mechanics. He had the good sense to use as a text the book by Dicke and Witke, which emphasized fundamental ideas at the expense of applications. Although modest in appearance, that text influenced many successful physicists of my generation. Eisner's own idiosyncratic style, his willingness to challenge fuzzy thinking, his raised eyebrow when something less than cogent was uttered, showed a young graduate student how to think about theoretical physics. That Mel was an experimentalist highlights his particular gifts as a teacher.

Of course I learned more by teaching quantum theory for over four decades than I did by sitting in a classroom. In this I had the pedagogical guidance of the texts by Dirac, Schiff, Messiah, Merzbacher, and Sakurai. Other classics that have enriched my knowledge of the subject are those by Landau and Lifschitz, Kursunoglu, and Davydov.

On the other hand, when I commenced this project, I had only the barest knowledge of the history of quantum mechanics, and I suspect that most of what I "knew" was wrong. In this quest I have had no guide, which may lend this account a personal character. My interest in and knowledge of the history, historiography, and even philosophy of physics, is, however, long-standing. Those interests and skills date, in the first instance, to long discussions I had with the late Frank Durham, beginning over 30 years ago. Brief but influential encounters with the likes of Bernard Cohen, Joseph Agassi, Henry Stapp, Sam Westfall, Jed Buchwald, and Michael Hunter, to name just a few, have on the one hand taught me humility and on the other widened my intellectual horizons and suggested new avenues to explore.

In the end, however, this book arose as a logical intersection of my years of studying, teaching, and applying quantum theory, with my interest in history of physics. My book on 19th-century physics began as an exploration into the transition from classical to modern physics at the turn of the century, but I never escaped the 19th. That, in some sense, is a motivation for this study.

After reading the late John Wheeler's autobiography, in which he notes the influence of Baltimore's City College on his development, as well as the Enoch Pratt Free

Library, I am moved to do the same for City's rival Baltimore Polytechnic Institute, which had an important impact on me, despite my brief time there. As for Enoch Pratt, it would be hard to overstate the importance that the riches of the ground-floor reading room had on a teenager well over a half-century ago.

As always, access to primary and secondary sources in the history of quantum mechanics has been essential. Much of this has been made possible by Tulane University's Howard-Tilton Library with its extensive collection of important journals in German, its digital and Internet resources, and interlibrary loan. Some of these widely available resources include JSTOR and the Archive for the History of Quantum Physics. Nonetheless, and despite the availability of almost all journals on the internet, when those digital resources fail, as they sometimes do, it is valuable to have complete or near complete runs of important journals like *Nature, Philosophical Magazine, Proceedings of the Royal Society of London, Annalen der Physik*, and *Zeitschrift fur Physik*, just down the hall, as it were.

PREFACE

As I write this, we have put the centenary of Bohr's theory of the hydrogen atom, perhaps the singular event in the history of quantum mechanics, behind us, and look forward to celebrating the 100th anniversary of the birth of quantum *theory* less than a decade hence. Several Bohr symposia spent 2013 trying to define precisely what Bohr's legacy is. His place in this narrative is somewhat odd and in a sense limited, because by the time the "new quantum theory" appeared in 1925, marking the starting point of our study of its literature and history, Bohr had virtually stopped contributing to the formalism of quantum mechanics, as opposed to its ontology.[1] At the same time, his authority had hardly waned, and in what follows few pages are totally devoid of his influence.

Quantum mechanics stands unchallenged as the great monument of 20th-century physics. Born at the very beginning of the century, it attained something like a definitive form by 1932, yet continued to evolve throughout the century, and its applications are fully a part of the modern world. Quantum computing, now so fashionable, may very well revolutionize contemporary life. In any case, although we live in a classical world, our lives are continually enriched on a daily basis by the applications of quantum theory.

It should come as no surprise that literature on the history of quantum theory is vast. Just one example of this is the monumental six- (or eight-) volume work by Jagdish Mehra and Helmut Rechenberg, *The Historical Development of Quantum Theory*,[2] written over two decades, and rivaled only by the 2000-page *Twentieth Century Physics* by Brown, Pais, and Pippard. Secondary works abound. But because the theory was essentially complete by the early 1930s, its basic history is actually manageable. The result is, that for the most part, the history of quantum mechanics has already been written, and many of the previous studies have benefited greatly from the fact that most of the founders survived into the 1950s and in a few cases, into the 1990s. One important consequence has been the oral history interviews of the Archive for the History of Quantum Physics project (AHQP),[3] consisting of first-person recollections of the early days of quantum theory. Of course the usual caveat applies here, that such recollections are often faulty, but it is probably fair to say that before quantum mechanics, no revolution in physics could have been documented and fleshed out from the oral histories of the major participants in the way that happened in this case. Although the journal literature continues to expand,[4] and many of these efforts will find their way into this narrative, for the most part my take on the events of 1925–1940 is based on my own reading of the primary sources.

So this is not a new story. It has been told in many places, superificially and exhaustively, successfully and otherwise. There are comprehensive, multivolume treatments like those of Mehra and Rechenberg, elegant, focused monographs such as that of John Hendry, idiosyncratic, episodic works along the lines of Beller, and so on. Abraham Pais's *Inward Bound* stands out as a wonderfully detailed and personal account of subatomic physics in the 20th century, but skips over most of the story told here. One might be tempted to write a better one-volume history of quantum physics than now exists, and I could be accused of trying to do just that, but my intent here is actually somewhat different. In short histories of ideas, the trade-off for brevity is often superficiality, a fate I have tried to avoid by showing in detail precisely where the important ideas on which quantum theory is based actually arose and usually where they first appeared in print. This information generally lies buried in papers by specialists focusing on narrow questions or in massive studies of the kind already mentioned. It will certainly not be found in the textbooks, and for the most part with good reason; the training of a physicist typically leaves very little time for contemplation and introspection. It is a cliché, but not less true because of that, that a major motivation for this work has been my inability to find a compact but comprehensive and detailed book on the subject.

Almost all of the sources used or cited in this work will be found at a good university library, and virtually all of the journal references are available online, even though access may not always be easy. The present work is only one way of looking at the subject, of course, focusing on the written record at the expense of correspondence among the principals that was so crucial to progress, the symposia and other meetings, and the hallway conversations that ensued. Although I have drawn heavily on these resources, to weave them into the narrative would simply have expanded it well beyond any reasonable size.[5] Quantum theory has a history that is important in its own right, and knowledge of that history not only enriches our understanding of the theory,[6] but an appreciation of how a particular idea or result came about may, and indeed should, offer important insights into how theoretical (or experimental) ideas emerge, and what their range of applicability or validity might be.[7]

Many of the papers relevant to this volume were originally published in German, of course,[8] frequently in *Annalen der Physik* or *Zeitschrift für Physik*, and only a small fraction of the important early papers have been translated into English.[9] This is largely a reflection of the fact that when they were published all physicists were expected to read, and even be able to lecture in, the German language. In some cases this has required me to personally translate papers into English, and where translations do exist I have relied on their accuracy. The assumption is that this will not introduce significant errors into this manuscript, but it remains at best an assumption. Frequently there will be no recourse but to cite the German original despite the lack of a translation. By the mid-1930s, as many Jewish scientists fled their homelands and as the *Physical Review* became increasingly important, supported by the continuing impact of British journals, the language of scientific discourse became English.

Without apology, this work takes as its starting point the current consensus and asks "how did we get here from there?" This is what historians (myself included)

would call "whig" history, or "presentism;" even "triumphalist" history. That this is not the way history ordinarily ought to be written is obvious. It selects from the physics of the time only those discoveries that led to our present understanding, ignoring wrong turns or blind alleys. An analogy in the history of astronomy or cosmology would be to emphasize only Aristarchus's advocacy of the heliocentric theory and discard the geocentric theories of Aristotle, Hipparchos, Ptolemy, and everyone else. Nonetheless, and intentionally, few of the many blind alleys that necessarily were part of the development of quantum theory are pursued in this narrative. This turns out to be less of a defect than one might imagine, however, because the formalism of quantum mechanics matured so quickly, in not much over seven years, and was materially shaped by less than a few dozen physicists, so that there is a much thinner record of wrong turns and controversies than there might otherwise be. Finally, and although scientists–historians and historians of science often do not agree on this point, it is fair to argue that because science does inexorably progress, though not without setbacks and periodic rethinking and retrenching, it does move forward, and I make use of that fact without apology.

Yet we all know that published work, that is, journal papers or review articles, fail to fully capture the history of an idea or discovery; we can look to our own work for that insight. The final paper is the polished end product of a typically complex, halting, and messy process that is typically moved forward by hunches and speculations that often as not are totally missing from the published papers. The road to a discovery might be quite formal and logical, but more frequently it will be almost devoid of these characteristics. Much of the evolution of a theory or understanding of an experiment will have taken place in correspondence, at conferences, over coffee or tea, in a bar, on a climb or a ski slope. Today it might be technology: email, the Internet. But for a discovery to become "official" or canonical, and thus enter the secondary literature and become part of everyday practice, it will have had to meet the test of "peer review," or at least receive an editor's stamp of approval, and come into print.[10] The peer-review process that we alternately deride and praise today was not nearly as well developed in the 1920s, but it is nonetheless true that what may have been discovered in a mountain cabin in Austria or in an office in Göttingen had to reach print before its import and validity could be judged and before it could become influential. Once on the page an idea becomes part of the literature, to be incorporated into textbooks for the next generation, or perhaps even to be shown wrong.

With the notable exception of the introductory chapters, which serve to bring the reader up to date on the situation before the new quantum mechanics appears in 1925–1926, this work concentrates on the decade-and-a half ending in 1940. If the choice of this period seems arbitrary, I think it is not. One could argue that the period between the wars is the natural period to treat, and in a sense I have done that by devoting considerable space to setting the stage for 1925. And terminating this narrative in 1940 (or 1939 or 1941) is appropriate for two reasons. In the first place, the hiatus caused by the war represents something of a period of gestation, so that quantum physics was very different in 1947 from that in 1939, in part because of the fruits of war-related research. But this hiatus meant that relatively little of importance was

published between 1939 and 1947. In the end, however, it is simply a matter of manageability. Prior to WWII, the community of quantum scientists was small, but grew rapidly after the conflict, with enormous resources spent on rebuilding the affected nations, and with the rise of large-scale funding of science by governments, fueled in part by the Cold War. The literature began to grow rapidly, making it impossible to try to continue to survey it and still retain some scale. The reader will notice a certain lack of discipline in this regard, however, so that in a few cases, nuclear physics and astrophysics in particular, it seemed appropriate to follow the trail of writing on a subject to its denouement as late as 1948–1949. Perhaps the most egregious example of ignoring our self-imposed constraints comes in the discussion of the interpretation of quantum mechanics. But because this issue hangs like a cloud over the theory, I have felt obligated to give some flavor of developments in the last four decades, as issues that for the most part arose in the 1920s and 1930s have not only been elaborated, but actually subjected to experimental tests. As an aside, it is worth noting that the period on which we concentrate here is essentially the same as that covered in Mehra and Rechenberg's vol. 6 (1926–1941), in well over 1000 pages.

As will become apparent, the formalism of quantum theory was substantially in hand by 1932, so that one might ask, why 1940? It turns out that many important implications of the theory were discovered in those prewar years, especially in the application of quantum mechanics to atoms, nuclei, and solids. Without some acknowledgment of these developments, the story would be incomplete.

It may seem strange that the interpretation of quantum theory is still very much an open question. Yet in the 80 years since von Neumann first wrote about the paradoxes inherent in the quantum theory of measurement, there has never been a hint that disagreements about interpretation have any bearing on the explanatory power of the theory. This remarkable situation is perhaps without parallel in the history of science, but, in any case, because much of the writing on the interpretation of quantum mechanics is fairly recent, if the last half-century can be seen as "recent," we will only be able to scratch the surface, so to speak. Although these open issues of interpretation are very unlikely to threaten its validity as a program for calculating the results of experiments, they touch on, in very profound ways, the *meaning* of quantum mechanics. I provide some guide to this literature, but because it is very much an open topic, I cannot linger too long over its details. How the reader decides to deal with these issues—if at all—is a matter of taste or strategy.

Although the theory had matured well before the outbreak of WWII, so that most of the material discussed in a modern textbook from the 1980s or 1990s will have been developed in those prewar years, a few recent topics of special relevance that would not be found in books written in the immediate postwar era (or would have been given short shrift) are also touched on here, if briefly, when coherence or completeness seems to require it. I do not try to cover the literature of quantum-field theory or even quantum electrodynamics in detail, but again, I do not avoid it altogether. Relativistic quantum theory is almost as old as quantum theory itself, with Schrödinger trying a relativistic theory before his nonrelativistic wave mechanics. Dirac developed the relativistic theory of the electron ("Dirac equation") as early as 1928, and for all practical

purposes founded quantum electrodynamics in those same years. But the great successes of quantum electrodynamics and quantum-field theory are mostly postwar.

There are, of course, many unanswered or open questions that qualify any consensus view of how quantum mechanics evolved, some of which originate in newly discovered biographical details of one or another of the founders, occasionally in some newly discovered correspondence. Most of the open issues, however, concern not the history of quantum mechanics, or its formalism, but rather its meaning and interpretation, in the form of questions that still haunt the theory the better part of a century after its creation. The caveat that might be added is one that arises in thinking about how to reconcile quantum theory and the theory of gravity, which for the moment is general relativity. There is no way to know the direction this exploration will take, but it could have a fundamental impact on how quantum theory is formulated. But that is for the next generation.

With the exception of those observations that fostered the quantum revolution, and especially atomic line spectra, I touch on experimental results only when they are essential to the narrative, and then only briefly. To some degree that decision is merely a matter of economy, and it certainly does not represent a judgment on the relative value of theory and experiment in this story. Indeed experimental results played an unusually direct role in the origins of quantum mechanics. But quantum *theory* is a theoretical construct, and for that reason the story has to be about how the theory evolved, however much that may have been driven by experiment.

There is naturally interest in what might be called the sociology of quantum mechanics, the cultural and philosophical milieu in which the theory was born and how that context affected the creation and even the nature of quantum theory. It is interesting, however, that Max Jammer, who wrote what is perhaps the definitive work on the philosophy of quantum mechanics, found little reason to address the question of how European philosophical movements, especially positivism, could be seen as laying the groundwork for the discoveries of Einstein, Bohr, Heisenberg, Schrödinger, Dirac, Pauli, and others. Nonetheless, we are not so naive as to believe that quantum mechanics was not influenced by its time and place in history.

Although this is not the place to survey the textbook literature on quantum mechanics in detail, there is arguably no other literature that shows so directly the evolution of the field; those ideas that have proven to be especially efficacious in advancing the understanding quantum systems quickly find their way there. There are many excellent texts on quantum mechanics for those who want to learn the theory and even some popular introductions that try to give some flavor of it.[11] Indeed there may not be another area of physics that has spawned so many excellent texts. A few even treat the history of the subject with skill and subtlety. And yet times change, fads, or at least emphases, come and go, even in the textbooks. The situation is complicated by the fact that not too much over a decade after the initial papers on the new quantum mechanics appeared, the world was plunged into war again. This means two things: First, that some discoveries in quantum mechanics and its progeny, nuclear physics, were not published in the open literature until well after the conclusion of the WWII,[12] and second, that for nearly a decade physicists were either occupied with war-related research

or were in areas where research and publication was impossible, from at least 1939 until 1945, or even later. If we add to that German anti-Semitism of the 1930s and the disruption in careers that resulted, we can see that the record, in both the primary and secondary literature, is spotty, with at least a semi-hiatus of over a decade. Thus the textbook literature is less revealing than might be otherwise.[13] It is also true that after the new quantum mechanics reached a kind of maturity in the early 1930s, much of the subsequent effort was in applications to molecules, nuclei, and solids. I provide a guide to this literature of applied quantum mechanics.

We should not forget that the physicists who created quantum mechanics in 1925–1932, with a small number of exceptions, were all from the generation that was born in the first decade of the 20th century: Pauli, Heisenberg, Jordan, Dirac, von Neumann, Bethe, and Gamow were all born between 1900 and 1906. Only Einstein, Born, Bohr, and, most surprisingly, Schrödinger, were of the previous generation.

The reader will not find many equations in this book, and only a few detailed developments or discussions of a particular discovery or proof of some result. To have elaborated in this way would have defeated my purpose and would have expanded this work beyond reasonable and practical bounds. The original sources are laboriously cited, as are, in many cases, secondary works that provide explication and context. The reader can pursue these developments at his or her leisure. The alternative would be a book many times the size of this one, and essentially a full-blown text on quantum mechanics, with historical asides. The principal exception to this is a brief discussion of Heisenberg's revolutionary paper that in many ways began the quantum revolution, in the Appendix.

A bibliographic essay had to be sacrificed to my prolixity in other areas, and it ought to be mentioned that the references to each chapter do not fully reflect the sources that went into the narrative; as is always the case, I have had to be judicious in the sources I have cited. Assume if you will, however, that your missing source has probably found its way into this work in some fashion.

NOTES

1. Although his career in the technical sense underwent a resurgence in the late 1930s with his compound nucleus model. See Chapter 15.
2. Indeed, Mehra was able to interview most of the founders of quantum theory. It has to be said that there are serious organizational problems in Mehra and Rechenberg (1982–2000) that do not, however, negate much of the evidence presented there. In fact, vol. 6, which is a sort of summation of what has come before, can profitably be read on its own. Its historical focus is almost precisely that of the present work, but its scope is quite different.
3. To which the *Sources for History of Quantum Physics* project provides a guide and overview The archives are monumental and indispensable. The way in which they can enrich the history of quantum theory can be seen in a work like John Hendry's gem, *The Creation of Quantum Mechanics and the Bohr-Pauil Dialogue* (Hendry, 1984).
4. Notably in *Historical Studies in the Physical Sciences* and *Archive for the History of Exact Sciences*.

5. For those whose interest is more in the personalities of the founders of quantum mechanics than in the theory, there is the somewhat glib and gossipy *The Quantum Ten* by Sheila Jones. Although not flawless, the history is sound enough to deserve a seriously qualified recommendation, and the same caveat applies to the science, which is a bit surprising from someone with a background in theoretical physics.
6. The point has been made that the history of a discipline, say, is the equivalent of an individual's personal memory. Without those memories, who are we?
7. Eric Scerri has expressed a somewhat different view: " . . . many argue . . . that it is actually a hindrance for the practitioner to get too involved in the historical aspects of the theory." It seems to me that there is little danger of that. See, for example, Elkana (1977).
8. And a few in French or Italian.
9. Some important contributions should, however, be mentioned. Pergamon's *Selected Readings in Physics* series published several volumes of papers that included many previously untranslated. Of special relevance here are *Nuclear Forces* by Brink (1965), *The Old Quantum Theory* by Ter Haar (1967), and *Wave Mechanics* by Ludwig (1968). Van der Waerden's indispensable *Sources of Quantum Mechanics* (1967) does much more than merely translate early works in matrix mechanics. His participation in these events has given him the perspective to provide much additional context.
10. This has been changed to some extent by the existence of the e-print archive arXiv.org and other forms of rapid, often barely reviewed, publications, but this is product of the digital era entirely. Preprints, of course, have been a major form of scientific communication for decades, but only rarely—if ever—will such a medium intrude into our discussions.
11. Notably the just-published *The Quantum Moment* by Crease and Goldberger (2014).
12. There was a similar lacuna during WWI, but quantum theory was in its infancy then.
13. In fact, a comparison between even the best and most up-to-date of the texts from the late 1930s, such as Rojansky, and those that appeared 3–4 years after the end of the war is very revealing and deserves further study.

PART I

Forbears

1

"CLOUDS ON THE HORIZON"
NINETEENTH-CENTURY ORIGINS AND THE BIRTH OF THE *OLD QUANTUM THEORY*

INTRODUCTION: *FIN DE SIÈCLE*

By the middle of the 19th century physics was evolving toward a form that most physicists would recognize today. The major figures in this consolidation of classical physics were James Clerk Maxwell, Lord Kelvin (William Thomson), G. G. Stokes, and a few others in Britain, along with Rudolf Clausius, Hermann Helmholtz, Gustav Kirchoff, and Ludwig Boltzmann in Austria and Germany.[1] Much of this work was built upon mathematical foundations laid down by Kelvin George Green, and their 18th-century predecessors (Augustin-Louis Cauchy, Leonhard Euler, etc.). Most of them were what we would think of today as theoretical physicists, though Maxwell, Kirchoff, and Helmholtz were quite at home in the laboratory. Although many will argue that today's strong separation between experimental and theoretical physics (or physicists) began in the 20th century, the trend was well under way before Maxwell's death in 1879.

At the same time that the science of thermodynamics, centering on its first and second laws, was being developed by Kelvin and Clausius, electromagnetic theory was being formulated by Kelvin, Maxwell, and Helmholtz, founded upon the experiments of Michael Faraday, André-Marie Ampère, and others. Even classical mechanics, which was largely an 18th-century science elaborated by Pierre-Simon Laplace, Joseph-Louis Lagrange, Euler, Pierre Louis Maupertuis, and others, saw important advances in the 19th century, including celestial mechanics, especially the three-body problem, the work of Carl Jacobi and W.R. Hamilton,[2] and eventually the work of Henri Poincaré at the century's end. Continuum mechanics, in the form of fluid dynamics and elasticity, lagged behind a bit, but was being advanced by Kelvin, Stokes, Claude-Louis Navier, and others.[3] Thus, by the end of the 19th century such a towering figure as Kelvin could see physics as essentially complete.[4] The first American Nobel Laureate Albert Michelson wrote that "the more important fundamental laws and facts of physical science have all been discovered."[5] This turned out to be a monumental error, as we all know,[6] and indeed there were "dark clouds" on the horizon, as Kelvin noted,[7] as early as the 1870s, that would force a complete rethinking of mechanics and electromagnetic theory and ultimately lead to the quantum revolution.[8]

It is a crucial point that although that other great revolution of the 20th century, the theory of relativity, had very little in the way of an empirical foundation, depending on how one incorporates the efforts of Michelson and Morley into the story,

quantum theory, by contrast, was built almost entirely upon a foundation of experimental results and observations that had been accumulating since just after 1850.[9] Together, these two theories, which so exemplify 20th-century physics, provide illuminating case studies in the nature of scientific progress and discovery through the sharp contrast between the ways each evolved. Some of this is due, of course, to the unique personal style of one man, Albert Einstein. The larger story, of the transition from classical to quantum physics, has been told in several places,[10] and for that reason only the briefest recounting is given here.

TRANSITION

Because a defining characteristic of the history of quantum mechanics is that it was so thoroughly experiment driven, we will take some time to examine the most important of the challenging and unsolved problems that loomed over theoretical physics as a result of experiments carried out in the last few decades of the nineteenth century.[11] It hardly needs to be added that there was little appreciation at the time of the impact these experiments would have in ushering in the revolution that was about to take place. This situation is not unusual; historically it is rare to find a situation in which there exists a clear sense that a series of perplexing experimental results or observations would require a total break with the past,[12] a paradigm shift if you like. In most cases the recognition comes long after it has happened, and a case in point is that of Arnold Sommerfeld, perhaps as representative of the transition as anyone, and certainly an important participant in it, who in 1929 thought that the new quantum theory, then 4 years old, "did not signify a radical change."[13]

One caution is in order as I emphasize the empirical roots of the quantum revolution, which is—and it does not take much sophistication in the philosophical underpinnings of science to understand this—that rarely is experiment unguided by theory, even theory that will eventually be abandoned, and even in the case of someone like Michael Faraday, seemingly the quintessentially naive experimenter. There are, however, episodes in the history of physics when existing theory is able to shed very little, if any, light on emerging experimental results, and it can be argued that this was one of those.

SPECIFIC HEATS

The kinetic theory of gases of Maxwell, Clausius, and Boltzmann,[14] and in particular the *equipartition theorem*, provided an explanation of how energy was apportioned among translational degrees of freedom of a monatomic gas and the additional vibrational and rotational degrees of freedom of a diatomic or triatomic molecule. Up to a point, the observed specific heats could be understood in terms of the still-young and somewhat controversial atomic theory, and, indeed, provided strong support for it. It was known from the observed specific heats of monatomic gases and others at low temperatures, along with kinetic theory, that each degree of freedom contributed $1/2kT$ of energy per atom or molecule, where k is Boltzmann's constant. In the case of a monatomic gas, with only 3 degrees of freedom, the specific heat at constant

volume, c_v, should be $3/2k$.[15] At constant pressure, some of the heat goes into expanding the gas (doing work), so that c_p, the specific heat at constant pressure, should be $(3/2k+k)=5/2k$. The ratio $\gamma=c_p/c_v$, which is independent of k (or R), i.e., a dimensionless quantity, should then be $5/3$. As early as 1857 Clausius was assuming that a diatomic molecule such as H_2 had 6 degrees of freedom (three translational, three rotational), and that γ should equal $4/3$.[16] Experimentally, however, it was found that γ was approximately 1.4. In 1860 Maxwell saw this as a great crisis, writing that this "overturns the hypothesis [of equipartition], however satisfactory the other results may be."[17] In 1875, 4 years before his death at the age of 48 from stomach cancer, he observed of this problem that "here we are brought face to face with the greatest difficulty that the molecular theory has encountered."[18] The measured value of 1.41 could be obtained only by assuming that 1 degree of freedom did not contribute to the energy (for then $c_v=5/2$ and $c_p=7/2$; $\gamma=7/5=1.4$). It was only in 1877 that Boltzmann made the proposal that rotation about the symmetry axis did not contribute to the energy, yielding the theoretical value $\gamma=7/5$, very close to experiment. It had also been found that γ for mercury vapor was about 1.67, exactly what would be expected from translational degrees of freedom alone.

Note that when Maxwell made his comment, vibrational degrees of freedom were not being taken into account, and they would have raised c_v to $7/2k$, lowering γ to $9/7=1.29$ (or 1.25 depending on the number of rotational degrees of freedom). Thus the situation was much worse than Maxwell thought, and in 1900 Lord Rayleigh (John William Strutt) noted that "the law of equal partition disregards potential energy," and went on to say that "what would appear to be wanted is some escape from the destructive simplicity of the general conclusion."[19] Soon the specific heats of molecular hydrogen were measured over an increasingly large range of temperatures, especially higher temperatures, and the behavior turned out to be very puzzling (Figure 1.1).

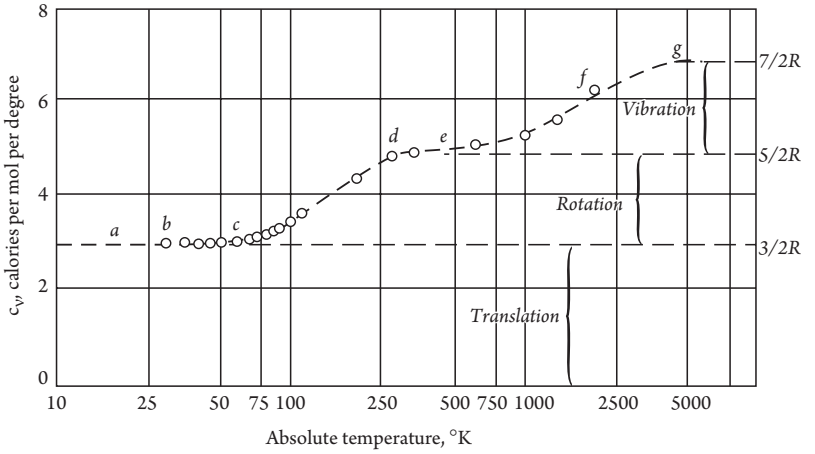

Figure 1.1. Specific heat of a typical gas as a function of temperature, showing excitation of rotational and vibrational degrees of freedom. Richtmyer and Kennard (1942), by permission of McGraw-Hill.

c_v was found to be approximately $5/2k$ at room temperatures ($\gamma = 7/5$), matching the "dumbbell model" with 2 rotational degrees of freedom, but was strongly temperature dependent, being approximately $3/2k$ below 60 K ($\gamma = 5/3$) and $7/2k$ ($\gamma = 9/7$) at very high temperatures. Clearly only translational degrees of freedom were excited at low temperatures; rotations began to be excited at around 100 K, and finally 2 additional degrees of freedom, evidently due to vibrations, were excited beginning near 500 K.[20] Instead of the rotational and vibrational degrees of freedom contributing to the energy and hence the specific heats at all temperatures, there were abrupt transitions from one value of the specific heat to another, as can be seen Figure 1.1. This was, indeed, one of the very first pieces of evidence that what we would call quantum phenomena existed, that as was later discovered, rotational or vibrational degrees of freedom were not excited until there were sufficient energy quanta available to cause the system to make a transition to a higher state. No explanation would be possible before the advent of quantum theory.[21]

A similar problem arose with the specific heats of solids and the law of Pierre Louis Dulong and Alexis Thérèse Petit that predicted the value $3k$ (or $3R$), contrary to what was observed at low temperatures.[22] As we shall see, Einstein's attack on this problem in 1907[23] was one of the decisive events in the unfolding evolution of the quantum theory, and one that is not widely appreciated. It was, as Martin Klein has emphasized,[24] the very first application of quantum theory to matter as opposed to radiation. Out of the latter had come Max Planck's 1900 paper and Einstein's analysis of the photoelectric effect, in 1905, introducing the energy quantum into radiation theory. But Einstein's treatment of the problem of specific heats of solids made clear, first, of course, to Einstein, and then to his audience, that the nascent quantum theory had to apply *everywhere*. This was truly revolutionary. I discuss the problem at greater length in Chapter 18.

BLACKBODY RADIATION

The problem of the spectrum of "cavity" or "blackbody" radiation dates back to the late 1850s and the early measurements of Kirchoff and others. Attempts using the thermodynamics and kinetic theory of the 1860s, that is, equipartition, the Maxwell–Boltzmann distribution, or Boltzmann's early statistical mechanics of the 1880s, were only partially successful, and, as is well known, suffered from an "ultraviolet catastrophe"[25] (Figure 1.2). This conundrum motivated Planck's search for the correct functional form of the blackbody spectrum and his "successful" attempts to justify it from statistical mechanics. Unlike the problem of atomic spectra, this one did not scream discontinuity at the outset. Whether Planck had a clear idea of what he had done is a matter for debate, but, in the sense of historical influence, there is no doubt that, right or wrong, it is in Planck's 1900 paper that the quantum was born.[26] His introduction of the new constant, h, with units of angular momentum,

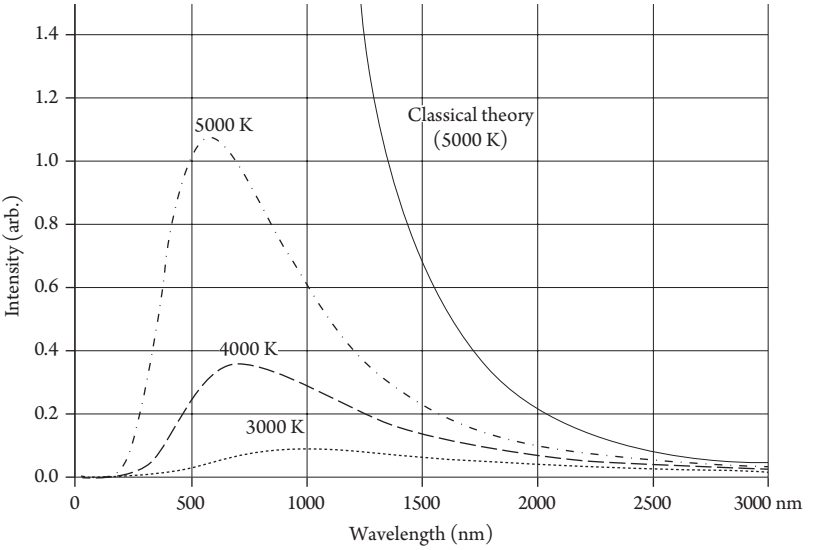

Figure 1.2. "Ultraviolet catastrophe," showing divergence of the classical Rayleigh-Jeans law at short wavelengths. Enge et al. (1972), by permission of Addison-Wesley.

meant that a fundamental unit of length could be derived from the electron charge e, its mass m, and h. That length, h^2 / me^2 , has the value 2×10^{-7} cm, a characteristic atomic size.[27]

PHOTOELECTRIC EFFECT

The photoelectric effect, in which electrons are ejected from a metal surface because of an incident electromagnetic wave, was first observed by Heinrich Hertz in 1887,[28] and it became known as the Hertz effect. The first serious studies of it were by J. J. Thomson in 1899, using ultraviolet light, and by Philipp Lenard, who in 1900–1902, showed that the effect defied explanation in classical terms.[29] Together they found that no matter what the intensity of electromagnetic radiation incident upon a metal surface, electrons were not ejected until the energy (frequency) was sufficiently high. Not long after, in his 1905 paper "On a Heuristic Point of View About the Creation and Conversion of Light,"[30] Einstein introduced the novel idea of the quantum of light to explain the effect.[31] In that paper and one the next year he essentially reinterpreted Planck's introduction of quanta in the 1900 paper, which was really only implicit, and, it can be argued, created the quantum concept then and there. His 1916–1917 papers on the emission (spontaneous and stimulated) and absorption of radiation further solidified the concept of the quantum of electromagnetic energy, carrying linear momentum hv / c.[32] The scattering of x-rays by electrons in the "Compton effect," discovered by the

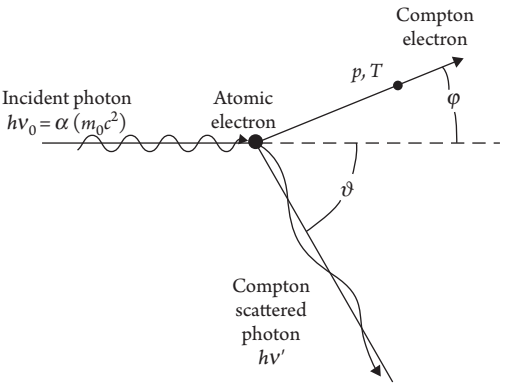

Figure 1.3. Compton scattering. From Evans (1955), by permission of McGraw-Hill.

American physicist Arthur Holly Compton in 1922–1923, convincingly demonstrated the importance of a particle-like description of electromagnetic radiation (Figure 1.3).

WAVE–PARTICLE DUALITY

The mysterious property of matter, *wave–particle duality*, was first mooted by Einstein in 1905, when in interpreting the photoelectric effect, he proposed what came to be known as the *photon*, the light quantum. Interference and diffraction phenomena had long made it clear that electromagnetic radiation consisted of wave motion,[33] but Einstein's analysis of the photoelectric effect, his decisive paper on the emission and absorption of radiation, and finally, the Compton effect,[34] showed that light exhibited discrete, particle-like properties as well. Eventually the understanding came to be that light is "something else," neither wave nor particle, but exhibits one or the other property depending on how it is observed.

Another decade would pass before symmetry would be restored to the wave–particle question. This happened in 1923–1924, when Louis de Broglie (Louis-Victor-Pierre-Raymond, seventh duc de Broglie) suggested that a particle of momentum p possessed (in some sense) a wavelength of $\lambda = h / p$. This daring proposal, that particles also ought to possess *wave* properties,[35] was at the time not much more than a conjecture, with essentially no experimental support, but soon the electron-diffraction experiments of Clinton Davisson, Charles Henry Kunsman, and Lester Germer at Bell Labs, as well as those of G. P. Thomson and Andrew Reid in Cambridge, beginning as early as 1923, but culminating in 1927,[36] made the conclusion that particles can exhibit wave properties that are almost inescapable (Figure 1.4). Eventually, the quantum-theoretical understanding of the Ramsauer–Townsend effect[37] buttressed this understanding.

Electron diffraction had already been predicted by Walter Elsasser after he read de Broglie's thesis.[38] He suggested that an experiment should be attempted to test the hypothesis, but supposedly the experimentalist James Franck, with whom the 21-year-old Elsasser was trying to work at Göttingen, replied that such an experiment was unnecessary because the phenomenon had already been observed in Davisson's

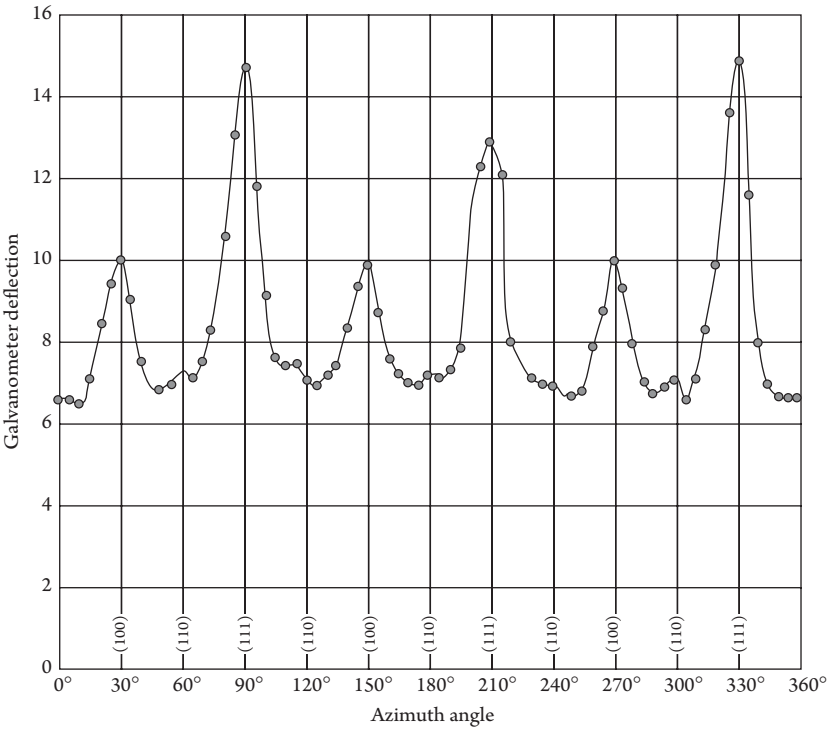

Figure 1.4. Electron diffraction experiment of Davisson and Germer. Intensity of electron scattering vs. azimuthal angle. Davisson and Germer (1927b), by permission of American Physical Society.

experiments.[39] By the time of this verification, Erwin Schrödinger had constructed his wave mechanics, drawing its inspiration from de Broglie's hypothesis and lending some plausibility to it.

ATOMIC SPECTRA

The existence of discrete emission lines in the spectra of excited atoms and the similar phenomena of discrete absorption spectra, including that of the sun (first noticed in 1802), posed a problem similar to that of specific heats, and one that arose much earlier.[40] Indeed, much of the effort in experimental physics in the late 19th century and the first two decades of the 20th was devoted to atomic and molecular spectra. It was suggested that the discrete lines represented periodic molecular vibrations, that is, classical normal modes, but it would have been very difficult to explain the discrete emission or absorption spectrum of monatomic hydrogen on this basis. Hydrogen, of course, was the canonical case, with its very familiar "Balmer series" (1885) of spectral lines in the visible spectrum. Investigations outside the visible spectrum led to the fundamental discoveries of Johannes Rydberg and Walter Ritz, and in particular the *Ritz combination principle* of 1908.[41] What was not yet understood was that the emission

or absorption lines represented energy *differences* between discrete states. But in 1913–1914, just as Niels Bohr was proposing his theory of hydrogen, Franck and Hertz found that electrons passing through mercury vapor were absorbed only if their energy reached 4.9 eV.[42] Soon Bohr showed that this could be interpreted as the discrete ionizing energy of mercury,[43] further establishing the existence of discrete levels, and characteristic x-ray spectra raised similar problems. The Bohr theory of the hydrogen atom would provide a convincing explanation of the discrete lines, and, of course, the details of the Balmer series. We explore these issues in detail in future chapters.

X-RAYS, RADIOACTIVITY, AND THE NUCLEAR ATOM

Although radioactivity, as a mostly nuclear phenomenon, did not immediately demand a quantum explanation, it seemed to be beyond the explanatory power of classical physics as understood in the years around 1900. For quite some time, studies of radioactivity were in a primitive, taxonomic stage, in which it was not even clear what the phenomena were. The discovery of x-rays by William Röntgen in 1895[44] raised a whole host of questions, including whether they were a form of electromagnetic radiation. And the discovery of characteristic x-rays by Henry Moseley[45] posed problems similar to those arising from discrete optical atomic spectra.

Henri Becquerel's[46] accidental discovery of radioactivity in 1896 complemented that of Röntgen in the previous year, and this was followed by Ernest Rutherford's discovery of α- and β-rays emitted in the decay of uranium and thorium sources in 1899. In 1903 he called the third kind of radiation from radium, discovered by Paul Ulrich Villard in 1900, γ-radiation. In only 8 years around the turn of the century, virtually all of the basic phenomena of radioactivity had been discovered. Soon after the discovery of α-rays, the α-scattering experiments of Rutherford and his colleagues[47] revealed the nuclear atom and hinted at the existence of new forces and hence entirely new physics, but again, the quantum nature of the problem became apparent only later. We discuss these experiments of Rutherford and his collaborators in detail in Chapter 15, but the nuclear atom, with its orbiting electrons, immediately raised the question of atomic stability, because in Maxwell's theory accelerated electrons would radiate energy and spiral into the nucleus. This problem, as it turned out, could be dealt with only quantum mechanically. Bohr's model of hydrogen, although a historical watershed, provided only a partial and tentative solution.

All of the issues associated with radioactive decay, including the nature of α- particle emission and β-decay, the identification of the parent and daughter nuclei, the quantization of electronic charge,[48] the radioactive inert gas radon, etc., were being enthusiastically studied by Marie and Pierre Curie, Rutherford, and others in the years leading up to the war, just as Bohr was about to publish his first paper on hydrogen.[49] Alpha-decay would turn out to be a fundamentally quantum phenomenon, involving quantum tunneling, a discovery made by George Gamow in 1928,[50] but only after quantum theory had been created. From these studies of radioactive decay, and

later scattering experiments carried out in Rutherford's laboratory, would eventually emerge the realization that there were two new forces of nature, the strong and weak nuclear forces.

ON THE THRESHOLD

Initially it was the Planck–Einstein idea of quanta of vibrational or electromagnetic energy that solved the problem of blackbody radiation, and, as we have seen, it was also in a paper of Einstein's that the riddle of the photoelectric effect was explained by invoking the quantum of electromagnetic energy. Although the general acceptance of the idea of the particle aspects of light may have had to wait for Compton's experiments, Einstein's Nobel Prize in 1921 reflected a growing acknowledgment of it.[51] The name *photon* was coined by G. N. Lewis 3 years after Compton's work.[52] And, as we have noted, the deployment by Einstein in 1907of these quantum ideas in attacking the problem of the specific heat of solids was the first application of the quantum to something other than radiation.

A decisive event in the history of the quantum theory was the first Solvay Conference in Brussels at the end of October 1911, involving Hendrik Lorentz, Planck, Einstein, Walther Nernst, and over a dozen other prominent figures, including the great turn-of-the-century mathematical physicist Jules-Henri Poincaré.[53] Much of the discussion at the conference centered on the meaning of the "quantum of action," h. At that point, special relativity had been embraced by most far-seeing physicists, and now the issue was the seeming fact of quantum discontinuities, exhibited in the empirical evidence we have just discussed, as well as in the theories of Planck and Einstein. Poincaré is an especially interesting case because he came to the conference pretty much ignorant of quantum theory, but within a month had written a major paper for *Journal de physique* on the subject.[54] In a real sense Poincaré epitomizes the transition that was just beginning. Among important ideas offered at the conference was the opinion that quantum discreteness seemed to imply that physics could no longer be described by differential equations.[55] This conundrum would be central to the controversies of 1925–1926, as matrix mechanics with its built-in discontinuities, and wave mechanics, framed in terms of differential equations, emerged and vied for supremacy.

THE OLD QUANTUM THEORY; THE BOHR THEORY AND ITS AFTERMATH

The term old quantum theory is traditionally restricted to the theory prior to de Broglie's hypothesis of 1923–1924, or perhaps Heisenberg's first paper 2 years later. It represents the attempt, largely within the classical paradigm, but nonetheless incorporating the idea of the quantum, to explain the troublesome experimental results I have enumerated. An excellent short summary of the old quantum theory, and especially the growing realization of the defects of the theory in 1924–1925, can be found in chapter 1 of Condon and Morse's book of 1929.[56] As late as 1925 Max Born, who

would be directly involved in breaking the impasse, wrote in his "Lectures on Atomic Mechanics" that "At present we have but a few vague indications about the kind of deviations from classical laws that must be introduced for the explanation of atomic properties . . . therefore perhaps the second volume [of this work] so-planned will remain for many years unwritten."[57] In fact it would only be a few months before the long-sought explanation would begin to emerge, and Born would be one of its parents.

The first and greatest triumph of the old quantum theory was Bohr's treatment of the hydrogen atom in three papers in the *Philosophical Magazine* in 1913, known colloquially as "The Trilogy."[58] But the place of the Bohr theory of hydrogen in the history of quantum mechanics is so central that a detailed discussion of it is left for the next chapter. Of course, Bohr's theory of hydrogen would have been impossible had it not been for Rutherford's discovery of the atomic nucleus only 2 years earlier and in the laboratory where Bohr would soon be working.

During the decade following Bohr's theory of hydrogen, the old quantum theory was elaborated with some qualitative successes, but in a patchwork manner and without anything that could be called a fundamental theoretical framework,[59] in spite of tireless efforts by Bohr, based on his correspondence principle, and by Arnold Sommerfeld and others.[60] Sommerfeld generalized the Bohr quantization condition (see Chapter 3) to the "action integral" $\int p_i \, \mathrm{d}p_i = n_i h$, where p and q are canonically conjugate momentum and coordinate variables (there is also a related *angle* variable) and n is an integer.[61] This came to be known as "the quantum principle" or "quantum condition." This formulation, which attempted to bridge the gap between classical and quantum theory, gave good results in simple systems, but had already failed when applied to the neutral helium atom, for example.[62] As Condon and Morse wrote in 1929, "Even when it gave correct results . . . there was an unsatisfactory looseness about the principles. The quantum conditions were added to ordinary mechanics as an afterthought, so to speak, instead of being an integral part of it."[63] As with much of the formalism that seemed promising in the post– WWI era, this rule foundered when more widely applied. More generally, wrote Bohr in 1925, ". . . one is faced not with a modification of the mechanical and electrodynamical theories describable in terms of the usual physical concepts, but with an essential failure of the pictures in space and time on which the description of natural phenomena has hitherto been based."[64]

The almost Olympian figure of Bohr dominated attempts to arrive at a description of quantum phenomena in this period of interregnum, so to speak, the decade between the Bohr theory of hydrogen and and de Broglie's thesis. Bohr's was the most respected voice, and after 1921 his institute in Copenhagen was a mecca for those attempting to solve the problems that nature was presenting.[65] His survey papers of 1916 and 1922[66] in many respects pointed the way for those who would take the torch from his hands and carry it forward, especially Werner Heisenberg, Pascual Jordan, and Wolfgang Pauli. If Bohr's writing failed to offer anything like a solution, it made clear where the problems lay.

More than any other single idea of the time, Bohr's *correspondence principle* guided attempts to create a quantum theory of atoms in the 1920s. Its assertion that

any valid quantum theory must merge with the corresponding classical theory in the limit of large quantum numbers could be taken as merely an expression of the fact that quantum mechanics is *the* theory of matter; that it applies for both large and small quantum numbers, and therefore a quantum description must merge into the classical one at some point. One statement of this principle by Bohr goes as follows: "we may expect that any theory capable of describing [these phenomena] in accordance with observation will form some sort of natural generalization of the ordinary theory of radiation."[67] If it is rarely spoken of today, its implications are nonetheless universally accepted. It is demonstrable that specific theoretical developments of the 1920s were directly motivated by the correspondence principle. Of this I will have more to say.

From the perspective of the early 21st century, it is undeniable that the most important developments in atomic physics in the first two decades of the previous century were experimental, not theoretical. Theoretical breakthroughs that took place between 1913 and 1923 were for the most part illusory, or at the very least, ad hoc. There are exceptions, however. For example, Sommerfeld and his student Pieter Debye discovered space quantization in 1916 in the process of providing an explanation of the Zeeman effect.[68] This discovery, that the projection of the angular momentum vector on a chosen axis was quantized, was a major discovery, one that provided further confirmation of the discrete character of the microscopic world, and in a realm somewhat removed from that of discrete energy levels and atomic transitions, though of course it was revealed in the same context of atomic spectra and the effect of applied magnetic fields. This result, which would be "confirmed" in the case of spin in the Stern–Gerlach experiment 5 years later, was based on the quantization rule discovered by Sommerfeld and Wilson[69] (previously mentioned), that the *action* $J = \int p_i \, \mathrm{d}p_i = n_i h$.

It was the speculative leap taken by de Broglie, in proposing that particles ought to possess wave properties, that opened the door for wave mechanics, one of the two early formulations of quantum theory. As we learn from his own words, Schrödinger's most immediate motivation for developing wave mechanics was de Broglie's work,[70] which, along with Einstein's explanation of the photoelectric effect, represented the origin of "wave–particle duality"; Schrödinger was quite explicit about his debt to Einstein.

In passing, the interested reader may want to explore the relationship between Einstein's general relativity and the first tentative gropings toward a quantum mechanics in the early 1920s. It might seem that there could not be much relationship between these two theories, but such is not entirely the case. Hermann Weyl, especially, as an expert in general relativity theory and a mathematical colleague of David Hilbert's, explored these implications of general relativity to the quantum theory.[71] Hilbert himself, whose mathematics, in the hands of John von Neumann and others provided the formal foundation for the quantum theory, very nearly beat Einstein to general relativity.[72]And although little came of these connections, such issues, that is, quantization of gravitation, would be at the forefront of theoretical physics as the 20th century closed.

CONCLUSION

In 1924, just after de Broglie took his decisive step toward wave–particle duality, Bohr, in a paper with Hendrik Kramers and John Slater, spoke pessimistically of the "doubt . . . whether the detailed interpretation of the interaction between matter and radiation can be given at all in terms of a causal description in space and time of the kind hitherto used for the interpretation of natural phenomena,"[73] signaling that something more than incremental extensions of existing theory would be required.

The state of attempts to explain atomic line spectra and other quantum phenomena was so frustrating to Pauli that in 1924, in the face of what he regarded as ad hoc attempts to play games with integral and half-integral quantum numbers, he declared his intention to give up on it, saying that "I myself have no taste for this sort of theoretical physics and retire from it." This fortunately did not last, and though one could not see it, physics was on the verge of the revolution that would clarify the issues that so troubled Pauli and that would dominate the next decade (and which in some sense is still in progress). Pauli would be one of the most important players. One could say, echoing Abraham Pais in his *Subtle is the Lord* when speaking of the conundrum of the ether, that Pauli's lament was not that "of a single individual, but of an era."[74]

NOTES

1. See, for example, my *Physics in the Nineteenth Century* (Purrington, 1997). Note that I said "major figures"; there were many others, of course.
2. Who virtually wrote down the Schrödinger equation, as Goldstein (1980) notes.
3. For example, Dugas (1955).
4. Although some oft-quoted statements to that effect cannot be verified.
5. Michelson (1903). In the course of expressing his conviction that " future discoveries must be looked for in the sixth place of decimals," Michelson concluded that "such examination almost surely leads, not to the overthrow of the law."
6. Arguably, perhaps, being repeated by those who think the "theory of everything" is almost at hand.
7. "Nineteenth-Century Clouds Over the Dynamical Theory of Heat and Light," (Kelvin, 1901), delivered in 1900. In a series of very elaborate arguments, he tried to show that the Maxwell–Boltzmann theory of equipartition had to be wrong.
8. There are, of course, problems in classical physics that have only partially succumbed to the vigorous assaults of both mathematicians and physicists, including turbulence and other problems in nonlinear dynamics.
9. The two revolutions, if that is the proper word, clearly also differ in the extent to which quantum mechanics was the offspring of the efforts of at least a dozen important physicists, whereas relativity, although not quite the product of one mind, was nearly so. On precursors such as Poincaré, see Pais (1982).
10. Including Stehle (1994), especially chapters 7–9, Rechenberg (1995), and the chapter *Fin de siecle* in Purrington (1997).

11. Fritz Reiche's *Die Quantentheorie* of 1921 gives an excellent summary of many of these issues. It was translated into English in 1924 by Henry L. Brose, and there was a second edition. In the next chapter, we will consider in greater detail important experimental results from the decade before the new quantum theory came on the scene, about 1915–25. Brose also translated Sommerfeld's work into Engllish.
12. Kuhn (1962).
13. Sommerfeld (1930). See Chapter 5.
14. Actually obtained by John Waterston a decade earlier, in work that was buried for 45 years in the archives of the Royal Society.
15. With $1/2KT$ of energy per degree of freedom (quadratic term in p or q in the energy; that is, v^2, x^2, L^2, etc.). The specific heat at constant volume, c_v is defined as $\partial U/\partial T$ at constant volume, where U is the internal energy. Thus each degree of freedom contributes $1/2k$ to the specific heat., and $c_v = 3/2k$ for a monatomic gas. Alternatively, the molar specific heat is $3/2R$, where R is the universal gas constant (1.99 cal K^{-1} $mole^{-1}$ or 8.3 J K^{-1} $mole^{-1}$). The relationship between k and R is $k = R/N_A$, where N_A is Avogadro's number. See any text on kinetic theory or thermodynamics. Boltzmann's constant k has the value 1.38×10^{-23} J/K. It should be noted that tabulated specific heats are usually given in J K^{-1} g^{-1}. In the past they were given in terms of calories per gram, and the calorie was defined in terms of the specific heat of water, as the amount of heat required to raise the temperature of 1 g of water 1 °C. Now the calorie is defined in terms of the joule, about 4.2 J. Molar specific heats are more convenient, being, in theory, nR, where n is the number of degrees of freedom and $R = 8.3\,\mathrm{J\,K^{-1}\,mole^{-1}}$. Admittedly, this is more information than is needed here.
16. Because $c_v = nkT/2$ and $c_p = nkT/2 + kT$; then $\gamma = (n+2)/n$ or $\gamma - 1 = 2/n$.
17. From a BAAS report, quoted in Goldman (1983), p. 118.
18. Maxwell (1875).
19. Rayleigh (1900).
20. The measured c_v makes smooth transitions from $3/2 \rightarrow 5/2$ and $5.2 \rightarrow 7/2$ as increasing fractions of molecules have rotational or vibrational degrees of freedom excited.
21. Thomson's (Kelvin) 1884 Baltimore lectures, as updated and published in 1904, show him pondering this conundrum at great length; it was one of his famous "clouds" that he saw as undermining the classical consensus just before 1900 (Kelvin,1904).
22. Although here the quantum nature of the phenomenon was more obscure, emerging only from its theoretical explanation by Einstein, and later others. The law was formulated in 1819. Petit and Dulong (1819). See Chapter 18. The value $3R$ is about $6\ \mathrm{cal}/K$ per mole or about 25 J/K per mole.
23. Einstein (1907).
24. Klein (1965).
25. The $1/\lambda^4$ dependence of the Rayleigh–Jeans law of 1900–1905, which of course blows up at short wavelengths. The term was supposedly coined by Ehrenfest in 1911.
26. Planck (1900). See Kuhn (1978, 1979) or Purrington (1997), pp. 156–7. Planck's introduction of the quantum was vigorously debated at the first Solvay Conference in 1911, where Sommerfeld expressed skepticism that it represented physical reality. See Mehra (1975), p. 39.
27. Before the symbol ħ ("h-bar") was introduced, Dirac employed the symbol h to mean "$h/2\pi$." Planck gave the value of h as 6.55×10^{-27} erg-s (Planck, 1900). The accepted value is $6.626\ldots \times 10^{-27}$ erg-s (6.6×10^{-34} J-s).

28. Hertz (1887).
29. Lenard (1902). Lenard was awarded the Nobel Prize in 1905, but became a strong proponent of "Deutsche physic," and an opponent of "jewish physics." Lenard is sometimes confused with the French physicist Alfred-Marie Liénard of the Liénard–Wiechert potential, and perhaps the English physicist John Lennard-Jones, who changed his name from J. E. Jones upon marrying "a Miss Lennard," as Mehra (1972) puts it.
30. Einstein (1905). In no more than two pages.
31. Although Lenard, as a Nazi sympathizer, became an opponent of both relativity and quantum mechanics, he apparently never rejected Einstein's explanation.
32. Einstein (1916b, 1916c, 1917a). The last of these is translated in van der Waerden (1967). Einstein (1916c) essentially established that photons had to carry momentum. These papers were written just as Einstein was revealing general relativity to the world.
33. The controversy that began with the opposing 17th-century views of Robert Hooke and Isaac Newton, up to the consensus achieved in the early 19th-century consensus by Thomas Young that light was a form of wave motion, was an argument about whether light consisted of waves *or* particles, not both.
34. Compton (1923).
35. De Broglie (1924, 1925). Proposed in his PhD thesis of 1924, refereed by Einstein. (See fn. 83 in Rechenberg, 1995.)
36. Davisson, Clinton, and Kunsman (1923), Davisson and Germer (1927a, 1927b; 1928). At Bell Labs after 1925. The entire fascinating story is told in Gehrenbeck (1976). Davisson and G. P. Thomson shared the 1937 Nobel Prize. The story of Thomson's elegant experiments is told in Moon (1977). His results were published in Thomson and Reid (1927), Thomson (1927), etc. It has been "quipped," to quote the AIP website, that J. J. Thomson received the Nobel Prize for showing that the electron was a particle, whereas his son, G. P. Thomson, received it (1937) for showing that it wasn't. Germer did not share the prize in 1937, which was awarded to Davisson and Thomson.
37. Bailey and Townsend (1921), and succeeding papers; Ramsauer (1921).
38. Elsasser (1925).
39. This would be Davisson and Kunsman (1923); Davisson and Germer, (1927a). See Jammer (1966, p. 249) for elaboration, including the contributions of Elsasser. See also the AIP Oral History interview with Elsasser, Nov. 21, 1985.
40. Characteristic x-ray spectra represented a similar issue, but this was discovered only in 1913.
41. Ritz (1908a). It stated that spectral line frequencies were either the sum or difference of another pair of lines. This was a first step toward the understanding that spectral lines represent the difference between the energies of two atomic levels.
42. Franck and Hertz (1914). Translated in Ter Haar (1967).
43. Bohr (1915b). That the results of the Franck–Hertz experiment were obtained in April 1914, not long after Bohr's first paper on hydrogen.
44. Röntgen (1895). A translation by Arthur Stanton appeared in *Nature* the next year (Röntgen, 1896). The discovery, made in Würzburg on Nov. 8, 1895, led to his being awarded the first Nobel Prize, in 1901. Element 111, Roentgenium, is named after him.
45. Moseley (1913, 1914). He obtained expressions for the frequency of these lines whose Z-dependence was modified by screening. . Moseley perished at the battle of Gallipoli on Aug.10, 1915, age 27, along with about 130,000 others.

46. Becquerel (1896).
47. Just over a century ago. His major assistants and collaborators were Soddy, Geiger, Marsden, and later Chadwick.
48. The "discovery," or identification, of the electron in 1897 by J. J. Thomson (Thomson 1897a,1897b) as the quantum of electrical charge, itself had implications not very different from those we have been discussing.
49. Again, Stehle (1994) provides an accessible summary of these developments.
50. Independently by Gurney and Condon. See Chapter 15.
51. As is well known, the 1921 Nobel Prize was awarded to Einstein for his explanation of the photoelectric effect (but was delayed until 1922), but not really for the notion of a quantum of electromagnetic energy. It would have been awarded for special relativity, but this had become conflated with general relativity, about which there was much skepticism. Nonethless, Einstein devoted his Nobel Lecture to relativity. It is also well known that Einstein ultimately rejected the offspring of his idea of the quantum of energy, standard or orthodox quantum theory. When confronted by Phillip Frank about this, with Frank saying that the viewpoint of Heisenberg and Bohr "was invented by you," Einstein supposedly replied that "a good joke should not be repeated too often." See Frank's notes on Einstein [Frank (1947), p. 216; quoted in Jammer (1974), p. 131]. Rosenfeld (1971) has pointed out that for some time an alternative explanation of the Compton effect in terms of the Doppler effect was possible.
52. Jammer (1974), p. 126. An obvious choice once "electron" had been coined by Stoney in 1894 for the quantum of electric charge.
53. See Mehra (1975) for details. The subject was "The Theory of Radiation and the Quanta." Sommerfeld and Rutherford were among the 20+ attendees as well, but not Bohr, who was just completing his PhD dissertation. The second Solvay Conference took place just weeks after Bohr's paper was published, and he was again not an attendee, and the third Solvay Conference was not held until after the war, in 1921.
54. Poincaré (1912).
55. See McCormmach (1967).
56. Condon and Morse (1929). ter Haar, (1967).
57. *Vorlesungen über Atommechanik*, 1925; quoted in Condon and Morse (1929), pp.7–8.
58. Bohr (1913a). "On the consititution of atoms *and molecules*." These are reproduced, in part, in French and Kennedy (1985). The initial paper is also reprinted in ter Haar (1967). For a secondary work, see Heilbron and Kuhn (1969).
59. It is interesting to see Bohr correctly concluding that there were closed shells involving 2, 8, and 18 electrons, well before the Pauli principle. But he had no real theory, and his 18 electrons were divided into three groups of six, rather than 2 + 8 + 10. Bohr (1921). See also Chapter 10.
60. The three centers of activity were Munich, under Sommerfeld, Göttingen, under Born, and Copenhagen, under Bohr.
61. On the technical meaning of "action" and the "principle of least action" in mechanics, see, for example, Goldstein (1980).
62. For example, Merzbacher (1998), p. 2.
63. Condon and Morse (1929), p. 8.
64. Bohr (1925). The paper is an excellent introduction to the situation in late 1925, shortly after Heisenberg's paper appeared and just before Born and Jordan (1925). It includes a

discussion of the "quantization rule." In some respects Bohr was the most conservative of the founders of the quantum theory, holding onto classical concepts to the last—around 1920. When he died in 1962 things were very different. See Hendry (1984), pp. 28–34.

65. It officially became the Neils Bohr Institute in 1965. Lorentz, who was still a towering figure, died in early 1928, age 75.
66. "Fundamental Postulates," Bohr (1922). See Hendry (1984), p.141
67. "On the quantum theory of line spectra," published in three parts between 1918 and 1922. See van der Waerden (1967), pp. 5–8. Van der Waerden printed only part I. The three papers are collected in the reprint volume, Bohr (2005). Bohr first used the term "correspondence principle" [*Korrespondenzprinzip*] in 1920 (Bohr, 1920). *Zeitschrift fur Physik* had just began publishing that year.
68. Sommerfeld (1916b). Debye (1916), the article succeeding Sommerfeld's.
69. Sommerfeld (1916b). See ter Haar (1967), p. 75; Wilson (1915). In this case, William Wilson.
70. De Broglie (1924). De Broglie received the 1929 Nobel Prize in Physics.
71. Rather than cite papers by Weyl in this case, I refer the reader to chapter 2 of Hendry's book (1984).
72. The subject of much controversy.
73. Bohr, Kramers, and Slater (1924).
74. Pais (1982), p. 115.

2

1913: THE BOHR THEORY OF THE HYDROGEN ATOM

Quantum *theory* was born in the first decade of the 20th century with the papers of Planck and Einstein.[1] But quantum *mechanics,* as a dynamical theory of the microscopic world, had its beginning in Niels Bohr's seminal paper in *Philosophical Magazine* in 1913,[2] showing how certain assumptions about the role of quanta could explain the Balmer series discrete spectrum of the hydrogen atom. This paper holds a deservedly honored place in the history of quantum mechanics, at least rivaling those of Heisenberg and Schrödinger a little over a decade later, and everything that took place between 1913 and 1927 built upon Bohr's theory.

The essential building block was Rutherford's hypothesis of 1911, based on his experiments with α-particles,[3] that the atom consisted of a small, massive central core and a surrounding electron cloud. After a couple of meetings with Rutherford, one in Manchester and the other at Cambridge, Bohr was invited to work in his laboratory in Manchester (see Figure 2.1). He spent less than 5 months with Rutherford, but there he became quite familiar with the latter's nuclear atom.[4] But he knew that the orbit of an electron circling a positively charged central body would be unstable because an accelerated charged particle must radiate electromagnetic energy according to Maxwell's electromagnetism. To explain the stability of the hydrogen atom, that is, the existence of "stationary states," and lacking any real theory other than classical mechanics and the notion of the quantum, Bohr simply *postulated* that an electron would be in a stable orbit if it satisfied certain integral or quantum conditions.[5] This was, of course, an ad hoc explanation—or, if you prefer, merely a recognition of an empirical fact that would require over a decade to find an explanation for. In part because of Bohr's chronic prolixity, or one might say, his penchant for thinking out loud in print, a reader might be excused for not seeing how what is taught as the "Bohr theory" emerged from his papers of 1913–1915. But it cannot be emphasized too strongly that it was Bohr's fundamental insight that spectral lines resulted from transitions *between* discreet stationary states; that is, a line did not itself correspond to a state. This, coupled with the assumption finally reached by Bohr that the energy difference given up in a transition between two states was radiated as a *single* photon, an argument that evolved in these papers, provided the basis for Bohr's theory of the atom. Of course, Bohr does not speak of photons, because the name would not appear for over a decade. Rather he uses the term "energy quanta," but there is more to the story. In fact, as late as 1920 (and beyond) Bohr was unable to accept the idea

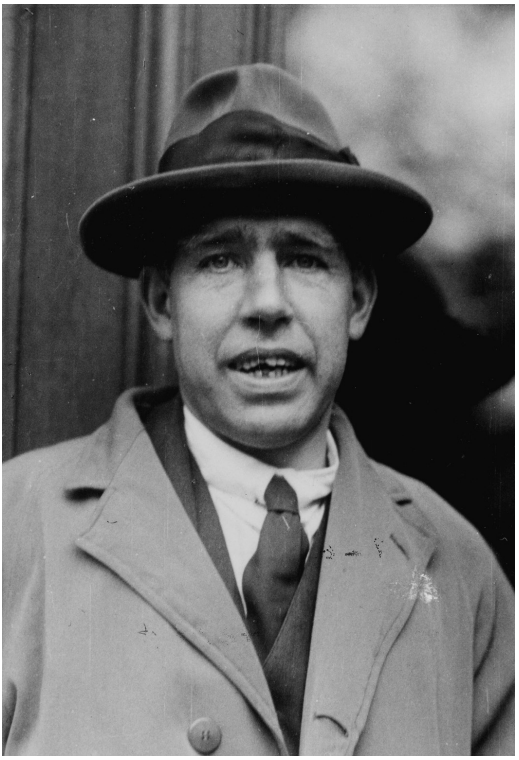

Figure 2.1. Niels Bohr (1885–1962). AIP Emilio Segrè Visual Archives, Segrè Collection.

of the photon. I recommend especially Pais's discussion of the issue in his *Niels Bohr's Times*.[6] Bohr's quantum postulate was that instead of radiating energy continuously as required by Maxwell's theory, the energy was emitted as electromagnetic quanta with energy $h\nu$,[7] and only when an electron changed orbits. This insight, for which Bohr credits Einstein's papers of 1905–1907, would lead to a quantization condition for the stable orbits themselves.[8]

But the road to the correct result was, and still is, a bumpy one. Bohr's starting point was the *assumption* that when an electron falls in from *infinity* to a stable orbit with orbital frequency ω, radiation with a frequency $\nu = \omega/2$ would be emitted,[9] and that the energy emitted, W, "from Planck's theory," would be an integral multiple of $h\nu$. That is, $W = nh\nu = nh\omega/2$, which would be the negative of the energy of the bound electron. This is the quantum condition, of which Leon Rosenfeld has written that "the daring (not to say scandalous) character of Bohr's quantum postulate cannot be stressed too strongly."[10] And in December of 1913, shortly after the final part of the trilogy appeared, Sir James Jeans complained that "The justification of his theoretical assumptions is only the very ponderous one of success."[11] Bohr's reasoning apparently was that if the orbital frequency at infinity is 0, and for the final orbit, ω, then the emitted radiation could be assumed to have frequency $\nu = \omega/2$. Not a very sound argument but one that led to the correct result, which was certainly a strong motivation for him.

Now it is easy to show, classically, that for a circular orbit, ω is proportional to $E^{3/2}$ (Kepler's Third Law; Bohr's Eq. 1), specifically,[12]

$$\omega = \left(2^{1/2}/m^{1/2}k\pi\right)W^{3/2}, \tag{2.1}$$

where E is the energy of the electron. The result is that the energy radiated by an electron falling in from infinity would be proportional to $\omega^{2/3}$. But Bohr had to introduce the quantum postulate, essentially $E = nh\nu$ and his leap of faith, or guess, was to take $\nu = \omega/2$. Then, using the assumption that $W = -E = nh\omega/2$ to eliminate ω, one finds that (Bohr's Eq. 3)

$$E = -2\pi^2 mk^2/\left(n^2h^2\right), \tag{2.2}$$

in which the Coulomb potential energy has been written[13] as $V = -k/r$. This appears to give the correct expression for the energies of the stationary states in hydrogen, except that the orbits are labeled by the number of quanta, n, emitted as the electron falls in from infinity. But Bohr noted that W is greatest when $n = 1$ corresponding to the ground state, and that this leads to $W = 13$ eV, the correct binding energy of an electron in the ground state, essentially the Rydberg constant. But this requires that a *single* quantum of energy be emitted in the transition to the ground state, which is what Bohr would eventually adopt, in his sec. 3. This is fine, but what are we to make of the states labeled by different values of n?

The way to look at this is to say that Bohr had an expressions for $E(\nu)$, the quantum one, and a classical expression for $E(\omega)$, both of which he took to be valid. This required a relation between ν and ω that he took to be $\nu = \omega/2$ a leap of faith with the dubious justification previously given. Then, eliminating ω led to Eq. (2.1) with W or E proportional to $1/n^2$.

In his sec. 2, we see Bohr beginning to sour on his original assumptions, for as he continued on with the Balmer series, in which the energy emitted in a transition from level n_2 to n_1 would be of the form $E_{2\to1} = 2\pi^2 mk^2\left(1/n_1^2 - 1/n_2^2\right)$, with $n_2 = 2$ and $n_1 > 2$, to get the correct expression for the frequencies, he now had to accept that the energy was emitted in the form of *a single* quantum, that is, $E_{2\to1} = h\nu$ abandoning, as was said, his original postulate. From this, however, followed the basic features of the emission or absorption spectra of hydrogen, and the Balmer formula, involving a transition from $n = 3, 4, 5, \ldots$ to $n = 2$, follows immediately. While doing all this, however, Bohr deferred a discussion of the validity of his assumptions until later in the paper. The result stood but the reasoning had to be revised. The meaning of the quantum number n had been reinterpreted, with considerable sleight of hand. Rarely has such an important proof rested on such flimsy foundations, something Bohr evidently recognized.

Then, in his sec. 3, Bohr says that "we will now return to the discussion of the special assumptions used in deducing the expressions . . . for the stationary states of the system. . . ." and describes the assumption that different numbers of quanta are emitted during transitions as "improbable." After a bit of effort, he concludes that "we are thus

led to assume that the interpretation . . . is not that the stationary states correspond to the emission of different numbers of energy-quanta, but that the energy emitted . . . is equal to different multiples of $\omega/2$." So rather than n quanta with frequency ν, only a single quantum is emitted, with energy $h\nu$ but $\nu = n\omega/2$. Why a *single* quantum? Again, the justification is that it worked. Bohr relaxed his original assumption but still assumed that W is still linearly related to ω: $W = f(n)h\omega$ and showed, using the correspondence principle, that $f(n) = n/2$. Of course it gives precisely the same result, but, as we have said, the meaning of n has changed. Unlike most scientific papers, which give only the finished product, the final reasoning, this one allows us to see how Bohr's thinking evolved as he struggled to justify what was obviously the correct formula, with little to guide him. The result was pretty much a muddle.

On the other hand, it is also easy to show from classical mechanics that for any level with energy E, the energy can be expressed as:

$$E = -mk^2/\left(2L^2\right), \tag{2.3}$$

where L is the orbital angular momentum, whence, by combining Eqs. (2.2) and (2.3), we have $L = nh/2\pi = n\hbar$, which is the quantization condition for angular momentum. Although Bohr makes note of this almost as an afterthought, and dismisses it with the statement that "there obviously can be no question of a mechanical foundation of the calculations given in this paper . . . ," the "Bohr postulate" is often taken to be just that: quantization of the orbital angular momentum. Despite the historical inaccuracy, we can then argue, ignoring the initial "proof," that the Bohr theory rests on this *postulate, L = nh*. Another writer, having discovered that the angular momentum was quantized, might have used that as his postulate and suppressed the earlier arguments, but not Bohr. And, in fact, in sec. 5 of the paper, and in the second installment, Bohr notes that in "the permanent state" of an atom, that is, the ground state, the angular momentum of an electron[14] is $h/2\pi$, and really doesn't look back.

A decade after Bohr's original papers, following de Broglie, it could be shown that this quantum condition $L = nh$ was equivalent to the postulate that an integral number of de Broglie wavelengths $(\lambda = h/p)$ would fit into one orbit.[15] Interestingly, had he been able to use the later Wilson–Sommerfeld quantization rule,[16] which would have said that $\int p\,\mathrm{d}q = nh = \int L\,\mathrm{d}\theta = 2\pi L$, he would have immediately found that $L = nh/2\pi = nh$.

Beyond the fundamental result of the paper, Bohr concluded more generally that bound or closed systems will possess discrete, stationary states, but that unbound systems will still have continuous spectra. The successful application of Bohr's theory to the experiments of E.C. Pickering and William Fowler on ionized helium was another great triumph,[17] but it was soon apparent that even two-electron atoms posed insurmountable problems. In the last two parts of the trilogy, Bohr attacked the problems of multielectron atoms and even molecules, without notable success. In part III, he attempted to explain the stability of multinuclear molecules by invoking the principle of "universal constancy of the angular momentum of the bound electrons."[18]

It is worth noting that the 27-year-old Bohr was not working in a vacuum.[19] He was strongly influenced by John William Nicholson, whose atomic models owed more to J. J. Thomson than to Rutherford, but did include quantization of angular momentum to attain stability.[20] Nicholson was thus the first to attempt a quantum-mechanical theory of the atom. And although Bohr's triumph (along with Rutherford's discoveries), provided the impetus for all that followed, the elation was short-lived, as attempts to extend his approach, by Bohr himself and by Sommerfeld and others, met with failure almost from the outset. The result was a decade of floundering attempts to find a theoretical description of the mass of spectroscopic data that was accumulating that bore little fruit.

CONCLUSION

Bohr's theory was embraced almost immediately, despite its logical shortcomings. It is likely that readers of his paper were able to look beyond these original shaky foundations and accept quantization of orbital angular momentum as a fundamental principle. Einstein, for example, quickly saw its importance, and in 1916 called it "a miracle," and "the highest musicality in the sphere of thought."[21] Many, like Moseley, took several months to be persuaded, and some, like Johannes Stark, were unconvinced a decade later. J. J. Thomson complained that the theory was only mathematical, not dynamical,[22] and some resistance was based, quite reasonably, on the fact that the theory was capable of explaining the structure of only a single element. Runge thought it was "the sheerest nonsense," and Paul Ehrenfest called it "completely monstrous." [23] Constraints of space will not allow a recount of the fascinating story of the reception of the Bohr theory, but it has been described in several places.[24] As we saw in the last chapter, the famous Franck–Hertz experiment of the year after the Bohr theory, in which electrons were found to be absorbed by mercury atoms only if their energies were 4.9 eV (to use modern terminology), provided strong support for the idea of discrete electronic states as in Bohr's theory.

In a sense that goes far beyond the Bohr theory of hydrogen or the failed Bohr–Sommerfeld theory, Neils Bohr was the father of quantum theory, even quantum theory as we understand it today. Bohr thought more deeply and more continuously than anyone else about the fundamental questions that led, almost inexorably, to the discoveries of the late 1920s, often aided by his correspondence principle, which, though much neglected today, was the guiding light for a generation of young quantum physicists.[25] All of the founders of quantum mechanics visited Bohr in Copenhagen at one time or another, and the long walks with Bohr, the arguments and discussions, gave impetus to the discoveries that would follow. Without Bohr's influence, it is doubtful that the revolution would have come when it did.[26]

While we have dwelt rather heavily on the deficiencies in Bohr's arguments, we have also noted that most authors would have suppressed the reasoning that Bohr himself found faulty and would have published a cleaned-up version. Bohr was not awarded the Nobel Prize in physics until 1922, simultaneously with Einstein, who was

belatedly awarded it for the year 1921, but the delay was as much the result of the war as of misgivings about the theory.[27]

NOTES

1. Planck (1900, 1901), Einstein (1905, 1907).
2. Actually a 71-page trilogy; Bohr (1913a). The three parts were published in July, September, and November. An excellent source is Heilbron and Kuhn (1969). See also Heilbron (1985) and Stachel (2009).
3. See Chapter 15.
4. See Rudolf Peierls's Rutherford Lecture, delivered in November 1987 (Peierls, 1997). He died in 1995. It has been said that Rutherford took to Bohr because he was a "footballer," depite their very different personalities and approach to physics.
5. The interested reader might consult the paper by Pais (1995), in which the contributions of Haas, Nicholson, and Bjerrum are detailed. On antecedents, see especially pp. 80–82.
6. Pais (1991).
7. Note that this is not equivalent to adopting the photon picture of light, which Bohr did not quickly do.
8. This is the birth of the idea of a quantum state. See Weisskopf (1985, in French) and Kennedy (1985).
9. Almost the only plausible basis for this assumption would appear to be simply that it leads to the correct expression for the hydrogen spectra, with the correct Rydberg constant. For background, see the detailed discussion in Heilbron (1985), pp. 45–6. Bohr was using an analogy with a Planck oscillator, which he eventually abandoned. Note that in Bohr, ω is frequency (s^{-1}), not angular frequency. The first part of the paper, beginning on p. 1 of vol. 26 of the *Philosophical Magazine* (Bohr, 1913a), is reproduced, with slight modification, in Ter Haar (1967). Unfortunately Bohr's endnotes are omitted.
10. Referring in part to the next assumption as well. Heilbron (1985), more gently, called it an invention and the derivation "unintelligible." The interpretation given here, however, is my own. The flaws in the proof don't stop there, as we shall see. In fairness to Bohr, however, one should note his caveat, "the question, however, of the rigorous validity of both assumptions . . . will be more closely discussed in § 3."
11. Quoted in Hund (1974), p. 74.
12. Bohr used W for the orbital energy; I am using both W and the conventional symbol E.
13. Bohr wrote it as Ee/r, and we would write Ze/r. He also used τ for the integral number of quanta rather than n.
14. Actually for" every electron" in a multielectron atom (Bohr, 1913a, part II, p. 477) Obviously the exclusion principle was over a decade away.
15. For a circular orbit the circumference C equals $2\pi r$, but with $L = n\hbar = mvr$, it follows that $C = 2\pi L/mv = 2\pi L/p$. With $p = h/\lambda$ from the de Broglie formula, $C = n\lambda$, de Broglie shows this more generally (de Broglie, 1924).
16. Wilson (1915), Sommerfeld (1916c). Sometimes called Bohr–Wilson–Sommerfeld.
17. Pickering (1896), Fowler (1912). Ionized helium, of course, is the same problem as hydrogen, with a larger nuclear mass and charge.
18. The quote is actually from part II, p. 502, but invoked as well in part III.
19. See Heilbron (1977), p. 40.

20. Nicholson (1911, 1912). See McCormmach (1966). Also an unpublished online paper by Jaume Navarro, "The structure of the atom before Bohr." See, as well, Nagaoka's "saturnian" model.
21. Quoted in Kragh (2010a).
22. Thomson (1919), p. 420.
23. Footnotes 9 and 154 in Kragh (2010). The entire paper is of interest.
24. For the period 1913–1915, see Kragh (2010a), and references therein.
25. Bohr (1920). English translation in *Neils Bohr, Collected Works* (1976), p. 241. Dirac once said that Bohr "seemed to be the deepest thinker that I ever met." Quoted in Kragh (1990), p. 38. John Slater felt quite differently, particularly regarding the apparent absence of mathematical underpinnings for his work. See the AHQP Oral History interview.
26. Unfortunately, Bohr died suddenly in 1962 before extensive interviews by historians of science could plumb the depths of his memory.
27. Kragh (2010).

3

TYRANNY OF THE DATA
ATOMIC SPECTROSCOPY TO 1925

INTRODUCTION

In the first chapter we surveyed a series of important empirical results from the period straddling the turn of the century that seemed to defy explanation in terms of accepted classical physics. Some of these phenomena, like blackbody radiation, the photoelectric effect, and (later) Compton scattering, required, or at least were a motivation for, the introduction of the quantum of electromagnetic energy, the photon.[1] Others, such as the problem of specific heats of gases, would eventually demand the quantization of internal degrees of freedom of a system. It was, however, in the problem of atomic line spectra and characteristic x-ray spectra that experiments most clearly established the need for a radical theoretical transformation. By 1920 an enormous mass of spectroscopic data awaited some kind of theoretical interpretation,[2] and because these empirical results were so crucial in forming the basis for the theoretical developments that are our main preoccupation, some time is now devoted to the recounting of these discoveries.[3]

Before embarking on this discussion of atomic spectra, however, we should note that although the scattering experiments of Rutherford and his colleagues established the reality of the nuclear atom in 1909–1911,[4] it had taken some time to arrive at the number of electrons per atom; hence the equality of the atomic number and the number of electrons (or about one electron per two units of atomic weight).[5] J. J. Thomson and Charles G. Barkla[6] played perhaps the most important roles in working this out by about 1911. In the Thomson or even Nicholson models of the atom, the charge was distributed uniformly, and the disparity between the mass of the atom and tiny electron mass meant that the number of charges had to be huge. But if the charge on the atom was approximately equal to the atomic number, there must be a large amount of "positive electrification" as well. Sommerfeld's classic and enormously influential *Atomic Spectra and Spectral Lines* [*Atombau und Spektrallinien*] noted that Phillipp Lenard had attempted to understand x-ray scattering from the atom by arguing in 1903 that matter had a "perforated structure," with only a "tiny part impenetrable to x-rays."[7] But by 1920, with the Bohr–Rutherford nuclear atom well established, James Chadwick was able to show that the observed deflections in Coulomb scattering from various nuclei confirmed the fact that the nuclear charge was the same as the atomic number.[8] We discuss this further in Chapter 15.

ATOMIC SPECTRA

To return to spectroscopy, for nearly a decade, from 1916 to 1925, physicists struggled to understand the bewildering complexities of atomic spectra with almost nothing in the way of a theoretical framework and, in the end, would have little to show for the effort, at least on the theory side. In the case of hydrogen and hydrogen-like atoms one had the semiclassical Bohr–Sommerfeld theory,[9] but it broke down spectacularly in more complex atoms and, before long, even in the simplest case of hydrogen. Much progress was being made in the phenomenology of spectroscopy, where, on a purely empirical basis, it was found possible to derive quantum numbers, selection rules, even intensity formulae, without, again, any real theory (except for the correspondence principle from 1920). Deciphering atomic spectra was an inherently difficult process, as spectral lines represented atomic *transitions* from one level (or "terms") to another, not the levels themselves, that is, *changes* or *differences* in quantum numbers, making the assignment of quantum numbers to a given level a major detective process. The *combination principle* or frequency sum rule discovered by the Swiss physicist Walter Ritz in 1908[10] aided in this, but there was little that could be called quantum *mechanics* at all. The state of affairs is nowhere better illustrated than in the several editions of Sommerfeld's book (revised through 1931, with further editions and a second volume, through at least 1944). Although Sommerfeld was a great theoretical physicist and extraordinary mentor,[11] his contact with empirical results was also very intimate.

It would be these data, which included the discovery of *fine structure* in hydrogen and the alkali metals as early as 1887, as well as the effect of applying external electric and magnetic fields to an atom in the Stark and Zeeman effects at the turn of the century, that as experimental dispersion and resolution increased, would lead to the discovery of the Pauli principle and electron spin in 1925. Everything seemed to converge on that year, that in many respects was the "golden year" of quantum mechanics, culminating in Heisenberg's creation of the "new quantum theory." Ultimately, Heisenberg's program of formulating a theory based only on observable quantities (see Chapter 5), the goal of which was to explain energies of spectral lines, intensities, etc., leaned crucially on the spectroscopic data.[12] Again I emphasize that the development of quantum theory was driven, to an uncommon degree, by experimental discoveries, especially those we discuss here.

Little progress had been made in spectroscopy from the time of Isaac Newton and James Gregory until Joseph von Fraunhofer invented the spectroscope, which allowed the cataloging of lines due to heated sources. In 1814, using sunlight as a source, he identified nearly 500 dark lines in the solar spectrum, some of which had already been seen in 1802 by William Wollaston.[13] Separately, Anders Ångström and Julius Plucker measured the frequencies of some of the lines in what we call the "Balmer series" of hydrogen in 1859–1860, but atomic spectroscopy might be said to have begun, or at least come into its own, with the experiments of Kirchoff and Robert Bunsen in Heidelberg in those same years,[14] in which they were able to clinch the identification of the solar absorption lines with emission lines from terrestrial sources. There

was little organization of these data until 1885, when the Swiss high school teacher J. J. Balmer devised his remarkable formula for the wavelenths of the Balmer lines in the form $\lambda = km^2/(m^2 - n^2)$, where m and n are integers and $m > n$.[15] This was written by Rydberg 3 years later in the form $\lambda = \mathrm{k}'(1/n_1^2 - 1/n_2^2)$, and with $n_2 = 2$ for the Balmer series transitions, it could be expressed as $\lambda = (4/R)/(1 - 4/m^2)$, where R is the Rydberg constant and $m > 2$. The meaning of this simple formula, which was really just a fit to the data but in which the differential nature of spectral lines was barely concealed, would continue to be a mystery for nearly 30 years, until Bohr offered his theory of discrete states in hydrogen in 1913.[16] As mentioned in the last chapter, it was Bohr, undoubtedly influenced by Ritz, who first understood that frequencies of the spectral lines are due to energy differences between stationary atomic states. By 1908 the Lyman ($n_2 = 1$) and Paschen ($n_2 = 3$) series in hydrogen, which are, respectively, in the ultraviolet and infrared, had also been identified. In the meantime, Pieter Zeeman had discovered the splitting of spectral lines in a magnetic field in 1897 (sharing the second Nobel Prize in 1902 for the discovery),[17] an effect that bears his name, and Johannes Stark did a similar thing for an applied electric field in 1913,[18] for which he became the 1919 Nobel Laureate.[19]

In the simplest case of all, hydrogen, Bohr's theory provided an explanation of Balmer's formula in terms of transitions between stable electronic orbits, each labeled by the principal quantum number n. The theory raised as many questions as it answered, but was obviously a great step forward. The hydrogen-like case, in particular He^+, was just as easily described by the Bohr theory,[20] but neutral helium proved intractable. The alkali metals (Group 1), including sodium, which came to be understood as a single-valence electron outside an at least approximately inert "core" (called by Sommerfeld an atomic trunk; *atomrumpf* in German), showed absorption spectra that resembled that of hydrogen, though with significant differences. But this important discovery meant that the spectrum of a complex atom with 11 electrons, say, could be understood, at least approximately, by considering the excitation of only a single electron, in this case outside a neon core. And so on.

But even in hydrogen, the simplest atom of all, improved resolution showed that levels with a given principal quantum number n were split potentially into $n - 1$ levels, in what came to be known as *fine structure*. Fine structure had been first seen by Michelson and Morley in 1887, when they found that Balmer series lines were actually multiplets.[21] Bohr, quite sensibly, had made no attempt to address fine structure in his original theory of 1913, and indeed he may not have known of it at the time.[22] In 1916 Sommerfeld[23] showed that there was a first-order relativistic correction that depended on the *azimuthal quantum number* k that was effectively the orbital angular momentum quantum number (or rather, $k = \ell + 1$), which could explain, at least in part, the fine structure.[24] The fact that the relativistic correction depended on ℓ, splitting the $2S$ and $2P$ states for example (Figure 3.1),[25] coupled with the empirical selection rule $\Delta\ell = \pm 1$ meant that spectral lines in the Balmer series of hydrogen ought to be comprised of three lines, because the $n = 3 \to 2$ transition (H_α line) could be $3D \to 2P$, $3P \to 2S$, or $3S \to 2P$.[26] In fact, the $3S \to 2P$ transition is very weak, effectively resulting in a doublet. The relativistic correction amounts to about

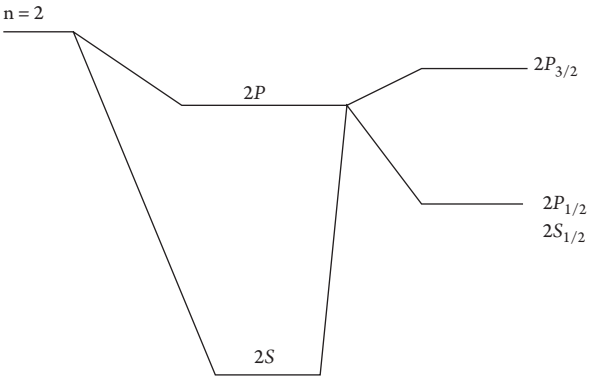

Figure 3.1. Fine structure of the $n = 2$ level in hydrogen. Center: Relativistic correction only. Right: Addition of spin–orbit term. Energies given in cm^{-1}, which was common practice. Richtmyer and Kennard (1942), by permission of McGraw-Hill.

1 part in 10^5, or of the order of 10^{-4} eV, or less than an ångstrom.[27] It depends on α^2, the square of the *fine-structure constant*,[28] and because it also depends on Z^2 (Z being the nuclear charge), it was more apparent in the heavier, alkali metals. It was also stronger in ionized helium, He+, than in hydrogen, because of the higher mass (less Doppler broadening) and higher charge.[29] In hydrogen, according to Sommerfeld, but in modern form,[30]

$$\Delta E_{\text{rel}} = -E_n^2 \Big/ (2mc^2)\Big[4n/(\ell + 1/2) - 3\Big]. \tag{3.1}$$

Thus the H_α Balmer series line in hydrogen, because of the $n = 3$ to $n = 2$ electronic transition, was found to be a narrow doublet, with the lines separated by 0.3 Å.[31]

The Bohr–Sommerfeld theory[32] attempted to explain these splittings in terms of the eccentricity of the electron orbits—implicitly the angular momentum, whence the quantum number k. The empirical selection rule (for electric dipole transitions[33]), Δk or $\Delta\ell = \pm 1$, could also be justified by the correspondence principle.[34] Other "forbidden" transitions were found to occur, with much reduced intensity, not all of which were resolved, less because of instrumental resolution than Doppler broadening coupled with the variable intensities of the lines.[35] Attempts by Sommerfeld and others to calculate the intensities of the spectral lines, in the absence of a real theory, were largely ad hoc. The classification of spectra into series was as much an art as a science, and it cannot be emphasized too strongly how difficult this process of deducing the appropriate quantum numbers from the transition data, that is, the spectra, was complicated by limited resolution and variations in intensity or transition rates. The complexity of unresolved structure is exemplified by the fact that the "diffuse" series was so named because of the "blurriness" of the spectra. But the details of the spectra led to empirical selection rules whose origin would eventually be understood theoretically, and for that reason, the issue is not belabored here. The reader is referred to Sommerfeld's book or other sources such as Andrade or Richtmyer and Kennard.[36]

Experimentally, two things had happened to clarify the situation. First, as spectral resolution increased (better diffraction gratings, for example[37]), it was found that lines were doubled in the alkali metals, as in the case of the well-known Fraunhofer sodium D-doublet,[38] with the large separation of 6 Å. And, as we have seen, under higher resolution, the H_α line in hydrogen was also found to be a narrow doublet.[39] Second, and dating back to 1896, when atoms were placed in a magnetic field, a splitting of the spectral lines that depended on the magnitude of the field was observed—the Zeeman effect. In fact, Zeeman observed only a broadening of the lines initially, which was sufficient to demonstrate that the new phenomenon of the effect of magnetism on light—long sought by Faraday[40]—had been discovered. Lorentz immediately offered a theory that predicted actual splitting of the lines, something that was confirmed when a stronger magnetic field was used (Figure 3.2).[41] Lorentz's theory could "explain" the "normal" Zeeman effect in some situations, as in the case of an atom in which the electron spins coupled to $S = 0$, where often a triplet was observed. But with greater resolution, much more structure became apparent, depending on the magnetic-field strength, with lines first splitting, and then as the field is increased, merging again. Evidently there were atomic energy levels that were degenerate in the absence of a magnetic field, whose energies changed in the presence of the field. Lorentz shared the 1902 physics Nobel Prize with Zeeman for the discovery of the effect and its "explanation."

The discovery, from an analysis of alkali spectra, that levels with a given $\{n, l\}$ were usually split further into doublets (e.g., the splitting of the $3P$ level into $3P_{3/2}$ and $3P_{1/2}$) provided the clue that led to a new quantum number that could take on odd multiples

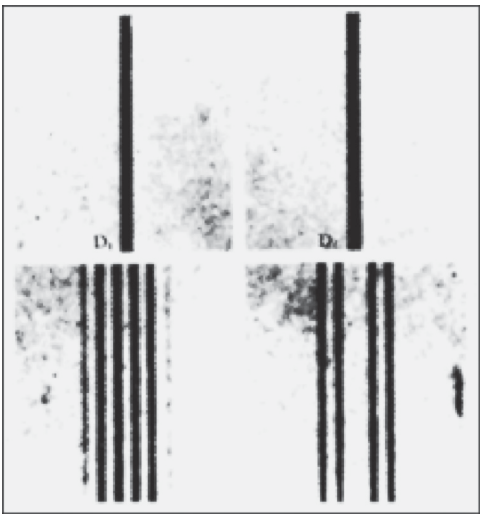

Figure 3.2. Zeeman splitting of the sodium D-doublet in a weak applied magnetic field. The $3p$ level is split by the spin–orbit interaction into $3p_{3/2}$ and $3p_{1/2}$. The transitions to the $3s_{1/2}$ level produce a doublet (top; D_1 and D_2, respectively). Under the applied field, the splitting of the $j = 3/2$ level into four magnetic substates and the $j = 1/2$ levels into 2 produces a pair of doublets for the D_2 line (right) and five lines for the D_1 (left), in Zeeman's photograph. For details, see White (1934), p. 152.

of $1/2$, that is, $\ell \pm 1/2$, resulting in doublets. This new quantum number, *j*, evidently reflected a new degree of freedom that might be a "hidden rotation" and was called the inner quantum number by Sommerfeld.[42] A simple example of this would be an unpaired electron outside an "inert" core, as in the alkali metals (see subsequent discussion). This introduction of half-integer quantum numbers was described by Andrade as "a grave and repulsive step," but one that "seems inevitable."[43] Of course, the situation was even more complicated in the alkaline earths (Group 2: Ca, etc.), where the spins of two electrons were coupled; triplets were observed rather than doublets, and so on.[44]

All of this meant that three quantum numbers were needed to label a state: *n, l, j*. Although it was generally understood that *j* represented a total angular momentum quantum number, the "duplexity" was thought to be due to internal motion of the core.[45] The solution to the problem awaited the introduction of the electron spin, the vector addition of the spin and orbital angular momentum, and the understanding that the fine-structure splitting of levels with different *j* depended on an $\mathbf{L} \cdot \mathbf{S}$ *spin–orbit interaction* (see Chapter 10).

To see how this manifested itself in the case of hydrogen, the *l*-degeneracy (energies depending only on the principle quantum number *n*) meant that the 2*S* and 2*P* levels had the same energy[46] in the absence of the relativistic correction (and the later spin–orbit force). But in fact what was observed with higher resolution and in the Zeeman effect was that the splitting of levels with a given $\{n, l\}$ actually depended on the new quantum number *j*, so that the $2S_{1/2}$ and $2P_{1/2}$ levels were degenerate,[47] but were depressed relative to the $2P_{3/2}$ state. The result was that for a given principle quantum number *n*, there would be *n* levels, all but one of which would be doubly degenerate, e.g., the $3D_{3/2}$ and $3P_{3/2}$ states ($2n - 1$ levels altogether). See Figure 3.1. The important selection rule turned out to be on *j* rather than ℓ: $\Delta j = \pm 1, 0$, though $\Delta \ell = \pm 1$ still obtained.[48]

Thus, to revisit our original analysis, if one takes spin into account, the H_α line should consist of seven distinct transitions (rather than three), i.e.,

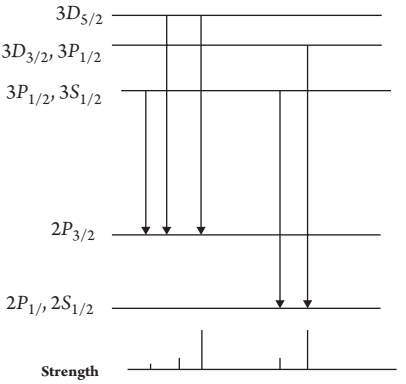

Figure 3.3. Structure of the hydrogen H_α doublet. The doublet results from the strength of the ($3D_{3/2}$, $3P_{3/2}$) → ($2P_{1/2}$, $2S_{1/2}$) and $3D_{5/2} \rightarrow 2P_{3/2}$ transitions. Richtmyer and Kennard (1942). McGraw-Hill, by permission. See the text.

$3D_{5/2} \rightarrow 2P_{3/2}$, $3D_{3/2} \rightarrow 2P_{3/2}$, $3D_{3/2} \rightarrow 2P_{1/2}$, $3P_{3/2} \rightarrow 2S_{1/2}$, $3P_{1/2} \rightarrow 2S_{1/2}$, $3S_{1/2} \rightarrow 2P_{3/2}$, and $3S_{1/2} \rightarrow 2P_{1/2}$.[49] In fact there are five lines, because the $3D_{3/2}$ and $3P_{3/2}$ states are degenerate, as are the $3P_{1/2}$ and $3S_{1/2}$ and the $2S_{1/2}$ and $2P_{1/2}$.[50] But what was actually seen was a doublet (as previously noted) because of a combination of poor resolution and the low intensity of some of the lines (Figure 3.3).[51] Remember that this splitting is due to an applied external magnetic field that removes some of the degeneracy. If nothing else, this shows the complexity faced by Sommefeld and others trying to decipher the spectra and deduce selection rules, even in the simplest case of hydrogen.

Investigation of the effects of external electric and magnetic fields on atoms began with Faraday, and, as we have seen, studies of their effect on atomic spectra date to at least 1896. Karl Schwarzschild and Paul Epstein (a former student of Sommerfeld) provided a successful theory of the *Stark effect* in the framework of the old quantum theory as early 1916.[52] This case was relatively straightforward because the application of an electric field to an atom involved only a perturbing term of the form $-eE_{ext}$ z. But it would be a decade before the Stark effect would be given an explanation in terms of matrix mechanics by Pauli and shortly thereafter by Schrödinger in his third-wave mechanics paper.[53]

In 1916, the same year that the Stark effect was first "explained," Sommerfeld[54] and Debye[55] provided a semiclassical, but nonetheless quantum, description of the Zeeman effect, but the proof was at best incomplete in that, as with Lorentz's classical theory, there were cases for which this semiclassical theory seemed to work, and others for which it did not. The obvious importance of the Zeeman effect was that the application of an external magnetic field exposed a hidden multiplicity, that what appeared to be single lines were actually multiplets.[56] In other words, there was a degeneracy (a symmetry) that was broken by the presence of a magnetic field. As was realized by George Uhlenbeck and Samuel Goudsmit in 1925, the introduction of an electron spin would result in an interaction between the external magnetic field and the coupled orbital and spin moments $[\mathbf{B} \bullet (\mathbf{L} + 2\mathbf{S})]$ that had previously not been suspected. For these reasons, the "anomalous" Zeeman effect (to use the language of the time[57]) was a powerful motivation for both the Pauli principle and the hypothesis of spin and provided a test of those hypotheses as well. Shortly after matrix mechanics was formulated, and not long after the acceptance of the intrinsic spin hypothesis, Heisenberg and Jordan[58] provided the first modern explanation of the Zeeman effect, and George Darwin elaborated upon it the next year.[59] See Chapter 10.

It would turn out that in the alkali metals (Li, Na, K . . .), with a single-valence electron outside an inert core (the so-called core model; later termed filled shells)[60] and where the spectra were found to resemble hydrogen, there were two physical processes involved in the splitting of levels with a given principal quantum number *n*. One was the fine structure previously mentioned—which itself had two distinct origins—and the second, which was understood as a measure of the mean attractive potential felt by the electron (screening[61]), was the degree to which the electron penetrated toward the nucleus, hence the eccentricity of the electron orbit. Thus in the alkalis, levels with a given quantum number *n* were split even without the fine structure. For example, the

3*S* ground state was well below the 3*P* level in sodium because of screening.[62] In the end, these alkali atoms exhibited spectra that resembled that of the Lyman series in hydrogen, but there were multiple series of lines with decreasing spacing and intensity, which came to be labeled *sharp, principal, diffuse,* and *fundamental* (or *Bergmann*).[63] These were explained by Sommerfeld in terms of the azimuthal quantum number *k* (or, alternatively, the eccentricity of the electron orbit). It was assumed that the angular momentum of the "core" was zero. Needless to say, the situation quickly became more complicated as one moved to the alkaline earths, e.g., calcium, but even in the case of helium, for different reasons.

To look more closely at these alkaline metals, with one electron (that we now know has $s = 1/2$) outside a closed shell, we find, as before, that there are two values of *j* for each ℓ: $j = \ell \pm 1/2$, with only the *S* terms[64] being single. The doublets with different *j*, e.g., the $D_{5/2}$ and $D_{3/2}$, are split by the spin–orbit interaction (see Chapter 10), with the higher *j* term usually higher in energy. Then for $D \rightarrow P$ transitions, for example, the allowed transitions between the $D_{5/2}$, $D_{3/2}$ doublet and the $P_{3/2}$, $P_{1/2}$ doublet would yield a triplet of lines: $D_{5/2} \rightarrow P_{3/2}$, $D_{3/2} \rightarrow P_{3/2}$, and $D_{3/2} \rightarrow P_{1/2}$. The result is that the alkali spectra would in general consist of doublets (or triplets with one line very weak).[65] Although spin has been introduced into the discussion, it is important to remember that all of this analysis was accomplished without any plausible theory; that is, was only a heuristic deduction from observation, well before the physical reason, electron spin, and any theoretical justification for odd half-integral quantum numbers.

Already in neutral helium, the complications resulting from two or more active elections became apparent, and the alkaline earths posed similar problems. Only limited progress could be made in classifying these spectra before spin was introduced, because a real understanding involved coupling of the spin and orbital angular momenta. The reader is referred to the many books on atomic structure, but especially those at by Condon and Shortley.[66] Even after the introduction of spin, understanding of the spectra of atoms with one and two electrons was mostly qualitative, dominated by empirical rules for intensities.

The case of neutral helium, however, has special historical interest, particularly because the inability of the Bohr or Bohr–Wilson–Sommerfeld theory to describe the optical spectrum highlighted the need for a much better theory. As Sommerfeld wrote of neutral He in 1919, " . . . to overcome the extraordinary mathematical difficulties, new methods will have to be worked out."[67] Eventually it was found that helium showed two series of terms, or levels, known as *orthohelium* and *parahelium*, with no transitions between the two.[68] After the discovery of spin, it was realized that the distinct systems were characterized by either spin triplet ($S = 1$; orthohelium) or singlet ($S = 0$; parahelium) states of the two electrons. This meant different spin symmetry, and, as a consequence, different spatial symmetry, by means of the exclusion principle. Transitions between the two would involve a parity change. Clearly this understanding was not possible before Pauli formulated the exclusion principle in 1924 and before electron spin was "discovered" the next year. By 1926, Heisenberg was able to give the first theoretical explanation.[69]

SPACE QUANTIZATION

There are two ironies associated with the Stern–Gerlach experiment of 1922,[70] one of the most famous experiments of modern physics, one that demonstrated the quantization of the direction of the angular momentum vector of the electron (Figure 3.4). The first is that it is almost never mentioned that the experiment was designed to *verify* the hypothesis of space quantization, discovered theoretically by Sommerfeld using the old Bohr–Sommerfeld quantization principle.[71] The second irony is that the experiment, using a beam of neutral silver atoms, although an experimental tour de force, was misunderstood at the time, because spin had not yet been discovered.[72] Thus the observed quantization was assumed at the time to involve the orbital angular momentum or, more specifically, the magnetic dipole moment of the atom. It was in fact spatial quantization of the electron spin, something that was not made fully clear until 1927, when hydrogen atoms were used, by which time the electron spin had been introduced.[73]

Otto Stern and Walther Gerlach took the angular momentum of the silver atoms to be $\ell = 1$, in which case, according to an argument of Bohr's, based on Sommerfeld's theory, the beam should split into two, which is what was observed, thus confirming space quantization.[74] But because the angular momentum of a silver atom in its ground state is $\ell = 0$,[75] they actually should have seen no effect at all, or if the ground state had had $\ell = 1$, they should have seen the beam split into three. The effect Stern and Gerlach saw was due to electron spin, which, in effect, they had discovered.[76]

By 1924–1925 it was becoming clear from the fine structure in alkali spectra that there was a "new non-relativistic cause, that however obeys an equation almost exactly like the relativity equation," to quote Robert Millikan and I. S. Bowen, a guess that turned out to be correct, as we will subsequently see.[77] In that year, 4 years after Sommerfeld introduced the inner quantum number *j*, his former student Pauli, again

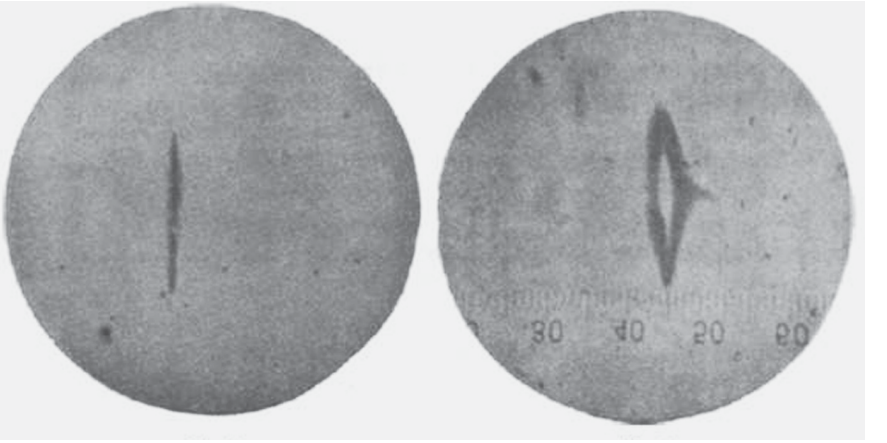

Figure 3.4. Deposits of silver showing splitting of the beam of silver atoms with (right) and without (left) an applied inhomogeneous magnetic field. Gerlach and Stern (1922b), by permission of Springer.

from purely spectroscopic considerations, emphasized the need for an additional double-valued quantum number to explain the "duplexity"—"a two-valuedness not describable classically"[78]—of the doublets. Pauli showed that the new angular momentum could not be due to rotation of the core,[79] and yet he rejected the idea that it might be due to a spinning electron as Ralph Kronig suggested to him in January 1925.[80] As it turned out, the additional fundamental quantum number would be the spin quantum number s rather than j, which could be then be derived from (l, s), depending on how the angular momenta were coupled.[81]

As we will see in Chapter 10, the proposal of electron spin had been made by Compton[82] as early as 1921, somewhat later by John Slater,[83] then by Kronig, and ultimately by Uhlenbeck and Goudsmit, who took the final step of introducing the electron spin, carrying angular momentum $\hbar/2$, at the end of 1925 and then early the next year.[84] The challenges presented by both fine structure and the Zeeman effect were pointing toward a new degree of freedom and a related interaction, that is, entirely new physics.[85]

ANGULAR MOMENTUM COUPLING

A theory of angular momentum coupling, which had to precede any calculation of spin–orbit coupling or the Zeeman effect, led to an exploration of alternative ways of carrying out that coupling. This would ultimately lead to consideration of mutually commuting angular momentum operators and to transformations from one coupling scheme to another, once quantum theory had been born.[86] These considerations would arise particularly in the case of the Zeeman effect because of the competition between the spin–orbit and Zeeman parts of the Hamiltonian, depending on the strength of the external field.[87] In the weak-field case, fine structure dominated and was part of the "unperturbed" Hamiltonian, whereas in the strong-field case, the Zeeman Hamiltonian dominated. Prior to 1925, there was much groping in the dark, attempting to understand the perplexing experiments, but as Condon and Shortley[88] wrote, "The Paschen-Back effect [strong-field Zeeman effect] was important in the pre-quantum-mechanical theories of atomic spectra for the information it gave about the coupling relations." The point here is that angular momentum coupling, that is, vector coupling, had to be addressed even before the quantum-mechanical implications were evident.

As early as 1921–1922, Alfred Landé had derived empirically what is now known as the Landé g-factor to which the weak-field Zeeman splitting is proportional:

$$E_Z = \mu_B g\, B_{\text{ext}} m_j,$$

where μ_B is the Bohr magneton $e\hbar/2m$. The g-factor is just a consequence of angular momentum coupling. Landé was the first to make the identification $J^2 \to j(j+1)$, again for empirical reasons, in the process of obtaining the factor that bears his name.[89] It is really in the Born–Heisenberg–Jordan (BHJ) paper that we discuss in Chapter 5,[90] however, that familiar angular momentum algebra appears for the first

time, and virtually the full apparatus appeared in a paper by Heisenberg and Jordan, published later the same year.[91] Our focus here, of course, is on the spectroscopic data that led to these discoveries, beginning in 1925.

Consideration of the Zeeman and Stark effects, especially the former, was important in clarifying some of these issues, and it was here, along with the 1922 Stern–Gerlach experiment, that magnetic quantum numbers (space quantization) emerged for the first time. After spin became routine, that is, after 1925, the spectroscopic notation of the form ${}^{2s+1}X_j$, became standard, where $X = S, P, D, F$, denoting the angular momentum quantum number ℓ, and the $2s + 1$ factor indicating the multiplicity of the electronic spin state. Between about 1916 and 1926, angular momentum coupling morphed from being a heuristic tool of spectroscopy and spectroscopists to an integral part of the theory and an example of the application of transformation theory, as the formal structure of quantum mechanics developed (Chapter 8).[92]

HYPERFINE STRUCTURE

Hyperfine structure, due to the nuclear magnetic moment, was observed by Michelson as early as 1881, over three decades before the Bohr theory, and over 40 years before the discovery of electron spin and its accompanying magnetic moment.[93] Ironically, in 1924 Pauli, had suggested that the *nucleus* might have a magnetic moment, well before he was willing to accept electron spin.[94] In the simplest case of hydrogen, hyperfine structure originates in the interaction between the spin magnetic moments of the proton and that of the electron. It is reduced in magnitude relative to fine-structure splitting by the ratio of the electron to proton mass, about 1/1836. This interaction splits the ground electronic state of hydrogen into a singlet state of the coupled spins and a higher triplet state, the difference being the cause of the well-known 21-cm radiation utilized in modern radio astronomy to map the interstellar distribution of hydrogen. An additional contribution to hyperfine structure in heavier nuclei comes from the interaction between the nuclear electric quadrupole moment and the gradient of the atomic electric field, which provided the first evidence of nuclear quadrupole moments, and in complex molecules there can be a contribution from the interaction of nuclear spins. We discuss the first attacks on hyperfine structure in the framework of the new quantum theory in Chapter 15.

CONCLUSION

In closing this survey of the spectral data up to about 1925 that the new quantum theory had to explain, it is worth recalling the enormous amount of effort by Arnold Sommerfeld and many others to organize and interpret the data and to find rules and regularities in them—some of which were important, others of which were not—a situation that is dramatically exhibited in the several editions of Sommerfeld's famous book on atomic and x-ray spectra, *Atombau und Spektrallinien* [*Atomic Structure and Spectral Lines*]; the English translation of the third German edition of 1922[95] runs to

over 600 pages. These data and their phenomenological interpretations were the raw material with which the younger generation of theorists had to work.

The theoretical tools available in the years leading up to 1925, in addition to the correspondence principle, consisted mainly in the Bohr–Sommerfeld–Wilson quantization condition $\int p_i \, dp_i = n_i \hbar$. This old quantum theory met its demise in 1924–1926 with the radical proposals of de Broglie, Heisenberg, and Schrödinger. To many it was a "paradigm shift" in the sense of Thomas Kuhn, but Sommerfeld did not see it that way. In the introduction to the *Wave Mechanics Supplement* to his *Atombau* published in 1928–1929, and reflecting the astonishing developments of the previous 3 years, he wrote that "the new development does not signify a radical change but a welcome evolution of the existing theory."[96]

Finally, it was during the first three decades of the century that the distinction between theoretical and experimental physicists began to be a very sharp one, one that has become sharper with time. Someone like Sommerfeld could play a universal role, even if he wasn't in the laboratory himself, and important experimentalists like Rutherford, Stark, Lenard, and Friedrich Paschen were held in the highest repute and usually held the most important professorships. Yet pure theorists like Planck, Einstein, Poincaré, and Bohr were making what would turn out to be the fundamental discoveries, despite some suspicion of them,[97] and the careers of Heisenberg, Born, Jordan, Pauli, and Dirac were about to blossom. Only Lorentz, perhaps, had a renown equal to that of the important experimentalists, who dominated the Nobel awards in this period.[98] And although the early development of quantum mechanics was driven entirely by the experimental results we have discussed, the conceptual revolution that the new quantum theory spawned, while by no means losing its contact with experiment, was above all a revolution in theoretical physics. The discoverers of the new quantum theory—Heisenberg, Born, Jordan, Dirac, Pauli, Eugene Wigner, von Neumann—all occupy an honored place in the history of physics, whereas the names of those experimentalists without whose results there would have been no quantum revolution are largely, and unjustly, forgotten.

NOTES

1. The conundrum of the localization of the quantum of light as against its familiar and obvious wave properties weighed heavily on the minds of people like Bohr until most were converted by Compton's arguments. See Rosenfeld (1971).
2. In a time when experiment had a status much superior to theory, unlike the present situation in physics.
3. An interesting source on the state of atomic spectroscopy is Andrade's (pronounced "ann draid") *The Structure of the Atom*, first published in 1923, with a third edition in 1927 (Andrade, 1927). He had worked with Rutherford a decade earlier. Another good source is the second volume of Whittaker's *A History of the Theories of Aether and Electricity* (Whittaker, 1953), especially chapter IV. See also Sommerfeld, *Atombau und Spektrallinien*, 1919 [*Atomic Structure and Spectral Lines*]; (Sommerfeld, 1919, 1923).
4. Geiger and Marsden (1909). See Chapter 15.

5. Here I speak of orbiting atomic electrons, and not the number of electrons thought to be in the nucleus to provide the attraction necessary to bind the nucleus. Again, Chapter 15.
6. Barkla (1911).
7. Sommerfeld (1923), p. 62 . After receiving his doctorate at Göttingen under Felix Klein, Sommerfeld found his way to Munich as professor of theoretical physics in 1906 and stayed there for 32 years. He died in 1951 in a traffic accident while walking his grandchildren (Wikipedia).
8. Something van den Broeck had suggested in 1913 (van den Broeck, 1911).
9. Well described by Sommerfeld himself (1923).
10. This was a recognition that a given line represented a transition between a pair of states or "terms," so that in general the number of terms was much less than the number of possible transitions. Specifically, the Rydberg–Ritz combination principle (1908) required that the frequency of a spectral line be either the sum or the difference of the frequencies of two other spectral lines (Ritz, 1908a). Ritz wrote that "By additive or subtractive combination . . . formulae are formed that allow us to calculate certain newly discovered lines from those known earlier." Quoted in Sommerfeld (1923) p. 205. Or, "every series term can be combined with any other to form a spectral line." Ibid, p. 334. Interestingly, David Hilbert was defeated by this problem much earlier, around the turn of the century, when he attempted to relate spectral lines to eigenvalues of linear operators. See Elsasser (1971).
11. Four of his students won Nobel Prizes, as did three of his postdoctoral students. He was reportedly nominated 81 times himself. See also n. 23 of this chapter.
12. This was especially true of the Zeeman effect.
13. Wollaston (1802).
14. Kirchoff and Bunsen (1860). See also Pais (1995), n. 117.
15. Balmer (1885).
16. For precursors of Bohr, including Conway, Bevan, Nicholson, and Ehrenfest, see Whittaker (1953), chapter IV.
17. Zeeman (1897b, 1897c). The splitting was first reported in the *Philosophical Magazine* for July 1897 (1897b) but was not reported in a March paper (1897a). Faraday had looked for such an effect of magnetism on light without success, because of poor resolution. In the first paper, in which he saw only broadening of the lines (but noted that Lorentz's theory predicted a triplet), Zeeman (1897a) quoted Faraday on his experiments.
18. Or "Stark–Lo Surdo" effect after the Italian Antonio Lo Surdo. Ironically both Stark and Lo Surdo supported Fascist movements in their respective countries (Stark et al., 1914). Stark was a prominent supporter of Nazism and Adolph Hitler, denounced "jewish physics" and especially Einstein, and called Heisenberg a "white jew."
19. It is perhaps worth noting that absorption and emission (arc, spark) spectra were quite different in that in general most atoms were in very low-lying or even ground states when they absorbed light.
20. Bohr (1913b), with a follow-up paper by Fowler. Also Bohr (1913a, parts I and II). The data were E. C. Pickering's measurements of absorption lines in the star ζ Puppis (Pickering, 1896). See Whittaker (1953), pp. 113–14. The Rydberg constant had to be modified to account for the different reduced mass.
21. Michelson and Morley (1887). There they speculate that the Hα line is a doublet in the final sentence of the paper.

22. Kragh (2003) says "ignored." It seems plausible that Bohr did not know of even the Balmer formula until the fateful year of 1913. See Pais (1995).
23. Because Sommerfeld's name does not appear often in subsequent chapters, his role in the transition from the old to the new quantum theory should be recognized here. He is generally regarded as the greatest mentor in the history of modern physics, having guided future Nobel Laureates Heisenberg, Pauli, Debye, and Bethe, plus dozens of influential physicists including Pauling, Rabi, von Laue, Peierls, Meissner, Landé, Brillouin, and many others. It is without apology that I recommend the Wikipedia article on Sommerfeld.
24. Shown by Sommerfeld in 1916, following a suggestion by Bohr. See Kragh (2003).This was taken to be an important confirmation of the still-controversial special relativity in 1916.
25. The somewhat archaic notation, in which $\ell = 0, 1, 2, 3\ldots$ states are labeled *S, P, D, F*. . . (or *s, p*, . . .) is a relic of the identification of spectral series in the alkalis: "sharp," "principal," diffuse," "fundamental," etc. We can see the evolution of this notation in chapter 10 of Ruark and Urey (1930), chapters 5 and 6 in Pauling and Goudsmit (1930), and chapters 5–8 in White (1934). In the latter, capital letters *S, P*, . . . are used for the states or "terms," whereas *s, p*, . . . are used for the electron orbitals. There is also the "Lamb shift," which is proportional to α^5, the fifth power of the fine-structure constant, in hydrogen, hence 2 orders of magnitude smaller than fine structure.
26. Note the subsequent discussion of further splitting. In slightly different notation, the doublet resulted from (n,ℓ) transitions from $(3,1)\rightarrow(2,0),(3,2)\rightarrow(2,1)$, and $(3,0)\rightarrow(2,1)$, with the last being weak.
27. The Balmer series lines being in the visible have wavelengths of the order of 4000–7000 Å.
28. Actually, α^2 relative to the Bohr energies. $\alpha = e^2/\hbar c = 1/137$, approximately (and dimensionless!), and introduced by Sommerfeld. For a time it was thought that it might be a "pure" number, i.e., 1/137 exactly. Whittaker (1953), for example, treats this as a fact.
29. Thus Paschen, who provided Sommerfeld with spectroscopic data, emphasized He^+. See Kragh (1985).
30. Derived in Griffiths (2005), p. 267, for hydrogen, but quantum mechanically. See also Ruark and Urey (1930), p. 135; White (1934), pp. 136–7. Sommerfeld (1923), p. 259, writes this, essentially, as $(\alpha^2/4n^4)Z^2(4n/n_\varphi - 3)$, where $\alpha = 2\pi e^2/hc$, the fine-structure constant and n_φ is the azimuthal quantum number, the same as k (equal to $\ell+1$). Heisenberg and Jordan (1926) carried out the first quantum-mechanical treatment of the relativistic correction.
31. See n. 25 in this chapter. The notation *K,L,M,*. . . ,for principle quantum number $n = 1,2,3,\ldots$ comes from early studies of x-ray spectra.
32. An essential ingredient of which was the Sommerfeld–Wilson quantization rule: $\int p_i \, dq_i = n_i h$. See, for example, Sommerfeld's book on atomic spectra (Sommerfeld, 1919, etc.); much attention is given to the Kepler problem.
33. Rubinowicz (1918a, 1918b).
34. Which would argue that a conclusion based on a calculation for small quantum numbers should merge with the classical result at large quantum numbers, which meant that, in practice, a quantum result could be inferred from the classical one.
35. For details, see Sommerfeld (1919, etc.) or Richtmyer and Kennard (1942), chapter VIII.
36. Richtmeyer and Kennard (1942); see also their 1928 and 1934 editions. Andrade (1927) includes the modern developments only in passing. Also Ruark and Urey (1930), White (1934). On Sommerfeld, see the several references given in previous notes.

37. See the AIP biography of Henry Rowland: (https://www.aip.org/history/gap/Rowland/Rowland.html).
38. Because of the difference in energy between the $3p_{3/2} \rightarrow 3s_{1/2}$ and $3p_{1/2} \rightarrow 3s_{1/2}$ transitions. Here D is the Fraunhoffer notation for the doublet in the yellow in the solar absorption spectrum due to sodium.
39. This as early as 1887, by Michelson and Morely (op. cit.)
40. Faraday had discovered the rotation of the plane of polarization of an electromagnetic wave in a magnetic field in 1845.
41. Zeeman was an assistant to Lorentz, and eventually a colleague, at Leiden, and shared the 1902 Nobel Prize in physics with his mentor. See Kox (1997). Lorentz's entirely classical theory predicted doublets ("longitudinal effect") or triplets ("transverse effect"), usually the latter. By the time his *The Theory of Electrons* was published in 1909, based on lectures given at Columbia nearly 3years earlier, it had been found that sometimes 4 or 6 or even more lines were seen (Lorentz, 1909, p. 103). At the time it was not understood that spectral lines resulted from *transitions between levels.* See also Ruark and Urey (1930), p. 143.
42. "innere quantenzahl," Sommerfeld (1920), p. 231. See also Sommerfeld (1923), p. 364. It was thought possibly to be due to angular momentum of the atom's core, which was not so radical in the context, k or l representing orbital motion. A state, then, would be characterized by the three quantum numbers n, ℓ, and j. Eventually $s = 1/2$ would be added, and of course $m_s = \pm 1/2$. This led to the notation nX_j that evolved in the early 1920s and has been standard since then. Whence the notation j (or J) for total angular momentum, and Landé thought the new quantum number represented a total angular momentum. Hendry has likened these almost ad hoc adjustments of the theory to Greek and medieval attempts to "save the appearances." Hendry (1984), pp. 39–41.
43. Andrade (1927), p. 510.
44. In the level structure; the spectra showed bands of five lines. See Millikan (1935), p. 286.
45. For example, Andrade, p. 299.
46. The "Lamb shift," from quantum electrodynamics, does remove the l-degeneracy in hydrogen, so that the $2P_{1/2}$ and $2S_{1/2}$ levels are split. (Lamb and Retherford, 1947).
47. The theoretical explanation (see Chapter 10) is that in a one-electron atom the relativistic and spin–orbit terms are of the same order of magnitude and can be combined into an expression that depends only on j. See, for example, Griffiths (2005). Note that the spectroscopic notation ($^2S_{1/2}$) has changed also. Perhaps this is the point at which I should emphasize that when we speak of an electronic energy level we are really talking about the energy of the atom when the electron is in a particular state. The change of state of a single electron affects the potential and kinetic energies of all electrons.
48. Although this could be ignored because a pair of levels with a given (n,j) could be treated as one level. See Richtmyer and Kennard (1942), sec. 149.
49. Neglecting transitions such as $3D_{1/2} \rightarrow 3P_{1/2}$ that involve small energy differences and would not be in the optical spectra.
50. So that the previous third and fourth transitions had the same energy, as did the fifth and seventh. This meant that the $3D \rightarrow 2P$ line was split into three lines (first–third), $3P \rightarrow 2S$ into two (fourth and fifth), and $3S \rightarrow 2P$ into two (sixth and seventh).
51. The way this was worked out was that when the broadened $3 \rightarrow 2$ Hα transition was resolved, it was found to consist of three closely spaced lines, as we saw earlier. This could be understood as consisting of $3D \rightarrow 2P$, $3P \rightarrow 2S$, and $3S \rightarrow 2P$ transitions [see fig. 1 in

Ladenburg (1921)]. But these lines were found to be broadened as well, and under higher resolution it was found that there were five lines contributing to the $3 \rightarrow 2$ transition. This is because the fine-structure correction depends only on *j*, levels with a given *j* but different *l* ($2P_{1/2}$, $2S_{1/2}$) are degenerate. Three of the transitions are weak or unresolved, resulting, effectively, in a doublet. See the earlier discussion in the body of the chapter. See also White (1934), sec. 9.3.

52. Epstein (1916). See Whittaker (1953), p. 121.
53. Pauli (1926a), Schrodinger (1926d), sec. II.
54. Sommerfeld (1916a). See also his discussion in chapter VI of his Spektalinien, pp. 406–12 (Sommerfeld, 1923).
55. Debye (1916).
56. Thus differing from other cases, as, for example, fine structure, for which the existing structure was revealed at higher resolution. It was not initially clear that the magnetic field had not *caused* the multiplicity, as opposed to revealing it.
57. Which was anomalous only because it disagreed with Lorentz's theory because spin had not yet been discovered. There is really only one Zeeman effect.
58. Heisenberg and Jordan (1926). On the process of carrying over the semiclassical "vector model" of angular momentum into quantum mechanics, see Back and Landé (1924) and also Biedenharn and van Dam (1965), p. 2.
59. Darwin (1927).
60. In the alkalis, for example, the core would have zero angular momentum. Bohr tried treating *all* atoms as a kernel or core with one electron outside it, without success. See Andrade (1927), p. 553.
61. So that the electron feels a potential different from that due to a point nucleus.
62. Similarly in lithium, the 2*S* level was well below the 2*P*, which was very close to the $n = 2$ level in hydrogen.
63. The principle series involved $nP \rightarrow 3S$ levels, the sharp, $nS \rightarrow 3P$, the diffuse, $nD \rightarrow 3P$, etc. The series corresponded to $k = 1,2,3,4$ or $l = 0,1,2,3$.
64. "Term" was widely used in the early empirical literature to mean, essentially, a "level," often expressed in terms of energy/*hc*. See, for example, "Atomic states and spectral terms," McLennan et al. (1926). From White (1934), p. 88: "The terms energy level, energy state, and term, are to be considered more or less synonymously and are often used indiscriminately."
65. See Richtmyer and Kennard (1942), sec. 147. See also White (1934), fig. 8.4 It is important to be careful about whether we are talking about levels (terms) or spectral lines, which of course involve transitions between two levels. In the example, the $D_{3/2} \rightarrow P_{3/2}$ line, with $\Delta j = 0$ and $\Delta \ell = -1$ would typically be weak.
66. Condon and Shortley (1935). Also White (1934).
67. Sommerfeld (1923), p. 69. He also expressed the hope that some of Bohr's new ideas would provide the solution, referring to Bohr (1921).
68. Motivating some to think that helium was a mixture of two gases.
69. Heisenberg (1926b).
70. Gerlach and Stern (1922a, 1922b, 1922c). They used a collimated beam of silver atoms from a furnace. See Bernstein (2010) or Bohm (1951).
71. Sommerfeld (1916a). It was, in fact, the principal theoretical triumph of that theory. As Pais (1991, p. 186) notes, this "quantum phase integral," most often associated with the

names of Bohr and Sommerfeld, was discovered by William Wilson, but credit is also due the Japanese physicist Ishiwara and Planck.

72. For example, Weinert (1995).
73. Phipps and Taylor (1927). Stern had written a paper in 1921 titled "A method using a magnetic field to demonstrate space quantization"; see Bernstein (2010).
74. Bernstein (2010). See also "Wrong theory—right experiment: The significance of the Stern–Gerlach experiments," Weinert, (1995). See also the elaborate discussion in Sommerfeld (1923), pp. 242–52.
75. That is, the valence electron is in the 5*s* state. The entire configuration is [Krypton] $5s^1 4d^{10}$. Neither the single *s*-electron or the 10 *d* electrons contribute to angular momentum in the group state.
76. Mehra and Rechenberg (1982–2000) give a detailed description of Stern and Gerlach's experimental efforts and the attempts to understand the results theoretically (vol. 1–2, chapter IV).
77. Millikan and Bowen (1925). The quote is on p. 122.
78. Pauli (1925b), p. 765.
79. Pauli (1925a), p. 373.
80. See Chapter 10.
81. Sommerfeld (1923) quotes Landé as having said that the two different values of the inner quantum number were due to "the two different possible ways of circulating of the atomic trunk [core]."
82. Compton (1921a, 1921b).
83. Slater (1925).
84. Uhlenbeck and Goudsmit (1925, 1926). Both were strongly influenced by Ehrenfest's mentorship Ehrenfest, in turn, was a student of Boltzman; both died by their own hands.
85. Namely, a precession of the electron spin about an axis defined by the magnetic field due to the electron's orbital motion in the field of the nucleus (Uhlenbeck and Goudsmit, 1925,1926). Indeed they said that "the introduction of the spinning electron was primarily suggested by the analysis of the anomalous Zeeman effect."
86. This is also discussed in Chapter 11. The original scheme of Sommerfeld involved the quantum numbers *r, k,* and *j*, where *r* represented the angular momentum of the atomic core, *k* (or ℓ) the angular momentum of the electron, and *j* the total angular momentum. Andrade, however, noted plaintively that "the quantum numbers chosen for compounding according to a vector scheme are not the simple r, k, j of our childhood's dreams, but numbers related to them" [Andrade (1927), p. 512].
87. See any text on quantum mechanics, e.g., Griffiths (2005), pp. 273–83.
88. Condon and Shortley (1935). Quoted from 1964 edition, p. 390.
89. Landé (1921). The Landé *g*-factor is essentially a Racah coefficient.
90. Born, Heisenberg, and Jordan (1926).
91. Heisenberg and Jordan (1926). The paper follows immediately that of Frenkel (1926).
92. White's *Introduction to Atomic Structure* of 1934 not only presents atomic theory as understood in that period, but gives an excellent historical introduction that elaborates on the Bohr–Wilson–Sommerfeld theory.
93. Hyperfine splitting in Cesium-133 is now used as the basis for the second, the SI unit of time.

94. Pauli (1924). To the extent that this represents the first suggestion of intrinsic angular momentum, it is interesting that Pauli was so resistant to the idea of electron spin, even if one understands why (Chapter10).
95. Sommerfeld (1923).
96. Sommerfeld (1930).
97. This took an ugly turn in the 1930s, in the form of a reaction against theoretical physics, and especially "jewish physics," at the hands of Stark, Lenard, Gehrcke, and other adovcates of "Aryan physics."
98. Lorentz was a laureate in 1902; the next theorist was Planck in 1918.

4

QUANTUM THEORY ADRIFT
WORLD WAR I

INTRODUCTION

The four decades or so between the Franco-Prussian War and the start of WWI represent a period of radical change, especially in the arts, that saw a near-complete overthrow of old ways of thinking. The conclusion that the radical changes in physics around the turn of the century [*fin de siècle*], in relativity and quantum mechanics, are part and parcel of this turn away from old ideas, is inescapable. So huge was the transformation that even the horrors of the war failed to halt it, though the optimism of the prewar years turned to widespread pessimism.[1] It was in this context that quantum theory was born, and although the way in which its origin and evolution was influenced by the cultural milieu is controversial and beyond the scope of this work, it should not be forgotten.

The 5 years of WWI produced something of a hiatus in the accumulation of spectroscopic data and attempts to explain it, and it was really not until 1920 that the problems could again be attacked with vigor. The war had been prosecuted mainly in France, but the human resources of Britain, France, and Germany were all devastated, as 16 million, mostly young, men died in the trenches or from disease.[2] It is ironic that this happened to the very age group that would have been expected to carry physics forward, and yet only 7 years after the Armistice the new quantum theory was born, in spite of the many obstacles of these postwar years. There is a further irony in the fact that the interregnum was appallingly brief and that only 8 years after the creation of quantum mechanics, burgeoning German anti-Semitism decimated the scientific capital of that nation again, as the scientific elite fled the new militarism and persecution. For all that, it was a remarkable decade-and-a-half, following the Armistice.

Progress on the development of a quantum theory was slow and halting until the war had finally run its course in 1918. Its aftereffects lingered for more than a decade and led, in due course, to the rise of National Socialism. As we saw earlier, in Germany everyone and every institution was affected by the war, and although many were eligible to fight, few established physicists actually saw combat, because their talents were put to use elsewhere. As hostilities drew to a close, the Spanish flu epidemic of 1918 added to the terrible human cost of the conflict,[3] and hyperinflation in the early 1920s made life miserable for everyone and, in particular, seriously affected the universities. The postwar economic hardships increased competition for funding, widened the gulf between the haves and have-nots, and gave rise to political divisions that in many cases

were exacerbated by the resistance of conservative physicists to relativity and quantum mechanics and a growing hostility to theoretical physics. This issue of "Jewish physics" came to a head in 1933, with the collapse of the Weimar Republic, but there was no shortage of anti-Semitism, even during the war when many German Jews fought for their country. Who can say how many young men who might have matured as physicists between 1914 and 1918, on both sides in the conflict, never began their careers because of the war? In the end, it may be that the main effect of the war on the development of quantum mechanics was to delay it by almost a decade, during which there was much mulling over of the issues, but it also skewed research efforts toward theory, given postwar privations, especially in Germany.

Important work was done in the years immediately preceding the conflict, notably by Sommerfeld, Bohr, Frank and Hertz, Moseley, and William Henry and William Lawrence Bragg, to name just a few. And in some centers research persisted throughout the war years, as at Munich, where Sommerfeld and his students[4] continued to explore the mysteries of quantization, including an attempt to quantize the elliptical Keplerian orbits. Beyond the direct effects on the lives of the figures who had, or might have had, a place in this narrative, the war, which was the most disruptive event in the entire history of Europe up to that time, deeply affected the culture that in a broad sense spawned quantum theory.[5]

At the start of the war Sommerfeld was 46, and thus exempt from service, and Einstein, who turned 35 in 1914, had been a Swiss citizen since 1901. Having just returned to Berlin in 1914, Einstein was one of a small number of physicists who opposed the war. In these prewar years he was struggling with the general theory of relativity, finishing it in 1916 and applying it to cosmology the following year, which was also when he published his famous paper on stimulated emission.[6] But even for those too old to serve, and of course for those who survived military service, the privations of the postwar period, with runaway inflation, the situation was difficult, which makes even more remarkable the achievements of the first decade following the war. Many physicists, especially in Germany but also in England, did contribute to the war effort, some of it quite willingly, and indeed there was an appalling amount of patriotic chauvinism, including that of Max Planck, who was nearing 60 in 1914—hence not vulnerable—but who was especially prominent in this movement.[7] Bohr was not quite 30 when the war began, but Denmark was neutral and he was unaffected; one of his most important papers was published in 1918, just as the war was ending. Schrödinger, who was slightly younger than Bohr, served during the entire war, including combat duty on the Italian and Hungarian fronts where he commanded an artillery battery, far from the greatest carnage. Other physicists were young enough to serve, of course, including the young Englishman H. G. J. Moseley, who died at Gallipoli in 1915, age 28.[8] There were many fewer students during the war years, and the impact of the slaughter in reducing the ranks of those who might have done physics was felt for several decades. The privations that resulted from Germany's loss in the war had an impact on research funding, which were further exacerbated by the effects of inflation. Especially in Germany, everyone suffered from the rapid decline in living standards.

Among examples of those whose careers were interrupted by WWI was Louis de Broglie, who spent the war working on radio communications, returning to school after the Armistice to obtain his doctorate in 1924 on wave–particle duality. Max Born, who was born in 1882, 3 years Einstein's junior, was of military age when the war began and spent some time in the German Army. Starting as a radio operator, he was soon transferred to artillery and acoustic research in Berlin.[9] Franck and Hertz both spent time in the German Army.

On the other hand, the cohort that would create quantum mechanics (not including Born and Schrödinger)—Pauli, Heisenberg, Jordan, Dirac, Wigner, and von Neumann—were all born within 3 years of the turn of the century[10] and were only teenagers during the war. Nonetheless, although Heisenberg and Pauli, from this next generation, were 13 and 14, respectively, when the war broke out, they would be affected by its aftermath and the buildup to the next one.[11]

It is clear, then, that the war produced a distinct hiatus in progress toward a coherent theory of quantum phenomena, whether because of economic chaos, difficulty of communication, nationalism, military service, or simply general distraction.[12] Finally, as conditions began to return to something like normalcy in 1919–1920, full attention could be given to the problems lurking in the phenomena of the microscopic world. The timing of the quantum revolution of 1925–1926 was determined to a significant degree by the effects of the war, and 7 years after the Armistice the new quantum theory was born. By this time Pauli, Heisenberg, Dirac, and Jordan were all in their early to mid-20s and ready to strike out in new directions.

IN SEARCH OF A THEORY

The period we concentrate on here is 1918–1925, when the search for theoretical understanding of the rapidly accumulating data was most intense. During most of this period, two figures, one in Germany and one in Denmark, led the halting efforts toward a final theory: Arnold Sommerfeld and Niels Bohr. Sommerfeld, the consummate theorist, more than anyone else made clear what the problems in atomic spectroscopy were, especially through his monumental *Atomic Structure and Spectral Lines*.[13] In the years following the Bohr theory of hydrogen, Sommerfeld, in concert with Bohr, offered much of what theory there was—the "Bohr–Wilson–Sommerfeld theory," despite its increasingly obvious failings. Bohr's role, as we shall see, eventually came to be more one of philosophical guidance, and in the end he provided the philosophical soil from which quantum theory would arise. With the founding of his institute in 1921 and the hospitality he provided there, the stage was set, and what happened was almost inevitable. Virtually all of the founders of the new theory visited Bohr in Copenhagen, had long talks there with him and his visitors, and the result was a deeper understanding of what a new theory might be like. The only rival to the Niels Bohr Institute (technically, the Institute for Theoretical Physics at the University of Copenhagen[14]) were the University of Göttingen, where Hilbert and Born spent almost their entire careers, and most of the founders of quantum theory, including

Heisenberg, Jordan, Pauli, Weyl, and von Neumann were trained or spent time there, and Sommerfeld's center in Munich.

The gropings, as it were, toward a theory are told in a number of places, including, of course, Mehra and Rechenberg's massive work.[15] Within a couple of years of the Bohr theory of 1913, the generalization of Bohr's circular orbits to elliptical ones was well under way.[16] The quantum phase integral, $\int pdq = nh$, found initially by William Wilson and apparently independently by Sommerfeld,[17] soon became the starting point for quantization of any theory. This amounted to quantizing the *action integral*, which is what Wilson did as a "hypothesis," and Bohr's final quantization condition for hydrogen, that the angular momentum is quantized, i.e., $L = n\hbar$, follows directly from it. Bohr gave his own "proof" of the quantum phase integral in 1918.[18] The first three editions of Sommerfeld's book, from 1919 to 1922, are excellent sources on the state of the Bohr–Wilson–Sommerfeld theory in the early 1920s.

BOHR AND THE CORRESPONDENCE PRINCIPLE

In view of Bohr's influence and the fact that his *correspondence principle* plays such an important role in Sommerfeld's book, we now take some time to consider the former's role and that of his correspondence principle. Despite the fact that it is barely given a nod today, it proved a powerful guide to the structure of a quantum theory for many physicists in this period. In the entire period covered by this narrative, and going back to his theory of hydrogen, no one had the influence that Bohr had on the development of quantum theory. For several years he and his collaborators, along with Sommerfeld, were at the forefront of detailed attempts to generalize the nascent quantum mechanics and to widen its application; any important new idea that failed to receive Bohr's stamp of approval faced a chilly reception. Beginning shortly after 1916 when Bohr became professor at the University of Copenhagen, every bright young quantum theorist was drawn to Copenhagen and eventually his institute, where, on long walks with him, their ideas were scrutinized, examined from every direction, and, with luck, shaped into final form.[19] Bohr was not always right, and the same was true of his interlocutors, but without those visits with Bohr and the discussions with the master and others at the institute, the history of quantum theory might have been very different.

Much of Bohr's direct influence on the evolution of the quantum theory resulted from his enunciations of two general principles: the correspondence principle and complementarity. Of these the first, although enormously influential, is relatively straightforward and clear in its import, if not in its application. The same, however, cannot be said of complementarity, which has puzzled many for almost the entire past century, and for this reason and because it dates from 1927, we turn our attention to the simpler of the two tasks, the correspondence principle. We will return to complementarity in Chapter 14.

If we accept the premise that quantum mechanics is ultimately *the* theory of nature, then it is self-evident that any quantum-mechanical description must merge with the confirmed classical description when applied to macroscopic objects, or, as

Bohr put it, it must be "a rational generalization of the classical theories."[20] Looked at another way, given the classical description of, say, an harmonic oscillator, the as-yet-unknown quantum theory is constrained by the condition that it must, in some appropriate sense, usually expressed as for large quantum numbers or states closely spaced ($\Delta n/n$ small), lead to or merge with the classical theory. Although this may seem obvious, this idea, which is the essence of Bohr's correspondence principle,[21] was enormously influential between 1920 when it was formulated (though it is implicit as early as Bohr's 1913 paper on the hydrogen spectrum) and the discovery of the new quantum theory in 1925–1926. Moreover, as we have noted, if it is given little more than lip service today, it was an important guide and motivation for most of the founders of the new theory.[22] The evidence for this is found in their own words, especially in the case of Heisenberg, who perhaps more than any of his contemporaries was influenced by the principle.[23] Yet, although some very concrete inferences were made solely on the basis of the correspondence principle, it is often unclear how it actually guided the construction of the quantum description of a system or how different a development might have been without it. It is, however, quite clear from the record that this guidance was real. Heisenberg was very explicit on the importance he attached to the correspondence principle in developing matrix mechanics,[24] and on almost every page of his paper he compares the classical result and the new, proposed, quantum analog. Of Heisenberg's reasoning, Leon Rosenfeld wrote that "Heisenberg's achievement was to derive from the rules establishing the correspondence between the quantal and classical amplitudes and frequencies a method for dealing directly with the former without referring at all to classical theory."[25] The current neglect of the correspondence principle—quantum-theory texts will frequently not even mention it or note its historical influence in passing—is mostly a reflection of the fact that it is, indeed, self-evident, or at least is a commonplace, a constraint on a theory that is hardly given a second thought. But that, we know, is hardly a measure its historical importance. We should remember, as a caveat, that many systems or phenomena have no classical counterparts.

The correspondence principle had been elaborated in 1918 in the paper "The quantum theory of line spectra,"[26] though something like it had clearly been on Bohr's mind during the previous half-decade. As we have noted, it imposed a very strong restriction on any quantal theory, and because it had the effect of ruling out any theory that did not converge to the classical description in the appropriate limit, it had a strong selective power. It is a measure of the uncertain state of affairs in 1918 and our present distance from them that what seems today to be a rather obvious restriction should have been such a powerful guide to future developments.[27] But there was then no real theory, leaving the field open for general, philosophical, guiding principles.

THE OLD QUANTUM THEORY, 1919–1925

Although the old quantum theory could claim few successes, great effort was expended after the war, especially in the early 1920s, in an attempt to break the impasse that

physics was facing. The problem was how to modify classical physics to incorporate quantum discontinuities or "jumps." Much of the effort was naturally devoted to the interaction between atoms and radiation, which, among other things, led to a theory of dispersion, involving John Slater, Max Born, Hendrick Kramers, and Werner Heisenberg, and in particular in a paper by the last two authors.[28] Heisenberg built his ultimate theory directly on these results, most especially in replacing classical amplitudes that depended on a continuous variable and were labeled by a single quantum number related to the energy, by an amplitude $a(n, m)$ that depended on the quantum numbers n and m of a *pair* of states between which a transition occurred. This is elaborated on in the next chapter.

The great discoveries of 1925–1932 that are about to be described built on the work of the previous 5 years as attention turned from war-related research and students returned. Pauli, who got his doctorate under Sommerfeld in 1921, moved to Göttingen in 1922 and Copenhagen the next year. Heisenberg also received his PhD at Munich under Sommerfeld, in 1923, but had already gone to Göttingen to work with Born, Franck, and Hilbert. Pascual Jordan came to Göttingen in the same year to work with the mathematician Richard Courant. All of this shuffling set the stage for what would happen there in 1925. In England, Paul Dirac, having failed to find work as an engineer after the war, switched to mathematics and physics and left Bristol for Cambridge, where he completed his doctorate under Ralph Fowler in 1926.[29]

CONCLUSION

This decade between the Bohr theory of the atom and de Broglie's thesis was one of consolidation, of searching for a theory. Important papers on radiation and spectra were written by Einstein and Bohr in 1917–1918, as the war was ending,[30] and the problem of dispersion, or the interaction of radiation with atoms, was gaining the attention of Bohr, Kramers, Heisenberg, and others near the end of this decade, in the years 1921–1924.[31] These tentative moves led directly to Heisenberg's landmark paper of 1925. Bohr's correspondence principle proved to be an effective guiding light to researchers in this period, and Ehrenfest's "adiabatic hypothesis" of 1916[32] served as a somewhat similar function, in that it allowed one to take a fundamental property of a fully understood system and apply it to one that could be reached by an adiabatic transformation. Wave–particle duality, in the form of de Broglie's hypothesis and the electron-diffraction experiments described earlier, which for a while seemed almost a dead end, provided the hint that would push Schrödinger toward wave mechanics.

It is at this point, then, that the real narrative begins.

NOTES

1. Although Mehra and Rechenberg (1982–2000) note that 1925–1928 were the most stable years of the old Weimar Republic.
2. In Germany, for example, over 7 million casualties, with nearly 2 million dead. Russia suffered even greater losses.

3. Many more lives were lost to the influenza outbreak than in the war, and unlike most flu epidemics, this one targeted young people, further decimating that important generation.
4. Including Pauli and Heisenberg, who did their doctoral research under him, receiving their degrees in 1921 and 1923, respectively.
5. Although see Kragh (1999).
6. Einstein (1917a).
7. Especially notable is the well-known case of the chemist Fritz Haber, who played a crucial role in the introduction of chemical warfare to the battlefield in 1915.
8. Karl Schwarzschild, who enlisted at age 40, succumbed to an autoimmune disease possibly related to his role in combat, in 1916 at the age of 43.
9. And saw Einstein nearly every day, as his office was near Einstein's home.
10. I realize that the century ended on Dec. 31, 1900, but try to convince anyone of that.
11. Jordan was born in 1902 and von Neumann the following year. Weyl was of the previous generation, having been born in 1885, the same year as Bohr.
12. Einstein, however, published over 40 papers during the war years.
13. Published in several editions throughout the decade of the 1920s, beginning in 1919. See the bibliography for details.
14. Becoming the Neils Bohr Insitute of the University of Copenhagen in 1965, on the occasion of Bohr's 80th birthday.
15. Mehra and Rechenberg (1982–2000).
16. Wilson (1916); Sommerfeld (1919, 1923). Also Peter Debye, as early as 1913.
17. Sommerfeld (1916c), a 95-page paper in which Wilson (1915) is cited.
18. Bohr (1918).
19. Especially after 1921, when the institute was founded.
20. Bohr (1928).
21. Or "correspondence argument," which Leon Rosenfeld says was Bohr's preferred usage [Rosenfeld (1973)]. Rosenfeld also says that Bohr used the term analogy before arriving at the "correspondence" language (p. 254). It should be added that in Bohr's hands, at least, the application of the principle was not limited to large numbers of quanta, but had a more general applicability, though in such cases its use as a guide was more a matter of intuition than of anything more specific. (p. 256).
22. See van der Waerden's comments in his introduction (van der Waerden, 1967).
23. In his important paper in *Physical Review* (Van Vleck, 1924), the American physicist J. H. Van Vleck employed the "correspondence principle" over 25 times. All of Van Vleck's doctoral students were notable and included two Nobel Laureates. Thomas Kuhn was also a student of his.
24. See, for example, the quote on p. 124 of Cassidy's biography of Heisenberg (Cassidy, 1991), in a letter to Landé: ". . .. I am beginning to want to consider [it] as important as the entire quantum theory."
25. Rosenfeld (1971); "Men and ideas in the history of atomic theory"; the quote is on p. 81. Rosenfeld was himself a collaborator of Bohr. Another quote from this paper, referring to John Slater, is intriguing: "No one who remembers the bewilderment he experienced on his first contact with Bohr will blame the young American physicist freshly landed in Copenhagen for finding Bohr's views "hazy" (p. 80).

26. Bohr (1918). See van der Waerden (1967), where some of the long paper is published. The actual term correspondence principle was first used by Bohr 2 years later in Bohr (1920, in German).
27. On the other hand, Pauli wrote of the "imperialism of the correspondence principle"; See n. 40 to chapter 10 in Cassidy (1991). Sommerfeld called it a "magic wand" (Wentzel, 1960, p. 49).
28. These papers are translated in van der Waerden (1967).
29. Fowler's list of students and their students rivals the record of Sommerfeld. Dirac's student Dennis Sciama had as PhD students Steven Hawking, G. F. R. Ellis, Martin Rees, Brandon Carter, and David Deutsch. Fred Hoyle was one of Dirac's PhD students. But can one imagine the luxury of having two students of the caliber of Pauli and Heisenberg at virtually the same time?
30. Einstein (1917a); Bohr (1918). Einstein's paper is translated in van der Waerden (1967).
31. See the papers in van der Waerden (1967) on dispersion (papers 4–11).
32. Ehrenfest (1916, 1917). The latter paper is reproduced in van der Waerden (1967).

PART II

Theory

5

AT THE CREATION
MATRIX MECHANICS AND THE NEW QUANTUM THEORY

INTRODUCTION

The uncertain state of quantum theory in the early 1920s is illustrated by Max Born's complaint to Einstein in 1922 that "the quanta really are a hopeless mess."[1] Bohr wrote to Landé in the same year that "the entire method of quantization . . . appears not to be reconcilable with the fundamental principles of quantum theory."[2] Three years on, his pessimism was even deeper: "it seems to follow . . . that one is faced . . . with an essential failure of the pictures in space and time on which the description of natural phenomena has heretofore been based."[3] Wolfgang Pauli, who would eventually play a seminal role in the development of the new theory, considered giving up on quantum theory altogether.[4] Despite enormous effort, interrupted of course by the war, the accumulation of data that was described in previous chapters had so far shed very little light on the theoretical situation.[5] There were some glimmers of hope, notably in attempts to treat dispersion, but little real progress. Even at the end of 1923, which had seen the confirmation of the particle nature of light—for most physicists at any rate—as well as the de Broglie hypothesis, there was still no hint of the way forward. But in 2 years the situation would change dramatically.[6]

In the event, and somewhat surprisingly, it was the study of dispersion, principally by Kramers, involving the discrete absorption of radiation by atomic electrons, that, as Hund put it, "smoothed the path to quantum mechanics."[7] The way in which this happened is quite technical, and one might want to read Hund and the original papers in van der Waerden, most of which were translated from the German. Aside from Heisenberg's seminal paper, his *Physical Principles of Quantum Theory*, based on lectures given in 1929, is fairly illuminating.

No one played as important role in guiding the slow progress of quantum theory in this period as did Niels Bohr. In the decade following his theory of the hydrogen atom, which can be seen as the birth of quantum *mechanics*,[8] much of his influence came through the vehicle of the *correspondence principle*, which we discussed in the previous chapter, and its influence on the young Werner Heisenberg was (figure 5.1) especially strong; 40 years later he gave a moving tribute to Bohr and the effect on him of a conversation between the two of them in Göttingen in 1922, when he (Heisenberg) was only 20.[9]

MATRIX MECHANICS: HEISENBERG, BORN, AND JORDAN

By any measure, Heisenberg's original paper, submitted to *Zeitschrift für Physik* in July 1925, during the University of Göttingen's summer vacation, was the beginning of it all.[10] It was there that the new quantum theory had its origin, or we might say, was discovered. For Heisenberg the starting point was the problem of measurement and his insight that it was necessary to abandon the thought of measuring certain dynamical variables that one would routinely measure in classical physics: ". . . it seems sensible to discard all hope of observing hitherto unobservable quantities . . . and to concede that the partial agreement of the quantum rules with experience is more or less fortuitous."[11] Thus Heisenberg's philosophical point of departure was his conviction that quantum mechanics should be formulated in terms of measureable quantities, such as intensities[12] *only*, which meant throwing nonobservable quantities, like orbits, out the window. As Heisenberg acknowledges, he was strongly influenced in this by Einstein's operationalist treatment of measurement in special relativity.[13] Writing to his friend Pauli, with whom he was in constant contact and who had a strong and continuing impact on his viewpoint, Heisenberg said that "The basic postulate is: In the calculation of whatever

Figure 5.1. Werner Heisenberg (1900–1976). AIP Emilio Segrè Visual Archives, Segrè Collection.

quantities, for example, energy, frequency, and so on, only relationships between quantities controllable in principle may appear."[14] This very positivist approach was a reaction against the rather ad hoc attempts to impose quantization conditions on conventional classical descriptions of microscopic phenomena, guided by the correspondence principle. Not only were such attempts aesthetically unpleasing, they failed in the sense that if they were successful in treating the problem for which they were tailored, they could not readily be generalized to another problem. But this period of floundering ended when Heisenberg's paper appeared in the early fall of 1925, aided by its recasting in the form of matrices 2 months later by his fellow Göttingeners Born and Jordan[15] and Dirac's nearly simultaneous reformulation in terms of Poisson brackets.

The reader who might consider taking advantage of translations of Heisenberg's paper (e.g., van der Waerden[16]) should be cautioned that it is anything but transparent. In his *Dreams of a Final Theory*, Steven Weinberg, arguably the most important physicist of his generation and someone with considerable historical sensitivity, wrote that "papers of magician-physicists are often incomprehensible . . . in this sense, Heisenberg's 1925 paper is pure magic."[17] Our discussion is necessarily very brief here, but it is hoped, helpful, and there are a number of summaries of Heisenberg's arguments available, freeing us from having to do the same in any detail.[18] But the essentials are given in the Appendix.

Although much of the halting progress that led to Heisenberg's paper was guided by Bohr's correspondence principle, Helmut Rechenberg[19] has noted that the somewhat ad hoc process of "more or less arbitrary hypotheses" that characterized quantum theory in the late teens and early 1920s might have continued indefinitely but for an insight of Pauli's, which appeared in a letter to Sommerfeld in Munich in July 1923,[20] and was likely arrived at independently by Born.[21] It was an analogy to Bohr's "frequency condition," $[E(n+n')-E(n)]/h = \nu$. Pauli's novel idea consisted in replacing a classical quantity involving a differential such as $\sum_k \tau_k \partial\Phi/\partial J_k$, by a discrete "difference quotient" $1/h\,[\Phi(n+\tau)-\Phi(n)]$.[22] It provided a way of bridging the gap between the fundamentally continuous nature of classical physics and the discrete world of the quantum, and of course, introduced Planck's constant into the description.

Pauli had just finished his doctorate under Sommerfeld in 1921 and followed this by part of a year as assistant to Born, who had just returned to Göttingen as professor of theoretical physics.[23] Heisenberg, who was also a student of Sommerfeld,[24] moved to Göttingen in the summer of 1922, also to work under Born, even though he had not yet completed his doctorate (Sommerfeld having gone to Wisconsin for the year).[25] Although Pauli's stay there was very brief as he headed on to Copenhagen, and Heisenberg himself soon left for Leipzig (1927), the two remained friends for life. Despite writing only a couple of papers together, they were in constant contact, and each was the greatest stimulus for the other. It is hardly surprising that quantum mechanics had its origin there not much more than 2 years later, aided by the fact that Pascual Jordan moved to Göttingen in 1923 to work under Born.

Heisenberg's paper, in vol. 33 of the 5-year-old *Zeitschrift für Physik*,[26] the journal in which most of the important developments in quantum mechanics in this

era were published, was the culmination of a frustrating attempt to find some way of understanding the spectroscopic data.[27] It is clear from a reading of this paper of Heisenberg that Kramer's dispersion theory[28] formed the basis for his invention of what we know as matrix mechanics. It was this problem of absorption and emission of radiation by atoms, attacked by Ladenburg, Kramers, and Born in the early 1920s treating the atom as a collection of virtual oscillators, that led to Heisenberg's discovery.[29] Especially important was the famous (or infamous) Bohr, Kramers, and Slater[30] paper, despite its radical approach in which energy conservation could be violated and the photon hypothesis rejected, views that experiments soon made untenable.[31]

Although there is much argument by analogy in Heisenberg's paper,[32] using the vehicle of the correspondence principle, the heart of the development involves trying to find a solution to the equation of motion for a system by providing a Fourier series representation that would include quantum jumps, and then applying, in modified form, the old Bohr–Wilson–Sommerfeld quantization condition: $\int p\,\mathrm{d}q = nh$.[33] Heisenberg was faced with the fact of transitions between discrete levels, which meant that the amplitudes for such transitions had to depend on quantum numbers for both levels. As his mentor Born said, "we knew that frequencies of vibrations were proportional to energy differences between two stationary states. It slowly became clear that this was the main feature of the new mechanics."[34] Heisenberg began what turned out to be the final attack on the problem by treating the problem of radiation from an anharmonic oscillator. Dynamical variables like $x(t)$ were given a Fourier representation in terms of virtual oscillators whose amplitudes were modified from their classical forms in a way that incorporated this idea that the emission or absorption of radiation of frequency ν involved a quantum jump between two states, n and $n-\alpha$ with energy difference $h\nu(n, n–\alpha)$. Because the square of the amplitudes would be a measure of the strength of the radiated field, Heisenberg had to work out quantities like $x(t)^2$ in terms of these Fourier representations. Objects like $x(t)y(t)$ then involved products of amplitudes of the form $A(n, n-\alpha)\,B(n-\alpha, n-\beta)$, in which, in retrospect, one can see a hint of matrix multiplication—and soon Born would.

In the course of this development, Heisenberg found to his surprise that "whereas in classical theory x(t)y(t) is always equal to y(t)x(t), this is not necessarily the case in quantum theory." This somewhat innocuous comment on noncommutivity would provide Born with the key to understanding Heisenberg's relations as involving matrices, something the latter knew nothing about.[35] One might be excused for being amazed that Heisenberg so readily accepted the idea that physical variables might not commute under multiplication. In any event, he employed the by-now-familiar quantum phase integral $\int p\,\mathrm{d}q = nh$, but in the form $\dfrac{\mathrm{d}}{\mathrm{d}n}\int p\,\mathrm{d}q = h$. By differentiating with respect to n and representing $p\mathrm{d}q$ as $m(\mathrm{d}x/\mathrm{d}t)^2\,\mathrm{d}t$ and replacing the integral by a sum, the following result was obtained:

$$h = 4\pi m \sum\nolimits_{\alpha} \left\{ \left| a(n, n+\alpha) \right|^2 \omega(n, n+\alpha) - \left| a(n, n-\alpha) \right|^2 \omega(n, n-\alpha) \right\}.$$

This was the fundamental relationship from which everything else followed. Some details of Heisenberg's derivation of this result are given in the Appendix.[36]

As is perhaps evident from the preceding discussion, even those intimately familiar with matrix mechanics as we now understand it[37] will find Heisenberg's 1925 paper daunting. But happily this obscurity is much less true of the article by Born and Jordan that followed Heisenberg's by about 2 months in the next volume of *Zeitschrift für Physik* and largely reformulated his theory in terms of matrix operations.[38]

It happened that while (or shortly after) reading Heisenberg's manuscript before it was submitted for publication in July of 1925, Born (Figure 5.2) quickly realized that the noncommutivity that Heisenberg had discovered could be interpreted in terms of matrices, which in general do not commute.[39] After Pauli declined, Born was able to induce his 23-year-old assistant Pascual Jordan,[40] who had studied with the mathematician Courant, to help him with the mathematics of the theory. They immediately began their very lucid reformulation of Heisenberg's paper, which they worked up in those 2 months, opening with an introduction to the properties of matrices,[41] including their noncommutivity, and adopting Heisenberg's assumption from the correspondence principle that Hamilton's equations of motion apply in the quantum theory as well as classically. In short order they discovered the operator, or matrix, expression $\mathbf{xp} - \mathbf{px} = h/2\pi i\mathbf{I}$.[42] With the Hamiltonian,[43] a function of p and q (or x), in

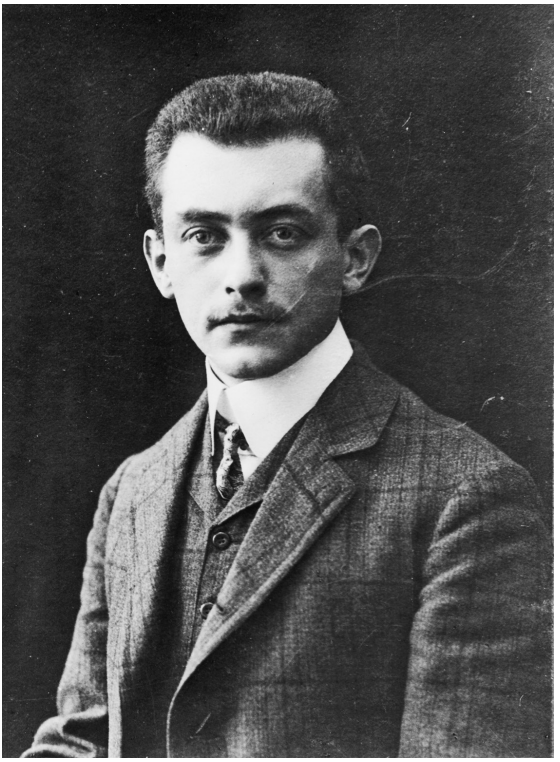

Figure 5.2. Max Born (1882–1970). AIP Emilio Segrè Visual Archives, Gift of Jost Lemmerich.

hand, they could obtain an expression for the time dependence of an operator $O(p, q)$ (see subsequent discussion), and using Hamilton's laws of motion, treat a problem like the harmonic oscillator.[44] Application was made to the one-dimensional oscillator, from which the now-familiar result $E = (n+1/2)\hbar\omega$ was obtained, and the simple rotor was treated as well. The paper is a tour de force, succinct, and clear. It is not at all hard to see why Born always felt that he (and Jordan) should have been given something like equal credit for the discovery of matrix mechanics, which was never the case.[45] The details of the paper, which hinted at the role of Hermitian bilinear or quadratic forms in representing observables (though the specific language of Hermitian operators on a Hilbert space was not yet used),[46] were mostly the work of Jordan.[47] The troubling problem of how to deal with continuous spectra in matrix mechanics was also touched upon, without any resolution.

The third paper, this one by all three, Born, Heisenberg, and Jordan[48] (BHJ), which is often known as the *Dreimännerarbeit* or "three-man work," submitted in November, 8 weeks after Born and Jordan's paper, introduced the language of Hermitian forms quite explicitly. So did Dirac's almost simultaneous paper (at least implicitly), which came out of the blue, as it were,[49] and to which BHJ referred in press. The BHJ paper was sent to *Zeitschrift für Physik* shortly after Born left for a series of lectures at MIT that he gave in the winter of 1925–1926 and in which he further elaborated the theory. These lectures were published as *Problems of Atomic Dynamics*[50] in 1926 and stand as one of the most complete expositions of matrix mechanics—certainly in English—as it existed in the late 1920s, just as it was confronted with Schrödinger's alternative formulation of quantum mechanics.

As was said, perhaps the most startling discovery by Heisenberg, and more explicitly by Born and Jordan, was that the products xp and px were different, that is, that as *operators* x and p do not commute in quantum mechanics. Thus a quantity like $pq - qp = [p,q]$ came, in the BHJ paper, to be known as a *commutation rule* or *commutation relation* [*Vertauschungsrelationen*], after the common notion of commutivity.[51] In this paper we also find the general expression for the time dependence of a dynamical variable, or, as the authors put it, "any quantum mechanical quantity," in terms of the commutator with the Hamiltonian, which is equivalent to giving the time dependence of an operator in what we know as the *Heisenberg picture*, $\mathrm{d}O_H/\mathrm{d}t = i/\hbar\,[O_H, H]$.[52] Throughout the development, emphasis is placed on the canonical transformations that lead to a diagonal matrix representing the dynamical variable, typically the energy (the Hamiltonian).

Another important application found in the BHJ paper is to time-independent perturbation theory. An examination of their chapter 2 reveals the equations for the energy eigenvalues in first- and higher-order perturbation theory in a fairly transparent form for even the modern reader (say, Schiff, 1968, chapter 8), and in the same chapter, degenerate perturbation theory is treated by diagonalizing a submatrix of the perturbing interaction, involving the degenerate states.[53]

In the next chapter of the paper, the challenging problems of continuous spectra, involving continuous matrices, are addressed, although in a less than mathematically rigorous way, therefore leaving some unanswered questions. It is worth noting that

Heisenberg was not entirely comfortable with Born and Jordan's casting the theory in what for the time was a fairly sophisticated mathematical form. He wrote Pauli, saying that "I am pretty unhappy about the whole theory and thus was glad that you were so completely on my side in your views on mathematics and physics. Here [Göttingen] I'm in an environment that thinks the exact opposite, and I do not know if I'm not just too stupid to understand mathematics." In the same vein, Pauli wrote Ralph Kronig that "one must next attempt to free Heisenberg's mechanics from Göttingen torrent of erudition."[54] Of course, these two founders of quantum mechanics would soon be proved wrong.

Schrödinger's first paper on wave mechanics (to which our next chapter is devoted) was published in January 1926, before the BHJ paper and while Born was still in the United States. It confronted physics with the startling and embarrassing situation of having two theories that apparently described the same phenomena, but that seemed to have nothing in common. Almost everyone, but specifically Born, Jordan, and Pauli, sought to find ways to reconcile the two approaches, which clearly had to be possible. In the event, as we shall see, it was Schrödinger who won the race.[55]

By the next July, Born had written the first paper on quantum-collision theory[56] in which he introduced the probabilistic interpretation of the wave function, having quickly seen the value of Schrődinger's approach in such problems. That fall (1926) he returned to MIT for a second series of lectures[57] at the invitation of Norbert Wiener. Born and Weiner had published a foundational paper, titled "The operator calculus," earlier in the year, reformulating matrix mechanics in terms of operators on what amounted to a Hilbert space.[58] Born's principal Göttingen collaborator, Jordan, took a somewhat different approach, leading to his version of what came to be known as "transformation theory," which he would pioneer with Dirac. As we noted, Jordan was especially well equipped to formulate quantum mechanics in this way, as a former student of David Hilbert's and an assistant to Courant.

The BHJ paper was titled "On quantum mechanics, II," thus deliberately announcing it as the successor to the Born–Jordan paper, rather than of Heisenberg's original work. Hilbert, whose role as a sort of midwife we explore later, since 1895 had been at Göttingen, where all three authors (BHJ) were working at the time—before Heisenberg's move to Leipzig.[59] It is in this paper (BHJ) that Jordan provided the first sketch of what would become transformation theory, which we subsequently discuss in this chapter and in Chapter 8. On the other hand, although dynamical variables are transformed, the states have not yet emerged as vectors in *Hilbert space*. But the relationship of these results to the eigenvalues[60] of Hermitian operators are clearly spelled out, and Hilbert's work is cited.

One of the most important aspects of the paper is to be found in its chapter 4, "Physical applications of the theory," the introductory section of which is titled "Laws of conservation of momentum and angular momentum: intensity formulae and selection rules." Here we see angular momentum algebra for the first time using the new commutation rules, which were obtained directly from the commutators for p and q, along with $\mathbf{L} = \mathbf{r} \times \mathbf{p}$.[61] Here are to be found the standard expressions for the commutators involving the angular momentum operators (not using that term, of course),

matrix elements of the angular momentum operators,[62] even matrix elements of the modern $L_{\pm} = L_x \pm i L_y$, which were recognized as being responsible for "jumps" between states of ℓ_z differing by one. Implicitly the "ladder operators" for angular momentum are thus introduced.[63] Thus the matrix elements of the components of $\boldsymbol{L}$, L^2, L_z, and, effectively, $L_{\pm}$ are constructed, that is, the matrix elements of vector operators in a spherical basis. Although the paper was submitted in November 1925, the advance over Heisenberg's original paper from the end of July is enormous. Among other things, it led directly to Pauli's treatment of the hydrogen atom, which we subsequently discuss. In all the early papers, including those of Heisenberg, of Born and Jordan, of BHJ, and even of Dirac, the problem of the hydrogen atom was ducked as being too difficult, in favor of the harmonic oscillator or the simple rotor, for example.

DIRAC'S ROLE

The 23-year-old Dirac's initiation into the process of creating quantum mechanics came when his advisor at Cambridge, Ralph Fowler, showed him proofs of the paper that he had received from Heisenberg in September 1925. Dirac quickly realized that the noncommutativity of complementary dynamical variables (p_x and q_x, for example) could be framed in terms of the Poisson brackets of classical mechanics, so that the commutator of two variables was equal to their Poisson bracket times $i\hbar$. Many years later he recalled that "noncommutivity was really the dominant characteristic" of the new theory.[64] The resulting paper was published on December 1, 1925,[65] and was followed quickly by works that reached print in March, May, and October of 1926, and then on the first day of 1927.[66]

Of Dirac's totally unexpected appearance on the scene, Born reminisced nearly 40 years later:

> "Our paper was sent in I think in November [1925; BHJ], and then I went to America and left Boston at the end of January to go on a lecture trip over the continent. And the day before I left there appeared a parcel of papers by Dirac, whose name I had never heard. And this contained exactly the same as was to be in our paper. In turning it in we were about four weeks earlier than him, but not in publication. And I was absolutely astonished. Never have I been so astonished in my life; that a completely unknown and apparently young man could write such a perfect paper."[67]

Very quickly both Dirac in Cambridge and Jordan in Göttingen began to pioneer a more abstract approach to the theory, essentially reconciling or unifying the techniques of matrix and wave mechanics and employing the theory of linear operators on a vector space that had been developed by Hilbert and others. This came more easily to Jordan, who at Göttingen was in a position to absorb Hilbert's mathematics, and indeed Dirac's embracing of the language of linear operators on a complex normed vector space seems a bit reluctant at times. This is ironic given how influential Dirac would be in establishing the abstract approach to quantum theory, but it reflected

his early training as an engineer and perhaps the difference between mathematics at Cambridge and at Göttingen in the 1920s.[68]

Dirac began to use the language of matrix algebra in a paper published in May 1926,[69] by which time both the Born–Jordan and the BHJ *Dreimännerarbeit* paper had been published.[70] In fact, as is revealed in the passage quoted earlier, Dirac realized that it was not the matrices, per se, that were fundamental, but the noncommunitive property of the dynamical variables represented by those matrices. In the next paper, "On the theory of quantum mechanics," published 5 months later, identification of the solutions of the Schrödinger equation with eigenfunctions of operators ("*q*-numbers") representing observables is quite clear.[71] That insight, of course, was a direct result of reading Schrödinger's first three papers on wave mechanics, the fourth of which was in press when Dirac submitted his paper to the *Proceedings*. In this same paper, somewhat surprisingly, Dirac went almost immediately to an application: the theory of an ideal gas in which the wave functions of the particles are either symmetric or antisymmetric functions of the coordinates of the particles. He could see no reason to favor one over the other, except that for electrons, the antisymmetric choice led to the Pauli principle and thus what is now known as "Fermi–Dirac statistics."[72] In the course of this development, "Slater determinants," as a way of representing multiparticle fermion states, appear for the first time.[73]

Dirac's next paper, "The physical interpretation of the quantum dynamics," was submitted in December 1926 from Copenhagen, where he was visiting Bohr. This paper represented the introduction of an early form of transformation theory and was a major step toward the crystallization of the theory enshrined in his classic *Princples of Quantum Mechanics* of 1930, which established more clearly than any other source the formal structure of the theory.[74] There is certainly some wave mechanics in the book, including the treatment of the hydrogen atom, but the emphasis is on what we would see as matrix mechanics and the transformation theory. Notably, the difference between what Dirac called the Heisenberg and Schrödinger called *representations* ("pictures" in today's parlance) is spelled out.

Of Dirac's *Principles*, and especially from the second edition forward, the theorist Behram Kursunoğlu has remarked that "the quantum theory as we know it and apply it today was formulated by Dirac,"[75] a statement that is substantially true, but one that does neglect the large impact that Jordan's similarly abstract formulation had.[76] Thus the second chapter of Born and Jordan's joint work of the same year as Dirac's book, the 400-page *Elementare Quantenmechanik*[77] (which is anything but elementary and played a role similar to Dirac's in the German literature), dealt with mathematical foundations, including the theory of vectors in a Hilbert space. The third chapter was devoted to developing matrix mechanics, including the solution to the one-dimensional anharmonic oscillator problem in terms of ladder operators of the familiar form $c_1 p \pm c_2 iq$. The fourth chapter treated angular momentum, something the BHJ paper had addressed earlier. The authors' original intent of following with a volume on wave mechanics never materialized, which partly explains the scathing review that Pauli gave the work and its relatively smaller influence.[78]

It is fairly clear that Dirac did not catch up to Born and Jordan in mathematical sophistication until the second edition of his book in 1935. Born and Jordan were, after all, steeped in the mathematical traditions of the Göttingen school, whereas Dirac was essentially self-taught. On the other hand, unlike the Göttingen pair, Dirac represented "each state of a dynamical system" by an abstract symbol ψ, which he called an "eigen- ψ," with all the properties of elements of a vector space (orthogonality, completeness, superposition, etc.). In discussing eigenvalue equations for observables, he assigns them properties that make the eigenvalues real and shows that eigenfunctions of these operators corresponding to different eigenvalues are orthogonal. No reference is made to Hilbert space or to Hermitian operators, and we might be pardoned for thinking that Dirac has "reinvented the wheel," so to speak, but the formal structure is all there.

VON NEUMANN ET AL.

In response to the matrix mechanics of the BHJ paper (as well as its recasting by Dirac), John von Neumann, who as much as anyone pioneered the application of operator methods to quantum mechanics as early as 1926, emphasized that one should ordinarily employ bounded operators on a Hilbert space, which if they are Hermitian correspond to observables rather than to matrices, and can be written down in only a particular coordinate system or basis.[79] This is elaborated on in Chapter 8, but the earliest explicit treatment of quantum mechanics in terms of state vectors on a Hilbert space is to be found in three papers by von Neumann in 1927[80] and, less axiomatically, in Hermann Weyl's book *Gruppentheorie und Quantenmechanik* of 1928, published in English 2 years later as *The Theory of Groups and Quantum Mechanics*.[81] Von Neumann's formulation was not only the first, but also the most rigorous, so much so that his 1932 book *Mathematical Foundations of Quantum Mechanics* is still widely read. Despite this greater rigor, Dirac's approach gained wider acceptance among physicists. Von Neumann's approach had much greater appeal to mathematicians than Dirac's less rigorous methods, but the latter for the most part prevailed, thereby fostering the use of that device that was so unpalatable to von Neumann, the *Dirac delta-function*.[82]

Von Neumann had been Hilbert's assistant at Göttingen, along with Lothar Nordheim, and the three together wrote an axiomatic paper on the mathematical foundations of the quantum theory in 1927.[83] This meant that among the most important founders of quantum mechanics in Germany, Born, Jordan, Weyl, and von Neumann were all protégés of Hilbert,[84] and Weyl would succeed Hilbert at Göttingen in 1930.[85] Weyl's book, which appeared the year after von Neumann's first paper, employs the language of operators on a Hilbert space and transformation groups unequivocally. He, along with Eugene Wigner, would also lay the foundations of the study of symmetry in physics beginning in the late 1920s.[86]

Dirac, Jordan, Weyl, and von Neumann together shaped the formalism of quantum mechanics into an abstract form that exhibited its relationship to the more general mathematical theory of self-adjoint operators on a Hilbert space. This was accomplished in

the half-decade before 1932, the crucial period in the birth of quantum theory, not least because they were able to incorporate Schrödinger's wave mechanics into the formalism and show that both matrix mechanics and wave mechanics were special cases, or at least alternative formulations, of a more general theory. Here we reprise Arnold Sommerfeld's surprising judgment that "the new development does not signify a radical change but a welcome evolution of the existing theory."[87] Clearly the torch had been passed.

MATRIX MECHANICS AND THE HYDROGEN ATOM

The hydrogen atom is the simplest atomic system and therefore a natural test case for any theory of the microscopic world. Further, as the system that in Bohr's hands launched the quantum (-mechanical) revolution, and in addition the problem that most dramatically demonstrated the efficacy of matrix mechanics only 5 months after its inception and of Schrödinger's mechanics less than 2 weeks later, it is surely deserving of special treatment in this narrative.

Although Bohr's triumph (along with Rutherford's discoveries) provided the impetus for all that followed, the elation was short-lived, as attempts to extend his approach, by Bohr himself and by Sommerfeld and others, met with failure almost from the outset. Even Bohr's theory of hydrogen left much to be desired and only succeeded because of the ℓ-degeneracy of the levels in hydrogen. It was quantum mechanics, to be sure, but just barely. The result was a decade of floundering attempts to find a theoretical description of the mass of spectroscopic data that was accumulating, with little to show for it. The impasse was broken with the papers of Heisenberg, Born, and Jordan in 1925–1926, and the inevitable applications of matrix mechanics to the hydrogen atom came immediately, by Pauli and Dirac in particular, and within the year had born fruit. Pauli won the "race," so to speak, submitting his remarkable paper "On the hydrogen spectrum from the standpoint of the new quantum mechanics" to *Zeitschrift für Physik* on January 17, 1926,[88] exactly 5 days before Dirac's was received by *Proceedings of the Royal Society*.[89] The importance of the problem is evidenced by the fact that within 10 days in January 1926, three distinct treatments of hydrogen were published, less than a half-year after quantum mechanics was born.

Although this gets us a bit ahead of ourselves (see the next chapter), we note that all of this took place just before Schrödinger's own effort reached *Annalen der Physik*, but only barely so, his paper having been received on January 27,[90] following his Christmas at Arosa, Switzerland. He found the correct expression for the energies of the bound electron in hydrogen, introducing the problem on the second page of this very first wave-mechanical paper. It would be in the third of his series of papers that he would obtain the now-familiar solution to the wave equation in terms of associated Laguerre polynomials.[91] Schrödinger's effort was the most successful of the three and certainly the most intuitive, but as a tour de force, Pauli's paper was unequaled.

Unfortunately, Pauli was unable to obtain a unique solution because of problems of degeneracy, and so he considered the effects of both an additional central field and

external electric and magnetic fields in breaking the degeneracy. To obtain matrices for L^2 and L_z, which are diagonal, Pauli needed a preferred direction in space, which he accomplished by imposing a weak electric or magnetic field in the z-direction.

As noted earlier, perhaps the clearest exposition of the early matrix mechanics (Göttingen mechanics) was that given by Born in his lectures at MIT in the winter of 1925–1926 and published as *Problems of Atomic Dynamics* in 1926. And in his 18th lecture, Born announced Pauli's solution to the problem of the hydrogen atom, which had not yet been submitted for publication. These 30 lectures (about 4 per week), were given between November 14 and January 22, so that Born laid out Pauli's derivation of the Balmer formula some time in December, before the latter submitted it to the *Zeitschrift* in January. Born also noted in the preface to the published lectures that his paper with Jordan was in press and that the BHJ paper was essentially complete (being submitted only 2 days after his lectures began), and also that "as the course proceeded, further achievements of the new method came to my notice . . . Pauli's theory of the hydrogen atom is a case in point." These were heady times.

Having been an assistant of Born, Pauli leaned heavily on the BHJ paper, submitted exactly 2 months before his own treatment of angular momentum on which his theory of hydrogen depended. Pauli's development closely follows the corresponding classical one and makes use of the classical Runge–Lenz vector,[92] which is a constant of the motion (conserved). In the short time he took to solve the hydrogen-atom problem, Pauli had to derive a whole set of commutators such as $[p_i, L_j]$, $[p_i, r]$, $[p_i, x_j / r]$, etc., which might even challenge a student today who is already steeped in the standard formulation of quantum mechanics. He defined the *quantum* Runge–Lenz vector **A**, showed that it too was a constant of the motion, and then obtained a simple formula for A^2 in terms of L^2 and the energy E. The problem of finding the matrix elements of **A** or A^2 and showing that they were quantized was more difficult, requiring an anzatz or two. This is fairly thoroughly described in Born's published MIT lectures, and Pauli's paper is translated in Van der Waerden's work,[93] but the proof still remains difficult, and one of the best summaries of this tour de force appears in Green's little *Matrix Methods in Quantum Mechanics*.[94]

Dirac's approach to the problem was quite distinct, being based on the use of Poisson brackets, which were essentially the corresponding commutators of matrix mechanics. He concentrated on the electron orbit, giving $1/r$ as a function of θ, which we now know is untenable because p and its components are determined by r or θ, thus violating the uncertainty principle. Of course, that principle was over a year away. In the end, Dirac's proof, which was not grounded in matrix mechanics per se, fell just short of establishing the $1/n^2$ dependence of the energy of the stationary states in hydrogen, or at least required a leap of faith to get there.

When Schrödinger's solution of the hydrogen atom using wave mechanics was published, it quickly became the standard treatment because of its greater simplicity and transparency, and the way it emerged from the solution of the (somewhat) familiar second-order partial-differential equation. In fact, the success of Schrödinger's treatment of the hydrogen atom was an important factor in the rapid acceptance of wave mechanics. By the time Dirac wrote his enormously influential

Principles of Quantum Mechanics in 1930, the power of Schrödinger's method had become clear, and Dirac gave the standard solution to the wave equation in terms of Laguerre polynomials,[95] as opposed to his earlier, somewhat awkward approach. In his *General Principles of Wave Mechanics* of 1933, Pauli acknowledged the problems of the matrix-mechanics approach caused by the existence of a continuous as well as a discrete spectrum.

CONCLUSION

Ninety years after its inception, "matrix mechanics" is in a rather odd ontological state. The term will appear in some textbooks (including Weinberg's very modern treatment), where it is shown that a quantum-mechanical operator may be expressed in matrix form and that its eigenfunctions are column matrices, and so on. But in many other texts, no special attention is given to matrix mechanics, even as the abstract formalism that allows such representation is fully developed. It has now been subsumed in the formalism in a way that wave mechanics has avoided, mainly for pedagogical reasons. As a result of its greater accessibility and intuitive character, the Schrödinger equation is regularly taught to college sophomores. The history, of course, naturally suffers. Even at the graduate level, only lip service is given to a brief account of the discovery in 1925 by Heisenberg of matrix mechanics, possibly prefaced with arguments from the uncertainty principle, which Heisenberg established in 1927, or perhaps stemming from the de Broglie hypothesis of 1923.[96] But the move on to the Schrödinger equation of 1926 and the development of wave mechanics as a more accessible vehicle for the introduction of the theory are typically very quick, leaning heavily on Born's statistical interpretation of the wave function.[97] In due course, a more abstract formulation (historically known as transformation theory) is introduced, essentially a unification of the two approaches, usually presented in Dirac's notation or something akin to it. But matrix mechanics, per se, certainly as it was understood in 1925–1926, is typically given short shrift.

This may make sense pedagogically, as the theories are equivalent or merely different versions of one theory, and matrix mechanics is no longer seen as a separate theory, but it does distort the origin and rapid evolution of the new quantum mechanics.[98] As we will see in the next chapter, this ahistorical strategy ignores the confusion that prevailed in the face of two competing and very different approaches to describing the same phenomena, as well as the soul-searching that accompanied the ensuing attempts to reconcile matrix and wave mechanics at both the technical and philosophical levels. This process of reconciliation stimulated deeper thinking about the meaning of the quantum theory than either formulation alone could have.

NOTES

1. Born and Einstein, *Letters*, pp. 57–9. Quoted in Hendry (1984), p. 39.
2. Quoted in Serwer (1977), and repeated in Hendry (1984), p. 39.
3. Bohr (1925).

4. Readers more interested in Pauli's psyche than his physics might consult Zabriskie's *Atoms and Archetypes* (2001), which deals with the Jung–Pauli correspondence.
5. The situation was not so different from that of the mid-1960s, just before the elements of the standard model began to be put together by Glashow, Weinberg, Salam, and others.
6. Hund (1974) gives an excellent introduction to the considerations that led up to matrix mechanics, although the translation is rather rough. See especially chapters 5, 6, and 10.
7. Ibid.
8. A term [*Quantenmechanik*] that first found its way into print as the title of Born's paper in *Zeitschrift für Physik* (Born, 1924).
9. See van der Waerden (1967), pp. 21–2. Bohr was 16 years Heisenberg's senior.
10. For this, the subsequent papers by Born and Jordan and BHJ, the most readily accessible translations are in van der Waerden (1967).
11. Heisenberg (1925). The quote is on p. 262 in van der Waerden (1967).
12. Einstein had introduced the concept of transition probabilities in his fundamental paper on spontaneous and stimulated emission in 1917 (Einstein, 1917a).
13. It is clear from Heisenberg's writing that Einstein was major influence because of his operationalist interpretation of spatially and temporally separated events in special relativity, that is, measurement, although this was tempered by Einstein's own caution to Heisenberg that "it is the theory which decides what we can observe." See the discussion in Jammer (1974), p. 57, and more generally in his sec. 3.1 . On further philosophical influences, consult Jammer. See Beller (1999), chapter 3, as well.
14. Heisenberg to Pauli, June 24, 1925; n. 92, chapter 10 in Cassidy (1991). Similarly, Born and Jordan (1925) wrote that "Only such terms enter into true natural laws that are in principle observable and determinable" [quoted in Cassidy (1991), p. 198]. See, for example, Folse (1985) or Rosenfeld (1971). In abandoning electron orbits, Heisenberg was strongly influenced by Pauli, who held even stronger views. See Hendry (1984), p. 19. It is interesting, given Heisenberg's philosophical commitment to an operationalist point of view, that Pauli wrote to Bohr that "If I think about his ideas they seem so monstrous . . ." and "because he is so unphilosophical, he pays no attention to clear presentation." Pauli to Bohr, February 11, 1924; Hendry (1984), n. 45, chapter 4.
15. Born and Jordan (1925). Most of this paper is translated in van der Waerden (1967). Heisenberg's paper was published on September 18 and Born and Jordan's on November 28. Jordan had been Born's student. He likely would have shared the 1954 Nobel Prize with Born but for his Nazism.
16. Van der Waerden (1967).
17. Weinberg (1992). Weinberg noted that he had "tried several times to read the paper that Heisenberg wrote . . . and although I think I understand quantum mechanics, I have never understood Heisenberg's motivations for the mathematical steps in his paper." Twenty years later Weinberg gave a useful précis of some of Heisenberg's arguments in his textbook (Weinberg, 2013), § 1.4. See also Mackey's comment in n. 32 of this chapter.
18. These include the introductory chapter to van der Waerden (1967), Jammer (1966), and Aitchison et al. (2004). In the latter, references are given to at least a dozen attempts to clarify Heisenberg's reasoning. Heisenberg's *Physics and Beyond* (1971) offers some insights into his thinking. In the Appendix a brief sketch of Heisenberg's arguments is given. Fair warning, however.
19. Rechenberg (1995), pp. 184–5.

20. Ibid, n. 138, p. 240.
21. And appears in Born's 1924 paper (Born, 1924), which is translated in van der Waerden (1967).
22. Born (1924), p. 388 [p. 191 in van der Waerden (1967) (VdW)]; Heisenberg (1925), p. 881 (p. 263 in VdW); Born and Jordan (1925), p. 870 (p. 291 in VdW). In particular the case in which Φ is the Hamiltonian and J is the action, so that the result is the frequency ν. See Born (1924), p. 190.
23. Minkowski invited Born to come to Gottingen in 1908 to work with him on relativity, but Minkowski died the next year from an appendix operation. Born struck up a friendship and collaboration with the great aerodynamicist Theodore von Kármán. After 2 years in Frankfort with Stern as his assistant, Born returned to Göttingen in 1921, succeeding Debye. Soon he took on as assistants Heisenberg and Pauli.
24. Pauli was a strong influence on Heisenberg during their 2 years together in Munich (under Sommerfeld), and they developed a friendship that lasted until Pauli died in 1958; Heisenberg lived another 18 years. Cassidy (1991) characterizes them as "so opposite and yet so similar" (p. 108).
25. In fact he nearly failed his doctoral oral exams, and Wien did fail him. Cassidy (1991), pp. 151–2.
26. Heisenberg (1925). Translated in van der Waerden (1967), p. 261. It is worth noting that there was essentially no peer review and that the time lapse between receipt and publication of a paper was very short, though frequently a paper would be submitted, hence vetted, by a more senior scientist. In particular, Leon Rosenfeld has said that the editor of the *Zeitschrift*, Scheel, did no refereeing at all. (American Institute of Physics Oral Transcript, interview with Charles Weiner, September 3, 1968). *Annalen der Physik* was the other major physics journal, which is where Schrödinger published his papers on quantum mechanics. Although the *Annalen* had been publishing since 1799, when the *Zeitschrift* appeared in 1920 (mostly through Sommerfeld's influence), as the journal of the German Physical Society, it soon became the more important journal, especially in quantum mechanics and then nuclear physics, despite the *Annalen* being edited by Planck and Wein. After WWII and before unification, the *Annalen* represented East German science, whereas the *Zeitschrift* was published in West Germany. See the Appendix.
27. As he tells it, retreating from Göttingen.to the island of Helgoland because of an attack of hay fever, Heisenberg had a sudden revelation: "It was about three o'clock at night when the final result of the calculation lay before me. At first I was deeply shaken. I was so excited that I could not think of sleep. So I left the house and awaited the sunrise on the top of a rock" [Heisenberg (1969)]. This has been called the most important attack of hay fever in history.
28. Kramers (1924); Kramers and Heisenberg (1925); Bohr, Kramers, and Slater (1924).
29. A good source is van der Waerden (1967), especially his introduction, pp. 14-18. See also Miller (1994), §1.3.
30. Bohr, Kramers, and Slater (1924). John Slater later claimed to have had no part in the writing of the paper or in its ideas.
31. Bothe and Geiger (1924, 1925); Compton (1925); Compton and Simon (1925).
32. Mackey (1963) described it thus: "by vague and mystical but inspired heuristic reasoning, he was led to consider analogs of the differential equations of mechanics in which the varying elements were infinite matrices" (p. 99).

33. The quantum phase rule is, essentially, a statement of the quantization of the action $A = \int L\,dt = \int p\,dq$ for a free particle. Here L is the *Lagrangian*. I am forced, here, to credit the reader with a knowledge of Fourier series and its application.
34. Quoted in van der Waerden (1967), p. 20.
35. Nor were most physicists at the time.
36. Van der Waerden's commentaries on the papers by Heisenberg, Born, and Jordan, and the three together, including correspondence among the principals (including Pauli) are very enlightening. (van der Waerden, 1967; introduction, part II).
37. For example, Schiff (1949, 1955, 1968), chapter 6.
38. Born and Jordan (1925). The paper was written and submitted while Heisenberg was in Copenhagen, recognizing that the two indices, *n* and *m*, say, used by Heisenberg to describe atomic transitions, could be understood as *nm* elements of a matrix and that everything could be cast in terms of matrices. Although most of this paper is translated in van der Waerden (1967), the material on Maxwell's theory was not. It is, however, available online at http://www.p;hys.psu.edu/~collins/563/born_jordan.pdf.
39. See the translation of a letter from Born to Einstein in van der Waerden (1967), p. 37.
40. Jordan evidently deserves most of the credit for the paper. Born wrote in his *Recollections* that "after only a few days [he] brought me the solution to the problem" [*My Life* (1978), p. 218]. See also van der Waerden (1967), p. 38. On Jordan's initial collaboration with Born, see §1.4 in vol. 3 of Mehra and Rechenberg. In German, Jordan's name is pronounced "yor'-don."
41. Heisenberg admitted that he knew nothing of matrices when he wrote the first paper; Born, on the other hand, recalled the lectures of Jakob Rosanes when he was an undergraduate at the University of Breslau, now in Wroclaw, Poland, but then in Germany. Born was born in Breslau in 1882. The Born and Jordan paper was submitted in late September 1925.
42. There are problems with Jordan's proof, as van der Waerden pointed out (1967), p. 39. Weinberg (2013) has called the proof "mathematically fallacious."
43. Which doesn't appear in Heisenberg's paper.
44. "The devil is in the details," of course, but the steps leading to the commutator of *p* and *q* are not too obscure.
45. Not just because of the reformulation of Heisenberg with Jordan, but also because of the groundwork he laid in papers like Born (1924). See Greenspan's *The End of the Certain World*, especially chapter 14 (Greenspan, 2005).
46. Among the useful analyses of the BJ paper is Fedak and Prentis (2009).
47. See n. 40 of this chapter.
48. Born, Heisenberg, and Jordan, 1926, 59 pages long. The lectures that Heisenberg gave at the University of Chicago in the spring of 1929, published as *The Physical Principles of the Quantum Theory* (Heisenberg, 1930), which includes both Heisenberg's and Schrődinger's methods, is much more accessible.
49. Dirac (1925).
50. Born (1926c).
51. Following common usage, we will often use *q* rather than *x* for the spatial coordinate, because it can be generalized to other related variables, such as angular coordinates, where *p* would then represent angular momentum.
52. On "pictures" and "representations," see Chapter 9.
53. Which also had classical counterparts.

54. Both passages quoted in Hendry (1984), p. 72. To Born, Pauli scornfully said that "I know you are fond of tedious and complicated formalism. You are only going to spoil Heisenberg's physical ideas by your futile mathematics." Related in van der Waerden (1967), p. 37. In this connection, it is interesting to note Pauli's work in group theory and on non-Abelian gauge theories in the context of Kaluza–Klein theory, thereby anticipating Yang and Mills (Straumann, 2009).
55. There are, of course, arguments over when the first *full* proof was given. Some would say it was not until von Neumann did it in the first chapter of his *Mathematical Foundations*.of 1932. See Chapter 6.
56. Born (1926a).
57. Recall that he lectured there the winter before, resulting in his *Problems of Atomic Dynamics* (1926).
58. Born and Weiner (1926), published in February. Wiener had visited Göttingen in 1925 as well. This very interesting paper seems to have been dismissed by Born (AIP QHP interview with Thomas Kuhn, October 17, 1962), but the work generalized the matrix approach to that of operators on a Hilbert space, that is, the standard eigenvalue problem. In the interview Born said the following: "I worked with Wiener. We introduced the operator calculus but in a very clumsy way. But for [the?] time we did the right thing. We expressed the energy as d/dt and we [w]rote [the] commutation law for energy and time as an identity by applying (t(d/dt) – (d/dt)t) to a function of t; it was absolutely the same as for q and p. But we didn't see that. And I never will forgive myself, for if we had done this, we would have had the whole wave mechanics derived from quantum mechanics at once, a few months before Schrödinger. That is absolutely unexplainable, that one didn't see that. It always makes me a little doubtful about the Intelligence of Wiener. I was then very tired. I had to give two sets of lectures at MIT and a lot of discussions with other people and so on, while he spent all his work on this paper. He showed it to me, and on it I made my remarks and suggestions, and why then did he not see this. He also had been working all the time on the functions. So I'm not so great an admirer of Wiener's."
59. Born learned his linear algebra from Rosanes at Breslau but was also helped in this area by his mathematician friend Otto Toeplitz. Göttingen's mathematical stars were Felix Klein, David Hilbert, and Rudolph Minkowski (in the great tradition of Gauss and Riemann). Mehra (in Mehra and Rechenberg, 1982–2000, vol. 1, part 1) says that Born turned to physics because of hostility from Klein. Mehra also notes that Born was noted for recasting the ideas of others into more rigorous mathematical terms, as he did with Heisenberg.
60. Or *Eigenwert* in German. Van der Waerden's comments on this paper and Born's familiarity with these methods are useful. Van der Waerden (1967), pp. 51–2. The paper was received by *Zeitschrift für Physik* hardly a week after Dirac's manuscript reached the *Proceedings of the Royal Society*.
61. In the German literature of the time, cross-products are written as [**a b**] and inner products as (**a b**).
62. Labelled M_x, M_y, etc, which was a common usage, rather than L_x, L_y, etc.
63. Of course such operators appear in the classical treatment of Lie groups, as illustrated in Weyl (1930), p. 180, where the application is to quantum mechanics. In the quantum-mechanical context, it appears that the first full treatment of angular momentum in which the full implications of these raising and lowering operators was worked out by Schwinger as late as 1952: reprinted in Biedenharn and van Damm (1965).

64. Dirac (1971). Also Mehra (1972). It almost certainly set him thinking about canonical transformations in quantum mechanics, foreshadowing the "transformation theory" that he and Jordan invented less than 2 years later. Dirac had a handful of important students, including Dennis Sciama and Fred Hoyle, but was not a notable mentor. Robert Oppenheimer had briefly been at Cambridge but fled rather quickly without having much interaction with Dirac, and did his PhD work under Born at Göttingen. But the two boarded together there when Dirac was visiting Born in 1927. See, for example, Farmelo's biography of Dirac (2009).
65. Dirac (1925). "The fundamental equations of quantum mechanics." Published 2 days after the Born and Jordan paper, but the latter was submitted 41 days before Dirac's. Dirac would not have seen it in print. Dirac's advisor, Ralph Fowler, managed to get his student's paper rushed into print (in 24 days).
66. All in *Proceedings of the Royal Society*: "Quantum mechanics and a preliminary investigation of the hydrogen atom" (1926a); "The elimination of the nodes in quantum mechanics" (1927b); "On the theory of quantum mechanics" (1926c); The physical interpretation of quantum dynamics" (1927a). Dirac almost never had a coauthor.
67. AIP Center for the History of Physics interview with Thomas Kuhn, October 17, 1962. Referring evidently to Dirac's first paper, "The fundamental equations of quantum mechanics" (Dirac, 1925), received by the *Proceedings* on November 7, 1925. Dirac had just turned 23 in August.
68. See the comments by Rudolf (Rudi) Peierls on Rutherford's impact on theoretical physics at Cambridge and the Cavendish Laboratory, where theoretical physics was kept alive only by Ralph Fowler. In Stuewer (1979). Fowler was Rutherford's son-in-law, though his wife, Eileen (née Rutherford) died at age 29 after the birth of their last child.
69. Dirac (1926b).
70. In this paper it is recognized that one could talk about eigenstates of any Hermitian operator, not just the Hamiltonian. See Hendry (1984), p. 95.
71. Dirac (1926c). On the subject one might consult Darrigol (1992). Dirac's use of the term "q-number" for an operator is unrelated to the q of p and q. See Duncan and Jannsen (2007), "Never mind your p's and q's."
72. We subsequently discuss this issue, but in anticipation, it should be noted that although Fermi and Dirac almost simultaneously discovered the statistics that carry their names, Jordan anticipated them both in a paper that he gave Born as editor of *Zeitschrift fur Physik*, but that Born misplaced in his briefcase for nearly a year. Jordan's reputation might now be very different had that not happened.
73. Dirac (1926b), p. 669.
74. In the interim he made the first attempt to formulate quantum electrodynamics (1927b) and introduced the "Dirac equation" in 1928. See subsequent discussion. The reception and influence of Dirac's book as against that of Born and Jordan of the same year could be explored at length. Of major importance was the fact that Dirac's book was continually revised during the following three decades.
75. In the introduction to Dirac's Oppenheimer Prize lecture (Dirac, 1971), p. 2. Kursunoğlu was a student of Dirac's.
76. Jordan (1927a, 1927b).
77. Born and Jordan (1930), *Elementary Quantum Mechanics.* This was the second volume of a projected three-volume work, *Lectures on Quantum Mechanics* (*Vorlesungen über Quantenmechanik*). The third volume never appeared.

78. Pauli's most positive comment in reviewing the work was one lauding the quality of the paper [Pauli (1932); translated in Beller (1999), p. 38]. Born and Jordan were separated in 1933 when the Nazi Party came to power and Jordan joined the party. Born, a Jew, took a position in Cambridge almost immediately, though he soon moved to Edinburgh where he stayed until 1952 as Tait Professor.
79. Hilbert et al. (1927). It is doubtful that Hilbert played an important role in developing the paper. Von Neumann was known as "Johnny," but was originally János Lajos Neumann or "Jancsi," Hungarian for Johnny.
80. Von Neumann (1927a, 1927b, 1927c)**.** At almost the same time, Norbert Wiener, in collaboration with Born (Born and Wiener, 1926) also introduced operator methods into quantum mechanics. Wiener had spent time in Gottingen in 1926, returning to the United States just as Born was visiting it. As Lothar Nordheim, who was Hilbert's physics assistant and a coauthor of the first paper, told it, he "tried at that time to cast the unifying Dirac-Jordan transformation theory into a simpler and more easily understandable form and to convey its essence to Hilbert. When von Neumann saw this he cast it in a few days into an elegant axiomatic form much to the liking of Hilbert." See Heims (1980), p. 431.
81. As recounted in Condon and Shortley (1935), when Dirac presented his theory at Princeton in 1928, with Weyl in the audience, the latter objected that although Dirac said he would use no group theory, everything the latter said was an application of group theory. Weyl's book was based on lectures he gave at Princeton during the 1928–1929 academic year. See Chapter 11.
82. Which Dirac introduced in 1928 (Dirac, 1928).
83. Hilbert et al (1927).
84. Weyl was a doctoral student of Hilbert. See *Hilbert*, by Constance Reid. According to Reid all of Hilbert's assistants were picked by Sommerfeld for him. After about 1922, Hilbert turned away from physics, abandoning his hopes of axiomatizing physics in the face of the proliferation of confusing experimental data.
85. Although he was soon forced out by Nazi anti-Semitism. When Hilbert died in 1943, Arnold Sommerfeld was among the six who attended his funeral (Wikipedia).
86. But also by Wigner (1931) and van der Waerden (1932). Wigner's mentors were Michael Polyani and Laszlo Ratz, but Wigner and von Neumann were boyhood friends in Budapest.
87. Sommerfeld (1930), preface; p. v in the English-language edition. The English translation, by Henry Brose, contained some changes from the original German edition. This statement was echoed by Wigner many years later in an AHQP interview.in April 1962. The last of his really important students finished in about 1930, including Hans Bethe in 1928, who would surpass the renown of his mentor, and Herbert Frölich in 1930.
88. Pauli (1926a), 2 months, almost to the day, after the BHJ paper was received. This paper is translated in van der Waerden (1967).
89. Dirac (1926a).
90. Schrodinger (1926a).
91. Schrödinger (1926d), p. 461 [p. 79 in Schrödinger (1928)]. In neither case is much attention given to the hydrogen atom wave functions per se. Schrödinger actually separated the PDE in parabolic coordinates. See Schiff (1968), p. 95. Also see the next chapter.
92. See Goldstein (1980), p. 103. Goldstein gives priority to Laplace.
93. Van der Waerden (1967).

94. Green (1965). Although the proof is somewhat different. See his chapter 6. Weinberg (2013) gives a very clear, modern version of Pauli's argument, as does Merzbacher (1998), pp. 268–9. Also the wonderful little book by Guillemin and Sternberg (1991).
95. In their 1926 paper on the anomalous Zeeman effect, Heisenberg and Jordan (1926) refer to the treatment of the hydrogen atom as the "Pauli-Dirac" theory.
96. Starting from Einstein's relation for the energy of a photon $E = h\nu$ and the relativistic relation between energy and momentum $E = pc$, de Broglie easily obtained the expression $\lambda = h / p$. This could be interpreted as suggesting that a particle of momentum p would have a wavelength λ associated with it. This was verified experimentally 3 years later by G. P. Thomson (1928) and by Davisson and Germer (1927a, 1927b, 1928).
97. In Slater and Frank's 1933 textbook of theoretical physics, one finds the following comment: ". . . there are some ways of stating wave [quantum] mechanics apparently somewhat more fundamental than the wave equation, but they are not the best methods to start one's study with" [Slater and Frank (1933), p. 345].
98. A similar point has been made by Aitchison et al. (2004), who noted that the pedagogical approach to quantum mechanics is quite different from that typically adopted in teaching special relativity, for which Einstein's original arguments are ordinarily employed. But, as we all know, it is not unusual for historical accuracy to be sacrificed for pedagogical convenience.

6

SCHRÖDINGER AND WAVE MECHANICS

THE WAVE EQUATION

In the fall of 1925, Pieter Debye suggested to Erwin Schrödinger that he should give a seminar at the University of Zurich—where Schrödinger been professor for 4 years—on Louis de Broglie's recently published work on the wave properties of particles.[1] Schrödinger was then 38, an age at which innovation or creativity by a theoretical physicist is commonly winding down. De Broglie had defended his thesis the previous November—at age 32 himself, having been delayed by the war—and Schrödinger had just managed to get a copy of it. The thesis represented the birth of the idea that particles have wave properties, but it failed to offer a program for describing physical systems, that is, there was no wave *mechanics*. Apparently Debye casually remarked, after hearing Schrödinger's exposition, that if one was going to talk about waves, one should have a wave *equation*. With that as a motivation, Schrödinger, already fascinated by de Broglie's startling idea, wrote down his first wave equation within a month. Felix Bloch reported that shortly thereafter Schrödinger announced that "My colleague Debye suggested that one should have a wave equation; well, I have found one."[2]

In his 1924 thesis for his doctorate at the Sorbonne, de Broglie had made the argument, largely from symmetry, that "it seems to us that the fundamental idea pertaining to quanta is the impossibility to consider an isolated quantity of energy without associating a particular frequency to it . . . energy = h x frequency."[3] Some fairly elaborate relativistic considerations led him, essentially, to conclude that if the momentum carried by light was given by $p = E/c$, then with the relation between energy and frequency, $E = h\nu$, we would obtain $p = h\nu/c = h/\lambda$.[4] Thus a particle with momentum p should have a wavelength λ associated with it. Later that year, as we saw in Chapter 1, Walter Elsasser suggested that an experiment could be attempted to test the hypothesis, only to find to his surprise that his mentor James Franck believed that the early experiments of Davisson and Kunsman had already verified it. Although the evidence for electron diffraction was at best equivocal in 1925, the waves postulated in de Broglie's thesis were the strongest motivation for Schrödinger (Figure 6.1), as he was about to embark on his attempt to find a wave equation.

Schrödinger's first unsuccessful attempt to obtain a wave equation that was relativistic apparently came within a few days of the late November seminar, but a Christmas retreat to the resort town of Arosa, Switzerland, led to success with a nonrelativistic equation.[5] He quickly finished his first paper on wave mechanics [*Wellenmechanik*] and sent it to the journal *Annalen der Physik*, which received it on January 27, 1926,

Figure 6.1. Erwin Schrödinger (1887–1961). Photograph by Francis Simon, courtesy AIP Emilio Segrè Visual Archives.

just 2 months after he had encountered de Broglie's thesis. It was also almost exactly 6 months after Heisenberg's paper founding matrix mechanics reached *Zeitschrift für Physik*.[6] The publication of these two papers, so close together yet so different, was the source of enormous consternation in the physics community, with both approaches being apparently valid and at the same time completely different in spirit. One emphasized relationships among observables, using as its starting point the fundamental discontinuities (in particular discrete energies) of quantum systems, whereas the other was based on nonobservable (being complex), continuous, square-integrable functions satisfying a linear partial-differential equation and whose meaning was entirely obscure. The motivations for the disparate approaches were identical: an attempt to reformulate classical mechanics—as required by the correspondence principle—in ways that would yield the observed discontinuities. But despite their congruence in time, the two approaches owed nothing to each other beyond the fact that they were attempts to solve the same set of empirical problems.

Schrödinger's path to wave mechanics during the winter of 1925–1926 has been described in many places, although never in detail by him.[7] It is clear that the main influences were, first, the hypotheses of de Broglie and Einstein, announcing wave–particle duality[8] and second, the well-known manner in which discrete solutions to partial-differential equations (including the classical wave equation) may emerge

from boundary-value problems in mathematical physics.[9] The conservative, middle-aged Schrödinger, "scared away, if not repulsed"[10] by Heisenberg's approach, searching as he was for a *continuum* theory of quantum mechanics, wrote in that first paper on wave mechanics that ". . . when integralness does appear, it arises in the same natural way as it does in the case of the *node-numbers* of a vibrating string,"[11] that is, in the classical eigenvalue problem.[12] That statement expressed the essence of Schrödinger's view of quantum discontinuities and their origin, and it contrasted sharply with the introduction of discontinuities from the outset in matrix mechanics.[13] In this way, Schrödinger could hope to preserve the central idea of classical mechanics that systems were described by differential equations in continuous variables, but also show how certain discrete quantum phenomena such as electronic states in hydrogen, could emerge.

FIRST PAPERS

In the opening paper, "Quantization as an eigenvalue problem, part I"[14] submitted to *Annalen der Physik* in January 1926, Schrödinger began by invoking the classical time-independent Hamilton–Jacobi equation[15] for the characteristic function S, the *action*, which he expressed as $K \log \psi$, which is the origin of the now-universal practice of using ψ for the "wave function," a term he introduced in his second paper a month later.[16] The January paper was the first of four with the same title, in which he progressively elaborated on the new theory. Strictly speaking, one cannot *derive* the Schrödinger equation from classical physics, so that there is necessarily some sleight of hand in Schrödinger's initial presentation.[17]

What we know is that Schrödinger was motivated to search for some kind of wave equation, a differential equation that would describe the de Broglie or matter waves. Although for the most part we are left to speculate about how he did this, we do know that he first arrived a relativistic wave equation, equivalent to what we know as the Klein–Gordon equation (see Chapter 13), but the results were unsatisfactory and it was never published. The development he offered in the first paper (part I) was later superseded by an attempt to provide a better justification in the later papers, primarily in part II. Here we see revealed that often messy process of justifying an idea or equation, which, despite very shaky foundations, soon becomes commonplace. The published paper sheds little light on how he arrived at the wave equation in the first instance, although it may well be that it was, indeed, through the vehicle of the Hamilton–Jacobi equation. On the other hand, he might have proceeded much as he did in parts II and IV, in which he began with the full, essentially classical, wave equation, second order in time, and then assumed a specific harmonic time dependence, $\exp(2\pi i \nu t)$, from which a form of the time-independent equation results immediately. Then the question of the actual form of the time-dependent equation could be revisited, as was done especially in part IV. But once he had framed quantum mechanics as an eigenvalue problem, there was no going back. In less than 2 months he was able to show the equivalence of the two approaches, his and matrix mechanics, and by the following year von Neumann, Dirac, and Jordan had virtually completed the

task that Schrödinger began, of formulating the theory in terms of eigenvectors on a Hilbert space.

In any event, having obtained the wave equation, the fundamental differential equation on which wave mechanics is based, Schrödinger applied it to the Kepler problem (hydrogen atom) right from the start.[18] He showed that in this case the eigenvalue spectrum had both discrete and continuous parts, and that for negative energy, solutions exist only for certain values of the separation constants, yielding discrete energy and angular momentum eigenvalues. The discrete energies of the bound hydrogen atom (and thus the Balmer frequencies) emerge directly in what Schrödinger could see as a "classical" treatment. *Voila*!

But, to give a bit more detail, in the initial paper the "derivation" proceeds as follows, beginning with the Hamilton–Jacobi (HJ) equation:

$$H\left(q_i, \partial S/\partial q_i\right) + \partial S/\partial t = 0. \tag{6.1}$$

For a stationary (time-independent) system, with $p_i = \partial S/\partial q_i$ (here is the crux of the matter, of course), $H(q, \partial S/\partial q) = E$. Given the classical Hamiltonian in Cartesian coordinates, Schrödinger obtained the corresponding time-independent (or reduced) HJ equation, which involved terms of the type $(\partial\psi/\partial x)^2$, where ψ replaced the classical action S in the form $S = K \log \psi$. He then introduced a variational method (Hamilton's principle), noting that "the quantum conditions are replaced by this variational problem." Requiring that ψ be real, single valued, finite, and have continuous second derivatives, and with $E = \sum p_i^2 + e^2/r$ (for the Kepler problem) written in terms of $p_i = \partial S/\partial q_i$, he obtained the quadratic form whose integral J over all space was required to be stationary $(\delta J = 0)$. From this variational principle, Schrödinger obtained a second-order partial-differential equation (PDE) for ψ. This was the "time-*independent* Schrödinger equation (SE),"[19]

$$\nabla^2\psi + 2/\hbar^2\,(E - V)\psi = 0, \tag{6.2}$$

It would not be long, however, before he came to reject this approach to obtaining the SE.

Having wasted no time in applying his theory to the problem of a $1/r$ potential, he obtained the solution to this *wave equation* by using the method of Laplace transforms, which he had learned from Schlesinger,[20] rather than by a power-series method, and when he found the solution, he did not recognize or did not know that the functions were in fact associated Laguerre polynomials.[21] After several pages he arrived at an expression for the bound-state energies, from which the wavelengths of the Balmer series lines can be obtained. In part III, published 4 months later, he used perturbation theory to treat the Stark effect in hydrogen and did give the unperturbed hydrogen-atom wave functions in terms of Laguerre polynomials, which he obtained by separating the SE in parabolic coordinates.[22] The solution to the angular equation again gave rise to "surface harmonics," (spherical harmonics), and the "separation constant" that

emerged was shown to equal $n\,(n+1)$, where n was an integer. Schrödinger did not explicitly refer to angular momentum [*Drehimpuls*], but he did say that "our ℓ is the principal quantum number. $n + 1$ is analogous to the azimuthal quantum number."[23] Notably, because the meaning of the wave function had not been explored, little attention was given to the eigenfunctions themselves, which would in due course give the radial and angular probability densities for the electron.

In the first paper, and in the others as well, Schrödinger specifically chose not to address spin and the related Zeeman effect, even as he acknowledged the importance of the recent discovery of "the paradoxical but happy conception of the spinning electron."[24]

More important, Schrödinger also declined, at least initially, to speculate about the meaning of ψ:

> It is of course strongly suggested that we should try to connect the function ψ with some vibration process in the atom, which would more nearly approach reality than the electronic orbits, the real existence of which is being very much questioned today. I originally intended to found the new quantum conditions in this more intuitive manner, but finally gave them the above mathematically neutral form, because it brings more clearly to light what is really essential.[25]

When Schrödinger wrote his second paper on wave mechanics (part II), received by the *Annalen* less than a month after the first, he rejected the earlier derivation that we have just sketched, describing the transformation $S = K \log \psi$ as "unintelligible," though he was being a bit hard on himself, and recognizing that his variational process was faulty (or "equally incomprehensible"). But the new "derivation" is not much more satisfying than the first, a situation that is not surprising because, as noted, there is virtually no way to *logically derive* the Schrödinger equation from classical physics.[26] Analogy, plausibility, and correspondence principle arguments would have to suffice. In the new approach Schrödinger emphasized the analogy between Hamiltonian mechanics and optics and thereby provided a new justification of the wave equation. Before moving to applications he hedged his bets, so to speak, saying that "our postulation is again dictated by the striving for simplicity," and that "I consider in this case that a wrong deduction is not out of the question."[27] He then labored mightily for some 21 pages, before simply writing down a wave equation that is second order in both space and time derivatives

$$\nabla^2\psi - 1/u^2\,\partial^2\psi/\partial t^2 = 0, \tag{6.3}$$

acknowledging that "It is not even decided that it must be definitely of second order. Only the striving for simplicity leads us to try this to begin with."[28] Assuming solutions of the form $\exp(-2\pi i\,\omega t)$, the wave equation became a parabolic PDE (Helmholz equation), the *time-independent SE*.[29] Schrödinger acknowledged that "the substitution of a partial differential equation for the equations of dynamics in atomic problems appears at first sight a very doubtful procedure." And he observed that "It seems to be

a bad beginning for a new attempt in this direction if the number of possible solutions has been *increased* rather than diminished." Moreover,

> Whatever the fear expressed about taking the equation (18) [our equation (6.2)] as the foundation of atomic dynamics comes to, I will not positively assert that no further additional definitions will be required with it. But these will probably no longer be of such a completely strange and incomprehensible nature as the previous "quantum conditions,"[30] but will be of the type that we are accustomed to find in physics with a partial differential equation[,] as initial or boundary conditions.[31]

But despite these misgivings, he didn't look back, but instead went on in that paper to treat the harmonic oscillator (in terms of Hermite polynomials) and the rigid rotor. In contrast to Heisenberg's first paper, this one (and the previous ones as well) is quite accessible and even transparent to modern readers.[32] The positive reception of Schrödinger's approach is not surprising.

In working out the problem of the three-dimensional rigid rotor, the process of separating the wave equation in spherical coordinates, again led to the angular equation and its solution in terms of surface harmonics and to integral values for the quantum number n (or ℓ).[33]

In part IV, submitted in June 1926, Schrödinger was still agonizing over the problem of establishing the wave equation on a firm foundation, and in particular its time dependence, because he was intending to treat perturbations that might vary with time. As we noted, in part II he had introduced a time-dependent wave equation that was second order in space and time [Eq. (6.3)]:
or, as he wrote shortly thereafter in Part IV:[34]

$$\nabla^2\psi - 2(E-V)/E^2\partial^2\psi/\partial t^2 = 0. \tag{6.4}$$

He notes that this equation as an alternative to our Eq. (6.2) "is not really any more general," so he is still floundering a bit. But to treat *time-dependent perturbations*, Schrödinger had to explore the consequences of this second-order time dependence. Again assuming the $\exp(\pm i\omega t) = \exp(\pm 2\pi i Et/h)$ time dependence, he obtained

$$\partial^2\psi/\partial t^2 = -(4\pi^2E^2/h^2)\psi, \tag{6.5}$$

which led, from Eq. (6.5) to the time-independent SE [Eq. 6.2)].

$$\nabla^2\psi + 8\pi^2/h^2\,(E-V)\psi = 0. \tag{6.6}$$

But as an alternative to Eq. (6.5), the $\exp(\pm 2\pi i\,Et/h)$ time dependence also implies that

$$\partial y\psi/\partial t = \pm 2\pi i/h\; E\psi, \tag{6.7}$$

whence $\partial^2\psi/\partial t^2 = \pm(2\pi\, iEt/h)\partial\,\psi/\partial t$, so that Eq. (6.e) becomes

$$\nabla^2\psi + 8\pi^2/h^2 V\psi \pm (4\pi i/h)\partial\psi/\partial t = 0, \tag{6.8}$$

which is the conventional time-dependent SE. Schrödinger saw Eq. (6.7) as eliminating E from the equation.[35]

Thus, without much obvious conviction, Schrödinger arrived at essentially the modern expression (6.8), which, written in terms of ħ, had the form

$$\nabla^2 y\psi - (2m/\hbar^2)V + i(2mi/\hbar^2)\partial\psi/\partial t = 0. \tag{6.9}$$

The only real justification was that "we need not raise the wave equation to [order] four, in order to get rid of the energy parameter."[36] That is, the second-order time dependence was not *necessary.*

Although necessarily lacking rigor, the development was plausible, and thus Schrödinger rather tentatively concluded that the wave equation had to be first order in time and also that ψ must be complex,[37] though he seemed to be content with Eq. (6.4) as well, at least for conservative systems, and commented, in favoring Eq. (6.9) over the alternative, only that "I have taken a somewhat different route, which is much easier for calculations, and which I consider is justified in principle." We look in vain for some serious justification of the first-order time dependence, such as the fact that the time dependence of $\psi(x,t)$ is determined solely by $\psi(x,0)$, though this may very well have been in his mind.[38] In any event, Eq. (6.9) is then, essentially, although it doesn't appear explicitly,

$$H\psi = i\hbar\,\partial\psi/\partial t,$$

with $H = -\hbar^2/2m\nabla^2 + V$, in terms of which the eigenvalue equation (6.) can be written as $H\psi = E\psi$.

Finally, in a series of lectures given at the Royal Institution in London in 1928,[39] Schrödinger toyed with the idea that one should only deal with the observable $|\psi|^2$ and try to find a differential equation for it, an idea that was quickly rejected. In the first of the lectures, he essentially reproduced the "derivation" of the time-dependent wave equation that appeared in part IV, using the full wave equation, assuming an $\exp(2\pi i\nu t)$ time dependence to obtain the time-independent equation (SE). But in the second lecture, he worked backwards from the latter, using this same time-dependence to obtain a differential equation (DE) that is first order in time, the time-dependent SE (TDSE) (see subsequent discussion). A further sleight of hand there.[40]

By May of 1926, in part III, Schrödinger had treated the Stark effect in hydrogen and even calculated transition probabilities or intensities of transitions among perturbed Balmer lines, though he first had to develop a form of *time-independent* perturbation theory. The subtitle of this paper was "Perturbation theory, with application to the Stark Effect of the Balmer lines."

WHAT KIND OF WAVE? UNDERSTANDING ψ

Interpreting ψ was another question entirely. Quite wisely, Schrödinger had initially chosen not to speculate about the meaning of the wave function. The fact that ψ had to be a complex function troubled Schrödinger but his conclusion that $e|\psi|^2$, where e is the electronic charge, gave the charge density made a complex ψ at least palatable. He was quite clear that "no special meaning is to be attached to . . . the position of the electron along its path" and that "all these assertions systematically contribute to the relinquishing of the ideas of "place of the electron" and "path of the electron."[41] He also noted that "the real existence [of electronic orbits] is being very much questioned today."[42]

But one of the most interesting aspects of his final paper on wave mechanics is that Schrödinger does finally attempt to give meaning to the wave function, despite earlier declining to do so. Noting that $e\psi^*\psi$ represented "the electrical density as a function of the space coordinates . . . ", he went on to say that it is "a kind of weight-function in the system's configuration space."[43] Going beyond that insight, which might have influenced Born in his understanding of ψ, Schrödinger considered the time derivative of $e\psi^*\psi$ and interpreted it as a *current density S*, in essentially the modern form.[44] This was not the *probability current density*, of course because it involves the charge (e) of a particle and thus is a real current density. On the other hand, he was quite clear that "the ψ-function itself cannot and may not be interpreted directly in terms of three-dimensional space—however much the one-electron problem tends to mislead us on this point—because it is in general a function in configuration space, not real space."[45] Then, in a paper in *Naturwissenschaften* the same year as his revolutionary quartet in *Annalen der Physik* (1926), Schrödinger used the idea of a wave packet [*Wellengruppe*[46]] to make a connection between microscopic and macroscopic theories.

Schrödinger did not abandon the hope of providing some additional physical basis for quantum mechanics, perhaps even a kind of visualization. He noted that "*in tendency*" Heisenberg's approach "stands very near the present one," although in its method it is "so totally different." He added that "The strength of Heisenberg's programme lies in the fact that it promises to give the *line-intensities*, a question that we have not approached as yet." But "the strength of the present attempt . . . lies in the guiding physical point of view, which creates a bridge between the macroscopic and microscopic mechanical processes."[47]

Although the term "matter wave" revealed a predisposition toward some sort of physical wave, a "pilot wave," perhaps guiding the particle in question, that view became difficult to maintain when it was realized that ψ had in general to be complex.[48] But de Broglie, the godfather of wave mechanics, was for some time still committed to the physical reality of the waves he had set in motion. In any case, because the wave equation was an eigenvalue equation, the question of the meaning of its eigenfunction ψ immediately became the central issue. Clearly ψ was attached in some way to a "state," an "eigenfunction," but how?

RECEPTION AND RECONCILIATION: EQUIVALENCE OF MATRIX AND WAVE MECHANICS

The reception of wave mechanics was cautious, and despite the obvious successes of the Schrödinger approach, there was much unease surrounding the meaning of the central feature of the theory, the *wave function*, and tension between the obvious efficacy of the theory and the mysterious "field scalar" [*Feldskalar*] ψ. By the end of 1926, Schrödinger had published a summary of his "undulatory theory" in English in the American Physical Society's *Physical Review*,[49] making his ideas more readily available to the Anglophone world. Although Born expressed annoyance that physicists so quickly embraced Schrödinger's theory at the expense of matrix mechanics, he was quick to take advantage of the new formulation.[50] Heisenberg, however, was much slower to come around.

The fact that quantum mechanics could be formulated in two apparently distinct ways made it almost certain that these approaches must be special cases of a more general, abstract formalism. If either approach had preceded the other by a much longer time, the evolution of quantum mechanics, and in particular the abstract formulation or "transformation theory" of Dirac and Jordan, might have taken a very different course. The crux of the problem for the adherents of matrix mechanics was that, on the one hand, Schrödinger's approach was clearly important and evidently valid, and yet it seemed fundamentally at odds with the understanding of quantum discontinuities that had evolved in the previous decade.[51] Schrödinger remarked that Heisenberg's approach "in its method is so totally different that I have not yet succeeding in finding the connecting link," but he was "distinctly hopeful that these two advances will not fight against one another."[52] Although Born immediately saw the importance of Schrödinger's method,[53] Heisenberg was much harder to convince, notably because Schrödinger's goal was to replace quantum discontinuities with classical modes of vibration and a continuous function ψ, which apparently was unobservable.[54]

Schrödinger published three remarkable papers in vol. 79 of *Annalen der Physik*,[55] and it was in the last one, published in May 1926, that he demonstrated the "equivalence" of wave and matrix mechanics in a paper titled "On the relation between the quantum mechanics of Heisenberg, Born, and Jordan, and that of Schrödinger."[56] Since March, the world of physics, long suffering from the lack of any quantum theory, had been faced with two viable theories, both of which seemed to explain the facts. One theory dealt only with observables and made no reference to eigenvectors or "states,"[57] whereas in the other, the eigenfunctions were primary. One was inherently discrete, with discontinuities imposed from the outset, whereas the other was framed in terms of PDEs involving continuous variables. Fortunately the uncertainty did not last long, as not only Schrödinger, but others, including Carl Eckart, Pauli, and Dirac, were able to show the essential equivalence of the approaches.[58]

So it was that in May 1926, between the second and third parts of his quartet of papers, Schrödinger showed that the system of algebraic equations connecting matrix elements of p and q with that of the Hamiltonian in Heisenberg's mechanics

was completely equivalent to the solution of a boundary-value problem in coordinate space involving the set of orthogonal functions that were solutions to his wave equation.[59] He accomplished this by recognizing, essentially from Hamilton–Jacobi theory, that the momentum p has to be replaced by the operator $K\,\partial/\partial q$, where $K = -i\hbar$.[60] He then introduced orthonormal eigenfunctions $u_i(x)$ (stand-ins for ψ) and defined the matrix element of an operator F as follows:

$$F_{kl} = K\int \rho(x)\, u_k(x)\big[F,\, u_l(x)\big]\, \mathrm{d}x, \tag{6.10}$$

where in this case $[F, u(x)]$ merely denoted F operating on $u(x)$. Thus, in Schrödinger's paper, $[H, u_i] = E_i u_i$ means $Hu_i = E_i ui$.

So, for example, the matrix elements of p_1 and q_1 are given by:

$$p_l^{\,ik} = K\int \rho(x)\, u_i(x)\, [\partial u_k(x)/\partial q_l]\, \mathrm{d}x, \tag{6.11}$$

where $K = -i\hbar$,

$$q_l^{\,ik} = \int q_{l(x)}\rho(x) u_i(x)\, u_k(x)\, \mathrm{d}x, \tag{6.12}$$

and so on. Thus he could show that the matrix elements of observables, i.e., p, q, q^2, H, etc., obtained from eigenfunctions of the SE, were the same as those obtained in Heisenberg's method. The result was, he said, that "the solution to the whole system of matrix equations of Heisenberg, Born, and Jordan is reduced to the natural boundary value problem of a liner partial differential equation."[61] He then could obtain matrix elements of the expression $[p_i, q_j]$ (not using commutator notation, of course), obtaining $\left[p_k, q_k\right] = p_k q_k - q_k p_k = -i\hbar$. All of this was based on the theory of self-adjoint linear operators that he knew from Courant and Hilbert's book[62] and from discussions with Weyl, who was at Zurich with him at the time.[63]

Thus Schrödinger had shown that by obtaining matrix elements of the Hamiltonian from the eigenvalue equation $H\psi = E\psi$, where the Hamiltonian H was a differential operator, he could reproduce the corresponding matrix elements in the Heisenberg–Born theory, justifying his statement that "we have . . . shown that matrices constructed . . . from well behaved functions by the agency of an arbitrary, complete, orthogonal system . . ., satisfy all of Heisenberg's calculations."[64] He even ventured that "from the formal mathematical standpoint, one might well speak of the *identity* of the two theories."[65]

Schrödinger's proof, although historically crucial, could hardly be considered definitive. In particular, his treatment considered only normalizable wave functions and was therefore incomplete. Dirac's subsequent introduction of the "Dirac delta-function," if something of a mathematical fiction or at least aberration, addressed that problem, but not to everyone's satisfaction.

Schrödinger's paper was received on March 18, and within a month Pauli had also established, somewhat more robustly, the equivalence of wave and matrix mechanics and informed Jordan of that fact by letter on April 12.[66] When Born returned from MIT in April Jordan told him of Pauli's result, and, before the summer was out, Born,

encouraged by the established equivalence, had made the crucial step forward by using wave mechanics to interpret the wave function probabilistically in the course of an attack on collision theory.

In that same spring, the American physicist Carl Eckart, at Cal Tech, independently demonstrated the equivalence of the two approaches, again showing that the matrix elements obtained in the Heisenberg approach could be obtained by simple integration in wave mechanics.[67] Dirac's paper "On the theory of quantum mechanics,"[68] in which the equivalence is also shown, was submitted in August of the same year, 1926, and published in October. In his more complete proof of the equivalence of the two approaches using his new transformation theory, submitted in December 1926,[69] Dirac noted that "*The eigenfunctions of Schrödinger's wave equation are just the transformation functions . . . that enable one to transform from the (q) scheme of matrix representation to a scheme in which the Hamiltonian is diagonal*" [Dirac's italics]. In other words, $\psi_E(x) = \langle x | E \rangle$ in modern ("Dirac") notation.[70]

Of the two theories (Schrödinger wrote "I might reasonably have used the singular") and which approach is to be preferred, Schrödinger observed that "as the natural advocate of one [point of view], I will not be blamed if I frankly—and not wholly impartially—bring forward the arguments in its favor."[71] He further explored the question of whether mathematical and physical equivalence meant the same thing, citing the 19th-century views of Kirchoff and Mach. And in defense of his own formulation, which actually had been criticized for its intuitiveness or visualizability, he argued that "the [wave] functions do not form, as it were, *arbitrary* and *special* "fleshly clothing" for the bare matrix skeleton, provided to the need to pander to intuitiveness." Were that the case, said Schrödinger, "this would really establish the superiority of the matrices, from the epistemological point of view." Heisenberg viewed the matter differently, of course. Even after Schrödinger demonstrated the equivalence of the two methods, Heisenberg wrote to Pauli that "The more I think of the physical part of the Schrödinger theory, the more abominable [repulsive] I find it."[72] On the other hand, the theorist Hans Thiring, a close friend of Schrödinger's, turned the tables by criticizing Heisenberg's theory as "phenomenological" because it only involved relations among observables, hence lacking any inner meaning. Further, he remarked, in favoring the wave theory, that ". . . the introduction of the noted fictitious [i.e., unobservable] concepts turns out to be a very helpful and profitable tool."[73]

Very soon, others were applying wave mechanics to a variety of problems, notably Kronig and I. I. Rabi, who, shortly after Schrödinger's third paper was published, used his method to treat the fairly complicated problem of the symmetric rotor, publishing a note giving their result in December 1926.[74]

CONCLUSION

In contrast with the incremental results that led to Heisenberg's paper in 1925, Schrödinger's bombshell theory came out of nowhere. Despite strong misgivings, Heisenberg, Born, and Jordan, the founders of matrix mechanics, very quickly found

it useful to explore Schrödinger's method themselves, even as they held a clear preference for their own.[75] Indeed, they continued to think of their theory as "quantum mechanics," as opposed to the alternative, wave mechanics. Even Pauli, who in a technical tour de force that has been described, showed that the Balmer series of hydrogen could be reproduced by matrix mechanics, only 5 months after Heisenberg's first paper (and before Schrödinger's wave mechanical treatment)[76] soon grudgingly realized the power of Schrödinger's method.

Schrödinger's papers were remarkable for their clarity, completeness, and their use of familiar mathematics, and so the years 1926 and 1927 were dominated by the search for a unified understanding of the relationship between the two competing theories and in particular the implications of the wave function ψ. No similar conundrum arose in matrix mechanics, which made the equivalence all the more mysterious. Although much of the exploration occurred in Germany, at Göttingen especially,[77] the real soul-searching can be said to have taken place in Copenhagen, involving three-sided discussions among Bohr, his 24-year old assistant Heisenberg, and the maverick Schrödinger, who was just 2 years Bohr's junior but a newcomer to the quantum debate. Little of this argumentation reached the primary literature, but as one reads the correspondence of the principals it becomes clear that these years were preoccupied with this process of understanding what it meant that the Göttingen–Cambridge and Schrödinger approaches could be reconciled, not just formally, but philosophically or ontologically as well.[78] The first step may have been the demonstration that the theories were mathematically equivalent, but the more important and prolonged process was that carried out by Dirac and Jordan, who showed very generally that wave mechanics and matrix mechanics are just two realizations of a more general theory, with firm mathematical foundations.

At one point Schrödinger had observed that "Considering the very different starting points . . . it is very strange that these two theories agree with one another . . .,"[79] and, indeed, it is hard to come up with another situation in which two so distinct formulations of a problem turned out to give the same results, and were, *ipso facto*, equivalent, in that sense at least.[80]

By late 1926, it had come to Heisenberg's notice that the tide had shifted away from matrix mechanics to the more intuitive wave mechanics, and worse, that people were reworking matrix-mechanics proofs in the hated framework of wave mechanics.[81] Pauli and Heisenberg saw eye to eye on this question, being unwilling to accept that a continuum theory like Schrödinger's could capture all of the physics of the microscopic world with all of its discontinuities.[82] Increasingly Heisenberg was at odds with Bohr and his followers at Copenhagen, who embraced wave mechanics enthusiastically. The less doctrinaire Max Born, while favoring matrix mechanics, would make extensive use of Schrödinger's method in his treatment of collisions, and wrote of Schrödinger's theory that he was "inclined to regard it as the most profound formulation of the quantum laws."[83] In the face of the popularity of wave mechanics, it gave Heisenberg little comfort that the two approaches could be shown to be equivalent.

In the fall of 1933, with Hitler in power, Schrödinger left his post at the University of Berlin for Oxford, but fatefully, and with some trepidation, returned to Austria

2 years later.[84] In 1938, he, who was unusual among non-Jewish scientists in opposing the Nazi regime but had tried to save his position by writing a groveling letter of appeasement to the Austrian authorities, was dismissed from his post in Graz for "political unreliability." Later that year, after the Anschluss, he fled for good. After brief stops at Oxford and in Belgium, he eventually found his way to Dublin, where he remained for 17 years.[85]

Rewards came quickly to the founders of both approaches to quantum theory, as Heisenberg was awarded the Nobel Prize in physics for 1932 and Schrödinger and Dirac shared the prize the following year. Born had to wait until 1954, splitting it with Walter Bothe, and Jordan would never be so honored.[86]

In 1927 Schrödinger was 40 years old, and by the time he reached Dublin he was in his 50s and further developments were destined to be carried out by the younger generation: Dirac, Pauli, Heisenberg, Jordan, and von Neumann, all born at the turn of the century. Even after Dirac's abstract formulation of quantum mechanics[87] and the development of transformation theory, there remained open questions, some of which von Neumann resolved in 1932,[88] at which point it could be said that quantum mechanics was virtually complete. We explore the details in Chapters 8 and 9.

NOTES

1. De Broglie (1925). De Broglie's paper had just appeared (de Broglie, 1925). Debye was professor at E. T. H. (*Eidgenössische Technische Hochschule)*also in Zurich. De Broglie wrote several papers leading up to his 1924 thesis.
2. Bloch (1976). Also quoted in Moore (1989), p. 192. As recounted in Condon and Morse (1929), p. vii, "The story is told that someone asked Schrödinger to report on de Broglie's thesis to the colloquium at Zurich, and that he thus came to read it and to build his famous series of papers on 'undulatory mechanics' upon it." The seminar, suggested by Peter Debye, was probably given on November 23. Moore (1989), pp. 191–2. Although not questioning this account, Raman and Forman (1969) do not consider this adequate as an explanation of why it was Schrödinger rather than someone else.
3. De Broglie (1925).
4. We could say, with Weinberg (2013), that de Broglie considered the four-vectors $k^\mu=(k, \omega)$ and $p^\mu=(p, E)$, with $p^\mu = h\, k^\mu$. Among other things, de Broglie showed that Bohr's final condition for stable orbits involving quantization of angular momentum was consistent with his ideas. As we now put it, an integral number of de Broglie wavelengths λ fit into the circumference of a Bohr orbit.
5. See Moore (1989), including the discussion of the relativistic equation on p. 194. He went on holiday to Arosa with a "mysterious" woman who has never been identified. See Moore (1989), pp. 194–5. He was teaching at Zurich at the time, moving to Berlin in 1927. As people will do, much has been made of the erotic context of the discovery.
6. The dates were July 29 and January 27, respectively. Schrödinger (1926a), part I of "Quantization as a problem of proper values," (or "Quantization as an eigenvalue problem," hereafter "part I" or "SI." The *Collected Papers on Wave Mechanics*, originally published in German in 1927, contained the first six papers (including parts I–IV) that Schrödinger published in vols. 79–81 of *Annalen der Physik* in 1926. Subsequently three more papers

from vols. 82 and 83 and some lectures were added. The first English edition was published in 1928 and the present one in 1982. The translator was J. F. Shearer. Four of these papers are also given, at least in part and in a different translation, in Ludwig (1968). It seems better to cite passages from the collected English translation, but the original references are given in the bibliography. The publication dates of parts I–IV were March 13, April 6, July 13, and September 8, 1926. The paper showing the equivalence of matrix and wave mechanics (Schrödinger, 1926c) was published on May 4, 1926. The average interval between receipt and publication for these five papers was 55 days, the last two being 64 and 77 days, still a very quick turnaround by today's standards. We note here in passing that Schrödinger rarely, if ever, published a paper with a coauthor.

7. See Moore (1989), p. 197.
8. Schrödinger wrote in part III (Schrödinger 1926d) that "My theory was stimulated by de Broglie and by brief, but infinitely far-seeing remarks of A. Einstein" [Schrödinger (1926d), fn. 1]. And in part I (Schrödinger, 1926a) he wrote that "Above all I wish to mention that I was led to these deliberations in the first place by the suggestive papers of M. Louis de Broglie." And of course de Broglie was himself directly inspired by Einstein's discovery of the particle properties of light, i.e., the photon. Jammer (1966) gives some background to de Broglie's hypothesis and to its influence on Schrödinger in his chapter 5. It is, however, of the utmost significance that Schrödinger was something of a loner and, in aligning himself with de Broglie and Einstein, was out of the mainstream. This is reflected in his decision to subsequently publish in the *Annalen* rather than in the newer, trendier, *Zeitschrift*. Some have seen Schödinger's 1922 paper as foreshadowing de Broglie.
9. In the first paper, Schrödinger wrote that "The essential thing seems . . . to be, that the postulation of "whole numbers" no longer enters . . . mysteriously, but that we have . . . found the 'integralness' to have its origin in the finiteness and single-valuedness of a certain space function"(p. 9 in the collected papers—Schrödinger, 1928). Schrödinger leaned on the text of Ludwig Schlesinger, *Introduction to the Theory of Differential Equations*, of 1900 (Schlesinger, 1900). See Moore (1989), p. 199.
10. Pais (1995), p. 281. Or, "discouraged, if not repelled." Schrödinger (1926c), p. 46 in the English translation by Shearer, read by Schrödinger himself (1928).
11. Schrödinger (1926a).
12. Schrödinger's conservatism, which represented a continuation of his important work in statistical mechanics, was welcomed by such figures as Lorentz, Planck, and Einstein. See Rosenfeld (1971).
13. That somewhat ad hoc process was described by Eckart as having "a frankly empirical basis."
14. Schrödinger (1926a) SI; "Quantisierung als eigenwertproblem, Erste mitteilung," which is translated in the English-language compilation (Shrödinger, 1928) as "Quantization as a problem of proper values," a decision made in consultation with Schrödinger and others, which was explained in a publisher's note. We would use "eigenvalue problem."
15. See José and Saletan (1998), chapter 6, Goldstein (1980), chapter 10, or any graduate analytic mechanics text. In fact, Schrödinger's Eq. (1) is found in precisely the same form in chapter 3 of de Broglie's 1925 paper, which was essentially his 1924 thesis.
16. *Wellenfunktion* in German.
17. Clearly there is no way to logically or uniquely derive quantum mechanics from classical mechanics for the simple reason that the latter is a limiting case of quantum mechanics.

The nearest thing would be to approach the problem as Schrödinger originally did, starting from the Hamilton–Jacobi equation of classical mechanics, though Schrödinger's original criticisms still apply. Writing down the full wave equation and then assuming a harmonic time dependence will lead to the time-independent SE in the form of a Helmholtz equation, but the physical content of the energy eigenvalue equation is missing and the time-dependent equation is wrong to begin with. One can, as Schrödinger did, then work backward to a time-dependent equation that is first order in time (Schrödinger, 1928, pp. 104, 176), but that is hardly palatable. One can also simply write down the most general differential equation that is second order in space and first order in time, but then the physical content is absent. Finally, recognizing that the SE is just the energy eigenvalue equation in a position representation, one can postulate quantum theory as a theory of states in a Hilbert space with observables represented by Hermitian operators and in particular the energy eigenvalue equation $H\psi = E\psi$. Making the identification $p \rightarrow -i\hbar\nabla$, one obtains the SE. This can be accomplished, as Sakurai shows (1985, p. 54), by using the properties of momentum as the infinitesimal generator of translations. The time-dependent Schrödinger equation (TDSE) $H\psi = i\hbar\partial\psi/\partial t$ can be similarly obtained by employing the property of the Hamiltonian operator in generating time displacements, as, again, Sakurai shows (pp. 71–2).

18. The first sentence addresses the Kepler problem: "In this paper I wish to consider, first, the simple case of the hydrogen atom."
19. On the second page of the paper, in essentially this form. SI, p. 27 (Schrödinger, 1926a). Weinstock (1952), pp. 262–3, reproduces Schrödinger's derivation. Or Eq. 18 in SII.
20. Separated in spherical coordinates with the angular functions being spherical or "surface" harmonics, which Eckart says were not widely known in 1926 (interview with Heilbron, May 31, 1962). Schlesinger (1900).
21. See n. 1 in part IV (SIV); Schrödinger (1926e).
22. Which turn out to be useful in problems in which a preferred direction is involved, as, for example, in the Stark effect, which is what Schrödinger was considering. See Schiff (1955), pp. 87–9.
23. Schrödinger (1928), p. 8; (1926a, p. 371). In Schrödinger's notation, ℓ was what we call the principal quantum number and n was the orbital angular momentum quantum number, the reverse of current practice. In Sommerfeld's notation, $k = \ell + 1$ was the orbital or azimuthal quantum number. When BHJ introduced angular momentum into the Göttingen mechanics, they used the generic j, which, of course, Sommerfeld had introduced as the "inner," i.e., total, quantum number. Again, nowhere in either parts I or II does Schrödinger use the term "angular momentum," despite working with it directly.
24. SIII; Schrödinger (1926d), p. 439; p. 64 in the English translation [Schrödinger (1927)]. Although this paper was submitted in May 1926, the first paper by Uhlenbeck and Goudsmit had appeared the previous November. See Chapter 10.
25. SI, p. 9 in Schrödinger (1928), p. 372 in the original (1926a). In this original the word *anschaulich*, illustrative or pictorial, is used rather than "intuitive." Pais (1994), p. 304, chose to translate this as "physical."
26. One argument would go like this: The de Broglie relation $\lambda = h/p \rightarrow p = \hbar k$. $E = p^2/2m \rightarrow \hbar^2/2\nu = hn = \hbar\omega$. Then, for a plane wave $\psi = \exp[i(kx - wt)]$, $k^2 \rightarrow -\mathrm{d}^2\psi/\mathrm{d}x^2$ and $\omega \rightarrow i\,\mathrm{d}\psi/\mathrm{d}t$. Hence $-(\hbar^2/2m)\,\mathrm{d}^2\psi/\mathrm{d}x^2 = i\hbar\,\mathrm{d}\psi/\mathrm{d}t$. One can also write down the most general second-order linear, homogeneous differential equation

that is of second order in its spatial derivatives and first order in time: $a\nabla^2\psi + b\partial\psi/\partial t + c\psi = 0$. Dimensional arguments then lead to the SE.

27. Simplicity, that seductive mistress . . . SII; Schrödinger (1926b), p. 510. Schrödinger (1928), p. 28.
28. SII, p. 27 in the translation (Schrödinger, 1928). Schrödinger effectively apologized for the "unintelligible" and "incomprehensible" features of the first derivation (SII). It was only in part IV, which he submitted in June 1926, that Schrödinger found what we know as the "time-dependent Schrödinger equation.
29. Schrödinger (1926b); SII, p. 27 in Schrödinger (1928); p. 510 in the original.
30. Referring to those used in Heisenberg's and earlier papers.
31. Schrödinger (1926b), p. 511, p. 28 in Schrödinger (1928).
32. Although Moore (1989, p. 200) has called it "almost deliberately cryptic."
33. Schrödinger (1926b), p. 521; Schrödinger (1928), p. 35. As in part I, nowhere in part II does Schrödinger use the term angular momentum, despite working with it directly. Schrödinger entertains the idea of odd half-integral [*halbzehlige*] values of *n* "from various arguments from experiment."
34. Pages 102–4 in Schrödinger (1928), or Schrödinger (1926e), p. 109. He wrote that "only the striving for simplicity leads us to try this to begin with." Schrödinger (1926b); p. 27 in Schrödinger (1928).
35. See the "second lecture" in Schrödinger (1928), pp. 177–8.
36. SIV, p. 104 in Schrödinger (1928).
37. Lorentz was very anxious to eliminate *i* from quantum theory, but von Neumann argued that this preoccupation was a waste of time Heilbron AIP interview with Eckart, May 31, 1926)]. Schrödinger wrote in 1926 that ". . . there is no doubt a certain crudeness in the use of a *complex* wave function" (Schrödinger, 1926e; 1928, p. 123). The justification is often used that specifying $\psi(x,0)$ should be sufficient to determine $\psi(x,t)$ for all time, requiring the SE to be first order in time and second order in space.
38. See Merzbacher (1998), p. 22. An interesting discussion follows, leading to the Hamilton–Jacobi equation.
39. At the invitation of Sir William Bragg. The lectures, given in March 1928, were printed with his other papers on wave mechanics in the third English edition of his *Collected Papers*, published in 1982. (Schrödinger, 1928).
40. One is reminded of Weinberg's comment (see Chapter 5) about proofs that are almost pure magic.
41. In Schrödinger (1928), p. 26 (p. 508 in the original (Schrödinger, 1926b).
42. Page 9 in Shrodinger (1928), p. 372 in SI.
43. Schrödinger (1928), p. 120 (p. 134 in original, Schrödinger, 1926e).
44. Ibid., p. 122, p. 138 in Schrödinger (1926e).
45. Ibid., pp. 120–1 (p. 135 in original). See Rosenfeld (1971), p, 34.
46. In German, *Wellenpaket* is used, alternatively.
47. Schrödinger (1926b), p. 514. In Schrödinger (1928), p. 30. He did address the problem of intensities in the next paper (SIII; 1926d).
48. But see the de Broglie–Bohm pilot wave theory.
49. Schrödinger (1926f), "An undulatory theory of the mechanics of atoms and molecules." Notably, being published in the *Physical Review*, providing something of an introduction for an American audience.

50. Admitting to Einstein that "it is true that I considered the scattering of particles with other particles as a scattering of waves." Quoted in Beller (1999), p. 42. For an elaboration on Born's changing views, see Beller, pp. 44–6. See also Chapter 12.
51. On this see the correspondence summarized in Hendry's chapter 7 (Hendry, 1984).
52. Schrödinger (1928), p. 30. In the original (1926b), it is on p. 514.
53. Although he did remark in the 1964 forward to Green's *Matrix Methods in Quantum Mechanics* [Green (1965)] that ". . . I am naturally a little prejudiced in favor of the Gottingen version . . .," which might be considered remarkable, considering how much had happened in the previous 38 years.
54. According to Born, much later, Heisenberg said of Born's flirting with wave mechanics that "you have deserted our camp; you have gone over to the enemy Schrödinger." From an interview with Thomas Kuhn and Friedrich Hund, October 17, 1962. AIP Center for the History of Physics. The case of Isaac Newton provides an important cautionary tale to those who are tempted to take literally the later recollections of scientists. Hund died at the age of 101 in 1997.
55. Including parts I and II. The paper in question, "On the relation between the quantum mechanics of Heisenberg, Born, and Jordan, and that of Schrödinger," is Schrödinger (1926c).
56. Schrödinger (1926c).
57. Even though they were there implicitly, as the theory dealt only with what we think of as stationary states and transitions between them.
58. In Pauli's case, it was revealed in a letter to Jordan. See subsequent discussion. Schrödinger's proof in March 1926 forestalled Pauli's own publication. Eckart's paper was submitted in June and Dirac's in August.
59. Schrödinger (1926c).
60. Various textbook authors show for a plane wave $\psi(x,t) = \exp[i(kx - \omega t)$, that with $p = \hbar k$ and $E = \hbar\omega$, it follows that $-i\hbar\partial\psi/\partial x = p\psi$, and $i\hbar\partial\psi/\partial t = E\psi$.
61. Schrödinger (1928), p. 56; in the original, Schrödinger (1926c), p. 749.
62. Courant and Hilbert (1924).
63. For those who might be interested, Schrödinger's domestic life was very complicated and was intertwined with Weyl's as well. See Moore (1989).
64. Schrödinger (1928), p. 52 [p. 744 in the original (Schrödinger, 1926c)].
65. Schrödinger (1928), p. 46. In the original German (1926c), this is on p. 735.
66. See Straumann (2009).
67. Eckart (1926). The paper was submitted to *Physical Review* on May 31, 2 months after Schrödinger's submission, and just short of 4 weeks after the latter's paper was published, but Eckart's note added in proof was dated September 2. After the United States entered WWII, Eckart had an important career as an oceanographer and geophysicist, contributing especially to underwater acoustics, and he eventually married von Neumann's widow. There was perhaps no more important "home-grown" American physicist in the prewar era, except for John Slater.
68. Dirac (1926b).
69. Dirac (1927a). Published on New Year's Day, 1927.
70. Dirac (1927a), p. 635. This "bra-ket" notation for states was introduced by Dirac only in 1939 (Dirac, 1939), although something resembling it was used from almost the very beginning.

71. This and the other qutotations in this paragraph are all from pp. 58–9 in Schrödinger (1928) [Schrödinger, 1926c), pp. 752–3 in the original].
72. In a letter to Pauli, quoted in Moore (1989), p. 221. More candidly, he wrote "I think it is bullshit." Despite this, Heisenberg also saw the connection between the two approaches as early as late 1926. Indeed, his paper on the helium atom, submitted July 24, 1926, adopts the " Schrödinger method of eigenfunctions . . ." (1926b), and in a letter to Pauli in June 1926 he wrote of the ease with which one could calculate the matric elements by using wave mechanics (see Miller, 1994, p. 10). Mehra provided an excellent 45-page overview of the turmoil of 1926 after Schrödinger's papers had appeared. Especially interesting is the account of a lecture by Schrödinger in Munich in July 1926, attended by Heisenberg, in Lahti and Mittelstaedt (1987).
73. Quoted in Mehra and Rechenberg, vol. 6, part 1, p. xxxii. Gregor Wentzel expressed a similar view, quoted in Mehra and Rechenberg, vol 6, p. 24.
74. The full development was published in Kronig and Rabi (1926, 1927), an early example of an important paper in *Physical Review* on quantum mechanics. Dennison had earlier treated the symmetric rotor by using matrix mechanics, also in *Physical Review,* taking advantage of Dirac's Poisson bracket approach. (Dennison, 1926). Reiche (1926) also applied wave mechanics to the problem in 1926, slightly ahead of Kronig and Rabi.
75. See n. 53 and 54.
76. Pauli (1926a).
77. Schrödinger moved to the professorship in Berlin in August 1927, having edged out Born for the chair. See Moore (1989), chapter 4. Six years later, in 1933, this would have grave consequences.
78. For example, Cassidy (1991), Jammer (1966), and especially Jammer (1974). Moore (1989) describes the intense and largely futile dialogue between Bohr and Schrödinger at Copenhage in 1927, which failed to bridge the gap between their views on quantum mechanics and made Schrödinger ill. See also Pais (1991).
79. Schrödinger (1926c), p. 734; Schrödinger (1928), p. 45. The full quote is as follows: "Considering the extraordinary differences between the starting-points and the concepts of Heisenberg's quantum mechanics and of the theory and which has been designated 'undulatory' or 'physical' mechanics, and has lately been described here, it is very strange that these two theories *agree with one another* with regard to the known facts.. . . 'Equivalence' may be too strong a word, though they yield the same results when applied to the same problems, and perhaps that is the best working definition of 'equivalent.' " For one take on the matter, see Muller (1997).
80. Although it does recall the case of the geocentric and heliocentric theories of the solar system in Copernicus's days, when both theories matched observation, if not well, as least equally well. But in that case, one theory was manifestly wrong, as observation would eventually show.
81. Cassidy (1991), pp. 229–30.
82. See the discussion in Mehra and Rechenberg (1982–2000), vol. 6, p. 137, of debates at Sommerfeld's institute between Schrödinger and Willy Wien.
83. Born (1926a).
84. He nearly got the position in Ediburgh that went to Born.

85. Born, who was Jewish, also left Germany for Cambridge in 1933, and Weyl fled to Princeton because of his Jewish wife. Should one be interested in such things, sexual liasons formed a huge part of Schrödinger's life, and his wife Anna had a long-term and serious affair with Weyl.
86. It is hard not to feel that Born and Jordan ought to have shared the prize with Heisenberg.
87. Which Rojansky (1938) called the "symbolic method" in his text of 1938. Dirac used the term in the first edition of his book in 1930.
88. Von Neumann (1932), published in English in 1955.

7

THE END OF CERTAINTY
UNCERTAINTY AND INDETERMINISM

PART I. INTRODUCTION: THE UNCERTAINTY PRINCIPLE

When the Fifth Solvay Conference (see Figure 7.1) convened in Brussels in October 1927—the first to which German scientists had been invited since the war[1]—the situation could not have been more different from that of the previous assembly 3 years earlier. Not only had both matrix and wave mechanics been developed in the interim, but the Dirac–Jordan transformation theory (see the next chapter) had appeared at the beginning of the year, and the meeting came on the heels of the publication of the *uncertainty principle* by Heisenberg, and immediately after Bohr's first enunciation of the complementary principle.

The almost simultaneous appearance of these two fundamental elements of quantum theory—uncertainty and complementarity—had an enormous influence on the physics community, even though their impact would be very different. Although the principle of complementarity was taken to be a profound statement about the microscopic world and its description and although it seemed to address or at least provide a framework for discussion of the epistemological problems facing quantum theory, its full meaning and implications were far from obvious. The uncertainty principle, on the other hand, developed from the very simplest physical ideas, was quite transparent, almost deceptively so, and yet pregnant with meaning. Although there is a real sense in which Bohr was midwife to the uncertainty principle, it was ultimately more a product of the new formalism and, specifically and somewhat surprisingly, of Schrödinger's mechanics, or at least of the wave–particle duality that had spawned it.

Max Born had taken a giant step toward understanding the meaning of the wave function by interpreting it as a probability wave in the summer of 1926.[2] This issue arose naturally in wave mechanics but not at all readily in matrix mechanics, which makes it ironic that it would be Born, a founder of the latter,[3] who accomplished this, despite his ambivalence toward wave mechanics.[4] His unease and that felt by Pauli, Heisenberg, and Jordan, the principal advocates of matrix mechanics, comes through clearly in their correspondence in this period,[5] with the tide seeming to be turning against the matrix theory. But in spite of these misgivings about the theory, Born asserted in his paper on scattering that "Of all the different forms of the theory only Schrodinger's has proved suitable for this process," though it has been translated more

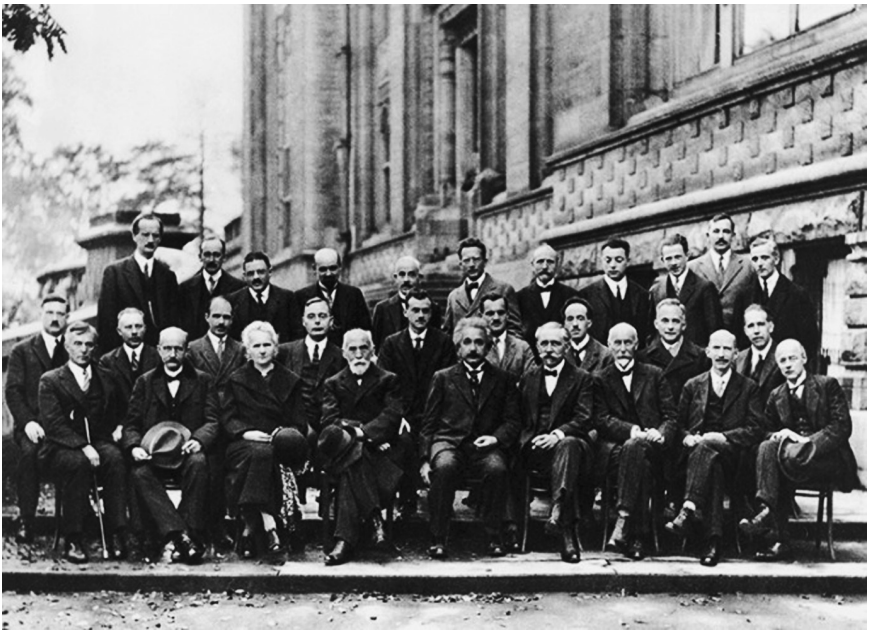

Figure 7.1. Attendees to the Fifth Solvay Conference in Brussels, October 24–29, 1927. From left to right, beginning in the first row: Langmuir, Planck, Mme. Curie, Lorentz, Einstein, Langevin, Guye, C. T. R. Wilson, Richardson; Debye, Knudsen, W. L. Bragg, Kramers, Dirac, Compton, de Broglie, Born, Bohr; Piccard, Henriot, Ehrenfest, Herzen, De Donder, Schrödinger, Verschaffelt, Pauli, Heisenberg, R.H. Fowler, Brillouin. Fourteen became Nobel Laureates. By permission of ETH Biliothek Image Archive.

generously as "Schrodinger's form of quantum mechanics appears to account for the facts in by far the easiest way."[6]

In the fall and winter of 1926–1927, while Heisenberg was Bohr's assistant in Copenhagen, both Schrödinger and Dirac paid visits to Bohr. Heisenberg was unrelenting in his antipathy to wave mechanics, but Dirac's visit and especially his paper on transformation theory, which appeared on the first day of 1927, had a strong impact. But in large measure, the uncertainty principle grew out of discussions of the measurement process that Heisenberg had with Bohr during that winter, and when Bohr went off to ski in Norway in early 1927, Heisenberg remained in Copenhagen where, without Bohr's often overbearing presence, he swiftly arrived at what we know as the uncertainty principle, wrote it up, and on March 23 submitted it to *Zeitschrift für Physik*.[7] Pauli's role was also crucial—as it so often was—something we know from Heisenberg's own words.[8] The two were in constant contact by the post, and Heisenberg sent Pauli a draft of the uncertainty paper before he showed it to Bohr.[9]

Heisenberg's paper, which appeared in May, was titled "On the perceptual content of quantum theoretical kinematics and mechanics,"[10] and he labeled the section in which he derived the uncertainty principle "The Dirac-Jordan theory," which, as we shall soon see, had subsumed both matrix and wave mechanics. His argument rested

on the idea of a probability wave, borrowed from Born, so that Schrödinger was a kind of godfather to it, something that Heisenberg only grudgingly admitted.[11] As for his own reasons, Schrödinger was already thoroughly repelled by matrix mechanics and was hardly receptive to the new result.[12]

The uncertainty principle exhibit in the clearest terms the indeterminism that is at the heart of the theory and thus, we assume, of nature, although it is important to note that "indeterminism" [*Unbestimmtheit*] and "uncertainty" [*Unsicherheit*] are not identical. When it comes to measurement, the two terms imply the same thing, that the outcome of a measurement is not determined, but can only be given probabilistically. Indeterminism, however, as the opposite of determinism, is a more subtle claim. Determinism is intimately connected with causality, but quantum mechanics is beset with the problem that systems evolve deterministically and causally according to the TDSE, but that the measurement process is acausal and indeterministic, something we will discuss at length in Chapter 14. Those, like Einstein, who believe that any physical theory must be causal and deterministic, hold that there must be some underlying determinism. But of course the uncertainty expressed in Heisenberg's principle—which is itself often called the "indeterminacy principle"—is a factor in indeterminacy. In any event, despite the radical nature of its claims, the reception of the uncertainty principle was fairly rapid and eased by the fact that a well-known analog arises in classical wave theory, lurking in the background, in effect waiting for wave mechanics or wave–particle duality to emerge.

It is clear that before Schrödinger's introduction of wave mechanics and the development of a consistent quantum-mechanical formalism in its wake by Dirac and Jordan (see the next chapter), the measurement questions with which the uncertainty principle contends did not arise. It is for this reason that the principle dates from 1927 rather than from 1925 or 1926. It is an offspring of wave mechanics, if only implicitly.[13] Yet Heisenberg arrived at the principle in early 1927 by means of an essentially classical argument, supplemented by the de Broglie relation expressing wave–particle duality. There was really not much quantum mechanics there, but it hinged on wave mechanics, as Heisenberg's "probability amplitude" [*Wahrsheinlichkeitsamplitude*] was essentially the wave function in coordinate or momentum space.

TOWARD UNCERTAINTY

Initially the Heisenberg–Born–Jordan theory of 1925 (see Chapter 5) was concerned solely with energies of stationary states, the energies or frequencies of atomic transitions, and, in some cases, transition probabilities, that is, strengths of spectral lines. The goal was to understand observable properties of the atom, eschewing unobservable quantities "such as the position or orbit of the electron."[14] The general question of measurement of the position or momentum of a particle did not arise directly in matrix mechanics, and the implications of the discovery, revealed in Heisenberg's first paper and elaborated in the Born–Heisenberg–Jordan (BHJ) paper, that p and q did not commute, were far from clear. As a practical matter, the measurement of the

position of a particle was largely a theoretical issue, but it was very important conceptually and epitomized the problem of measurement on a quantum system. From the start Heisenberg explicitly rejected the possibility of associating a particle with a specific space–time point or trajectory, saying that ". . . it is necessary to bear in mind that in quantum theory it has not been possible to associate the electron with a point in space, considered as a function of time, by means of observable quantities."[15] Thus did he banish the concept of orbits, and yet his continued mulling over the problem is evidenced by an exchange with Pauli in October 1926, in which he was clearly flirting with the uncertainty principle: "it is meaningless to talk of the position of a particle with fixed velocity," he wrote, "But if one accepts as less accurate position and velocity, that does indeed have a meaning."[16]

In late 1926 Dirac submitted his paper titled "The physical interpretation of quantum dynamics" to the *Proceedings of the Royal Society*, concluding that "one cannot actually set up a one-one correspondence between those values of these coordinates and momenta initially and their values at a subsequent time." In an earlier passage he asserted that "One cannot answer any question on the quantum theory which refers to numerical values for both the q_{ro} and the p_{ro}."[17] As Cassidy points out in his Heisenberg biography,[18] it was not a large step for Heisenberg from this insight to the uncertainty principle, though, as we have seen, he had already said something similar in October and was being urged in that direction by Pauli.[19] And as we acknowledge precursors of the uncertainty principle, we should note that Born, in his celebrated paper on collision theory, wrote that "we have the result that a cell of the extension in length $\Delta x = 1$ and the extension in momentum $\Delta p = h$ has the weight 1."[20] In other words, $\Delta x \Delta p = h$ defines a phase-space cell.

There are several interesting aspects to Heisenberg's paper. The first is that he says that the result $p_1 q_1 \sim h$ "is a straightforward mathematical consequence of the rule $pq - qp = h/2\pi i$ . . ." despite the fact that it is only used implicitly, and, one could argue, not at all.[21] Furthermore, he mentions almost in passing that the previous result can be "generalized to any canonically conjugate quantities whatsoever."[22] This important insight was not proved, and it fell to others to establish it (see subsequent discussion).

Importantly, in the first section of the paper, Heisenberg gives a familiar discussion of the measurement process in which an electron is imaged with an optical or γ-ray microscope. He purports to show that the observation, which determines the position of the electron, disturbs its momentum and that the precision with which each, the position and momentum of the electron, is fixed, satisfies the uncertainty principle. Whatever the merits of this argument may be, and it was roundly criticized by Bohr, it is not unique to quantum physics and does not capture the real meaning of the principle, as we shall see in the next section.[23]

"PROOF" OF THE UNCERTAINTY PRINCIPLE

It was well known in classical wave theory that if one considers a wave pulse that has a spread in wave number Δk, its extent in x, Δx, is constrained by the relation $\Delta x\, \Delta k \geq 1/2$.[24] This result is essentially a consequence of a Fourier integral

representation of a solution to the Helmholtz equation of electromagnetism in coordinate space, with appropriate spread $A(k)$ in wave-number space and the corresponding Fourier transform. This is often shown using a Gaussian wave packet, which is what Heisenberg employed.

In his paper Heisenberg essentially utilized the preceding classical argument, making it a quantum result by combining it with the de Broglie relation $\mathrm{p} = \hbar \mathrm{k}$ $\left(\text{or } \lambda = \mathrm{h}/\mathrm{p}\right)$. He wrote down the expression for a Gaussian wave packet in coordinate (q-) space, with a width $\Delta q = q_{1,}$ then Fourier transformed it, in effect, into momentum space, obtaining a Gaussian wave packet with width $\Delta p = p_1$, with the condition that $p_1 q_1 = h/2\pi = \hbar$. This was later generalized by others to $p_1 q_1 \geq \hbar$; thus, the *uncertainty relation.*

To fully understand the proof, let us add a bit more detail. Heisenberg considered a Gaussian wave packet for the probability amplitude $S(\eta, q)$ (where η is some arbitrary "state variable") of width $q_1 = \Delta q$ in coordinate (q) space, and then transformed it into momentum (p) space. The absolute square of the amplitude, $|S|^2$, had the form $\exp[-(q-q')^2/q_1{}^2]$. In this case q_1 is a measure of the width of the packet in coordinate space. Then the probability amplitude in momentum space $S(\eta, p)$ was obtained from the coordinate space wave function or probability amplitude $S(\eta, q)$ as follows:

$$S(\eta, p) = \int S(\eta, q)\, S(q, p)\, \mathrm{d}q.$$

For $S(q,p)$, which would be the probability function (wave function) describing a particle of momentum p in coordinate space [and that we would write as $\psi_p(x)$], Heisenberg used an "ansatz" due to Jordan, $S(q, p) = \exp(2\pi i pq/h)$, that is, a plane wave. $S(\eta, p)$ was then the Fourier transform of $S(\eta, q)$. Carrying out the integral resulted in the amplitude $|S|^2$ in momentum space having the form $\exp[-(p-p')^2/p_1^2]$, with a width $p_1 = \Delta p$ in momentum space equal to $h/(2\pi q_1)$, that is, $p_1 q_1 = h/2\pi$, or $\Delta p\, \Delta q = h/2\pi$. The result was incomplete because the equal sign was valid only for the "minimum uncertainty" wave packet, the Gaussian.[25] In a very dense paper sent to *Zeitschrift für Physik* on July 17, just short of 4 months after Heisenberg's submission to the same journal, E. H. Kennard of Cornell University obtained the uncertainty principle in its usual inequality form: $\Delta p\, \Delta q \geq h/2\pi$, making substantial use of the commutator of p with q, which Heisenberg had not done. This inequality is thus sometimes called the "Kennard Bound."[26] Kennard's paper is one of the most overlooked in the story of the development of quantum theory in this critical 1927–1928 period, having been overshadowed by those of Jordan and Dirac, described in the next chapter.

Thus there is really nothing new in Heisenberg's proof, which is essentially a classical one, except that the quantum is introduced by writing the momentum p as h/k, which is de Broglie's formula.[27] From the preceding classical result, we easily obtain the relation $\Delta x\, \Delta p \geq \hbar$ (or $h/2\pi$). From this point of view, the uncertainty principle follows from wave–particle duality, or alternatively, expresses it, as Heisenberg employs both the particle and the wave descriptions. The implications, however, are

enormous, because of the de Broglie relation associating wave properties with particles. For an electromagnetic wave, the result $\Delta k\,\Delta x \geq 1$ means that if the width of a pulse is infinite, it is a plane wave of wave number k and $\Delta k = 0$. Or in order for it to be localized in space (a narrow pulse, $\Delta x = 0$), it must contain an infinite range of frequencies or wave numbers.[28] But this is now true for a particle, with momentum $p = \hbar k$. For this reason, and because Heisenberg described the particle by using a wave packet and interpreted the square of the amplitude as a probability, the result was quantum mechanical rather than classical, though still a somewhat hybrid result. Having obtained the uncertainty or indeterminacy principle, Heisenberg then applied it to a variety of experimental situations.[29]

GENERALIZED UNCERTAINTY PRINCIPLE

At the risk of repetition, it is worth emphasizing the important fact that although Heisenberg says that the result $p_1 q_1 \sim h$ is a straightforward consequence of the fact that $\mathbf{pq} - \mathbf{qp} = h/2\pi i$, he does not prove the statement. On the other hand, he is evidently fully aware, or at least conjecturing, that the principle he is enunciating applies to any pair of "canonically conjugate quantities."[30] Nonetheless, in Heisenberg's hands the principle imposed a limit on only the measurability of position and momentum. At the time, then, there was only a hint of the generality of the uncertainty principle, but that would emerge in the year or so following Heisenberg's published result. The discovery of these wider implications, which began to happen almost immediately, was possible because of the Dirac–Jordan transformation theory, which appeared at the end of 1926.[31]

In 1928, a year after Heisenberg's paper, Hermann Weyl offered in print what might be called the first formal *derivation* of the uncertainty principle (still limited to p and q) from within the framework of quantum theory, a proof that was capable of being generalized.[32] Weyl credited Pauli, but in the latter's *General Principles of Quantum Mechanics* of 1933, Pauli clouded the picture by citing the proof by Weyl.[33] And although this was just a proof of the (p, q) uncertainty relation, $\Delta x\,\Delta p \geq \hbar/2$, not its generalization to other pairs of noncommuting observables, in it we see the understanding that uncertainty or indeterminism is an intrinsic feature of quantum mechanics, rather than being merely an expression of the practical difficulty of measuring a property of the system without disturbing it. Although Weyl's proof of this general result, using the Schwarz inequality, is by now familiar, it still depended on the particular form of p in a coordinate representation, that is $p = i\hbar\,\mathrm{d}/\mathrm{d}x$.[34] It is shown in all graduate quantum textbooks that for operators A and B corresponding to noncommuting observables, where $[A, B] = iC$, then $\Delta A\,\Delta B \geq 1/2\,|\langle C\rangle|$, expressing the reciprocity in the spreads of conjugate variables.[35] Seen this way, the generalized uncertainty principle is a consequence of the noncommutivity of the operators A and B, as indeed Heisenberg noted. Kennard and E. U. Condon seem to have first raised in print the question of a generalization to any pair of noncommuting observables, and the general proof was soon given by Robertson.[36]

THE TIME–ENERGY UNCERTAINTY RELATION

The "time-energy uncertainty relation" has a very different ontological status from that involving p and q, or for that matter, any other pair of noncommuting observables. This is because time cannot be represented by an Hermitian operator T whose eigenvalues are the time t, nor is there a commutator of T with H of the form $[T, H] = i\hbar$, something Pauli was one of the first to emphasize: "We therefore conclude that the introduction of an operator t is basically forbidden."[37] Quite surprisingly, however, Heisenberg introduced that very expression, $Et - tE = h/2\pi i$, as a "familiar equation," without any explanation, before proceeding to derive the p, q relation.[38]

Time is not an "observable" (dynamical variable) in the usual sense, but simply a parameter; Δt has a meaning only with respect to some dynamical variable. Landau is supposed to have observed that "to violate the time-energy uncertainty relation all I have to do is measure the energy very precisely and then look at my watch."[39] In other words, its meaning and implications are frequently misunderstood. David Bohm and Yakir Aharanov have attempted to clear up that misunderstanding, but their arguments have been attacked as well.[40]

The imperatives of special relativity that spatial and time variables be treated on an equal footing are such that, as we noted, Schrödinger initially attempted to obtain a relativistic wave equation before moving on to conventional nonrelativistic form.[41] And although some, including Dirac at one point, were motivated to try to find an Hermitian operator corresponding to time, in relativistic quantum-field theory, the problem is solved in a very different way, because here neither x nor t is a dynamical variable, both being only parameters.[42] In the process of quantization, the field variables $\varphi\ (x, t)$ and the canonically conjugate momentum $\partial L/\partial\varphi$ become Hermitian operators satisfying commutation relations.

The standard derivation of the energy–time uncertainty relation is as given in *Messiah*, in which the dispersion in energy of a system ΔE and the time variation Δt of its dynamical variables are related.[43] It is shown that in the measurement of any statistically distributed dynamical variable R, the time Δt during which $\langle R \rangle$ changes by an amount equal to its width ΔR, results in a time–energy uncertainty relation, $\Delta t \Delta E \geq \hbar/2$.[44] This is known as the Mandelstam–Tamm interpretation.[45] Classically, if a wave packet has a spread ΔE in energy, there will be an uncertainty Δt in the time it can be said to pass a particular point, a result that becomes quantum mechanical only through wave–particle duality.

SUMMARIZING

In concluding our discussion of the uncertainty principle, a few further comments are in order. Because it depends on the commutator of incompatible observables, it not only refers to the results of measurement, but to *knowledge*, in the sense that, for example, we cannot simultaneously *know* the x and z components of the spin of an electron (because s_x and s_z do not commute). Of course, the only way to obtain knowledge of the system is to make a measurement. But we cannot measure the x-component

of the spin and then measure the z-component and still retain knowledge of the x-component. For compatible variables such as the operators corresponding to the magnitude of the angular momentum **L** and its z-component, a measurement of the z-component of the angular momentum, L_z, following a measurement of the magnitude of the angular momentum (essentially L^2), does not change the state of the system because $[L^2, L_z] = 0$. The resulting state, an eigenstate of L^2 and L_z, is the "ket" $|\ell,m\rangle$.[46] Again, we can *know* the magnitude and projection (say, the z-component) of the angular momentum vector, but if we know, from measurement, the z-component, the x-component is indeterminate (not just unknown) and can be determined only by measurement, destroying our knowledge of the z-component.

So there is no question of a *simultaneous* precise or sharp (noiseless) measurement of noncommuting dynamical variables such as p and q, because this would make the state a simultaneous eigenstate of p and q, which is not possible.[47] If we know that a system is in a given state, the eigenstate of some operator, perhaps p, then we cannot measure x and still retain the knowledge of p. Of course, no real measurement is precise, although it may have an arbitrarily small uncertainty associated with it. So, in a sense, eigenstates are almost always a useful fiction, and we need to be clear whether we are speaking of a real, unsharp measurement or an idealized measurement.[48] If we localize a particle, represented by a wave packet, in a region Δx, then the spread in its momentum is at least $\Delta p = \hbar/(2\Delta x)$.

To be specific, let us imagine that a particle is confined in a cavity—in one dimension for simplicity—and thus is described by a wave function $\psi(x)$, which might be a simple energy eigenfunction, or perhaps an arbitrary superposition, giving the probability distribution of x, the position of the particle at some instant in time (say $t = 0$). In an unspecified way, this is the result of preparation of the system. We can *calculate*, using the Fourier transform of $\psi(x)$, the momentum distribution $\varphi(p)$ at $t = 0$ and hence the *probability* that a momentum measurement will yield a certain value in dp at p. The dispersions in x and p, obtained from $\psi(x)$ and $\varphi(p)$ must obey the uncertainty principle.[49] But if we then immediately measure p precisely, say by scattering a photon from the particle, we lose all information about its position, other than that it is in the cavity. It will not in general be in an energy eigenstate and so $\varphi(p)$, call it $\varphi(p, 0)$, will evolve in time in a complicated way. But if we immediately measure the position precisely, we lose all knowledge of its momentum, and so on. This is the message of the uncertainty principle, but ultimately of the quantum formalism.

As a further, somewhat different example of the use of the uncertainty principle, let us imagine an atom confined to a cavity as in a laser trap or an electron confined to the dimensions of an atomic nucleus. The uncertainty in position can be used to derive a spread in momentum, and in the 1930s this argument, with the further assumption that the spread in the momentum ought to be of the order of the momentum itself, was used to show qualitatively that free electrons cannot exist in the nucleus (see Chapter 15). We can use the same argument to estimate the size of the hydrogen atom (its electron probability distribution) from the uncertainty principle, because if it were smaller, its kinetic energy from the uncertainty principle would exceed its attractive potential energy, and it would be unbound. In the context of quantum-field theory, the

uncertainty principle plays a role in understanding how virtual particles can "borrow" energy from the vacuum and then give it back, as long as the time–energy relation is not violated.[50] A typical argument goes like this: We take the range of a force to be limited by $R = c\Delta t$, where c is the velocity of light. From the uncertainty principle, $\Delta t \geq \hbar/\Delta E$, where $E \sim \Delta E$. If we use for E the rest energy mc^2, then $R \leq \hbar/mc$. For the pion, with a rest energy of 135–140 MeV, the range of the force turns out to be of the order of 1.5×10^{-15} m or 1.5 fm, a typical nuclear dimension.

Many textbooks attempt to demonstrate the uncertainty principle by considering a *gedanken* experiment in which a particle is observed with an optical microscope or, in Heisenberg's case, a γ-ray microscope.[51] It is then shown that in localizing a particle by using light of a specified wavelength, a change in the momentum of the particle occurs, such that the uncertainty principle is again observed.[52] Although very suggestive, this disturbance argument for the uncertainty principle is essentially a classical one, or at least a hybrid result, and can be shown to be invalid.[53]

In an ironic twist, Bohr had strong disagreements with details of Heisenberg's arguments on this very point in the paper that he wanted to treat as a "rough draft," and he persuaded Heisenberg to add a note in proof, apologizing for questionable points that would be clarified in a forthcoming paper by Bohr.[54] In Rosenfeld's words, "it is not often that the announcement of a decisive insight into the workings of nature is qualified by such a warning."

As an aside, it may be useful to point out that a track in a Wilson cloud chamber gives a graphic account of the position and momentum of a particle, but entirely within the constraints of the uncertainty principle. Measurement, in short, is a very complex phenomenon and breezy or naive statements about measuring this or that observable may bear little relation to the actual measurement process.

PART II. INDETERMINACY

The creation of quantum mechanics that was detailed in previous chapters (1925–1927), put in the hands of physicists the tools, still evolving in those heady days, for describing the microscopic world. It is in this ability to describe fundamental physical systems, which we now know to be inherently quantum mechanical, that the profound importance of the new theory lay. In this sense the new quantum theory was thoroughly revolutionary. But it was revolutionary in another sense as well, one that soon came to be seen as a defining characteristic of the theory, and that was quantum indeterminism.

Thus, with the caveat just given, we can say that the truly crucial break with classical physics that quantum theory represents centers on *quantum indeterminacy* and the fundamentally statistical nature of quantum mechanics. The understanding that the statements of quantum theory are probabilistic in nature came fairly early on, certainly no later than Born's 1926 papers on collisions, but there were earlier hints.[55] Quantum indeterminacy goes beyond mere probability, however, and carries the implication that our knowledge of the properties of a system is inherently incomplete and that at any time certain properties are not simply unknown, or even unknowable, but

indeterminate or undefined. This began to be understood after Heisenberg introduced the uncertainty principle, but it was inherent in the formalism of Dirac and Jordan and was soon explicitly stated by Dirac. There are, of course, those who continue to resist the fundamentally indeterminate nature of the physical world in favor of some underlying determinism, a question we will explore later.[56] But, however we see this issue, quantum indeterminacy was a definitive, even radical, departure from the predictive powers of classical mechanics.

Although quantum theory was floundering in the early 1920s, Bohr for a while ventured into uncharted territory by advocating a statistical treatment of energy and momentum conservation, which appeared in the Bohr–Kramers–Slater paper of 1924.[57] This proved to be a blind alley, but almost from the outset wave mechanics seemed to demand a probabilistic or statistical *interpretation*, despite resistance from some quarters (including Einstein, and ultimately Schrödinger, who would reject the implications of his own theory). It was not immediately evident that matrix mechanics had this statistical character, but once the two disparate approaches to quantum theory were shown to be equivalent, the fundamental probablistic nature of the theory became fully apparent. Born is usually given principal credit for this, but in the end, it was the Dirac–Jordan "transformation theory," that is, the formal structure of quantum mechanics, that showed that indeterminism arose in a natural way and was found to be inseparable from the problem of measurement. This is explicit in Dirac's *Principles of Quantum Mechanics*, where early in the first chapter there is a section titled "Superposition and indeterminacy," in which the situation as we understand it today is clearly elaborated.[58] The formal aspects of this grounding of indeterminacy in quantum theory are explored in the next chapter in this narrative.

Interpretation, in this context, is a loaded term. It describes an understanding of a theory that is implied by the formalism but is not inherent in it or in the mathematical structure itself, because, by implication, more than one interpretation is compatible with the structure. This immediately raises an important philosophical question: Does a theory have *meaning* beyond its formal mathematical structure? We can argue whether any interpretation of quantum mechanics is necessary or useful if it has no effect on the structure of the theory itself or the results of measurement, but that would seem to be a minority view to judge by the millions of words that have been written about it. There are many interpretations of orthodox quantum mechanics (OQM), but the issue at hand has to do with the probabilistic interpretation and the so-called *Born Rule*, which emerged in his 1926 papers on collision theory. There he found the probability that a particle will emerge in a particular direction [or solid angle, to be technical (see Chapter 12)], which depends on the square of the wave function.[59] But the question is whether this is an *interpretation* or merely an understanding of what the imperatives of the theory are. I would argue the latter, that the statistical interpretation emerges from the theory, but there continues to be debate over whether the Born Rule can be derived from within the theory. Born seems to have believed that it could.[60]

Born's interpretation of the wave function obviously had to await Schrödinger's formulation of wave mechanics.[61] How much else Born may have taken away from the latter's papers, including the conjecture that $\psi^*\psi$ was "a kind of weight function in the

system's configuration space,"[62] is an open question. But Born wrote that "determinism has to be abandoned," extending, as it were, earlier statements of Schrödinger, including that "we can never assert that an electron at a definite instant is to be found on *any definite one* of the quantum paths."[63] The degree of credit Born deserves for introducing the probabilistic interpretation of quantum mechanics is a matter for debate, but historically there is no denying his influence, and this was the basis for the Nobel Prize that was belatedly awarded him in 1954. The citation read "for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wavefunction."[64] By December of 1926 Dirac was writing without apology that "the square of the amplitude of the wave function in certain cases determines a probability," citing Born.[65]

The ground had been tilled even earlier by Bohr,[66] who in turn had been strongly influenced by Einstein in his famous paper on the emission and absorption of radiation. Probability arguments are not foreign to classical physics, of course, and Einstein's role is ironic, given his staunch opposition to indeterminism in quantum theory.[67] There is no less irony in Schrödinger's skepticism of indeterminism, given that his formulation of quantum mechanics first raised the issue of its statistical character, and that he acknowledged Einstein, along with de Broglie, as his greatest influences. He is famously quoted as having rued the day when he set indeterminism in motion,[68] and referring to "probability theory," he told Einstein in 1946 that he had "hated it from the first moment when our dear friend Max Born gave it birth."[69]

Born's first short paper on collisions reached the editors of the *Zeitschrift* just 2 days after Schrödinger's final article on wave mechanics was received by *Annalen der Physik,* in June of 1926.[70] Although preferring his and Heisenberg's formulation of quantum mechanics, Born saw the utility of wave mechanics in describing the scattering process (and the reader is reminded that he called it "the most profound formulation of the quantum laws"[71]). In this paper Born hinted at the probabilistic interpretation of the wave function in a note added in proof and elaborated on this interpretation a month later,[72] crediting Einstein with the germ of the idea.

The argument can be made that because Born introduced the probabilistic interpretation only in the context of scattering theory in which the issue was the probability of particles emerging in a certain direction, it is a poor model for the more general idea of the probabilistic interpretation of the wave function, and later in the summer of 1926 Born made a much stronger and more general statement to a Britsh Association for the Advancement of Science meeting in Oxford.[73] But in an October letter to Heisenberg, interpreting $\left|\psi\left(p\right)\right|^2\,\mathrm{d}p$ as the probability of a particle having a momentum between p and $p + \mathrm{d}p$, Pauli first stated clearly the generality of the probabilistic interpretation,[74] and in his fundamental paper on the foundations of quantum mechanics of 1927, von Neumann gave the credit for the principle to Pauli alone.[75] What is clear is that during the 4 months between June and October 1926, the now-standard interpretation of the wave function, the Born Rule, slowly emerged.

In a historical sense, then, the statistical or probabilistic "interpretation" of quantum mechanics can be seen as the evolution of thinking about the problems of measurement that began with early ruminations of Bohr, moved along by the discovery by

Heisenberg, Born, and Jordan of the noncommutivity of p and q in matrix mechanics, Born's description of the scattering process, and finally the uncertainty principle. Heisenberg was very clear about "the statistical nature of quantum theory" and went further, concluding his uncertainty paper by saying that "it follows that quantum mechanics establishes the final failure of causality."[76] Whether that is true is a question for a later chapter.

Indeterminacy (including the uncertainty principle) emerges naturally from the formalism of quantum mechanics—that is, the mathematics—as Dirac asserted when he wrote that "when an observation is made on any atomic system that has been prepared in a given way and is thus in a given state, the result will not in general be determinate,"[77] a statement that comes directly from the principle of superposition. This claim is not without controversy, and the fact that there are so many different "interpretations" would seem to belie it. But if the raging controversies over "meaning," or how something like decoherence happens, whether measurement causes the universe to split into copies of itself, are matters of interpretation, indeterminacy is nonetheless an inescapable property of quantum mechanics as it is currently understood.[78]

Over the span of about 2 years, beginning with the founding of the new quantum theory by Heisenberg (and of course Born and Jordan) and Schrödinger in 1925–1926, and given a huge boost by the uncertainty principle and principle of complementarity, quantum indeterminacy became real. If by the time Dirac's book was published in 1930 there was a general consensus that had been reached, that did not mean an unequivocal or unqualified reception. There would be those for whom the statistical nature of the theory would always be a sign of its incompleteness, and some still cling to the idea that a superposition reflects a lack of *knowledge* of the state the system is in rather than a real indeterminate state. It was not difficult to at least imagine that the statistical character of the formalism simply means, by analogy with thermodynamics, that there is an underlying deterministic theory to which quantum theory is an approximation. But this was and is a minority view, not really compatible with the formalism, or, for that matter, with recent experiments.[79] A controversial view, which may continue to have some adherents, was expressed by A. E. Ruark and Harold Urey, in 1930, when they attributed to Born the belief that ψ described not an individual atom, but only the "average behavior of the atom."[80] The formalism speaks for itself on this issue, but it will always be with us as we proceed in this narrative, and especially when the quantum theory of measurement, which is intimately tied up with indeterminacy, is addressed.

MEASUREMENT AND THE COPENHAGEN INTERPRETATION: A FIRST LOOK

Despite the fact that as far as we know, everything in the universe obeys the laws of quantum mechanics even if we do not fully understand those laws, measurement is simultaneously a thoroughly classical activity, involving macroscopic measuring devices and a profoundly quantum-mechanical process designed to probe the

properties of microscopic systems. It is, of course, the activity by which we test the theory itself, with the potential to show that it is wrong. In view of this, it should not come as a surprise that measurement is at the heart of the problem of understanding and interpreting quantum theory. It is there that the major open questions in quantum mechanics today lie. We will discuss these issues at length, but it seems appropriate here, while speaking of indeterminsm, to at least set the stage for the deeper discussion. It should be noted, however, that in practice, issues of interpretation almost never arise in the taking of real data, even though they may influence the process of understanding it.

The puzzling nature of measurement in the face of quantum indeterminacy was the subject of discussions involving Bohr, Heisenberg, and Dirac at the 1927 Solvay Conference, which also featured the famous debate between Bohr and Einstein that continued into the mid-1930s. At Göttingen, von Neumann was exploring similar problems, which grew out of the mathematical structure of the theory. Dirac, a largely unphilosophical person, thought the formalism should speak for itself, or, as he put it very near the beginning of his classic book in 1930, "*The only object of theoretical physics is to calculate results that can be compared with experiment*" [his italics].[81] It is in Dirac's presentation of the formalism of quantum mechanics, including the nature of the quantum state, the meaning of the quantum algebra, quantum states as superpositions, how the probabilities of the outcome of measurement were to be calculated, and so on, that the theory first appeared in almost a complete form. And one could say, with only a modicum of exaggeration, that von Neumann did the rest. What emerged in 1930 was a mature formulation of quantum mechanics that needed only a bit of polishing to put it in the Hilbert space language of observables, Hermitian operators, and canonical transformations induced by unitary operators, which von Neumann did with characteristic rigor. But with Dirac it was all there, including the manner in which a superposition is collapsed by the process of measurement. Much of the formalism appeared as well in Weyl's book of 1928,[82] which emphasized symmetry principles above all.

At this point in the narrative we briefly touch on the consensus known as the "Copenhagen Interpretation" (CI) because it represented, in some sense, a codification of indeterminacy in the measurement process in the form of a loose understanding that crystallized between 1927 and 1930. Although it can be thought of as OQM, it is still a subject of vigorous debate, and we return to it in due course. Unfortunately, it is often not clear what one means by the CI. Of it, Rudolf Peierls is supposed to have said that "the Copenhagen interpretation *is* quantum mechanics," but Josef-Maria Jauch, a major figure in postwar foundational studies, called it the "skeleton in the closet."[83]

We have seen, or will see, that in a period of a few months around the beginning of 1927, the Dirac–Jordan transformation theory (the next chapter) and the Heisenberg uncertainty principle came into being. Fortuitously, as noted at the beginning of this chapter, the Fifth Solvay Conference was being held in Brussels in late October of that year, allowing these developments to be absorbed before the start of the conference, whose topic was "electrons and photons." Most of the major figures introduced so far,

Bohr, Heisenberg, Pauli, Dirac, and Schrodinger—but not Jordan—were present,[84] and it was there that a very uneasy peace was struck among the various camps, eventually resulting (at least in retrospect) in what we call the Copenhagen interpretation. The term, as distinct from the supposed consensus, which especially involved the trio of Bohr, Heisenberg, and Pauli, evidently dates only from the 1950s.[85]

Questions of interpretation got very little traction between the late 1930s and the 1960s, for a variety of reasons, some obvious, some not. And if it is not entirely clear what the CI was (or even is), some general comments can be made.[86] Its relevance to this chapter is the extent to which it put indeterminism at the heart of orthodox quantum theory. But because there was still vigorous disagreement among the principals, what emerged was a rather weak consensus that, to begin with, accepted the uncertainty principle and the Dirac–Jordan theory, as well as wave–particle duality. Dirac, more conservative and generally avoiding interpretation, argued that the wave function contained all possible knowledge of the system and that quantum mechanics was about our knowledge, not reality. Bohr's complementarity principle, only just presented at Como, Italy, in September following the Solvay Conference, was accepted as an overarching principle that could guide future developments, but whether that was ever the case is arguable. What is often considered the heart of the CI, the collapse or reduction of the wave function upon measurement, while lurking in the formalism, had not yet been explicitly stated, either in print or correspondence. Indeed, it is not clear that, prior to the appearance of Weyl's and Dirac's books of 1928–1930, the fundamental measurement questions had been explicitly raised, namely, what is the state of a system before or between measurements, and how does measurement discontinuously change the wave function from a superposition to a unique eigenstate?[87]

The CI can be taken to be the understanding that an arbitrary observable of a system is undetermined prior to measurement, that the state of a system is a coherent mixture or superposition of the possible results of measurement of that observable, that only potentialities or probabilities of the subsequent measurement can be given, and that the act of measurement realizes one of those potentialities, that is, *determines* the state of the system.[88] This view is stated very clearly in von Neumann's book of 1932, in which he describes this "acausal" process in which the coherent superposition is reduced to a single state upon measurement. Heisenberg came close to detailing the consensus interpretation in his compact *Physical Principles of the Quantum Theory*,[89] based on lectures given at the University of Chicago in the spring of 1929, when he said that "states are determined only by measurement." Although the term Copenhagen interpretation seems to have been coined by him in lectures given in 1955 that were collected in his *Physics and Philosophy*,[90] his statement in the preface to his Chicago lectures that "the purpose of the book seems to me to be fulfilled if it contributes somewhat to the diffusion of that '*Kopenhagener Geist der Quantentheorie*' [Copenhagen spirit of quantum theory] . . . which has directed the entire development of modern atomic physics" is pretty unambiguous.[91] One thing is clear, and that is that if the CI had its birth, or very nearly so, at the Fifth Solvay Conference, it continued to jell, as it were, in the next few years, culminating in the books by Weyl, Dirac, and von Neumann.

CONCLUSION

An understanding of the fundamentally indeterminate nature of quantum mechanics was achieved during those critical years 1927–1930, centering on the uncertainty principle, the Fifth Solvay Conference, and especially the clash between the giants Bohr and Einstein, in which Borh was seen to be the victor. But the issue was really joined in 1935 when the now-famous Einstein–Podolsky–Rosen (EPR) paper[92] appeared in *Physical Review* and Schrödinger published his three-part article[93] in *Naturwissenschaften* in which "Schrödinger's cat" was born. The latter emphasized the paradoxes of the standard interpretation, namely, that a physical property, an observable, has no existence until it is measured, introduced "entanglement" (*Verschränkung*), and noted more than once that in a system, "the whole is in a definite state, the parts taken individually are not." EPR's goal was to show the incompleteness of the theory, thus challenging the newly achieved consensus, including even the uncertainty principle. The implications of the EPR paper languished until almost 1960, when John Bell appeared on the scene, and eventually the possibility of an experimental test emerged. Schrödinger's exploration of "the present situation in quantum mechanics" was much more personal and reflective, and one might say more perplexed, than EPR's sharp and detailed critique of OQM, but both served to sharpen the debates over the quantum theory and indeterminacy. Much more on this in Chapter 14.

Although the uncertainty principle does not entirely capture the essence of quantum indeterminism, it does exhibit in the clearest way the fundamental difference between measurement in quantum and classical mechanics. In Heisenberg's hands it was really a hybrid result, as was emphasized, but it also has a much deeper meaning, as was shown. It has, however, for better or worse, captured the popular imagination in ways that have led to its being unwisely co-opted by fields of intellectual pursuit far removed from quantum physics, which is, of course, its only realm of applicability. The commonplace idea that making an observation of something may modify its properties has been widely accepted; indeed is something of a cliché. As a metaphor it may or may not be useful, but there is no logical connection between these uses and its fundamental role in quantum mechanics, and, to make matters worse, it distorts the meaning of the uncertainty principle.[94]

NOTES

1. See Mehra (1975), for example. Ernst Solvay convened the first *conseil de physique* in 1911, and six more followed, through 1933. They continue to this day. But here we see dramatically the continuing effects of the war; German scientists were not invited to the third and fourth conferences in 1921 and 1924, respectively. Interestingly, Schrödinger was invited to the Fourth Solvay Conference from his post in Zurich, though he was born in Vienna. Jordan, who was only 25 at the time of the Fifth Solvay, was not invited, but Pauli and Heisenberg were barely older. Jordan did have a serious stutter. Although the uncertainty principle was undoubtedly on everyone's mind at the Fifth Solvay Conference, it was not formally on the

agenda. Talks given by de Broglie, Born, Heisenberg, Schrödinger, and Bohr, among others, had as an undercurrent the question of indeterminism, with de Broglie and Schrödinger, backed by Einstein, on the "conservative" side.

2. In his paper on collisions. Born (1926a), p. 865. See Chapter 12, but also the following discussion.
3. One could almost say *the* founder.
4. It continues to be interesting that he so quickly embraced wave mechanics, as not everyone was convinced, in 1926–1927, that the essential discontinuities of quantum mechanics could all emerge from a continuum theory.
5. For a brief summary, one should consult Hendry's chapter 7 and references therein (Hendry, 1984).
6. Born (1926a) p. 864. [I have given Wheeler and Zurek's (1983, p. 52) translation.] Hendry's (1984) translation is virtually the same: "Of all the forms of this theory only Schrödinger's has proved suitable here." He has translated several passages from Born's papers. I have rendered this passage slightly more modestly (previously) as "of all the forms of the theory, that of Schrodinger has proven suitable in this connection."
7. Apparently arriving at it as soon as the night of Bohr's departure. (Rosenfeld, 1971); Heisenberg (1927b).
8. Heisenberg (1927b), p. 174. See Wheeler and Zurek (1983), p. 63, and again Hendry (1984), chapter 9. See also Cassidy (1992), pp. 229–33, as well as Rosenfeld's comments in Zurek and Wheeler (1983), p.60, which are from Rosenfeld (1971).
9. Letter to Pauli; February 23, 1927; see Cassidy (1991), p. 233.
10. Wheeler and Zurek (1983) translate the entire paper. The German title, "Über den anschaulichen Inhalt der quantentheortischen Kinematik und Mechanik," was translated by them as "The physical content of quantum kinematics and mechanics." There is also a translation in NASA TM-77379.
11. Schrödinger's name is mentioned in the paper in four places. Most interesting is a final critical comment. There it is a bit disengenuous of Heisenberg not to fully acknowledge his debt to Schrödinger's theory, though he does give a nod to the "mathematical mastery of the quantum-mechanical laws" of it. He also readily acknowledge both Bohr and Einstein as influences.
12. "If all this damned quantum jumping were really to stay, I should be sorry I ever got involved with quantum theory." See Jammer (1974), p. 57. At the end of his uncertainty paper, Heisenberg noted that Schrödinger had characterized matrix mechanics "as a formal theory of frightening, indeed repulsive, abstractness" (Wheeler and Zurek, 1983, p. 82).
13. In particular Dirac (1927a), published January 1. Wave mechanics is not present explicitly in Heisenberg's paper, but the wave analogy that Heisenberg uses would be impossible before Schrödinger. The probability amplitude he employs, $S(p,q)$, is just a momentum eigenfunction as a function of q, that is, a plane wave solution to the SE. See subsequent discussion.
14. Heisenberg (1925), p. 880 [p. 262 in van der Waerden (1967)].
15. Heisenberg (1925), p. 881; p. 263 in van der Waerden (1967).
16. The quote is in Hendry (1984), p. 111; from Pauli's correspondence or *Briefwechsel*.
17. Dirac (1927a). The quotes are from pp. 641 and 623. Dirac was then in Copenhagen.
18. Cassidy (1991), p. 240.

19. In October, Pauli had written to Heisenberg, "The first question is . . . why not the p's as well as the q's can be described with arbitrary precision. . . . One can look at the world with the p-eye and one can look at it with the q-eye but when one would like to open both eyes, then one gets dizzy." Quoted in Pais (1991), p. 304. The importance of this letter has led me to break with my intention to refer only to the published literature. The discovery of the uncertainty principle offers ample demonstration of how important correspondence and personal conversions very often are in the evolution of an idea or a theory. The Heisenberg–Pauli correspondence in this period was especially crucial to both men. See also Cassidy (1991), pp. 232–3.
20. Born (1926b), p. 808; p. 213 in Ludwig (1968).
21. We would take his p_1 and q_1 to mean Δp and Δq.
22. The quotes are on pp. 65 and 68 in Wheeler and Zurek (1983). In the original German, pp. 175 and 179.
23. And, indeed, it is not really sound. It implicitly assumes that the particle possesses a position and momentum and that one is disturbed if the other is measured. This is at odds with orthodox quantum mechanics.
24. With the inequality applying for something other than a Gaussian wave packet. See, for example, Jackson,. 3rd ed. (1999), pp. 323–4. There are some technical details having to do with defining the width Δx and Δk . A monochromatic plane wave would have $\Delta k = 0$. The wave number k is related to the wavelength λ by $k = 2\pi/\lambda$.
25. Comments on the proof include Jammer (1974), pp. 62–3; Rechenberg in Brown et al. (1995), pp. 201–4. The proof given in detail by Bohm (1951) in his chapters 3 and 5 is in the same spirit as Heisenberg's.
26. Kennard (1927). Heisenberg's proof is equivalent to the statement that one cannot simultaneously localize, or bound, both a function and its Fourier transform. In his *Physical Principles* of 1930, Heisenberg is happy to point out that Kennard derived the uncertainty principle without recourse to wave mechanics. Kennard spent a sabbatical year in Göttingen during 1926–1927 (age 41), which led to his familiarity with the uncertainty principle. "Squeezed coherent states" are states in which the Heisenberg inequality is said to be "saturated"; that is, $\Delta x\ \Delta p = \hbar/2$.
27. Dirac seems to have introduced ħ on p. 95 of his *Principles of Quantum Mechanics* in 1930. There is now an "h-Bar" drinking establishment at Imperial College in London.
28. That is, to localize a pulse in a small region Δx, a large range of frequencies is necessary; hence Δk is large and given by the "uncertainty principle."
29. There is a bit of irony here. In his AIPQuantum History Project interview, Born makes the interesting point that what Heisenberg had to do to prove the uncertainty principle was essentially what Wien almost failed him for on his doctoral oral exam in July 1923! The word Heisenberg used, *ungenauigkeit*, would ordinarily be translated as "inaccuracy" rather than "indeterminacy," as Wheeler and Zurek rendered it.
30. In the translation in Wheeler and Zurek (1983), starting on p. 68. There is a typo in the development on p.69.
31. Jordan (1926a, 1926b), Dirac (1927a).
32. In his *Gruppentheorie und Quantenmechanik* (Weyl, 1928). Kennard's proof was earlier, but less transparent and more strongly rooted in what Heisenberg had done.
33. Weyl (1928), pp. 77 and 393 (in the German original, pp. 67 and 272). This is identical to the proof in Landau and Lifschitz (1977) and close to the more general proof one finds on

pp. 217–20 in Merzbacher (1998). In fact, his Eq. 10.66 is identical to Heisenberg's starting point. Modern students of quantum mechanics may have difficulty in following Weyl's proof, because of the way he writes expectation values and diagonal matrix elements of x, x^2, p, etc. Interestingly, Weyl thought that the uncertainty principle and the correspondence principle were incompatible. See Beller (1999), p. 296.

34. From which the commutator follows.
35. See, for example, Merzbacher (1998), p. 218. Here I have used Jammer's wording.
36. Kennard (1927) deserves some credit for being the first to speculate that this was the case, although he provided no proof: "In all cases you can probably assert that the precision of simultaneous measurements of a pair of canonically conjugate variables will always be subject to the [same uncertainty relation]"(p.340). Condon (1929) commented that it was generally assumed that there was an uncertainty principle for general noncommuting observables. Wigner (1983) credits Robertson (1929) for being the first to recognize this generality, which is clearly wrong, but he gave the first general proof. Heisenberg, himself, credited Kennard (Heisenberg, 1930). Schrödinger (1930) provided another generalization, and understanding the uncertainty principle in all its implications is still an active field. I would recommend the Wikipedia article "Uncertainty Principle," but. . . .

    In 1933 Bohr and Rosenfeld showed that the uncertainty principle applied to the electromagnetic field, giving rise to fluctuations in the field, thus showing the universal application of Heisenberg's principle. Bohr and Rosenfeld (1933).
37. See Pauli (1933), p. 63, n. 2, or the original, German version, in vol. 24 of Geiger and Sheel's *Handbuch der Physik* (*HdP*) in 1933. This was reprinted in Flugge's *HdP* in 1958, vol. 5. When the English translation appeared in 1980, some material that had been removed in 1958 was restored. Otherwise, however, all versions are identical, even to the typesetting.
38. Heisenberg (1927b), p. 177.
39. Quoted in Jansson (2008). In 1950 Fermi used the term "time-energy complementarity" (Fermi, 1951).
40. Aharanov and Bohm (1961). See especially sec. 5.4 in Jammer (1974), pp. 150–1.
41. Having obtained, as already noted, what he obtained was what is known as the Klein–Gordon equation, appropriate to a spinless particle.
42. I acknowledge enlightening discussions with Lev Kaplan on this subject.
43. Messiah (1961), vol. I, pp. 135–6 and 319–20. Also Jammer (1974), p. 146.
44. Messiah (1961), vol. I, p. 320. In Ballantine's words (1970), "the spread of energies associated with any state is related to the characteristic rate of change associated with the same state."
45. Mandlestam and Tamm (1945), p. 249. See Jammer (1974), pp. 136–56.
46. Here we use the Dirac notation for quantum state vectors that he introduced just before WWII. $|l, m\rangle$ is an eigenstate of L^2 and L_z. See Chapter 11 on angular momentum or a quantum text such as Weinberg (2013) for details.
47. For a different take on this issue, see Suppes (1961). The problem of *simultaneous* measurement of any two observables is another question. What we usually mean is that one measurement is followed *immediately* by the other.
48. The modern example of laser trapping, that is, what is known as a MOT or magneto-optical trap, provides the opportunity to achieve a highly localized position.
49. With Δx being the dispersion in x or $\left(\langle x^2\rangle - \langle x\rangle^2\right)^{1/2}$.
50. See, for example, Kaiser (2005).

51. Heisenberg (1927b, 1930). Popper (1935, 1959) has shown that a gedanken experiment cannot prove a theory. See Ballantine (1970)
52. For example, Messiah (1961), pp. 143–5. It might be noted that often the uncertainty principle for x and p is written as $\Delta x \Delta p \approx \hbar$.
53. Ballantine (1970); Ozawa (2003, 2014). Called the "noise-disturbance uncertainty relation" by Ozawa. It has been demonstrated that the uncertainty principle, if viewed as a restriction on the accuracy of measurements rather than a statement about the dispersion in the values of incompatible or noncommuting observables (as an intrinsic feature of the theory), can be violated. Ozawa (2003), and references therein. Also Rozema et al. (2012). For an overview of these issues, including preparation of states, see Yamamoto and Haus (1986).
54. "After the conclusion of the foregoing paper, more recent investigations of Bohr have led to a point of view which permits an essential deepening and sharpening of the analysis of quantum-mechanical correlations attempted in this work." Translation by and in Wheeler and Zurek (1983). Bohr's paper never really appeared. Rosenfeld (1971), p. 89. To the extent that it did, it was in the published version of his Como lecture. Rosenfeld adds some fascinating details to this entire episode (p. 89).In Weiner (1972), there is general agreement that "Bohr never wrote anything, if he could help it;" and that his ideas were disseminated by travel and letters long before anything reached print (Bethe, Weisskopf).
55. In a footnote in his uncertainty paper, Heisenberg cites Einstein, BHJ, himself, and papers by Jordan that earlier raised the issues of the "statistical interpretation of de Brogle waves" [Heisenberg (1927b), p. 176 (p. 66 in Wheeler and Zurek)]. We ignore here the arguments over the meaning of "probability," referring on the one hand to ignorance or knowledge (Bayesian) and on the other to the frequency with which a result will occur in a long series of measurements (frequentist). An interpretation of quantum mechanics known as QBism is based on the former (Fuchs et al., 2014).
56. If truth be told, I could have written "many." See, for example, Omnes (1994), chapter 1. There is no better analysis of the problem of interpreting quantum mechanics than this work. Einstein wrote to Ehrenfest that he viewed quantum mechanics "with admiration and suspicion" (Mehra, 1987, p. 59). See also Chapter 14.
57. The paper was mostly written by Bohr. See McKinnon (1985) in French and Kennedy (1985). Bohr returned to a version of it a decade later when the continuous β-decay spectrum was an issue.
58. The difference between Dirac and Jordan (or Born–Jordan) being the greater focus on states and eigenfunctions in the former. Jordan's 1936 textbook (Jordan, 1936) was another matter, but the combined effects of turmoil in Germany and the fact that Jordan had largely stopped contributing to quantum theory, as well as his unpopular embracing of ideas of Jewish scientists, all lessened its impact. See Howard (2013). It may be worth noting that in the uncertainty paper, Heisenberg observed that "In this circumstance," referring to superposition, "we see the deep significance of the Schrödinger wave equation." Wheeler and Zurek (1983), p. 72.
59. Born wrote the following "note added in proof": "Exact consideration shows that the probability is proportional to the square of the Φ_{nm}." Born (1926a), p. 865.
60. Among many examples, Greenberger et al. (2009), *Compendium of Quantum Physics*. The "Born Rule" (Born–Pauli Rule; probability postulate) gives the probability that a measurement will yield a specified result. But from the formalism, if we write $|\psi\rangle = \Sigma_i a_i |\psi_i\rangle$,

the probability that the system will be found in the state *i* upon measurement is $|a_i|^2$. However, this was not Born's concern in his 1926 paper, because he was describing the fraction of particles emerging in a certain direction in a scattering experiment.

61. And, as previously noted, this all took place in the summer of 1926.
62. Schrödinger (1926e). In the compilation (Schrödinger, 1928), this is found on p. 120.
63. Schrödinger (1926b), p. 26 in Schrödinger (1928). This is especially interesting in view of Schrödinger's ultimate rejection of the Born interpretation, and also the fact that one can argue that Schrödinger's statement that $|\psi|^2$ was a kind of weight function (see previous discussion) actually bore more directly on the interpretation of the wave function than did Born's. It was, however, only a vague conjecture.
64. The author prefers "probabilistic" over "statistical," which implies the analysis of frequencies of occurrence. We might note that there seems to be no agreement about whether it should be "wave function" or "wavefunction."
65. Dirac (1927a). The quote is on p. 621. How rapidly this idea spread in the late summer and early fall of 1926!
66. Including the famous Bohr–Kramers–Slater paper (1924).
67. See the discussion in Jammer's (1974) sec. 3.1
68. It is interesting to see Schrödinger attempting to "evade" the Bose–Einstein distribution law for a photon gas—quantum statistics—by employing standing de Broglie waves. See Pais (1982), p. 439.
69. Quoted in Moore (1989), p. 435.
70. Schrödinger (1926e). Received June 23, 1926, published September 8, so that it was submitted just before Born's first paper, but reached print only a week before the latter's second paper. Born's initial paper (1926a) was received June 25 and published July 10. Schrödinger's fundamental assumption was that $\psi\psi^*$ multiplied by the electron charge represented a real charge density, so that he did not have an interpretation of $\psi\psi^*$ per se.
71. The is Jammer's translation. See the previous chapter and also Jammer (1974), p. 39.
72. Born (1926b); received July 21, published September 14. Translated in Ludwig (1968),
73. Quoted in Jammer (1966), p. 288. Born's use of wave mechanics in this paper is clear and sure-handed, with a general wave function ψ expanded in a familiar fashion, $\psi = \sum c_n \varphi_n$, with $\sum |c_n|^2 = 1$, etc.
74. Pauli to Heisenberg, October 19, 1926. (Pauli, 1979). It was written a month after Born's second paper (1926b), but he and Born had undoubtedly been in contact well before that. Much of the letter is given in Hendry (1984).
75. Hilbert, von Neumann, and Nordheim (1928). But in their second paper on α-particle tunneling in 1929, Gurney and Condon (1929) state that "Born has shown that its square may be satisfactorily interpreted as giving the probability that the particle lies between x and x + dx when it is in the state of energy W." The history had already been distorted. Thus, as pointed out already, although Born interpreted the wave function in the context of the theory of collisions, it was actually Pauli who arrived at the modern understanding, that $|\psi(x)|^2 dx$ is the probability of finding the particle described by ψ in the infinitesimal interval d*x* in one dimension. See Cassidy (1992), p. 232. Pauli to Heisenberg, October 19, 1926.
76. Heisenberg (1927); p. 83 in the translation in Wheeler and Zurek (1983). Which, of course, is another question entirely, because indeterminism does not, *ipso facto*, destroy causality. See Chapter 14.

77. Chapter I of his *Principles* of 1930, especially §§3–4. He made much more equivocal statements 3 years earlier (Dirac, 1927a), p. 641.
78. See Chapter 14.
79. We discuss Bell's inequality and resulting experiments in Chapter 14.
80. Ruark and Urey (1930).
81. Dirac (1927a). It is notable that although he began writing about transformation theory in 1927, his preoccupation in the next 2 years was mainly with the theory of the electron (the Dirac equation), many electron systems, and the first foray into quantum electrodynamics (quantum-field theory).
82. Weyl (1928). Again, Weyl was a student of Hilbert.
83. Peierls in von Weiszäcker (1987); Jauch (1971), p. 21. He actually wrote that "for many thoughtful physicists of a more practical bend of mind it has remained a 'skeleton in the closet.' "
84. Of just over 30 participants, the only female was Madame Curie.
85. Kragh (1999); Howard (2004). Also, a very good Wikipedia entry. And see subsequent discussion.
86. Many believe that it should not be called an "interpretation," because there is a substantial consensus that this is how nature is, and this follows from the theory. Even the *many-worlds interpretation* was devised to explain why or how a single state is selected by the measurement process.
87. Especially in sec. 18, pp. 48–9 (Dirac, 1930). On p. 12 Dirac puts it this way: "the first observation spoils the state of the system."
88. More formally, the essential elements of the CI are that (1) quantum states can be represented by vectors in a Hilbert space, (2) that observables are represented by Hermitian operators on that space, (3) that the principle of superposition holds, (4) that observables do not in general have values until they are measured, (5) that a measurement of some observable will yield one of the eigenvalues of the corresponding operator (collapse postulate), and (6) that in wave mechanics the square of the wave function is a probability density function. These ideas are not entirely independent, and they would not have been fully subscribed to by the participants in the Fifth Solvay Conference. But they do represent what has come to be called the Copenhagen Interpretation.
89. Heisenberg (1930).
90. Heisenberg (1958). Howard (2004) suggests that Heisenberg was attempting to associate himself with the Copenhagen view as a matter of rehabilitation following his role in the German A-bomb project in WWII.
91. Dated March 3, 1930.
92. Einstein, Podolsky, and Rosen (1935). Prior to the 1930s, not many important papers in quantum theory had been published in *Physical Review*, but Einstein had emigrated to the United States in 1933. Boris Podolsky and Nathan Rosen were postdoctoral candidates at the Institute for Advanced Study at Princeton. On EPR, see Chapter 14.
93. Schrodinger (1935). "The present situation in quantum mechanics.". The paper has been translated into English by John Trimmer (1980) and reprinted in Wheeler and Zurek (1983), p. 152.
94. For examples of this misuse of the uncertainty principle, see the excellent book by Crease and Goldhaber (2014), and in particular pp. 151–61.

8

FORMALISM
"TRANSFORMATION THEORY"

INTRODUCTION

By the fall of 1927 the broad outlines of quantum mechanics had been established. Matrix and wave mechanics had been created, and several figures in this narrative, Schrödinger and Pauli in particular, had shown that the theories were equivalent and could be transformed into one another, evidently giving the same results when applied to the same problems. Born, with the help of Pauli, had shown the way toward understanding the meaning of the wave function as a probability amplitude [*Wahrsheinlichkeit*]. The implications of the noncommutivity of p and q (or noncommuting dynamical variables in general) were in the process of being understood, and there was a growing sense that measurement in quantum mechanics was a very different proposition from the same process in classical physics, something Bohr had been long emphasizing. But equivalence of the two theories did not necessarily mean full acceptance, and for various reasons advocates of one theory or the other still strongly defended their approach as the right, or at least the best, one. Not unsurprisingly, the two founders, Heisenberg and Schrödinger, were ardent defenders of their creations. Heisenberg found wave mechanics "abominable." The objections were partly over matters of interpretation or philosophy, centering on how discontinuities arise in the two theories, and partly a distaste for the "visualizable" character of wave mechanics, which seemed thoroughly naive. It must be said, however, that much of the almost vituperative disagreement that prevailed throughout 1926 (especially on Heisenberg's part) stemmed from simply envy, as wave mechanics seemed to be winning the day, a desire to salvage what had seemed to be a momentous discovery in 1925.[1] In the end, the knowledge that the theories were equivalent strongly motivated the attempt, carried out by Dirac and Jordan, to combine or fuse them; to show that they were two aspects of *one* theory.

What was lacking as this critical year of 1927 approached was a robust and coherent mathematical structure that would not only encompass both matrix and wave mechanics,[2] but would provide a foundation on which to build a theory of measurement that would clarify the issues of meaning and interpretation and allow them to be addressed from within the theory. A critical threshold had been crossed when it became clear that it was not a matter of two alternative theories, different in their structure and philosophy, but rather two aspects of a more general formulation. The ensuing process, this search for a unifying theory, which was begun by Dirac and Jordan at

the end of 1926, would occupy the next 3 years and culminate in the books by Dirac and Born and Jordan, in 1930, and finally by von Neumann 2 years later, establishing quantum mechanics in very nearly its present form. That story is the focus of this and the next chapter. We begin by reviewing the formative years, 1925–1926, as the competing theories evolved to the point that a unification became possible, in the form of what was once widely known as "transformation theory."[3]

The decisive events in the creation of quantum mechanics were, of course, the publication of the papers by Heisenberg and Schrödinger, barely a half-year apart in 1925–1926, with essentially no influence on each another.[4] As we have already seen, this was just the beginning of the process that evolved a unified theory, one that would occupy much of the next 7 years. When Born and Jordan initially reformulated Heisenberg's mechanics,[5] they immediately gave it a coherence and mathematical structure it had lacked, and the subsequent wider application of the theory in the Born–Heisenberg–Jordan (BHJ; *dreimännerarbiet*) paper made quite clear the scope and power of matrix mechanics. The appearance of Schrödinger's own revolutionary theory, offering an entirely different approach to quantum phenomena, meant that when he and others were able to show that the two methods were "equivalent,"[6] the stage was set for a unification of the competing theories at a fundamental level. That this controversy was resolved so quickly meant that little time was wasted on the conundrum of two distinct approaches to quantum theory. That in itself is one of the most remarkable aspects of the year 1926.

TOWARD TRANSFORMATION THEORY: DIRAC

It is not really so surprising that it fell to Dirac to initiate this process, coming as he did from the outside, being in neither the Zurich (Schrödinger) nor the Göttingen (BHJ) camp.[7] It was indeed Dirac who first explored the possibility of incorporating wave and matrix mechanics into a formal, mostly rigorous mathematical framework, *transformation theory*, in the process clarifying many of the issues of interpretation.[8] But the simultaneous contributions of Jordan, who was the unsung hero among the founders of quantum mechanics, were no less important, and the transformation theory rightly bears the names of both Dirac *and* Jordan.[9] Jordan's more axiomatic approach was quite different from that of his English counterpart, and even Heisenberg was put off by it, expressing a particular distaste in letters to Pauli.

Dirac's work naturally had a strong influence in the English-speaking world, but quantum mechanics was born in Germany at the hands of mostly German and Austrian physicists, and in the 1920s and 1930s German was the language of scientific discourse. This began to change as Jewish scientists fled Germany after 1933, often to England or the United States, in the face of German anti-Semitism and the approaching war.[10] The result was that by the mid-1930s English began to take on an equally important role, eventually becoming dominant, the *lingua franca* of scientific discourse. This, along with the post-1933 disruptions, helped *Dirac* become the standard resource.

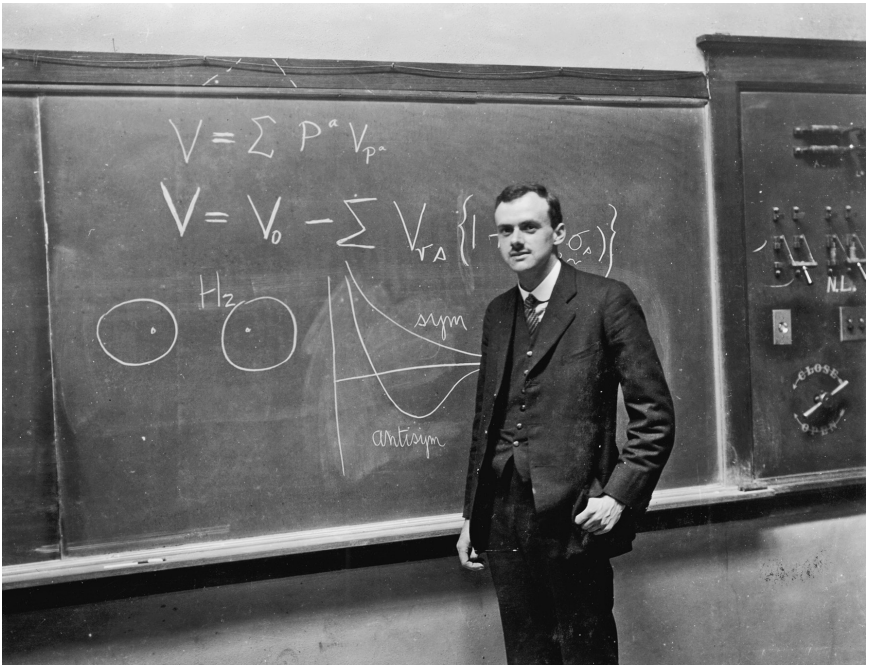

Figure 8.1. Paul Dirac (1902–1984). AIP Emilio Segrè Visual Archives, Gift of Mrs. Mark Zemansky.

Whether, as was suggested, Dirac's crucial role in the development of the formalism of quantum mechanics was in part a product of his independence from the dominant Göttingen school in the late 1920s, there is no doubt of the influence and productivity of the latter. The many-sided collaborations involving Born, Heisenberg, Jordan, Pauli, and even Schrödinger,[11] facilitated above all by Bohr's hospitality in Copenhagen, were obviously crucial. But then there was Dirac (Figure 8.1), working alone. He was an important figure for another reason, because before him, and despite major contributions on the experimental side, there had been no really important British contribution to the development of the theory of the quantum, and he represented a welcome break with the British predilection for mechanical models in treating physical systems. Charles Galton Darwin had written to Bohr in 1919 that "physics and applied mathematics here [Cambridge] are in an awful state."[12]

The opening salvo in this program of constructing a formal foundation for quantum mechanics was a brief paper by Dirac in 1925 (received by *Proceedings of the Royal Society* in early November 1925),[13] stressing the analogy between Poisson brackets of classical mechanics and the commutators obeyed by quantum-mechanical variables such as x and p. He understood as well as anyone the centrality of the noncommutivity of these variables that Heisenberg had discovered and saw the analogy between what we now call the commutator of two variables, $[p, x] = px - xp$, with the Poisson bracket and its role in canonical transformations. In that first paper from the end of 1925, after establishing that in general $xp \neq px$, he made the assumption (!) that "*. . . the difference*

between the Heisenberg products of two quantum quantities is equal to ih/2π times their Poisson bracket expression. In symbols, $xy - yx = ih/2\pi[x, y]$."[14] The importance of this for transformation theory lies in the fact that in classical mechanics, the Poisson brackets are invariant under canonical transformations.[15] Dirac had not yet taken the step of explicitly identifying such products as matrix multiplication, though he did speak of the (nm)-components of the *Heisenberg products* and thus writes down what are, in effect, matrix elements of, for example, the Hamiltonian.

All of this was elaborated further in a paper submitted in early 1926 titled "Quantum mechanics and a preliminary investigation of the hydrogen atom."[16] In this paper and in the nearly simultaneous BHJ paper, canonical transformations of the dynamical variables were considered, though in Dirac's case he wrote, rather skeptically, that "these formulae do not appear to be of any great practical value."[17] It was in this paper that he introduced his idiosyncratic "q-numbers" and "c-numbers," the former being noncommutative and hence operators, whereas the latter were just complex numbers.[18] In fact, the subsequent exploration of canonical transformations, by analogy with classical physics, formed the basis for transformation theory and eventually morphed into unitary transformations in the space of eigenvectors. In other words, it is important to note here that from the BHJ paper through the work of Dirac and Jordan, the emphasis was on *canonical transformations* involving the variables *p* and *q*, which diagonalized the Hamiltonian and carried over from classical mechanics. It would take von Neumann's special genius and background to generalize this idea to unitary transformations on a Hilbert space, in which the vectors are Schrödinger's eigenfunctions, that is, of the Hamiltonian. This important turning point in the theory is well described by Jammer and also in a large paper by Duncan and Jannsen.[19] On the other hand, between 1927 and 1930, Dirac was developing much of the mathematics on his own.[20]

In the 13 months between December 1, 1925, and January 1, 1927, Dirac published six important papers on quantum mechanics. In August 1926, after digesting Schrödinger's papers on wave mechanics that were published in *Annalen der Physik* in March, April, and May, Dirac began to explore the implications of the superposition principle,[21] something Schrödinger had already done without any fanfare, and that followed from the linearity of the wave equation. Dirac provided his own, somewhat more systematic, proof that the matrix elements obtained from solutions to the Schrödinger equation were just elements of Heisenberg's matrices, noted Schrödinger's "new development of the theory," and remarked that, in Schrödinger's hands, "the mathematical equivalence of the two theories is . . . established."[22] In his own personal way, the necessary linear algebra is introduced, and it is shown how to find matrix elements of an operator and how to diagonalize such a matrix, thus exhibiting the connections with matrix mechanics. Dirac is, however, making things up as he goes along, and any sense that there is an existing mathematical structure that his results could be mapped onto is missing, except for the well-known properties of solutions of linear differential equations. Although there is still no explicit vector-space language in this paper, which bore the ambitious title "On the theory of quantum mechanics,"[23] the importance of the eigenfunctions ψ_n of the Hamiltonian, which result from solving the Schrödinger equation, is made clear for the first time: "in this way we can have eigenfunctions

representing stationary states of an atomic system with definite values for the energy, angular momentum." One imagines that anyone with von Neumann's knowledge of complex vector spaces would jump at the chance to work out the implications of this statement, and this would soon be the case.

Recall that up to this point the Göttingen approach dealt only with matrix elements of Hermitian operators and the diagonalization of such matrices, not the states or eigenvectors themselves. Thus there are *eigenvalues* [*eigenwerte*] but not *eigenvectors* [*eigenvektoren*] to be identified with states of the system, and in chapter 3 of the BHJ paper, titled "Connection with the theory of eigenvalues of Hermitian forms," eigenvalues are discussed, but, again, not quantum states as eigenvectors. Although stationary states of a system—that is, physical states—are being considered, e.g., "the individual states of the atom," in connection with their discussion of angular momentum, there is no explicit identification of the state itself with an abstract mathematical object, no"eigenstates," to use the etymologically mongrel common usage. As van der Waerden noted, Born (and Jordan) failed to make the connection between the eigenvalue problem that he treated in the BHJ paper and the atomic stationary states, so that "the physical significance of the eigenvectors was not made clear before Schrödinger."[24] And, one might say, before Dirac.

Thus, although Dirac introduced the language of *q*-numbers in his first paper of early 1926, the idea of state vectors or eigenfunctions spanning a vector space had not yet appeared, and essentially could not, until Schrödinger's first paper appeared, and thus the transformations used to diagonalize the appropriate Hermitian matrices are canonical transformations, not unitary transformations on a vector space. But by late 1926 ("On the theory of quantum mechanics" and "The physical interpretation of the quantum dynamics").[25] Dirac had moved far beyond simply reinterpreting Heisenberg to a nearly complete understanding of how matrix and wave mechanics could be reconciled and what that implied for the formalism of quantum mechanics, transformation theory.

While Dirac was, almost alone, groping his way toward a mathematical structure that was already well known in Göttingen, Pascual Jordan was the major force in amplifying the mathematical foundations of matrix mechanics in the paper with Born and in the *dreimännerarbeit*, BHJ,[26] which reached print in early 1926. Later in that year he published two short papers on canonical transformations in quantum mechanics,[27] but it was the large paper "On a new foundation for quantum mechanics," finished in December and published early in 1927, almost simultaneously with Dirac's, that established him as cofounder of transformation theory.[28] The first sentence of the paper contains the Schrödinger equation, a big step for one of the founders of matrix mechanics, but the goal of the paper was to unify the existing versions of quantum mechanics.

TRANSFORMATION THEORY

In the paper "The physical interpretation of quantum dynamics,"[29] whose title clearly revealed his intensions, Dirac consolidated his theory of canonical transformations in quantum mechanics and showed how they could be used to transform from one

matrix scheme to another, transformations sufficiently abstract as to allow them to be thought of more generally, although the complex vector-space language is still not there. He also considered the "general" case in which the matrices[30] are labeled with continuous indices, that is, continuous eigenvalues, which motivated him to introduce what we know as the "Dirac delta-function," $\delta(x)$, to incorporate operators that have a continuous spectrum into quantum mechanics.[31] Finally, in a section titled "Comparison with previous methods," he again showed the equivalence of matrix and wave mechanics, with greater generality, and then demonstrated that his formalism was consistent with Born's idea that "that the square of the amplitude of the wave function in certain cases determines a probability."[32] Although he derived the properties of the appropriate similarity transformations, the term unitary was not yet used, and the generality of the quantum-mechanical transformations was not fully appreciated.[33]. However, the states themselves, as eigenfunctions of the Hamiltonian, for example, are quite prominent.

This was the first of a flurry of papers in 1927 by Dirac, Jordan, and von Neumann, as well as by Hilbert, von Neumann, and Nordheim[34] that went a long way toward creating the formalism of quantum theory as we now know it. Just 16 days after Dirac's "physical interpretation" paper was submitted to the *Proceedings* (December 2, 1926), Jordan sent to the *Zeitschrift* a major, and in many ways remarkable, "new foundation" paper, which showed that the several formulations that were out there[35] could be subsumed into one framework that was essentially equivalent to Dirac's transformation theory—whose work he acknowledged—if a bit more ambitious and perhaps more

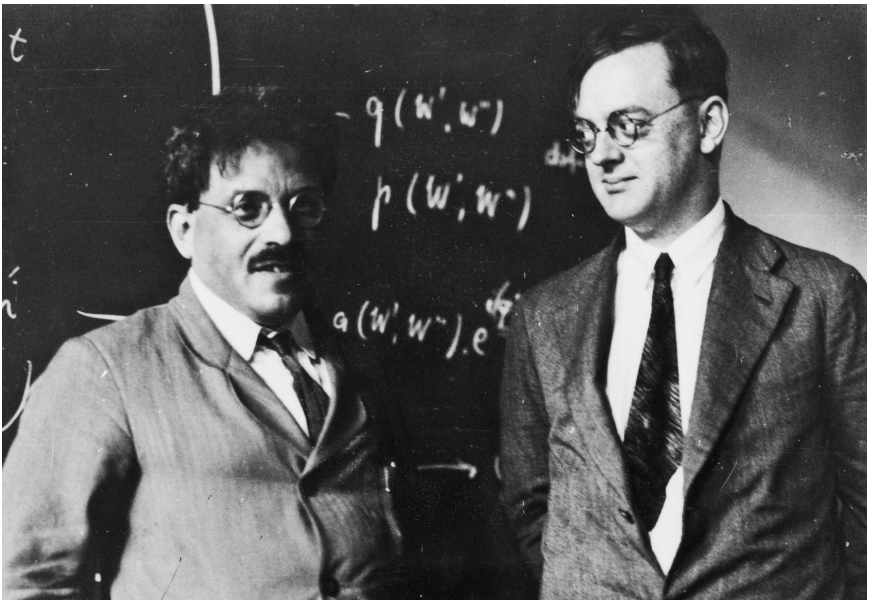

Figure 8.2. Paul Ehrenfest (1880–1933) and Pascual Jordan (1902–1980). AIP Emilio Segrè Visual Archives, Segrè Collection.

modern.[36] His §2 is titled "Statistical foundations of quantum mechanics," perhaps the first time such a phrase had been used (in print). We note in passing that at one point Jordan states that "for a given value of q all values of p are equally probable"(!); clearly the uncertainty principle is not far away (and indeed Heisenberg would submit it within 3 months). As was said, for this paper more than any other, Jordan deserves to be considered cofounder of the transformation theory, or the abstract formulation of quantum theory. But for a variety of reasons Jordan's fundamental contributions to the formal structure of quantum mechanics are often overlooked, especially in the English-speaking world. Dirac's formulation of transformation theory was developed patiently during 1925–1926, in contrast to Jordan's big paper at the beginning of 1927, when his entire theory was laid out. A more important reason why in the end Dirac's approach became the standard was probably the publication of his *Principles of Quantum Theory* in 1930, by which time the theory had been framed in terms of Hilbert space. The decision of Born and Jordan, in their book, not to incorporate wave mechanics, with its eigenfunctions of Hermitian operators in coordinate space, undoubtedly lessened its ultimate influence, and the projected volume on wave mechanics never appeared, at least partially a victim of changing political conditions in Germany.[37]

The label "transformation theory" was first used by Dirac because of the way it made use of canonical transformations to diagonalize an Hermitian operator representing an observable, usually the Hamiltonian. Eventually the transformation was from one basis in a Hilbert space of state vectors to another under the action of a *unitary* operator, hence a unitary transformation. "Transformation theory" became the title of chapter V in the first edition of Dirac's *Principles* and was employed by von Neumann in the first paragraph of the preface to his *Mathematical Foundations* ("the so-called 'transformation theory' "), and elsewhere in the work.[38] In summing up transformation theory in the preface to the first edition of his book, Dirac wrote of the laws of nature that

> The formulation of these laws requires the use of the mathematics of transformations. The important things in the world appear as invariants . . . of these transformations. . . . Further progress lies in the direction of making our equations invariant under wider and still wider transformations.[39]

Transformation theory has long since ceased to be common usage even as the theory has been codified. Once the identification between states of a quantum-mechanical system and vectors in an abstract vector space was made, the formalism of transformation theory followed almost immediately, but the original development largely went in the other direction. Einstein, who was initially hostile to Dirac's approach, later honored him as "Dirac, to whom in my opinion we owe the most logically perfect presentation of quantum mechanics."[40]

Above all, it is interesting to watch, in the papers previously mentioned, the slow and somewhat halting evolution of the formal structure of quantum mechanics, as the importance of canonical transformations in matrix mechanics comes to be recognized by both Jordan and Dirac, and as Dirac examines the implications of superposition

of the solutions of the Schrödinger equation, leaving transformation theory on the verge of a vector-space theory of quantum-mechanical states. The ingredients were there, in these two papers of Dirac and in Jordan's, of a realization that the quantum-mechanical states introduced by wave mechanics must be vectors in a complex vector space on which there are operators, or *q*-numbers, that undergo appropriate transformations. But neither Dirac nor Jordan was prepared to take the final step. This last stage in the development of transformation theory would be quickly carried out by John von Neumann and his collaborators along with Hermann Weyl,[41] who were able to recast the work of Dirac and Jordan in in the already existing language of Hermitian operators and vectors in a Hilbert space subject to unitary transformations, all before the end of 1927, which, of course, was also the year of the uncertainty principle.

SUMMARY

Initially, in Dirac's hands, transformation theory described the transformation from one matrix scheme to another, say, one that would diagonalize the matrices of some observable. Eigenfunctions do appear, though almost only in passing. They are, in Dirac's notation (ξ/α'), and are shown to be "just the transformation functions that enable one to transform from the (q) scheme of matrix representation to a scheme in which the Hamiltonian is diagonal." He demonstrated the time dependence of these eigenfunctions in the process of, essentially, carrying out the transformation from the Heisenberg scheme (picture) to the Schrödinger scheme. Dirac's language, which he is inventing, and his notation, which is not easy to decipher, are both challenging. The reader who wants to understand Dirac's paper might well consult chapter V in his 1930 *Principles*, even though much had happened between 1927 and 1930.

In Jordan's case, the paper's abstract announced his intention to show that the four approaches to quantum mechanics: wave mechanics and matrix mechanics, the Born–Wiener operator method, and Dirac's *q*-number theory are all special cases of a general theory.[42] The development, which shows how these different schemes transform into one another, makes use of canonical transformations from variables (p, q) to (P, Q), by which the Hamiltonian can be diagonalized. In the section titled "The statistical foundations of quantum mechanics," he explored the properties of the probability *amplitudes*, their role as against that of the probabilities themselves, how they combined and interfered, and so on. All in all, it was a much clearer and more logical development than Dirac's, but less general.[43]

Dirac's position on the probabilistic nature of quantum mechanics was very equivocal, and he concluded his paper by saying that "the notion of probabilities does not enter into the ultimate description of mechanical processes," despite earlier statements that seem to say something very different. But his discussion of matrices represented arbitrary observables, and the use of transformed bases to diagonallize them is rather general.

In short, the two approaches are substantially different, but are converging on the same answer, and together they showed that a general formulation of quantum mechanics that subsumed both matrix and wave mechanics, was possible. Further details on transformation theory can be found in, among other places, sec. 21 of

Gottfried's book or, of course, in any edition of Dirac. Steven Weinberg gives an appropriate nod to the term.[44] It is, in fact, orthodox quantum mechanics as is now taught, so that an full elaboration would be quite extensive.

1930: *DIRAC*, AND *BORN AND JORDAN*

In his *Principles of Quantum Mechanics* of 1930,[45] Dirac made explicit the identification of physical states with vectors in a vector space (still not using the term Hilbert space), following the lead of Weyl, who had 2 years earlier made a definitive statement of that fact in his book *Group Theory and Quantum Mechanics*, reflecting von Neumann's influence. Dirac also showed no ambiguity about whether a system possesses a value of a general dynamical variable before measurement: "In classical mechanics an observable always has a particular value for any state. This is not so in quantum mechanics, where a special condition [i.e., being an eigenstate] is necessary for an observable to have a particular value for a certain state."[46] Thus were revealed the central truths of quantum mechanics, though their reception was not without controversy. Three years after his transformation theory paper, Dirac had made his peace with the probabilistic nature of the theory.[47]

In the first two chapters of the book, Dirac very carefully explained what was meant in saying that a system was in a particular state and what the result of the measurement of an observable on that state would be.[48] This required the notion of superposition, which Dirac pointed out was a consequence of the linearity of the wave equation. He quite explicitly postulated that the state of a system after a measurement is completely determined by the result of that measurement and is independent of its previous state. Without agonizing over the implications, he identified the state of a system with a vector in an abstract vector space, which would turn out to be a Hilbert space, a name that was in use by 1930,[49] but not used by Dirac even in his second edition 5 years later. There, however, if somewhat reluctantly perhaps, Dirac does identify transformations such as time displacements as "unitary" transformations. The formal theory of states of a system as vectors in a complex vector space, with the implications of superposition, is patiently spelled out and the nature of the measurement process is fully described. In particular Dirac poses the problem that arises when deciding whether to consider an external influence to be outside the system or part of it, which he argues is largely a matter of convenience, except when that outside influence is an *observation*.[50] Here we have what is arguably the earliest clear and precise explanation of the implications of the measurement process as it would come to be embodied in the Copenhagen interpretation. Specifically, the fact that observations, which change or determine the state of a system, have a different ontological status from that of other interactions is accepted by Dirac without comment. Since then, tens of thousands of pages have been written debating that issue.

Just as Dirac's contributions, represented by those papers in 1926–1927 that we have examined, gave rise to his *Principles* (hereafter cited as *Dirac*) in 1930, Born and Jordan's *Elementare Quantenmechanik* (hereafter cited as *Born and Jordan*) of the same year mostly reflects Jordan's papers in that same period that culminated in his "New

foundations of quantum mechanics," of January 1927. It was shown that along with Dirac's paper of the same month, this work can be thought of as having created transformation theory, which generalized abstract formulation of quantum mechanics that freed it from its roots in both matrix and wave mechanics, but incorporated both. Compared with Dirac's book, *Born and Jordan* is considerably more modern in its treatment of the abstract theory of linear vector spaces, explicitly referring to the properties of unitary transformations in Hilbert space. The book would look more familiar to the modern reader than Dirac's somewhat idiosyncratic first edition, though unfortunately there is no English translation and no further edition appeared.[51] Born was nearing 50 in 1930, but Jordan was only 28, would publish an important paper with von Neumann and Wigner in 1934,[52] and was one of the founders of quantum-field theory. As a Jew, Born would lose his position at Göttingen in 1933 and Jordan became caught up in the politics of National Socialism, with disastrous results for his reputation.

At 430 pages *Born and Jordan* was also of somewhat larger scope than *Dirac*, in part because of a greater emphasis on applications, but also because of the elegant brevity that was so characteristic of Dirac. On the other hand, although there is only a moderate amount of explicit wave mechanics in *Dirac*, there is none in *Born and Jordan*. Instead, by design, they concentrated on matrix mechanics and on transformation theory in that context. One notable feature is the introduction of the algebraic approach to the one-dimensional harmonic oscillator, using ladder or creation and annihilation operators that cycle through the eigenvalue spectrum.[53] Angular momentum is treated in detail, including spin, and the hydrogen atom is discussed in what is essentially Pauli's approach.[54] The representation of quantum states in terms of vectors in a Hilbert space is explored in detail, though in the abstract sense, that is, no recourse to a position representation, as wave mechanics is absent. Significantly, there is no discussion of collision theory, which Born himself had introduced over 3 years earlier,[55] but that would have required resorting to wave mechanics as well. The influence of their large and important book might have been much greater had they had the will and opportunity to write the projected companion volume on wave mechanics.

DIRAC REDUX

When Dirac prepared to publish the second edition of his book in 1935, his understanding of the formal basis of the theory was much more clearly and directly expressed, but by this time von Neumann's formulation[56] had been in print for 3 years and was well known.[57] Notwithstanding this fact, Dirac's clarity (and, ironically, his device of the Dirac delta-function) carried the day at the moment when German militarism and anti-Semitism was changing the scientific landscape in Europe. The second edition was a wholesale revision, emphasizing what Dirac called the "symbolic method," that is, the abstract theory of states of a quantum system as vectors in a Hilbert space, making contact with matrix mechanics or wave mechanics only when necessary. That term, "symbolic method," gained wide currency at the time, though it was also known as the "algebraic method," in contrast to the more familiar methods

used in wave mechanics or matrix mechanics ("according to which physical things receive emphasis in the treatment, the states of a system or its dynamical variables"[58]). The symbolic method, Dirac says, "seems to go more deeply into the nature of things." It was this formal character, its elegance, the lack of a real competitor, and, of course, the impact of the political changes in Europe, that helped *Dirac* achieve the status it did, and indeed continued to hold, into at least the 1960s.[59]

CONCLUSION

In closing this chapter, it is appropriate to further emphasize Jordan's contributions to the origins of quantum theory, as they often go unacknowledged, despite the fact that in his early 20s he was the major force in the mathematization of Heisenberg's theory, and with Dirac and von Neumann was instrumental in creating the abstract formulation of quantum theory.[60] His relative obscurity is due largely to his membership in the Nazi party, and he likely would otherwise have been awarded the Nobel Prize for his work, probably with Born, and indeed was nominated both in the 1930s and in the postwar era (by Eugene Wigner).[61] Not only was he a co-inventor of matrix mechanics and of transformation theory, but he was, again with Dirac, a co-creator of quantum-field theory.

If nothing else, this story of the evolution of the basic formalism of quantum theory in the hands of a small number of physicists, which will be completed in the next chapter, is a testimony to the fact that there is not one single way to do physics. It further ought to be clear that there are almost forgotten figures who contributed importantly to these developments, but who have received little or no attention thus far, including, for example, Fritz London, who became known for his work on chemical bonding and superfluidity. In 1927 London wrote an important paper on canonical transformations in wave mechanics in which there is an early appearance of the term Hilbert space.[62] Other examples include the Americans Carl Eckart, E. H. Kennard, and Ralph Kronig, each of whom made major contributions.[63] As we move forward toward WWII, the number of important physicists will multiply, of course, especially as we begin to look at applications of quantum theory. But up to 1932, when the theory could be said to have been virtually complete, the number of major contributors, as must be evident, was really quite small. Such is the nature of a scientific "revolution," when only a few innovators see the way forward.

NOTES

1. Among discussions of this period, that of Cassidy (1991) is recommended, especially pp. 213–225.
2. We note here that Jordan, in his seminal paper, saw himself as unifying four theories: matrix mechanics, the operator calculus formalism of Born and Wiener, wave mechanics, and the q-number formalism of Dirac.
3. A usage rarely seen today, despite the fact that unitary transformations are at the heart of the theory. Gottfried (1966) subtitled his chapter V, "Transformation theory," and cited the

development of Dirac, but also a later formulation by Julian Schwinger. In fact, Gottfried's book was heavily dependent on Schwinger's lectures.

4. What influence there was probably negative, as Schrödinger had a strong aversion to matrix mechanics.
5. Born and Jordan (1925).
6. Depending on what one means by "equivalent." We would say that they are "unitarily equivalent." See also Pauli to Jordan, April 12, 1926, in *Wolfgang Pauli Scientific Correspondence*, vol I [quoted in Rechenberg (1995), in Brown et al. (1995) n. 164]. Ultimately the transformation theory of Dirac and Jordan clinched the case.

   On some technical aspects, including Dirac's use of the delta-function in his proof and von Neumann's more "sanitary" version, see Muller (1997), "The equivalence myth of quantum mechanics."
7. The impact of Dirac's papers and then the first edition of his *Principles of Quantum Mechanics* in 1930 is illustrated in this passage from Jammer, quoting John Lennard-Jones: "An eminent European physicist, who is fortunate enough to possess a bound set of reprints of Dr. Dirac's original papers, has been heard to refer to them affectionately as his 'bible.' Those not so fortunate have now at any rate an opportunity of acquiring a copy of the authorized version," Jammer (1966), p. 367.
8. Dirac is quoted [Brown et al. (1995), p. 211] as having said that the mid-1920s to late 1920s were "a golden age in theoretical physics, and for a few years after that it was easy for any second-rate student to do first rate physics." Dirac also wrote that "The growth of the use of transformation theory, as applied first to relativity and later to quantum theory, is the essence of the new method in theoretical physics. Further progress lies in the direction of making our equations invariant under wider and still wider transformations."
9. For example, Heisenberg's paper on uncertainty, in which he talks about the "Dirac-Jordan formulation." Heisenberg (1927b). See the previous chapter.
10. As well as the "Anschluss" of 1938, when Germany annexed Austria, eliminating any possibility of refuge in Austria.
11. Or the Göttingen–Munich–Berlin nexus, with a fourth major center being, of course, Copenhagen. Schrödinger generally worked alone, but was always in contact with his friend Weyl. Despite sometimes voluminous correspondence, there were almost no coauthored works; the good friends Pauli and Heisenberg published two papers together.
12. See Navarro (2013). Jeans had been attempting to arouse interest in the new theory as early as 1913. Ralph Fowler was a pivotal figure who not only mentored Dirac and Chandresekhar, but even Garrett Birkhoff, who eventually switched to pure mathematics and became a major figure in American mathematics in the 1930s and 1940s.
13. And published 24 days later. Dirac (1925). This was not the first paper Dirac wrote, nor even the first on quantum theory, e.g., his paper "The adiabatic invariants of the quantum integrals" submitted in late 1924. But it was the paper that followed Heisenberg's invention of matrix mechanics. See *The Collected Works of P.A.M. Dirac*, 1924–1948, R. H. Dalitz, 1995, Cambridge (Dirac, 1995).
14. Dirac (1925), p. 648. Received November 7, 1925.
15. On canonical transformations, see chapter 9 in Goldstein (1981) or any other book on classical mechanics.
16. Dirac (1926a). Dirac's paper was received on January 22, 1926, and published March 1, whereas the BHJ paper was received November 16, 1925, and published February 4.
17. Dirac (1926a), p. 565.

18. Much of the paper deals with his not entirely successful attempt to treat the hydrogen atom. Recall that this paper was submitted just 5 days after Pauli's more successful treatment of the hydrogen atom. In his next paper (Dirac, 1926b), he says (of *q*-numbers) that they "may be considered numbers of a special kind (which may be called q-numbers)."
19. Jammer (1966), p. 293; Duncan and Jannsen (2013). The latter also describe the "race" between Dirac and Jordan at the end of 1926, though neither knew of the other's work, though Heisenberg warned Jordan that Dirac was about to "scoop" him. See Duncan and Jannsen (2013).
20. He had been influenced by a paper of Lanczos (1926), which he cited.
21. Dirac (1926c).
22. Schrödinger (1926c), "On the relationship of the quantum mechanics of Heisenberg, Born, and Jordan, and mine." Translation in Schrödinger (1928). See Chapter 6. Also Jammer (1966), pp. 275–6.
23. Dirac (1926c). In was in May of this year that Dirac submitted his dissertation at Cambridge.
24. Van der Waerden (1967), p. 52.
25. Dirac (1926c, 1927a), received August 26 and December 2, 1926. In this period and for Dirac's papers, at least, publication came within a month of receipt, or a few days either way. There was no formal peer review process. The latter paper (1927a) was published on January 1, 1927. The slightly shorter interval between receipt and publication in the *Proceedings* resulted in Dirac's paper on transformation theory, submitted after Jordan's (1927a), being published over 2 weeks earlier.
26. Born and Jordan (1925); Born, Heisenberg, and Jordan (1926).
27. Jordan (1926a, 1926b), "On canonical transformations in quantum mechanics," parts I and II, which contains no reference to Schrödinger's wave mechanics. He was evidently responsible for the earlier use of "canonical transformations" to diagonalize the Hamiltonian in the BHJ paper, Secs. 1.3 and 2.1.
28. Jordan (1927a).
29. Dirac (1927a).
30. In his first paper Dirac did not use the term matrix and indeed may not have known that the (nm) notation he was using was best interpreted as a matrix element. By the time of the "Physical interpretation" paper a year later, matrices are used without note or apology. He had evidently learned much from a paper by Lanczos (1926), and, of course, the Born and Jordan (1925) paper. Although matrix methods were used in one form or another by Leibniz, Cramer, Gauss, J. J. Sylvester, Cayley, and others, they were not well known at the turn of the century. Dirac did use the term in his 1926 PhD dissertation. Titled simply "Quantum mechanics," and handwritten, portions of it along with various notations can be found at the Florida State University library site.
31. Which Jammer points out was actually introduced by Kirchoff in 1882, later used by Oliver Heaviside; others have said Fourier. Dirac, as initially an electrical engineer, knew of at least Heaviside's use of the delta function [Jammer (1966), p. 301]. It is interesting to see that Kennard's paper on the uncertainty principle, submitted to *Zeitschrift für Physik* in July 1927 (Kennard, 1927), makes wide use of the Dirac δ-function.
32. The quote is Dirac's (1927a), p. 621. Born (1926a, 1926b).
33. This does appear in Weyl (1928), where he writes "we arrive at the result that *the unitary correspondences of system space on itself in quantum theory: r′=Ur correspond to the canonical transformations of classical mechanics*." (p. 98 in translation, 1932).

34. Hilbert, von Neumann, and Nordheim (1928); von Neumann (1927b, 1927c); Jordan (1927a, 1927b); Dirac (1927a). See Jammer (1966), pp. 309–10.
35. Jordan (1927a). See n. 2. The paper by London (1926) should also be mentioned. See Jammer (1966), chapter 6, "The statistical transformation theory."
36. The personal styles of the authors are very apparent in the two papers. Despite Dirac's reputation for elegance and brevity, he is much more discursive than Jordan. For example, Dirac's first four pages have no equations at all. Jammer (1966, p. 307) has made the point that Kennard's 1927 paper, which he calls "lucidly written," helped to make Jordan's ideas more widely known.
37. Jordan's name was also always linked with that of the more famous Born, despite the fact that much of the formalism in their papers was Jordan's.
38. Von Neumann (1932).
39. This preface was reprinted as late as the fourth edition.
40. Pais (1982), p. 441. In a letter to Paul Ehrenfest in 1926 Einstein wrote, however, that "I have trouble with Dirac. This balancing on the dizzying path between genius and madness is awful."
41. Von Neumann (1927a); Hilbert, von Neumann, and Nordheim (1928); Kennard (1927); Weyl (1927, 1928).
42. Jordan (1927a).
43. It was an axiomatic approach, which Heisenberg disliked. From Kuhn's AHQP project interview with Heisenberg. Quoted in Duncan and Jannsen (2013).
44. Gottfried (1966); Weinberg (2013). Here we pay the price of talking about the theory without being able to give it.
45. A modern *Principia* in a way (referring to Newton).
46. Dirac (1930a), p. 31.
47. See his §18, for example.
48. See especially his chapter II.
49. In the 1928 German original, Weyl calls it a "Hilbert space" [*Hilbertsche Raum*], p. 29. In the English translation of 1930, this is on p. 32.
50. *Principles*, p. 9. In his chapter IV, "Representation of states an observables," Dirac introduced the idea of a representative of an abstract state. In the following chapter he introduced a new notation, which had first appeared a year earlier (Dirac, 1929), in which matrix elements are given in a bracket form $(\xi\,|\alpha\,|\xi')$, where the matrix element would imply either a sum or an integral over the appropriate variable, say x. There is not yet a separate bracket notation $|\alpha)$ for a state, per se.
51. It goes without saying that one is needed, for historical reasons, but after 80 years that seems unlikely to happen. Currently a copy can be had from booksellers for about $200. Dirac's book was widely translated, including a Russian edition in 1932. The Russian physicist Pyotr (Peter) Kapitza was not only a friend at Cambridge but editor, with Ralph Fowler, of the *International Series of Monographs on Physics* in which Dirac's book was published. Kapitza shared the 1978 Nobel Prize with Penzias and Wilson.
52. Jordan, von Neumann, and Wigner (1934).
53. Found in sec. 23.
54. I will have to say that while reading the laborious matrix-mechanical development in Born and Jordan I can't help thinking "haven't you read Schrödinger?" For which I apologize.
55. Born (1926a, 1926b).

56. Von Neumann (1932).
57. Dirac rarely cited earlier literature, somewhat obscuring his debt to others, and thus his priority. He was, however, remarkably independent, often inventing the mathematics he needed.
58. Dirac (1930a), p. vi.
59. As noted earlier, Rojansky's textbook of 1938, for example, speaks of the "symbolic method," meaning Dirac's. Rojansky gives an extensive introduction to linear algebra before proceeding to talk about the "Heisenberg method," the "Schrödinger method," and the "symbolic method."
60. If there were five major figures who created quantum mechanics, Jordan was one of those five.
61. Jordan's controversial career, including his membership in the Nazi Party, has been written about at length. Although Pauli declared him "rehabilitated" after WWII, he failed to share the Nobel Prize with Born in 1954, ostensibly because of his politics. He was a Christian Democratic representative to the West German Parliament from 1967 to 1971.
62. London (1927a). "Hilbertschen Funktionenraume." See Born's comments on London in his AIP CHP interview. London started out as a philosopher, studied with Sommerfeld in 1925, and then was assistant to Schrödinger in Zurich and Berlin, fleeing to England in 1933.
63. Beginning in about 1920, American physicists began to play a more important role at the frontiers of theoretical physics, and the same came to be true of the *Physical Review*, then, as now, the premier physics journal in the United States. It is, however, not quite fair to call Kronig an American physicist, because although he was born of American parents and educated at Columbia, he spent his entire professional life in Germany and the Netherlands. To continue that thread for just a bit longer, we could mention Compton, Oppenheimer, Millikan, Michelson, Anderson, and others. Six Americans received Nobel Prizes before the beginning of WWII, all essentially experimentalists.

9

HILBERT SPACE AND UNITARITY

INTRODUCTION

Quantum mechanics is the intellectual framework of modern physics. This has been essentially true since the fall of 1927. But what it lacked as that year began was an agreed-upon formalism which would provide the foundation for tackling any problem in the microscopic world. In the previous chapter it was described how the necessary formalism was created by Jordan and Dirac. But perhaps the single most important event in the creation of the *formal* structure of quantum mechanics was the recognition that states of quantum systems could be represented by vectors in a linear vector space. One of the first widely disseminated statements of this identification was by Weyl in his *Gruppentheorie und Quantenmechanik* of 1928, in which he wrote that "each particular state, each individual case of . . . a system, is represented by a vector **r** in a unitary system space. Each physical quantity associated with the system is represented by an Hermitian form in this space."[1] But these ideas have an older and much more uncertain pedigree, including the transformation theory of Dirac and Jordan, where they may be found in their infancy. They are even implicit in Schrödinger's papers of 1926, where stationary states in the hydrogen atom are labeled by the wave function (or "field scalar") ψ, buttressed by the well-known properties of solutions to the second-order, linear differential equation that he had introduced, namely, under proper circumstances, orthogonality, completeness, and so on. But Schrödinger's mathematical knowledge did not carry him further. Dirac, whose exploration of the implications of wave mechanics and its relation to the matrix formalism went further than anyone else, also could not quite take the final step. As we will see, this identification actually comes indirectly from the aging David Hilbert, largely through the vehicle of the Hungarian mathematician John von Neumann.[2]

QUANTUM MECHANICS AND LINEAR VECTOR SPACES

Although the theory of vector spaces was well developed by the 1920s, its formal origins go back to about 1888 at the hands of Giuseppi Peano (1858–1932), who is better known for his other contributions to mathematics and mathematical logic.[3] His close contemporary Hilbert (1862–1943), often considered the founder of *abstract algebra*, which deals with rings, fields, and groups, introduced the normed, complex, inner-product space that we now know as "Hilbert space" [*Hibertischen Raum*]—a

name *apparently* coined by von Neumann well after Hilbert, who along with Erhard Schmidt, Frigyes Riesz, and others, had developed the theory of these vector spaces in the first decade of the 20th century.[4] Hilbert and his protégé Hermann Weyl termed it "unitary space." Although Hilbert was the most important mathematician of his day, he was not averse to venturing into the messy world of physics, in pursuit of his desire to axiomatize all of it. His role in the creation of general relativity is somewhat controversial, but he certainly played a role in its genesis. The same is true here.

It was something of a lucky accident that the development of functional analysis by Hilbert and others coincided with the crystallization of experimental efforts in atomic spectroscopy and the failure of the semiclassical methods of Bohr and Sommerfeld to explain these data. More to the point, Hilbert was at Göttingen in 1925 when quantum mechanics was born, and although he was by then in his 60s and increasingly inactive, his influence on Born and Jordan, and particularly on von Neumann and Weyl, is quite clear.[5]

The formal mathematical developments took place in the space of about two decades, from 1910 to 1930, and once the mathematical imperatives came to be recognized, the application to quantum mechanics was carried out in only a few months. The question, of course, is how did this happen?

To begin with, the identification of states of a quantum-mechanical system with vectors (or rays) in a Hilbert space was essentially impossible before Schrödinger introduced wave mechanics with its wave functions, which would become *state vectors*. As we have noted, in matrix mechanics the states themselves were not initially an issue because they were not observable; rather, the observables that the theory emphasized were the dynamical variables of the system, or, like transition rates, could be computed from them. It took Schrödinger's very different formulation, based on classical analysis, in which the states (eigenfunctions) played the central role, to stimulate the imposition of the Hilbert-space mathematical structure. In the fourth paper in his series "Quantization as an eigenvalue problem" of 1926, Schrödinger made the first unequivocal statement of the wave function as representing a superposition of states: "The wave mechanical configuration of the system is a superposition of many, indeed strictly of all, point-mechanical configurations kinematically possible." And "If we like paradoxes, we may say the system exists, as it were, simultaneously in all the positions kinematically imaginable."[6] The first insight came directly from the classical theory of second-order linear differential equations, but the second was much more daring. At best this view is suggestive, and it is more a product of the theory of differential equations, stemming from issues of orthogonality and completeness than from an identification of quantum states with elements of a vector space, but there it was, as a statement of the physics of the problem with deep ontological implications. Schrödinger clearly identified the wave function ψ_n with electronic states in the hydrogen atom, though he was not yet thinking of states in a unitary space of square-integrable functions.[7] This understanding became much clearer with Dirac's abstract approach that reduced Schrödinger's method to quantum mechanics in a "position representation" by 1930.

THE CRUCIAL YEAR: 1927

By the fall of 1926, all four of Schrödinger's papers had appeared, bringing the eigenfunctions to the forefront, and Dirac's paper, "On the theory of quantum mechanics," appeared in October. Then in "The physical interpretation of the quantum dynamics" 2 months later,[8] we see him almost thinking out loud, as he develops the properties of "*q*-numbers" (operators) and "*c*-numbers" (complex numbers), superposition, Hermiticity, the need to consider matrices that depend on continuous indices—hence the delta-function, and so on (see the previous chapter). By the end of this paper the identification of the eigenfunctions of Schrödinger's equation with quantum states was clear, but Dirac could have benefited from having a mathematician looking over his shoulder, telling him that what he was constructing involved familiar mathematics,[9] quite familiar indeed to those, like Jordan in Göttingen.

Fortuitously, Hilbert was one of Born's mathematical mentors at Göttingen, and when Jordan arrived there in 1923, he first worked with Courant before becoming Born's assistant. Courant, of course, "collaborated" on the famous book on mathematical physics with Hilbert, though in fact it was really Courant's book, based on Hilbert's lectures. And Weyl got his doctorate under Hilbert in 1908 before moving to Zurich. It would be hard to imagine a situation better suited to the creation and mathematization of a revolutionary theory of nature than that which existed in Göttingen in 1925.[10]

Perhaps most important for the goal of this chapter, John von Neumann (see Figure 9.1) visited Göttingen in 1926–1927 on a Rockefeller fellowship and attended Hilbert's lectures on the foundations of quantum mechanics, which led to his groundbreaking paper "Mathematical foundations of quantum mechanics," and a collaboration with Hilbert and Luther Nordheim on another paper with almost the same title.[11] If Jordan and Dirac gave quantum mechanics much of the shape it has today, the completion of this program culminated in the specific identification of quantum states with vectors in Hilbert space. This took place in three monumental papers by von Neumann on the foundations of quantum mechanics, published in 1927, and the one with Hilbert and Nordheim in 1928. At the outset (in the initial paper) von Neumann explicitly introduced Hilbert space [*Hilbertischen Raum*] as the space in which the eigenvectors live and established many important results over the course of the 50+-page paper.[12] Considerable attention was given to the problem of continuous eigenvalues and therefore continuous matrices and thus to his disagreement with Dirac over the delta-function, which the latter had introduced at the beginning of this same year, 1927.[13] It is fair to say that with the publication of these papers of von Neumann, the foundations of quantum mechanics had been completed. Weyl's paper *Quantenmechanik und Gruppentheorie* of late 1927 in *Zeitschrift für Physik* and his monograph with the terms reversed in the title, which appeared the next year, brought wider attention to these ideas even as it promoted an entirely (well, perhaps not entirely) different agenda, that is, *group theory* in quantum mechanics.[14]

It is interesting that when Heisenberg gave his lectures at the University of Chicago in the spring of 1929[15] he spoke of vectors in unitary (Hilbert) space whose directions were the principle axes of tensors in infinite dimensions. A measurement along the

Figure 9.1. John von Neumann (1903–1957). Photograph by Alan W. Richards, courtesy AIP Emilio Segrè Visual Archives.

*k*th principal axis gave a value of the corresponding observable that was the diagonal element T_{kk} of the tensor. A superposition would be represented by a mixture of principal-axis directions with varying probabilities.

The process of convergence on a canonical formulation that culminated in von Neumann's book in 1932, proceeded rapidly, as one can see from Dirac's *Principles of Quantum Mechanics*, which appeared the year after Heisenberg's Chicago lectures. All of the expected terminology of state vectors ("eigen-ψ's") as solutions to the Schrödinger equation satisfying an eigenvalue equation involving observables (operators) is there. Yet explicit vector-space language is still absent, and Dirac develops everything without any reference to existing mathematics, including Hermitian operators, although it will all be very familiar to the modern reader.[16]

The symbols Dirac employs for eigenvectors, say ψ_r or φ_r denote abstract vectors, are not wave functions, which he would write as $(x|)$, indicating a position representation. Applications to the Schrödinger equation and its eigenfunctions in coordinate space appear only occasionally, as in the case of the harmonic oscillator or hydrogen atom. For the most part, Dirac had by then (1930) moved beyond the language of *q*-numbers and *c*-numbers (see subsequent discussion) to "observables" and "constants." Familiar results, such as the orthogonality of eigenfunctions of Hermitian

operators belonging to different eigenvalues are established, but without the notion of Hermitian. All this despite the fact that both von Neumann and Weyl had provided the necessary formal mathematics 2–3 years before. Typical Dirac, one is tempted to say.

It must be said that Dirac and von Neumann had different goals. The latter's emphasis on rigor was much greater, which resulted in his finding Dirac's delta-function unacceptable, among other things.[17] Von Neumann's papers were not published in either of the most important German scientific journals, the *Zeitschrift* and the *Annalen*, although the journals were well known to mathematicians, something that made them marginally less accessible. Dirac does not acknowledge von Neumann's work in his first edition, but then he was always very stingy with his attributions, in part reflecting his notorious independence.[18] Interestingly, he had spent 5 months in Göttingen, talking with Born and others, in the first half of that crucial year of 1927. The question of the influence of von Neumann, or rather the apparent lack of it, on Dirac is thus left unanswered. Indeed the influence may have gone both ways. Dirac surely knew what was happening in Göttingen, but we would not know that from reading his papers.

Early in the 1935 second edition of his *Princples of Quantum Mechanics*, in a section titled "The vector space representing the states," Dirac discusses the relationship between the mathematics of a linear vector space and the states of a physical system. Although he notes that "This results in the states . . . being represented by mathematical quantities of different natures from those ordinarily used," he does not linger over the issue, but instead quickly proceeds to develop the theory from the properties of Hilbert spaces, still without using that label. This was well after von Neumann's papers and Weyl's unequivocal statement of the identification of quantum states with vectors in Hilbert space. It also followed the publication of the von Neumann's foundational book, *Mathematical Foundations of Quantum Mechanics,* in 1932, in which the process of developing a mathematical structure for quantum mechanics was completed, so that Dirac was hardly breaking new ground. His influence, nonetheless, was enormous.

Although Dirac was not moved to adopt the linear vector-space language until the second edition of his book, his abstract formulation of quantum theory that began to emerge in 1926[19] was entirely consistent with it. It is there in the first edition, as we have noted, but *sub rosa*, as it were. It is thus not a little ironic that in his later years Dirac would come to be identified as putting mathematical elegance ahead of physical considerations, overcoming his early training as an engineer, which continued to be evident in his development of the abstract formulation of quantum mechanics without explicitly using vector-space language, and his initial reluctance to embrace group theory in quantum mechanics.

In contrast, Jordan's formulation of transformation theory, most clearly expressed in the Born–Jordan *Elementare Quantenmechanik* of 1930, unabashedly invoked the properties of Hilbert space. This was largely the result of the very different mathematical backgrounds of Dirac, on the one hand, and Jordan, on the other, who at Göttingen was influenced by Born and Hilbert, and, of course, von Neumann's work. The influence, as we have seen, went both ways.

One final contributor to this consolidation of quantum theory in 1926–1927 was Norbert Wiener, whom Born met when he lectured at MIT in the winter of

1925–1926. Wiener saw how to generalize Born's matrices to an operator calculus, and two joint papers resulted.[20] Wiener, whose mathematical genius had a breadth and depth comparable to von Neumann's, went on to other areas of applied mathematics as did von Neumann.[21]

UNITARITY

Just as observables had to be represented by Hermitian operators in the Hilbert-space formulation of quantum mechanics, so the transformations from one complete set of basis vectors to another had to have the property of *unitarity* in order to preserve the Hermitian character of the corresponding operators. Thus, for a unitary operator U on a Hilbert space, with $UU^{\dagger} = I$ or $U^{\dagger} = U^{-1}$ (where $U^{\dagger}$ is the adjoint or Hermitian conjugate of U), the similarity transformation $O \rightarrow O' = UOU^{\dagger}$ preserves the Hermitian character of operators representing observables. Unitarity was already a feature of the classical spectral theory of operators on linear vector spaces, so that the mathematics could be taken over immediately into quantum mechanics.[22] In quantum mechanics the relevant unitary transformations often correspond to space–time symmetries, e.g., invariance under displacements in space or time, or under rotations or reflections, or they may involve internal symmetries, and in either case these transformations will have group properties and will therefore be unitary groups. Common examples are $U(1)$, $SU(2)$, $SU(3)$, and so on. But early developments, especially in Dirac's hands, were devoid of the apparatus of group theory, and that is true of von Neumann's axiomatization of the theory as well, though the situation changed quickly in the papers of Weyl and Wigner, which we will explore further in Chapter 11. In the present discussion we review the way in which unitary transformations and the requirement of unitarity came to play a central role in the formulation of quantum theory, giving only a nod to group theory.

The transformation theory central to quantum theory in 1927–1929 had as its antecedents the: coordinate transformations of Lagrangian mechanics, which include, among other things, proper orthogonal transformations in three dimensions, that is, the rotation group $SO(3)$, which shares a Lie algebra with $SU(2)$, and the canonical transformations of classical Hamiltonian mechanics. The extension of these ideas to unitary transformations of vectors in a Hilbert space completed the process of defining a coherent mathematical structure for quantum mechanics. Thus unitary operators in quantum mechanics play a role similar to that of coordinate transformations in classical mechanics. That these are intimately connected is apparent from the fact that we can discuss the rotation of a coordinate system in three dimensions due to an orthogonal transformation R, which induces a corresponding unitary transformation U on the Hilbert space of the quantum states.[23] A unitary transformation is a rotation in Hilbert space whereas an orthogonal transformation is a rotation in real coordinate space R^3. Similarly, just as a matrix representing an inertia tensor in three-dimensional Cartesian coordinates can be diagonalized by an orthogonal similarity transformation (principal-axis transformation), a Hermitian operator (matrix) may be diagonalized by a unitary transformation.[24] The implications of invariance under canonical and

unitary transformations for symmetry and conservation laws are also identical. Thus the invariance of a system (e.g., of its Hamiltonian) under transformations of the rotation group $SO(3)$ or $R(3)$, which implies conservation of angular momentum, means that the Hamiltonian for the quantum system is invariant under the elements of the unitary group $SU(2)$, which in turn means $[H, \mathbf{L}] = 0$, because the components L_i are the infinitesimal generators of $SU(2)$.[25] The relationship between symmetries and such unitary transformations are explored below. Anti-unitary operators play a somewhat specialized role in quantum mechanics, principally in considerations of time-reversal invariance.[26]

REPRESENTING: PICTURES AND REPRESENTATIONS

In passing, we note that the term representation appears commonly in any discussion of basis states in Hilbert space and how they are related by unitary transformations. The term has both a colloquial and a technical meaning and we might wonder why it is singled out here for special attention. Technically representation is widely used in expositions of group theory, and so it is no surprise to find it extensively employed by Weyl and Wigner in their books on group theory and quantum mechanics.[27] A representation is a collection of entities that is homomorphic to an original group, and typically representations arise in obtaining concrete realizations of observables in a linear vector space. Frequently, then, a representation is taken to be the particular form that members or elements of an abstract group have in a specific basis, which therefore is a basis for a representation of the group.[28] For example, the spin-up and spin-down Pauli spin vectors $(1, 0)$ and $(0, 1)$ form a basis for the two-dimensional fundamental representation of $SU(2)$, which consists of the 2×2 Pauli spin matrices. In effect this means choosing a coordinate system, because the basis states $|1/2\rangle$ and $|-1/2\rangle$ would be $(1,0)$ and $(0,1)$, referring to a specific z-axis. Thus the term "matrix realization" or "matrix representation" of operators on a Hilbert space is an example of this use of the term.

But representation has been used in the literature in several different, but not totally unrelated ways, often carelessly. In some hands, it would simply refer to a particular complete orthonormal set of basis vectors, perhaps energy eigenvectors, so that often "basis" and "representation" are used interchangeably. Such basic states might be energy eigenkets, $|E_n\rangle$, or, alternatively, eigenstates of position or momentum, $|x\rangle$ or $|p\rangle$, and the term position representation or momentum representation might be used. This use of the term can cause confusion, however, because the term position representation and its momentum counterpart are used in another very different and standard sense, as we will see.

Another example would be the angular momentum states $|\ell m<$ or $|j, m_j\rangle$. Thus a representation would be specified by a complete set of mutually commuting Hermitian operators, say $\{J^2, J_z, J_1, J_2\}$ in which the basis states might be written as $|j, m, j_1, j_2\rangle$, consisting of the eigenstates of the set of operators $\{J^2, J_z, J_1, J_2\}$. As Messiah put it, "there are as many possible representations of the Theory as there are distinct bases,"[29]

which may seem tautological. In this last example there is a unitary transformation from a basis or representation in which the eigenvalues of J^2 and J_z are good quantum numbers to one in which L_z and S_z are diagonal, and the elements of the transformation matrix are "Clebsch–Gordan coefficients."[30]

Now Dirac would say that the way in which abstract vectors are replaced by numbers is a "representation." He is especially thinking of a position representation (or momentum representation), in which the vector is replaced by a function that has numerical values (though complex) as a function of position. For example, an energy eigenstate in a position representation would be written as $\psi_E(x) = \langle x|E\rangle$, where the ket $|E\rangle$ is the abstract energy eigenvector. These functions $\langle x|E\rangle$ satisfy the Schrödinger equation in coordinate space.[31] Alternatively, the basis might consist of functions $\varphi(p)$ in momentum space, satisfying the momentum-space Schrödinger equation. We would say that the representative of an abstract vector $|E\rangle$ in a position representation is $\langle x|E\rangle = \psi_E(x)$.[32] In a momentum representation, $\langle p|E\rangle = j\phi_E(p)$, which, because of the relationship between p and q (or x), would take the form of a Fourier transform:[33]

$$\langle p|E\rangle = \int < p|x\rangle\langle x|E\rangle \mathrm{d}x.$$

This usage is quite standard.

The development of transformation theory, which included (but was not restricted to) transforming from the Schrödinger approach or method (wave mechanics) to the Heisenberg method (matrix mechanics), left the theory ripe for the generalization carried out by von Neumann in 1927. The result is that quite frequently, especially in the early literature, the form of quantum mechanics in which the states are time dependent but the operators are not is known as the Schrödinger representation and that in which the states are time independent and the operators are time dependent is known as the Heisenberg representation. For example, in Born and Jordan,[34] one finds, for an operator O, $\mathrm{d}O/\mathrm{d}t = 2i/h\,[H,O]$ in Heisenberg's representation. In the Schrödinger representation, the time dependence of matrix elements of an operator comes from the time dependence of the appropriate state, which satisfies the time-dependent Schrödinger equation (TDSE).[35] There is a unitary transformation that takes one from the Heisenberg representation to the Schrödinger representation, which really means that they are not fundamentally different.

In the first edition of his book, Dirac used the term representation in at least two of the ways that were just enumerated,[36] but by the second edition (1935), he had introduced the term picture to refer to the different ways in which the equations of motion were obtained in the Heisenberg and Schrödinger methods, that is, whether the operators or states were time dependent. Today it is preferred practice to adopt Dirac's terminology in referring to these formulations, and others, as pictures rather than representations or methods; hence the Heisenberg picture or the Dirac (or interaction[37]) picture. They are, again, related by unitary transformations. The terminology was in

a state of flux for some time, so that Dirac's language did not become fully accepted until after the war. In his 1938 text, Vladimir Rojansky used representation in this older sense, but only once, otherwise employing the generic term method. In the postwar era, David Bohm used Heisenberg representation and Schrödinger representation in 1951, and Leonard Schiff, in the 1955 second edition of his famous text, referred to the *r*-representation, that is, a coordinate representation, but used no language to distinguish the two *methods*. In 1960 Robert Dicke and James P. Wittke still used the older language, but Eugen Merzbacher adopted Dirac's terminology in his textbook of the following year, probably influenced by the fourth edition of Dirac's book, published 2 years earlier. By his third edition in 1968,[38] Schiff had been converted to the use of Schrödinger, Heisenberg, and interaction *pictures*, so there was not much doubt how the tide was running. Still, old habits died hard, and Alexander Davydov (in translation, admittedly) was adhering to the old usage a year later, and even as late as 1973 Lev Landau and Evgeny Lifschitz (or their translators Sykes and Bell) were still using representation" in both senses.

Perhaps Albert Messiah's classic text of 1961 illustrates as well as any the confusion over the use of the term representation, employing it in all three senses. His chapter VIII was devoted entirely to the task of distinguishing the Heisenberg and the Schrödinger (and other) representations,[39] continuing to use the old terminology, albeit with some apology. He complicated the matter and caused more confusion by referring to, for example, an energy basis $|E\rangle$, in which the energy is diagonal as an "energy representation" whereas the state $\psi_E(x) = \langle E|x\rangle$ is an energy eigenstate in a "position representation." Similarly, he refers to the "momentum representation" as one in which the momentum is diagonal, that is, $|p>$. He then refers to the "wave function in momentum space" $\varphi(p) = \langle p|\psi\rangle$, or "wave function $\psi(q) = \langle q|\psi\rangle$ of configuration space" refraining from using the term representation. Then he declares that "Wave Mechanics is obtained by formulating the Quantum Theory in the Schrödinger 'representation' and in a representation in which the position variables are diagonal."[40] Thus we see representation used in both technical and commonplace senses of the word in the same sentence, which undoubtedly has confused a large numbers of students.

Eventually, by the 1980s, the use of Dirac's picture had become almost universal.[41] This is all purely a matter of terminology and convention, of course, confusing to students, perhaps, but it does show the syntax of the theory evolving even as its structure or substance went largely unchanged from the form that Dirac, Jordan, and von Neumann gave it.

To add just a bit more detail, states are propagated in time in the Schrödinger picture by the TDSE. A state is transformed from the latter to the Heisenberg picture as follows: $|\psi_H(t)\rangle = U(t)\,|\psi_S\rangle = \exp(iHt/\hbar)\,|\psi_S\rangle$. Any operator would transform according to $O_H(t) = U^{\dagger}(t)O_S U(t)$ and propagate in time according to ("Heisenberg equation of motion")

$$\mathrm{d}O/\mathrm{d}t = -\frac{2\pi}{h}[H,O].$$

A state in the interaction or Dirac picture, which is appropriate to perturbation theory, with $H = H_0 + H'$, is related to one in the Schrödinger picture by

$$|\psi_I(t)\rangle = \exp(H_0 t/\hbar)\,|\psi_S(t)\rangle.$$

The observables are also time dependent:

$$O_I(t) = \exp(-iH_0 t/\hbar)\,O_S(t)\exp(H_0 t/\hbar),$$

and their equation of motion is

$$\mathrm{d}O_I(t)/\mathrm{d}t = -i/\hbar\,[O_I, H_0].$$

This proved to be especially powerful in quantum-field theory, where it leads to the Dyson expansion.[42]

PURE AND MIXED STATES

Before we leave the question of formalism, to which this and the previous chapters have been devoted, we address the fact that many quantum-mechanical states are not "pure states." A pure state can be represented by a ket vector $|\psi\rangle$, a ray in Hilbert space that may also be a linear combination of other ket vectors. "Mixed states," on the other hand, are *statistical ensembles* of pure states, cannot be described by a single ket vector, and are most conveniently represented by a density operator or density matrix.[43] For a pure state $|\psi\rangle$, the density matrix would be given by $\rho = |\psi\rangle\langle\psi|$, and the expectation of an operator O would be $\langle O\rangle = \mathrm{Tr}(\rho O)$.[44] On the other hand, the density matrix corresponding to a mixed state, which is a statistical mixture of pure states, would be $\rho = \Sigma_k p_k |\psi_k\rangle\langle\psi_k|$, where p_k is the contribution of the state $|\psi_k\rangle$ to the mixture. An example would be a collection of hydrogen atoms at a given temperature T, each in an energy eigenstate $|E_n\rangle$ (that is, the electron is in that state), with the probability of being in the state n determined by a Boltzmann factor $p_n = \exp(-E_n/kT)$. Other examples include an unpolarized beam of light, or a beam of atoms, each with spin-1/2, which cannot be represented as a linear combination $a|+1/2\rangle + b|-1/2\rangle$, because in such a state the spin would point in a specific direction; the unpolarized state is an incoherent mixture of the spin-up and spin-down states.[45] In a mixed state, Albert Messiah wrote, "the dynamical state of the system is known incompletely."[46] This is because in a mixed state, the relative probabilities of the contributing pure states are of the form $|a_i|^2$, and the phase information of the states is lost. Looked at another way, in a pure state, described by a state vector $|\psi\rangle$, we have complete knowledge about the system (consistent with quantum mechanics). If the state is an eigenstate of an Hermitian operator O, measurement of the associated observable will give a definite, predictable value. In a mixed state, our knowledge is probabilistic; we can have only partial knowledge of a system; only the probability that the system is in a

particular state is known. An important consequence is that a mixed state cannot be reduced to a pure state by a measurement.[47] Landau and Lifschitz give a particularly clear description of the difference between mixed and pure states.[48] One can argue that every system is in a mixed state because of interaction with the environment, and that has important consequences for "decoherence."

CONCLUSION

Von Neumann, the great Hungarian–American mathematician and Hilbert, the prince of Göttingen mathematics, perhaps deserve a few additional comments. In von Neumann's case, although his name is generally not associated with a specific discovery in quantum mechanics, it was he, more than anyone else, who was responsible for the program of representing quantum states as vectors in a Hilbert space. As one of the most important mathematicians of his era, the task fell to him to carry out the axiomatization of quantum mechanics, beginning in 1927 and fulfilling an old dream of his mentor Hilbert, who wanted to do this for all of physics; von Neumann's *Mathematical Foundations of Quantum Mechanics* of 1932 is still hugely influential. As is well known, von Neumann helped create the fundamental basis of digital computing and was a founder of game theory and mathematical economics. He died at age 54 in 1957 with U.S. intelligence agents at his bedside because of his involvement in national security issues.[49]

As for Hilbert and his role as the godfather of modern quantum theory, we might again recall his intellectual descendants. Weyl and von Neumann, in particular, were directly influenced by him, von Neumann having studied under him and Weyl having received his PhD with him. Born had been close to Hilbert since 1904, as well as to Hilbert's colleague, Hermann Minkowski, and he served briefly as Hilbert's assistant. Jordan worked with Courant, who got his doctorate under Hilbert, before getting his PhD under Born. Born's other students included Lothar Nordheim, Robert Oppenheimer, and Victor Weisskopf, and although Heisenberg and Pauli were Sommerfeld's students, neither wasted much time in coming to Göttingen to work with Born.[50] In any event, if indirectly, Hilbert was responsible for the mathematical structure upon which quantum theory was built.

Finally, as we close this chapter on the mathematical formalism of quantum mechanics, we briefly touch on the unreasonable success of the Hilbert-space formulation of quantum mechanics, paraphrasing a comment by Wigner on the "unreasonable effectiveness of mathematics."[51] By adopting the Hilbert-space (or operator calculus) formulation of quantum theory, we have imposed a mathematical structure on the physical world whose range of validity only experience, that is, observation, can determine. We return to this idea briefly in Chapter 14.

In the case of classical physics, it is clear that the mathematical structure, primarily the use of second-order partial-differential equations to describe heat flow, fluid dynamics, electromagnetism, and celestial mechanics, emerges entirely from the phenomena; the mathematics were created to describe the physical world. We cannot really say the same thing about quantum mechanics, especially when it comes to

application of the theory of linear vector spaces to the quantum world. It is true that the mathematical structure evolved organically from Schrödinger's wave mechanics in a way entirely consonant with the treatment of other differential equations of mathematical physics, whose solutions could be expressed in terms of a complete set of orthonormal functions that spanned a linear vector space. In other words, the Hilbert-space formalism had a certain kind of inevitability. So it is not an accident that we can identify the state of a system with a vector in Hilbert space, but was it really inevitable?[52] We know that Hilbert and von Neumann recognized that the structure of quantum mechanics could be mapped onto Hilbert space, but why should nature be faithfully described by this abstract formalism, and is it, in the end? That, of course, is a question long debated by philosophers. That the mapping of the structure of self-adjoint operators on a Hilbert space onto the real world (or vice versa) actually works ought to be considered something of a mystery.[53] After more than 80 years, there is not a hint that the physics has been "shoehorned" into a mathematical structure that fails to fully capture it. This is, of course, only one example, if a most important one, of the problem of the relation between mathematics and the real world. Is mathematics merely a beautiful tautology? Or, to what extent is it dependent on experience, and is that the reason it seems to describe the real world? Much has been written on the subject, but there is no better distillation of the problem than von Neumann's "The mathematician: The works of the mind," found in vol. I of his *Collected Works*. Despite the efficacy of mathematics in describing the real world, he observed that "it is very hard for any mathematician to believe that mathematics is a purely empirical science or that all mathematical ideas originate in empirical subjects." Yet "it is undeniable that some of the best inspirations in mathematics . . . have come from the natural sciences."[54]. In the end, if the mathematical description of a particular phenomenon fails, it doesn't mean the mathematics is wrong, but only that its use in describing nature was at best approximate, or even wrong.

NOTES

1. That is, a "Hilbert space." Weyl (1928). In the 1932 English translation this is on p. 74. In the original, first German edition, the passage is on pp. 64–5. Weyl might have been able to reach this conclusion even before von Neumann, sometime in 1926, when both he and Schrödinger were at Zurich and close friends. But see Weyl's comments in his obituary of Hilbert (n. 5 of this chapter). The 1930 second German version of Weyl's book and the 1932 English edition differ very little.
2. Von Neumann (19927a, 1927b); Hilbert, von Neumann, and Nordheim (1928). It seems fair to say that we will never know precisely what Hilbert's role was: as leader, resuming his old goal of axiomatizing all of physics, including quantum mechanics, or only a token role, honored by having his name listed as primary author, though that was alphabetical. Nordheim went on to have an important career in nuclear physics in the United States.
3. Others might point to the work of Grassmann in 1844.
4. In the paper "On the mathematical foundations of quantum mechanics," written with Hilbert and Nordheim (Hilbert et al., 1928), the term is used. Fritz London used it in 1927 as well (1927a).

5. On Weyl and Hilbert, see Hilbert's obituary in Weyl (1944), where the latter wrote "The story would be dramatic enough had it ended there. But then a sort of miracle happened: the spectrum theory in Hilbert space was discovered to be the adequate mathematical instrument of the new quantum physics inaugurated by Heisenberg and Schrodinger in 1925. This latter impulse led to a reexamination of the entire complex of problems with refined means (J. von Neumann, A. Wintner, M. H. Stone, K. Friedrichs). As J. von Neumann was Hilbert's collaborator toward the close of that epoch when his interest was divided between quantum physics and foundations, the historic continuity with Hilbert's own scientific activities is unbroken, even for this later phase" (p. 651). According to Weyl, the period in which Hilbert engaged with physics was 1910–1922. See also the *Stanford Encyclopedia of Philosophy* article "Hermann Weyl," by Bell and Korté. As noted in Chapter 3, according to Elsasser (1971), Hilbert had much earlier ("around the turn of the century") tried to find a linear operator whose eigenvalues would represent the frequency of spectral lines. Weyl was almost an exact contemporary of Einstein, and died in 1955, 8 months after him.
6. Schrödinger (1926e), p. 120 in Schrödinger (1928). But see Jammer (1974), pp. 42–3, on how Schrödinger and Born interpreted such a superposition as applied to a single atom.
7. At the time both Schrödinger and Weyl were at Zurich, where they became close friends, and in his first paper Schrödinger acknowledges Weyl's help with the solution to the wave equation with an inverse-square force. The distinction between the space spanned by solutions to Laplace's equation in three-dimensional spherical coordinates and those of the Schrödinger equation for the hydrogen atom, say, is the presence of $\hbar$, or rather $\hbar^2$. The angular momentum operator L^2 differs from the angular part of the Laplacian by that factor of $\hbar^2$, so that $L^2 Y_{lm} = \hbar^2\, \ell(\ell+1)\, Y_{lm}$. Classically, of course, the observables are solutions to the partial-differential equations or are obtained from them, whereas in quantum mechanics, the observables are the eigenvalues of the operators. But the differential equations are the same.
8. Dirac (1927a).
9. Dirac finally cites Weyl's book in a paper published in April 1929 (Dirac, 1929). Dirac's situation is reminiscent of Heisenberg's when it fell to Born to point out that what he was doing was manipulating matrices.
10. Born was at Göttingen during much of the 20 years prior to his taking Heisenberg as a student, though he spent some time at the University of Berlin, where he became friends with Einstein. In mathematics, he was also influenced by Klein and Minkowski, both of whom were at Göttingen when Born became an ordinarius professor there in 1921. On the matter of mathematizing physics in this era, see Jungnickel and McCormmach (1986). Göttingen's heritage as a center of mathematical learning went all the way back to Gauss and Riemann.
11. Von Neumann (1927b); Hilbert, von Neumann, and Nordheim (1928).
12. Von Neumann (1927a). The third paper is titled "The probability-theoretic structure of quantum mechanics" (von Neumann, 1927c).
13. Dirac (1927a).
14. Weyl (1927, 1928), as well as the English version of 1932. This work of Weyl, on group theory and quantum mechanics, grew out of lectures in Zurich in 1927–1928 and at Princeton in 1928–1929. The latter lectures were translated by H. P. Robertson and published as *The Theory of Groups and Quantum Mechanics* (1932). In addition, some fundamental work on

mathematical foundations is given by Stone (1932). Stone, an American mathematician, son of Chief Justice of the Supreme Court Harlan Stone, studied under Birkhoff at Harvard.

15. Heisenberg (1930).
16. Dirac (1930a). See the first five chapters, especially II and III.
17. Which ultimately found a place in what is called "rigged Hilbert space." See Bohm et al. (1998).
18. In his papers in the *Proceedings*, he shows no reluctance to acknowledge others, but that is not true of his book of 1930, where citations are few and far between. He did acknowledge Weyl's work in 1929 (see n. 9 of this chapter). It is worth noting at this point that in the development of his abstract theory, Dirac cites no previous work in either the first or second editions of his book. There are, if I am correct, four citations in the first edition, to Weyl, Bohr, Schrödinger, and Einstein. We can watch his thinking evolve as he apparently learns more about linear vector spaces, but without any hint as to how he was influenced in his thinking.
19. Notably in the two papers: "On the theory of quantum mechanics" (Dirac, 1926c), and then four months later in "The physical interpretation of the quantum dynamics" (Dirac, 1927a).
20. Born and Wiener (1926). Wiener is considered the founder of the science of cybernetics. Recall that Jordan cited Wiener in his 1927 attempt to merge the disparate forms of quantum theory; Jordan (1927a).
21. Notably in game theory, stored-program computers, etc.
22. For example, Friedman (1956), p. 100. In some hands, unitarity has taken on a sort of metaphysical status, as a constraint on any theory, whether of the universe or of some simpler system.
23. Othogonality and unitarity thus play similar roles, the one preserving the length or norm of a vector in three dimensions (or its generalization), the other preserving normalization.
24. With suitable qualification.
25. See, in this connection, Goldstein (1980), chapter 9.
26. Wigner (1939). See also Weinberg (2013).
27. Weyl (1928), Wigner (1931). Weyl credits this to Frobenius.
28. Often "realization" is used, e.g., Weyl (1928), who took "representation" to apply only to an abstract group that is linear and homogeneous.
29. Messiah (1961), p. 323.
30. See Chapter 11.
31. These $\psi(x)$ also span a Hilbert space of complex-valued square-integrable functions.
32. So that $|\langle x|E\rangle|^2$ is the probability that if the energy is E, a measurement of position will yield the value x. Or rather, that $|\langle x|E\rangle|^2\, dx$ is the probability of finding the object in dx.
33. See, for example, Gottfried (1966). The chapter in his book (1930) devoted to these matters, chapter IV, is titled "Representation of states and observables."
34. Born and Jordan (1925), Eq. 43, written slightly differently.
35. See, for example, the third edition of Schiff (1968), p. 169.
36. Dirac (1930a), p. 115, where he speaks of the "fundamental states of the Heisenberg representation," and p. 55, where he talks of representations of the abstract vectors.
37. Discussed in all quantum texts, e.g, Davydov (1965), pp. 104–5, as the "interaction representation." The interaction picture, in which both the operators and wave functions are both time dependent, was introduced by Dirac in 1927.

38. The previous editions having been published in 1949 and 1955.
39. Because of the technical use of the term representation in group theory. Messiah, vol. I (1961), pp. 312–26. Messiah then introduces the terms position and momentum representations, somewhat clouding the issue (p. 326). Messiah's footnote (1961) on p. 314 cautions the reader not to "confuse this concept of 'representation' with the notion of the representation of vectors and operators of vector spaces by matrices." He suggests using the cumbersome terminology "Schrödinger mode of description" instead, though he eventually settles for putting representation in quotes when the meaning is what we now call "picture." The excellent 35-page appendix on group theory in vol. II of course uses representation in the technical sense. Messiah was originally published in French in 1958.
40. Messiah (1961), vol I, p. 324.
41. For example, Sakurai (1993), Bransden and Joachain (1989), Cohen-Tannoudji (1992), etc.
42. Dirac (1930a), §52. See Gottfired (1966), §54. But see also the implications of Haag's theorem;. Roman (1969), §8.4, or Earman and Fraser (2006).
43. Von Neumann (1932); Landau (1927). The idea of pure and mixed states appears in print for the first time in Weyl's long paper of 1927 (Weyl, 1927, pp. 7–9). He reported that von Neumann had also arrived at this idea (p. 1).
44. "Tr" stands for "trace," which in a matrix representation is the sum of the diagonal elements.
45. See Sakurai (1985, sec. 3.4). Most earlier textbooks ignored the problem, Davydov (1965) being an important exception.
46. Messiah (1961). The quote is from p. 204 in the 1964 paperback edition. Messiah played an important role in the French Resistance in WWII and died in 2013.
47. Another way to look at this is that a pure state has zero von Neumann entrophy, a mixed state has a nonzero entropy. The von Neumann entropy is defined as $S = -\mathrm{Tr}\left(\rho \ln \rho\right)$, where ρ is the density operator (matrix).
48. Landau and Liftschitz (1958), sec. 12. Or in the 1977 third edition, sec. 14.
49. As an aside, Pauli died the next year at age 58. Einstein and Weyl died in 1955, but were of an earlier generation. Born died in 1970, Heisenberg in 1974, and Dirac a decade later. Hans Bethe died in 2005 at the age of 99.
50. Paradoxically, this genealogy makes the crucial contributions of Dirac, who was initially trained as an engineer, to the formalism of quantum mechanics all the more remarkable, lacking as he did the Hilbert pedigree
51. The lecture "The unreasonable effectiveness of mathematics in the natural sciences," Wigner (1960). This was the Richard Courant Lecture in mathematical sciences delivered at New York University, May 11, 1959. The issue is, of course, larger than the question of Hilbert space, having an impact on any mathematical theory of nature, or as Einstein asked, "How is it that mathematics, a product of human thought that is independent of experience, fits so excellently the objects physical reality?" See also S. French, "The reasonable effectiveness of mathematics: partial structures and the application of group theory to physcis," in *Synthese* 125 (2000), p. 103. Also articles by Alex Harvey, Grattan-Guiness, Mauro Dorato, etc.
52. Mackey (1963) discusses some parallels in classical physics. As to the matter of formulating quantum mechanics in Hilbert space, Mackey gives as an axiom: "The partially ordered set of all questions in quantum mechanics is isomorphic to the partially ordered set of all closed subspaces of a separable, infinite dimensional Hilbert space." Among other sources

on the mathematical foundations of quantum mechanics, see Jauch (1971). It would, of course, be possible to say that Hilbert space replaced the phase space of classical mechanics.

53. Operators on a Hilbert space are mappings of the space onto itself.
54. Von Neumann (1961–1963), vol. I. "The work of the mind," pp. 1–9. "I think it is a relatively good approximation to the truth . . . that mathematical ideas originate in empirics" (p. 9). As an aside, Wigner said that "there are two kinds of people in the world: Johnny von Neumann and the rest of us." In a similar vein, the regard for unitarity is occasionally so great and it is so fundamental a part of quantum theory that it is preserved in almost any conceivable extension of the theory. For example, unitarity is very much involved in discussions of information loss in black holes, and belief in it is so universal, in part for reasons that were mentioned, that it has even been argued that the universe must be closed because otherwise unitarity would be violated. Whether that makes sense is an argument for another place, but it does show how important the concept of unitarity is, and, in a way, how belief in mathematical symmetry or beauty may be seen as constraining nature (the hubris there is self-evident, of course).

10

INTRINSIC SPIN AND THE EXCLUSION PRINCIPLE

INTRODUCTION

The discovery of intrinsic spin is one of the most fascinating episodes in the history of quantum mechanics. Beginning in 1911 and continuing up to the present, experiments, bolstered by new technologies, have revealed the existence of previously unknown entities, from Rutherford's α-particles to today's quarks, and in virtually every case, the new object has carried with it new physics. In a few cases a new particle was predicted before it was found, a most recent example being the Higgs boson, but for the most part these were fundamentally experimental discoveries. Over time, theories connecting these newly discovered particles have evolved, come and gone, finally settling on the current uneasy consensus, the "standard model." But the discovery of spin, at the very dawn of the new quantum theory, was quite different. Spin was discovered by theorists trying to understand experiments in a way that was untypical, and it provided an immediate explanation of a range of puzzling phenomena. It was the discovery of a *property* of matter, whose existence had been hidden in the data, clearing a veritable fog that had obscured understanding of the spectroscopic data.

But spin itself in some sense still continues to defy explanation. It is ubiquitous, at least partly responsible for the existence of normal matter, deeply involved in the issue of quantum entanglement, and yet we don't know why there is spin. For now, and this has been the case for 90 years, it is simply another degree of freedom, an angular momentum that couples neatly with ordinary orbital angular momentum, but has no classical counterpart. Fortunately our task here is to trace the history of its discovery, not to explain what it is.

The point could be made that neither the problem of intrinsic spin nor the Pauli exclusion principle—the two are inseparable—is central to the basic structure or formalism of quantum theory that we have discussed in the previous five chapters. Although spin is an important property of all elementary particles, quantum *theory* would be simpler without it, but not fundamentally different. The world would be, of course. Without spin there would be no exclusion principle, and that is because of the intimate connection between spin and statistics. And if fermions did not have the property that the exclusion principle describes, the universe as we know it would not exist.[1] Dirac showed that the electron *had* to have spin, and the photon spin is surely even more fundamental. By extension the same is true of the other vector bosons, the force carriers, but this does not really answer

the question "what is spin?" Lest our reach exceed our grasp, as promised that question is left for others.

> The problem of the doubling of spectral lines in the alkali spectra (Chapter 3) was a huge puzzle in the early 1920s, and the "anomalous Zeeman effect," as the name implies, thoroughly defied explanation. Years later, in a 1945 lecture at the Institute for Advanced Studies at Princeton, following his receipt of the Nobel Prize, Pauli recounted an event which happened in 1922, when he had been invited to Copenhagen by Bohr. In what is by now an oft-told story, Pauli, while "strolling rather aimlessly in the beautiful streets of Copenhagen," encountered a colleague who said that he looked very unhappy. "How can a person look happy," Pauli replied, "when he is thinking about the anomalous Zeeman effect?"[2] In the end, and despite the fact that Pauli would be hard to convince, it was the discovery of electron spin that provided a solution to the problem.[3]

Arthur Holley Compton, then at Washington University in St. Louis,[4] had advanced the idea of a spinning electron in print in 1921, and although his paper attracted little interest,[5] he is often cited—for example in the Heisenberg–Jordan paper on the anomalous Zeeman effect[6]—as the first to consider electron spin. In 1923 Bohr had timidly proposed a generic "non-mechanical strain" to address the troubling spectroscopic problems,[7] and by the next year it had become clear to Pauli that there was a new double-valued degree of freedom [*zweideutigkeit*] demanded by the spectroscopic data.[8] In retrospect it may seem surprising that the brilliant young Pauli would not be the one to conceive the idea of a spinning electron himself (or, more properly, *spin*), but, as we shall see, his distaste for the introduction of classical, pictorial ideas into the new mechanics was very firm. One unfortunate consequence was that when on January 8, 1925, a 20-year-old Columbia University graduate student, Ralph Kronig, making his "grand tour" of European physics centers, met Pauli in Tübingen, Germany, and suggested to him that the additional degree of freedom could result from an electron spin, Pauli dismissed the idea of the electron—as a sort of spinning top—as ludicrous, almost a joke. It was, he thought, a "very funny idea."[9] Heisenberg's similar negative reaction, shortly thereafter, was also unsurprising, given his attempt to banish nonobservable quantities from quantum mechanics. Eventually, after having been rebuffed by Pauli, Heisenberg, and even by Kramers and Bohr on a visit he made to Copenhagen, Kronig decided against publishing his conjecture. In one of those ironies of history, in the face of implacable opposition, despite having raised the question for the first time in the context of the unfolding quantum theory, Kronig capitulated, thereby missing his chance at a Nobel Prize.[10] As a further irony, Pauli had actually proposed the idea of a *nuclear* spin (or rather a nuclear magnetic moment) at just about the same time (the close of 1924) that he was talking Kronig out of the idea of *electron* spin.[11] Finally, Kronig's meeting with Pauli, in which the latter rejected the idea of electron spin, took place just as Pauli was submitting his paper on the exclusion principle. Of such paradoxes is the history of physics constructed. Still, there is no reason not to credit Kronig as *a*, if not *the*, discoverer of spin. In the event, it fell to a pair of Dutch physicists, still graduate students at the University of Leiden, George

Uhlenbeck and Samuel Goudsmit, who apparently knew nothing of Kronig's ideas, to publicly offer the suggestion that the electron had an intrinsic angular momentum, i.e., spin.[12] Kronig, who died in 1995, clearly deserves some share of the credit for the "discovery," and there are those who have wanted to give the honor to Pauli himself, but in view of his hostility to the idea, that doesn't seem entirely fair. On the other hand, Pauli's reasons for rejecting the spinning electron were philosophically sound, and because spin has no classical counterpart, we can argue that whether we calls it "spin" or a new "double-valued" degree of freedom may not be important.

To explain the motivation for Uhlenbeck and Goldsmith's suggestion that would come in late 1925, we need to discuss two phenomena that were troubling those like Pauli, who were trying to find an explanation for them, namely "fine structure" and the"anomalous Zeeman effect." Both of them were alluded to in an earlier chapter, but now, as the new quantum mechanics was unfolding, they again begged for a real explanation. Sommerfeld had given a partial explanation of fine structure as being a relativistic phenomenon, but there was still something missing, and Landé, in an analysis of the anomalous Zeeman effect, had shown phenomenologically that there was much more to it. His result is usually given in the form of the Landé "*g*-factor," and though that doesn't capture all that he actually did in 1921,[13] he did show that this quantity, whose meaning we subsequently explore, depended on the "inner quantum number" *j* as well as on the double-valued magnetic quantum number, corresponding to the still-undiscovered spin 1/2. The situation then was that when Pauli wrote an important paper on the Zeeman effect in 1923, there was a partial explanation of fine structure and an "explanation" of the Zeeman effect in terms of the Landé *g*-factor,[14]

$$g = (3/2) - \tfrac{1}{2}\left(\frac{\left[k - \frac{1}{2}\right]^2 - i^2}{j(j-1)} \right),$$

which in modern terms could be written as

$$g = 1 + \frac{j(j+1) - l(l+1) + (3/4)}{2j(j+1)},$$

and depended on quantum numbers whose origin was unknown; hence Pauli's frustration.[15]

FINE STRUCTURE

To appreciate what Uhlenbeck and Goudsmit actually did, it is probably best to describe both fine structure and the Zeeman effect in modern terms, thereby highlighting what was missing before the proposal of electron spin. With the interjection of spin, it followed that if there were two angular momentum vectors **L** and **S** associated with the electron, there would be a total angular momentum **J** = **L** + **S**, and there should be an interaction between the two magnetic moments of the form $\boldsymbol{\mu}_L \cdot \boldsymbol{\mu}_S$, based on the assumption that the electron spin represented the rotation of a

charged particle. This also can be seen as the interaction between the electron magnetic moment and the magnetic field due to its orbital motion. This would lead, then, to an interaction that depended on the product $\mathbf{L} \cdot \mathbf{S}$, which could be treated as a perturbation to the Hamiltonian. This was the "spin–orbit" force,[16] which would turn out to provide an explanation of fine structure, e.g., the alkali doublets. The result was that the fine-structure contribution would be [compare Eq. (3.1), Chapter 3]:

$$\Delta E_{fs} = E_n^2/2mc^2\left[3 - 4n/(j + 1/2)\right]. \tag{10.1}$$

In 1925 this result was still in the future,[17] but it is this composite correction that explains the fine structure of simple atomic spectra. To revisit hydrogen again, the vectors **L** and **S** couple to **J** and, with the fine-structure splitting depending on the quantum number j, the $n = 2$ state in hydrogen (with $\ell = 0,1$) is split by the relativistic correction, depending on l [Eq. (10.1)], but the spin–orbit interaction raises the $2S$ state and splits the $2P$ state, so that the final result is the doublet shown in Figures 3.1 and 3.3.[18] Similar considerations apply to the $n = 3$ ($l = 0, 1, 2$) state, which is split into five (as we have seen), with the states of the same j being degenerate. There is an additional contribution to the fine structure represented by the so-called Darwin term, which contributes for only $l = 0$.[19]

THE ANOMALOUS ZEEMAN EFFECT

The normal Zeeman effect had been given a quasi-explanation by Lorentz[20] on the basis of a classical theory that worked in some cases but failed in others, when the spectra of an atom in an applied magnetic field was found to be more complex than predicted. The normal Zeeman effect occurs only when spin does not play a role, so that already in atoms with only one unpaired electron (such as the alkali metals), the spectra were perplexing. This would be the simplest case of the anomalous Zeeman effect, which, under the hypothesis of Uhlenbeck and Goudsmit (as we shall see), would depend on $\mathbf{L} + 2\mathbf{S}$. This comes about because if there is a spin angular momentum **S**, there will be an interaction between the external field and the total magnetic moment of the form $\boldsymbol{\mu} \cdot \mathbf{B}$, $\boldsymbol{\mu}$ involving both orbital and spin moments: $\boldsymbol{\mu} = g_L\mathbf{L} + g_s\mathbf{S}$. But to explain the data, it was necessary to imagine that the ratio of the spin magnetic moment to its angular momentum differed from the classical result by a factor of 2 (see subsequent discussion).[21]

UHLENBECK AND GOUDSMIT

To describe in detail what happened, we begin with the revelation to the world of electron spin in letters submitted to the journal *Naturwissenshaften* in October 1925 and to the editor of *Nature* in December, which reached print in February.[22] In the first, breakthrough paper, titled "Replacement of the hypothesis of the non-mechanical strain by a requirement relating to the internal behavior of each electron," published November 20,[23] Uhlenbeck and Goudsmit were initially concerned with explaining

the empirical Landé *g*-factor, which arose in the weak-field Zeeman effect[24] and contained a factor that previously had been attributed to the inert core of an alkali atom. This was merely a matter of angular momentum coupling (or finding the projection of **S** on **J**), and with an electron spin angular momentum quantum number of 1/2 and spin *g*-factor (g_s) of 2, the Landé *g*-factor could be reproduced. Their crucial, even daring, conclusion, motivated by the Zeeman effect, was that "the ratio of the magnetic moment of the electron to the [mechanical] angular momentum must be twice as large for the self-rotation [spin] as for the orbital motion." They proposed that it was due to an intrinsic, "nonmechanical" angular momentum of the electron, with quantum number 1/2.[25]

By the time the two-page February letter to *Nature*, titled "Spinning electrons and the structure of spectra," was published, the Dutch physicsts had gained substantial confidence in their idea, and spin was explicitly advanced in explanation of the Zeeman effect as well as fine structure, concentrating on the latter, which did not require an anomalous value of g_s.[26] But when they turned their attention to the anomalous Zeeman effect, they again noted that agreement with experiment would require an electron magnetic moment twice as large as would be expected classically, if it behaved like a mechanical angular momentum. That hypothesis would immediately provide a coherent explanation of the appearance of the anomalous Zeeman effect in these atoms, but only if the troubling factor of 2 could be theoretically justified. In the author's words, describing the Zeeman effect, it "has heretofore presented very grave difficulties. However, these difficulties disappear at once when, as assumed, the electron has a spin and the ratio between the magnetic moment and angular momentum of this spin is different from that corresponding to the revolution of the electron in an orbit." As in the earlier paper, "It seems possible on these lines to develop a quantitative theory of the Zeeman effect, if it is assumed that the ratio between magnetic moment and angular momentum due to the spin is twice the ratio corresponding to an orbital revolution."[27] That leap of faith was daring indeed.

This episode is an excellent example of the way in which a portion of the physics community, essentially in concert, could manage to embrace a revolutionary new mechanism, electron spin, despite a nagging numerical discrepancy, for the simple reason that it would give a rational explanation of the observations. Initially no theoretical support for the basic idea existed; just the phenomena themselves. The hope or, if you like, the expectation, was that they (Uhlenbeck and Goudsmit) would be rescued by theory, and they were.

As all this was taking place, in May 1926, Schrödinger was submitting part III of his sequence of papers creating wave mechanics, in which he mentions the "paradoxical but happy conception of the spinning electron,"[28] but doesn't attempt a theory of the anomalous Zeeman effect. He does express his understanding that the electron is no longer seen as a point charge, though one suspects Pauli would have bridled at that suggestion.

By December 1925, before the second Uhlenbeck–Goudsmit paper was published, Bohr had convinced Heisenberg that the spin hypothesis was correct, and by

late March he had written a decisive paper on the subject with Jordan. They developed a detailed theory of both fine structure and of the anomalous Zeeman effect, which depend on $\mathbf{L} \cdot \mathbf{S}$ and $\mathbf{L} + 2\mathbf{S}$ respectively,[29] developing (or taking from the BHJ paper) virtually all of the now-familiar angular momentum coupling results (see the next chapter). They obtained matrix elements of $\mathbf{L}_{\pm}$ and $\mathbf{S}_{\pm}$, showed how one obtains $\mathbf{L} \cdot \mathbf{S}$ from $\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2$, and obtained the fine-structure formula including both relativistic and spin–orbit effects for the cases $j = \ell \pm 1/2$.[30] Uhlenbeck and Goudsmit leaned heavily on this calculation, the results of which they learned from Heisenberg before publication. For their part, Heisenberg and Jordan refer to Thomas's paper, which resolved the factor of 2.

THE PHYSICS

The magnetic moment of a charged particle possessing an angular momentum $\mathbf{L}$ can be written as $\boldsymbol{\mu} = \gamma \mathbf{L}$, where γ is the gyromagnetic ratio. Classically $\gamma = e/2m$ (or $e/2mc$, depending on units). If we write this slightly more generally as $\boldsymbol{\mu} = \left[g(e/2m) \right] \mathbf{L}$, where g is the g-factor, then the ratio of the magnetic moment to the angular momentum is $g(e/2m)$. Classically, we would have $g = 1$ and the ratio would be $(e/2m)$. Quantum mechanically, the ratio of the magnetic moment to the angular momentum (divided by $\hbar$) would be $g(e\hbar/2m)$. What Uhlenbeck and Goudsmit were suggesting was that $g = 2$ for the electron spin! Why? Simply because it worked. Initially the hypothesis worked because the spin quantum number of 1/2 could reproduce the Landé g-factor. But that was the easy part.

The Zeeman effect immediately raised the problem of the factor of 2. Paradoxically, it seemed that $g_s = 2$ was required for the Zeeman effect and $g_s = 1$ for fine structure. As Uhlenbeck and Goudsmit wrote, "at present . . . it seems difficult to reconcile this assumption $[g_s = 2]$ with a quantitative analysis of our explanation of the fine structure of levels,"[31] e.g., the doublet spectra of the alkalis, which, it would turn out, depended on the spin–orbit interaction, $\mathbf{L} + \mathbf{S}$, which was obtained from $(\mathbf{L} + \mathbf{S})^2$. They could explain one or the other of the phenomena, but not both, even with $g_s = 2$, because $g_s = 2$ ruined the agreement with the fine structure, the calculated splittings being only one-half what was observed.[32] In spite of these problems, they concluded the paper optimistically.

RESOLUTION

For a time, the ad hoc introduction of spin to explain the anomalous Zeeman effect was just a leap of faith, because of the missing factor of 2. But once the problem of an electron spin processing about a magnetic field due to a charged nucleus moving relative to the electron with velocity $\mathbf{v}$ was correctly treated relativistically by Llewelyn Thomas,[33] that leap of faith was fully justified. Then a spin g-factor of 2 $(g_s = 2)$ did give simultaneously the right Zeeman splitting and the correct description of fine structure, as Heisenberg and Jordan showed.[34] Although their paper was not completed

until March, both Pauli and Heisenberg had communicated preliminary results to Bohr, to which Thomas referred in his February submission. Heisenberg and Jordan, in turn, referred to Thomas's result, which had not yet been published when they originally submitted their paper (the precise dates are in the notes).[35] This simultaneous solution to the outstanding problems of the anomalous Zeeman effect and fine structure, accomplished between December and March of 1926, gives dramatic evidence of the close communication among European researchers and of the limited peer review in the publication process that allowed quick publication.[36]

To further complicate matters, the great Russian physicist Yakov Frenkel also worked out the theory of the precession of a spin vector in a magnetic field and submitted it to *Zeitschrift für Physik* in the spring of 1926,[37] well before Thomas's full development was published at the end of the year. This paper appeared immediately preceding that of Heisenberg and Jordan,[38] which, as we have seen, made use of Thomas's development. Although Heisenberg and Jordan's paper was received by the journal 6 weeks before Frenkel's, evidently an editorial decision was made to publish them together, as Frenkel's paper was received on May 2 and published 3 days later.[39] Interestingly, both the papers of Thomas and of Frenkel showed, or at least hinted at, how fine structure and the anomalous Zeeman effect could be correctly treated, but neither explicitly invoked quantum mechanics. This was left to Heisenberg and Jordan.

Unlike the earlier conjectures by Compton and Kronig, the proposal of electron spin by Uhlenbeck and Goudsmit soon won acceptance because of its explanatory power, depending critically on Thomas's letter to *Nature,* and then Frenkel's submission, both of which provided the needed theoretical justification. Of further help was the fact that the Dutch authors had the imprimatur of their teacher Paul Ehrenfest, who urged them to submit their initial paper for publication,[40] despite some misgivings, and of Bohr, who followed their *Nature* letter with one throwing his support to the idea ("promises to be a very welcome supplement to our ideas of atomic structure").[41]

Pauli, however, held out against the proposal longer than most, remaining unconvinced until the bitter end (4 months), which was when Thomas's paper appeared in *Nature* in April.[42] His position had considerable merit, however, rejecting the concept of a classical spinning particle, because, aside from philosophical prejudices, there were good physical reasons to be skeptical of the idea, including the fact that a tiny spherical electron seemed to have to rotate at a velocity greater than c (at its surface). And, of course, as with many others, Pauli was well aware that the hypothesis of a spinning electron, treated in terms of the new quantum mechanics, would lead to a spin magnetic moment of one Bohr magneton $(e\hbar/2m_e c)$,[43] just one-half the value required to explain the anomalous Zeeman effect in the alkali atoms.[44] We have seen how that was resolved.

Despite his initial scepticism, only a year after its discovery and with the concept of spin thoroughly established, Pauli (Figure 10.1) published a long paper developing a comprehensive theory of electron spin.[45] In it he introduced the famous "spinor" formalism of 2×2 "Pauli spin matrices,"[46] though in many respects the earlier paper

Figure 10.1. Wolfgang Pauli (1900–1958), by permission of CERN.

of Heisenberg and Jordan, giving the detailed solution to the problem of the anomalous Zeeman effect and spin–orbit coupling, went further.[47] When Weyl's book appeared in 1928, he identified the spin matrices as constituting the fundamental representation of $SU(2)$.[48]

Adding irony to this story of the discovery of spin is a letter from Kronig to *Nature* a week after Thomas's, on April 17, 1926, in which he took issue with Uhlenbeck and Goudsmit, concluding with the comment that "The new hypothesis . . . appears rather to effect the removal of the family ghost from the basement to the sub-basement, instead of expelling it definitely from the house."[49] And in fact the question "what is spin?" remained, and still does. Three weeks later, the May 8, 1926, issue of *Nature* featured communications on the problem of spin, by Eddington, Richardson, and Frenkel. These were indeed heady times.

At the start of 1928, Dirac published his groundbreaking paper on the relativistic theory of the electron, featuring the "Dirac equation," showing that electron spin emerged naturally from relativistic considerations, that is, Lorentz invariance, along with angular momentum conservation.[50] The puzzling g-factor was finally given an explanation. Intrinsic spin is a truly fundamental property of elementary particles, specifically leptons and quarks, which are fermions, as well as of the force-carrying bosons. But in the end, the mystery remains.

THE EXCLUSION PRINCIPLE

According to the discoverer himself, the origin of the "Pauli principle" goes back to his student days in Munich in 1919–1921 when he was studying under Sommerfeld.[51] The immediate problem to be solved was that of understanding the periodic table of elements and the significance of the numbers 2, 8, 18, and 32 of electrons that seemed to imply some sort of closed atomic "shells."[52] In 1921 Bohr advanced a purely phenomenological theory of the periodic table that attempted to explain these numbers, but without much success.[53] He did clarify the problem somewhat with the principle that when an electron is added to an atom, say to an inert gas, the quantum numbers of *bound* electrons would not change, the so-called "permanence principle." Of equal importance was the *aufbauprinzip*[54] or "building-up principle," of both he and Pauli, which said that the electron orbits of lowest energy were filled before levels of higher energy. These principles were forerunners of the atomic shell model, which would successfully explain the "magic numbers," but only after the Pauli principle was formulated.

By the time of his inaugural lecture as a new *Privatdozent* at Hamburg in 1923 after leaving Göttingen, Pauli was focusing on the doublet structure of one-electron atoms, the alkalis, which exhibited the problem of complex atomic structure in the simplest fashion, though he later described the contents of the lecture as very unsatisfactory. Then, as he tells it, it was a remark by Edmund Stoner, in a March 1924 paper in the *Philosophical Magazine* pregnantly titled "On the distribution of electrons among atomic levels,"[55] that gave him the key to the exclusion principle. Stoner saw the process of adding electrons to an atom as one of beginning with an inert gas core and progressively filling subgroups until another inert gas core is reached. Specifically, he concluded that the number of electrons in a subshell was twice the inner quantum number, that is, $2j$. This quantum number took on values k or $k - 1$, where $k = \ell + 1$ and ℓ is the angular momentum quantum number. Thus for $n = 1$, where $\ell = 0$, the $\{k, j\}$ states were $\{1, 1\}$ and $\{1, 0\}$, and for $n = 2$ ($\ell = 0,1$) the states or subshells were $\{1, 0\}$, $\{1, 1\}$, $\{2, 1\}$, and $\{2 ,2\}$. Then for $n = 1$ there were 2 electrons and for $n = 2$ there would be $2 + 2 + 4 = 8$ electrons, reproducing the "magic numbers" 2 and 8, but grouped differently from Pauli's ultimate $1s^2 2s^2 2p^6$ arrangement. What Pauli took Stoner to be saying, according to the former's Princeton lecture in 1946 (as well as his Nobel lecture), was that "the number of energy levels of a single electron in the alkali metal spectra for a given value of the principle quantum number $[2n^2]$ in an external magnetic field is the same as the number of electrons in the closed shells of the rare gases which corresponds to this principal quantum number."[56] Although this does not appear to be what Stoner said, it nonetheless led Pauli in the right direction. Stoner's scheme did "explain" the magic numbers and thus represented at least a partial explanation of the periodic table. Bohr 's earlier attempt had divided the 8 electrons outside the closed shell of helium into two subshells with 4 electrons each, so that Stoner's approach was slightly nearer the truth. Bohr had attributed the doublet structure in the alkali metals to a nonzero angular momentum of the atomic core, but for Pauli, the splitting was due to a new, fourth degree of freedom

or quantum number, a "two-valuedness not describable classically."[57] Citing Bohr and particularly Stoner as influences, Pauli proposed that if a state was defined in terms of four quantum numbers n, ℓ(or k), j, and m_j, with the dual-valued number m_s $(=\pm 1/2)$—which within the year would be identified with the electron spin—hidden in j,[58] there could only be 1 electron per state, that is, the electron would have a unique set of the four quantum numbers. As he put it, "there can never be two or more equivalent electrons in an atom for which . . . the values of all quantum numbers n, k_1, k_2, m_1 (or, equivalently, n, k_1, m_1, m_2) are the same."[59] Here

$$k_1 = \ell + 1, \quad k_2 = j + 1/2 = \ell \pm 1/2$$

and m_1 is the projection of j, so that this is equivalent to the set $\{n, \ell, j, m_j\}$ previously given. Consider the $3d(n=3, \ell=2)$ state. In this case $j = \ell \pm 1/2 = (5/2, 3/2)$. For $j = 5/2$, m_j takes on 6 values, and for $j = 3/2$, there are 4 m_j values, totaling 10; identically equal to $2(2\ell+1)$, or 10 electrons in a subgroup. Pauli's notation, $\{n, k_1, k_2, m_1\}$, which is equivalent to the set $\{n, \ell+1, j+1/2, m_j\}$. An alternative set would consist of the quantum numbers $\{n, k_1, m_1, m_2\}$, or $\{n, \ell, m_\ell, m_s\}$, but spin had not yet been identified as a new degree of freedom, thus no projection m_s. In quantum mechanics—then still a few months away—these are different *bases*, obtained from one another by unitary transformations.

Stoner's paper had been submitted in July 1924, and by the fall Pauli had arrived at the first formulation of the exclusion principle,[60] without knowing what the two-valued quantum number would represent; spin, which he would initially reject, was still a year away. It was for this discovery, the exclusion principle, that Pauli received the 1945 Nobel Prize in physics, somewhat belatedly, the first in the postwar era.[61] Stoner missed getting credit for that discovery by an eyelash, and it would not be the last time.[62]

In any event, in 1925 the exclusion principle was no more than an empirical fact, of unknown scope,[63] but the following year Dirac formulated it in terms of the symmetry properties of the two-electron wave function, and it is in that paper that what we now know as the "Slater determinant"[64] was introduced as means of expressing the antisymmetric state. Thus he wrote

> If the positions of two of the electrons [in an atom] are interchanged, the new state of the atom is physically indistinguishable from the original one
>
> . . . It is found that this allows one to obtain two solutions . . . satisfying all the necessary conditions. . . . One of the solutions leads to Pauli's principle that not more than one electron can be in any given orbit, and the other, when applied to the analogous problem of the ideal gas, leads to the Einstein-Bose statistical mechanics."[65]

The representation of a multifermion wave function in terms of Slater determinants immediately embodies the Pauli principle, because if any two rows or columns were the same (any pair of particles had all the same quantum numbers), the determinant would vanish (zero probability). Enrico Fermi attacked the antisymmetric case at about the same time as Dirac, somewhat less generally, creating the foundation

for "Fermi–Dirac" statistics.[66] Interestingly, Heisenberg had arrived at similar results 2 months before Dirac,[67] and added a note in press acknowledging that Born had informed him of that fact. Dirac credited Fermi with the result, but in any case, Heisenberg's contribution has mostly gone unnoticed. Bose and then Einstein had examined the problem in 1924,[68] before the discovery of spin and the advent of the new quantum theory.

The discovery of the electron spin as a fundamental property of the constituents of nature in 1925–1926, along with Pauli's conclusion in 1924 that only a single electron could have the same set of quantum numbers, set the stage for a full understanding of the structure of the atom. Finally the complex structure of the Balmer series lines in hydrogen, seen at high dispersion or in a magnetic field, could be explained in other than purely ad hoc terms. As Bohr commented after reading the paper of Uhlenbeck and Goudsmit, "this hypothesis throws new light on many of the difficulties that have puzzled workers in this field during the last few years."[69]

THE CONNECTION BETWEEN SPIN AND STATISTICS

By 1926 it was understood from the work of Dirac and Fermi that pairs of electrons were described by a wave function that was antisymmetric with respect to interchange of the coordinates of the particles and that there were, or ought to be, particles whose wave functions were symmetric under such interchange. Much later Dirac called these particles "bosons," after Satyendranath Bose, and "fermions," after Enrico Fermi.[70] Today we call the related statistics Bose–Einstein or Fermi–Dirac. But a "proof" of the connection between spin and statistics, the so-called "spin–statistics theorem," was not trivial, and indeed was only obtained by Markus Fierz and his mentor Pauli from quantum field theory in 1939–1940.[71] That is, although the statistics obeyed by fermions and bosons is an empirical fact, can it be understood in a more fundamental way? The answer seems to be yes, but the argument involves relativistic quantum-field theory, and is left to the reader to pursue.[72]

The known elementary bosons are "force carriers," the exception being the no longer hypothetical[73] spin-0 Higgs boson. Some have suggested that all bosons are composites of fermions, but that seems untenable, and supersymmetry, if true, requires bosonic counterparts of fermions and vice versa. But what is of interest to us here is how this question was understood in the 1930s. For example, as described in Chapter 15, when the neutron was discovered it was variously speculated that it was the bound state of a proton and an electron, or even that the proton was a composite particle consisting of a neutron and a positron, both of those particles having been recently discovered. Of course neither possibility is consistent with the spin–statistics theorem,[74] or, when they were measured, the nucleon magnetic moments. When ^{14}N was shown to obey Bose–Einstein statistics in 1929 by Heitler and Herzberg,[75] thus burying the proton–electron notion of the nucleus, it was a testament to the growing conviction that spin and statistics were inseparable.

CONCLUSION

In the end, one question is left unanswered: What is spin? It is no less mysterious today than 90 years ago. The electron is, or seems to be, a singularity, that is, a point particle, and yet it possesses this property called spin, along with a magnetic moment.[76] Despite the importance of intrinsic spin in nature, it is not clear what its origin is, if it can be said to have an "origin." As for the exclusion principle, the point has often been made that it is what keeps matter from collapsing on itself, with all that that implies. Twenty years after his discovery, Pauli was still bothered by the fact that his exclusion principle could not be deduced from quantum mechanics, but rather "remains an independent principle which excludes a class of mathematically possible solutions of the wave equation."[77]

NOTES

1. This is true on many levels. Obviously certain phenomena would not exist, such as the "anomalous" Zeeman effect, fine structure, and so on. Atomic spectroscopy would be very much simpler. More to the point, the absence of a spin–orbit force and the pairing interaction in nuclei would dramatically affect nuclear stability. But without the exclusion principle, nuclei would collapse, there would be no stars, no life, no quantum theory . . . etc.
2. Pauli (1946), p. 214. Also, van der Waerden (1960). These comments came in a dinner lecture at the Institute of Advanced Study on December 10, 1945, in honor of Pauli's Nobel Prize. Pauli had recently joined the Institute. Weyl, Einstein, and Panofsky offered toasts. In the same earlier period (ca. 1923), Sommerfeld was perhaps more optimistic:

   > "whereas initially the departures from theory . . . appeared discouraging . . . now it is just the laws which underlie these departures that claim the greatest interest" Sommerfeld (1923), p. 384.

3. I might have put "discovery" in quotes because it was not one in the usual sense, being more a recognition of something that was lurking in the unexplained physics than a discovery. But that would be splitting hairs.
4. Of which he eventually became chancellor. His two brothers became university presidents as well.
5. To regress the pedigree of the electron spin one step further, Compton wrote that

   > ". . . many of the magnetic properties of matter receive a satisfactory explanation on Parson's [A.L. Parson, 1915] hypothesis, that the electron is a continuous ring of negative electricity spinning rapidly about an axis perpendicular to its plane, and therefore possessing a magnetic moment as well as an electric charge." Compton concluded that the charge was likely concentrated at a center rather than being spread out into a ring (Compton, 1921a). Finally, Ternov and Bordovitsyn (1980) cite a 1903 paper by Schwarzschild as a precursor [*Nachr. Akad. Wiss. Gottingen, Math. Phys*. **K1. 2** (1903) 245].

6. Heisenberg and Jordan (1926).

7. Bohr (1923).
8. Pauli (1925a).
9. According to Kronig, Pauli said "das ist ja ein ganz witziger einfall," or "that is, yes, a very funny thing," but that it had no basis in reality. See Kronig (1960), "The turning point," in the Pauli memorial volume; Fierz and Weisskopf (1960), especially p. 21. As an aside, Pauli was renowned for his penchant for the dismissive judgement on a theory as "not even wrong." As late as 1927, Andrade reluctantly acknowledged that in "any scheme so far suggested . . . half quantum numbers must be introduced, so that we may as well accept them, and ascribe their occurrence to features of the mechanism of the interaction between the core and electron which we do not understand" (Andrade, 1927).
10. See van der Waerden (1960) as well as Kronig (1960), both in the Pauli memorial volume. Jammer (1966, pp. 146–8) also gives a good account of Kronig's work. Kronig (1904–1995) was born in Dresden, but educated at Columbia, where he taught briefly before returning to the United States. Most of his career was spent in the Netherlands. He is perhaps best known for the Kramers–Kronig relation.
11. Pauli (1924).
12. There is a wonderfully personal recollection of the discovery by Goudsmit, delivered at the golden jubilee of the Dutch Physical Society in 1971, which has since been translated into English by J. H. van der Waals. See also Goudsmit's 1976 comments in which he characterized the physics community in those days as "Peyton Place without the sex" (Goudsmit, 1976). Apparently Uhlenbeck tried to stop submission of the joint paper but Ehrenfest had already sent it off. Finally, there is Goudsmit's *Alsos*, the story of his leadership of a team sent to Germany to find out the state of the German nuclear weapons program, just as WWII was ending (Goudsmit, 1947).
13. Landé (1921).
14. This is equation (5) on pl 164 in Pauli (1923).
15. Pauli's "i" was a stand-in for the electron spin of 1/2 (Pauli, 1923). The factor 3/4 is $s(s+1)$, where $s = 1/2$.
16. An interesting elaboration on the spin–orbit interaction, with a summary of the arguments of Thomas and Frenkel is Kholmetskii et al. (2010).
17. Until Heisenberg and Jordan (1926). Adding the spin-orbit term to Sommerfeld's relativistic expression gives Equation 10.1.
18. Richtmeyer and Kennard (1942), p. 366. The 2*P* state was split into $j = 1/2$ and 3/2 states, and the 2*S* state became $2S_{1/2}$. The two $j = 1/2$ states have the same energy because, as we have seen, the fine-structure correction depends only on j (Eq. 10.1).
19. Darwin (1928).
20. Sommerfeld, (1923), pp. 295–300.
21. Consider the weak-field Zeeman effect. The shift in energy is given by $\Delta E = -\mu_z B_{\text{ext}}$, where $\boldsymbol{\mu} = -\mu_B\left(g_l\mathbf{L} + g_s\mathbf{S}\right)$ is the magnetic moment of a single electron, which one would have to average over all electrons in the atom, μ_B is the Bohr magneton $e\hbar/2m_e$. This will lead to $\Delta E = \mu_B m_j B_{ext} g_j$, where g_j is the Landé *g*-factor. For a single electron, $g_j = 1 + \frac{g_{s-1}}{2l+1}$. So the result depends on the value of g_s, i.e., 1 or 2. The $P_{3/2} \rightarrow S_{1/2}$ Lyman-α in hydrogen would split into six lines. See Griffiths (2005).
22. Uhlenbeck and Goudsmit (1925, 1926), published November 20, 1925, and February 20, 1926, respectively. Goudsmit's recollections of this episode, 45 years later, are wonderful.

In the published version is reproduced a letter to him from Thomas, saying of Pauli that "the infallibility of the Deity does not extend to his self-styled vicar on earth." Apparently Bohr and Heisenberg were convinced by December 1925 and Pauli only in March–April of the following year. See van der Waerden (1960).

23. Uhlenbeck and Goudsmit (1925). A short note (about 25 column-inches) in *Naturwissenschaften* [*Natural Sciences*], the German counterpart of *Nature*.
24. See any quantum text, e.g., Griffiths (2005), p. 278. But the implications were much greater. The model of a new, intrinsic angular momentum in the Landé vector model, propagated back to the interaction term $\boldsymbol{\mu} \bullet \mathbf{B}$ in the weak-field Zeeman effect, and thence to the electron magnetic moment. .
25. This understanding was already there in the first paper, indeed in the first paragraph: In German, "daß für den atomrest das verhältnis des magnetischen momentes zum mechanischen doppelt so groß ist, als man klassisch erwarten würde," or "the ratio of the magnetic moment is twice as large as one would expect classically" Uhlenbeck and Goudsmit (1925), p. 954. After reading the *Naturwissenschaften* paper, Bichowsk and Urey submitted a seven-page paper in December also advocating for an electron spin, an ideal that they say had "occurred to us quite independently" Bichowsky and Urey (1926).
26. Only dealing with the Zeeman effect in the last three paragraphs. Aside from a relativistic correction due to Sommerfeld (discussed earlier), fine structure depended on what we know as the spin–orbit interaction, a term in the Hamiltonian of the form $H = \xi \mathbf{L} \bullet \mathbf{S}$. See subsequent discussion
27. Uhlenbeck and Goudsmit (1926), p. 265. Although they do thank Heisenberg "for a letter containing some calculations on the quantitative side of the problem," which undoubtedly gave them a great deal of confidence. Heisenberg and Jordan (1926) published their calculation of the anomalous Zeeman effect based on a spinning electron in a paper submitted on March 16, 1926, less than a month after Uhlenbeck and Goudsmit's *Nature* letter appeared. Thus they (U&G) were aware of Heisenberg and Jordan's as-yet-unpublished efforts in which the perturbing Hamiltonian is seen to involve $\mathbf{B} \bullet \left(\mathbf{L} + 2\mathbf{S}\right)$.
28. Schrödinger (1926d), (1928), p. 64.
29. Heisenberg and Jordan (1926).Their paper was submitted in March, 4 months after the BHJ paper, in which the hope was expressed that "the hypothesis of Uhlenbeck and Goudsmit might later provide a quantitative description [of the Zeeman effect]." Uhlenbeck and Goudsmit's first paper, in *Naturwissenschaften*, had been submitted a month before BHJ, hence their knowledge of it.
30. It is important to note here that the spin–orbit interaction is of the form $\boldsymbol{\mu}_s \bullet \mathbf{B}$, where $\boldsymbol{\mu}_s$ is the electron spin magnetic moment and $\mathbf{B}$ is a magnetic field due to the electron's orbital motion, but actually has its origin in the gradient of the scalar Coulomb potential, producing an electric field $\mathbf{E}$ that in turn yields a magnetic field $\mathbf{B} = -\, 1/c2\mathbf{v} \times \mathbf{E}$. The result is a term of the form $\mathbf{L} + \mathbf{S}$, containing the Larmour and Thomas contributions to the energy. See Sakurai (1985), pp. 304–5. It is the Thomas correction that solved the factor of 2 problem.
31. Uhlenbeck and Goudsmit (1926), p. 265.
32. To elaborate further, for orbital angular momentum $\mathbf{L}$, the relation between $\mathbf{L}$ and the magnetic moment $\boldsymbol{\mu}$ is written as $\boldsymbol{\mu} = \gamma \mathbf{L}$, where γ is the gyromagnetic ratio, classically equal to $q/2m$. Thus $\boldsymbol{\mu} = \left(e/2m_e\right)\mathbf{L}$ for an orbiting electron. Or, with g = 1, one could write $\boldsymbol{\mu} = g\left(e/2m_e\right)\mathbf{L}$. In the case of spin angular momentum $\mathbf{S}$, one would have

$\boldsymbol{\mu} = (e\hbar/2m_e)\, g_s(\mathbf{S}/\hbar)$, where, because $s = \hbar/2, |S| = \sqrt{3/4}\,\hbar$ The factor $(e\hbar/2m_e)$ is known as the Bohr magneton. It turned out that one had to have $g_s = 2$ to get an electron magnetic moment large enough to reproduce the Zeeman splitting. The coupling of **L** and **S** yields $\mathbf{J} = \mathbf{L} + \mathbf{S}$, but the resulting magnetic moment is $\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = g_L\mathbf{L} + g_S\mathbf{S}$, within a factor of e/mc. With $g_L = 1$ and $g_S = 2$ (approximately), what is involved in the Zeeman effect is $\mathbf{L} + 2\mathbf{S}$. In the Heisenberg–Jordan paper, fine structure is treated in §4, pp. 273–7. Equation (46) is the same as Griffiths (2005) Eq. 6.66. See also the discussion in the text.

33. Thomas (1926), submitted February 20, published April 10. Full treatment: the following January (Thomas, 1927b). For details, including the contributions of Bichowski and Urey, see the discussion in Mehra and Rechenberg (1982–2000), vol. 1, p. 708. For a derivation, see Jackson (3rd ed. 1999), p. 552, in particular, Eq. 11.121. Jackson gives two derivations of "Thomas precession." A factor $g_s = 1$ seemed to work in the case of fine structure because the Thomas precession contains a $(g_s - 1)$ term, effectively reducing g_s by a factor of 2.
34. Heisenberg and Jordan (1926). The paper was received by *Zeitschrift für Physik* (*ZfP*) on March 16 and published May 5.
35. To reiterate, U&G's German-language paper was submitted in October 1925, and their *Nature* paper in December. Although Heisenberg and Jordan (H&J) submitted their paper the next May, the results had been communicated to U&G before their second paper appeared in December. Similarly, Thomas's paper was submitted in February 1926, but his result was communicated to H&J before they submitted their paper in March. Not so different from what happens today.
36. Thomas's submission to *Nature*, written while he was in Copenhagen, came on the very day, February 20, 1926, that Uhlenbeck and Goudsmit's letter to the same journal was published. In Thomas's letter the result was merely stated, and the full treatment reached print only 9 months later, in the *Philosophical Magazine* for January 1927. By then the spin hypothesis had already been widely absorbed. This paper Thomas (1927b), which developed the theory in detail, was 22 pages long, instead of the 1-1/2 columns of the original letter. Thomas acknowledged Max Abraham's theory of a spinning charged electron in 1903 (p.1). The article was communicated by Bohr. Thomas, who was still a PhD candidate, had been urged to work the relativistic theory out by Kramers. See Jackson (2009).
37. Frenkel (1926). For a modern analysis, see "Modern interpretation of J. I. Frenkel's classical spin theory" (Ternov and Bordovitsyn, 1980). Frenkel's only peer in Russian theoretical physics was Lev Landau. See his biography in Lopatnikov and Cheng (2005). Frenkel died in 1952 at age 58. He made important contributions to the theory of excitons, solitons, nuclear fission, the nature of white dwarf stars, and the physics of nuclei.
38. In *ZfP*, vol. 37.
39. This is based on the official publication date of the issue of *ZfP*, printed on the cover, May 5. Heisenberg's paper was received on March 16 and Frenkel's on May 2.
40. He also appended a rather neutral note to the *Naturwissenschaften* paper. Ehrenfest was one of the great mentors of his age (Einstein said "the best"), whose influence was nearly as great as Sommerfeld's. He died of a self-inflicted gunshot wound in 1933 in Leiden, where he had taught for over two decades. Ironically, perhaps, his mentor Ludwig Boltzmann also took his own life.
41. Bohr (1926).

42. In his Nobel lecture Pauli said that "although at first I strongly doubted the correctness of this idea because of its classical mechanical character, I was finally converted to it by Thomas' calculations on the magnitude of doublet splitting." An excellent source is van der Waerden, (1960), "Exclusion principle and spin." See also Straumann (2004), "The role of the exclusion principle for atoms to stars: an historical account." Interestingly, Pauli's name is mentioned six times in the first Uhlenbeck–Goudsmit paper.
43. In so-called Gaussian units. In the now-standard "SI units," the expression is $e\hbar/2m_e$.
44. In sodium, for example, the ground electronic state is $3s_{1/2}$. With no orbital angular momentum, the electron magnetic moment would be due entirely to the electron spin. The splitting depended on $\boldsymbol{\mu} \bullet \mathbf{B}$ and hence on the electron magnetic moment.
45. Pauli (1927c); submitted in May and published in July. George Darwin published a similar theory in the same year (Darwin, 1927). It is interesting that Pauli viewed the issue in terms of the strong-field Zeeman effect in the alkali metals, in which all of the magnetic substates were split. In this case, the Zeeman term in the Hamiltonian $H = e/2m\, B_{ext} \bullet (\mathbf{L} + 2\mathbf{S})$ dominates over the spin–orbit term, which is treated perturbatively. The result is that the splitting depends on ℓ, m_ℓ, and m_s (and, of course, $s = 1/2$ for a single-electron case). This is commonly known as the Paschen–Back effect, first treated quantum mechanically by Heisenberg and Jordan. See, for example, Griffiths (2005), p. 279.
46. Pauli (1927c); As mathematical objects, spinors were first introduced by Cartan (1913).
47. Heisenberg and Jordan (1926). Including what we know as the Pauli spin matrices.
48. Weyl (1928).
49. Kronig (1926).
50. Dirac (1928a, b). This is not, however, an explanation of the *origin* of spin, which is a much deeper question. For a possible explanation, see Ohanian (1986). There are other proposals as well.
51. Pauli (1946), and his Nobel lecture, delivered on December 13, 1946. He received the 1945 prize. No prize was awarded in 1940–1942.
52. Although Rydberg had noticed that the numbers 2, 8, 18, 32 are of the form $2n^2$, with $n = 1, 2, 3, 4$, little emerged immediately from that observation.
53. Bohr (1921).
54. Or, often "aufbau principle."
55. Stoner (1924).
56. These numbers are of the form $2n^2$, something realized by Rydberg, but more fundamentally, they result from
$(n=1)1s^2 = 2; (n=2)2s^2\,2p^6 = 8; (n=3)3s^2\,3p^6\,3d^{10} = 18; (n=4)4s^2\,4p^6\,4d^{10}\,4f^{14} = 32.$
That is, in the case of $n = 3$, for example, there are 10 $3d$ states, 6 $3p$ states, and 2 $3s$ states, totaling 18, which is $2n^2$. This is the number of $3d$ electrons in argon, and also the number of states available to an electron in the alkali metal Na, where the $n = 3$ states are filling. Similarly, there are 6 $2p$ states, 2 $2s$ states (total of $2n^2 = 8$), and 2 $1s$ states. Stoner, of course, only had 3 quantum numbers, n, k $(\ell + 1)$, and j, the "inner quantum number."
57. Pauli (1925a).
58. These are, of course, the principle quantum number, the orbital angular momentum quantum number, the "magnetic" quantum number, or z-component of the angular momentum, and the z-component of the spin, in modern terms. In his Nobel lecture Pauli recounted his cautious use of term "classically non-describable two-valuedness" Pauli (1925a). This was the first of two papers in vol. 31 of the *Zeitschrift*. The second (Pauli, 1925b) contained

the first statement of the exclusion principle. The latter paper was received in January and published in March. Pauli died of pancreatic cancer in Zurich in 1958, in room 137 of the hospital (fine-structure constant).

59. Pauli (1925b), p. 196, in ter Haar's translation.
60. Ibid. The paper is translated in ter Haar (1967).
61. Like Einstein and perhaps others, Pauli made several discoveries that would have warranted another Nobel.
62. Stoner derived a mass limit and an equation of state for white dwarf stars, following Fowler, that prefigured the Nobel Prize–winning work of Chandresekhar. (Stoner, 1929, 1930, 1932). See Chapter 16.
63. As quoted in Jammer (1966), p. 144, Pauli noted with chagrin that "no deeper motivation of the rule can be provided."
64. Slater (1929).
65. (1926b). In connection with the antisymmetric wave functions, Dirac comments in a footnote, added in proof, that "Prof. Born has informed me that Heisenberg has independently obtained results equivalent to these."
66. Fermi's independent discovery was also published in 1926: E. Fermi (1926a, 1926b). Finally, according to Born, Jordan was the first to discover what we know as Fermi–Dirac statistics, but Born forgot Jordan's paper in his briefcase when he went to MIT to deliver his lectures in the fall and winter of 1925.
67. Heisenberg (1926a).
68. Bose(1924); Einstein (1924).
69. Bohr (1926).
70. Apparently at a conference in Paris on December 6, 1945. See Farmelo (2009), p. 331 and note 64; Kragh (1990), p. 36.
71. Fierz (1939); Pauli (1940). Pauli's paper was being prepared for the what would have been the Eighth Solvay Conference, in 1939, which was not held. There were none between 1933 and 1948, one measure of the disruption.
72. Possible sources are Duck and Sudarshan (1997), the review of that work by Wightman (1999), or Jabs (2010). An argument is that the Pauli principle follows from applying a rotation operator in imaginary time to particles of half-integer spin (Wikipedia author). But see the letter by Romer (2002). Beyond this we cannot go.
73. The Nobel Prize having just been awarded to Peter Higgs and Francois Englert who predicted its existence. Still. . . .
74. Or rather it would be hard to justify it. Not impossible, perhaps, because of the angular momentum of relative motion of the proton and electron. This issue arises in the problem of the anomalous magnetic moment of the proton, consisting of three quarks.
75. Heitler and Herzberg (1929).
76. I once maintained to Wigner that nature does not allow singularities, to which he replied reasonably, "isn't the electron a singularity?" The six spin-1/2 leptons presumably all have magnetic moments, but the neutrino moments should be smaller than that of the electron by a factor of about 10^{20}; they, of course, are not charged. The six spin-1/2 quarks have magnetic moments that contribute to the moments of the neutron and proton, for example.
77. Pauli (1946).

11

ANGULAR MOMENTUM, SYMMETRIES, AND CONSERVATION LAWS

INTRODUCTION

Angular momentum became an important issue as soon as problems in more than one dimension were considered. This was the case in classical physics, of course, but what was clear after 1913, despite circular electron orbits, was that the orbital angular momentum, like the energy, was subject to quantization. In the Bohr theory of hydrogen, stable orbits had quantized energy *and* angular momentum, which were directly related. As was the case in the classical Kepler problem, the energies of the stationary states were independent of the angular momentum. But with higher resolution and the application of external fields (see Chapter 3), it became clear that an energy level (in hydrogen, say) characterized by a principle quantum number n was n-fold degenerate; evidently a new quantum number k (or ℓ) was needed. Classical reasoning suggested that differing values of the angular momentum quantum number implied elliptical orbits with varying eccentricity, and an additional degree of freedom could describe the orientation of the orbit. This way of viewing atomic structure, exemplified by the decade or so of the Bohr–Sommerfeld theory, was obviously pre–uncertainty principle, after which "orbits" in the classical sense became untenable.[1]

There was a long history of phenomenological work on atomic line spectra that involved assigning integral (and eventually half-integral) angular momentum quantum numbers, leading to empirical selection rules (Chapter 3). In 1922, the Stern–Gerlach experiment established *space quantization*,[2] when it showed that not only was the angular momentum quantized, but a component of the angular momentum vector along a particular direction, say the direction of a magnetic field, or just the "z-direction," was subject to quantization. Sommerfeld had already concluded that that degree of freedom, the orientation of the orbit, also had to be quantized and introduced a "latitudinal quantum number," n_2. Although we discussed the Stern–Gerlach experiment in Chapter 3, it is worth mentioning again that it was done before spin had been discovered and was mistakenly taken as a verification of the spatial quantization of *orbital* angular momentum.[3]

The first attempt to treat angular momentum in a fundamental way from within the newly formulated quantum mechanics was made in the "three-man work" that has been labeled BHJ.[4] There the commutation rules for the components of the angular momentum operator $\mathbf{M}$ (which BHJ used instead of the now-universal $\mathbf{L}$)[5] are worked out from the corresponding commutator of p and q. It is noted that all three components

of **M** cannot be simultaneously diagonalized, the result $[M_x, M_y] = i\hbar M_z$ is established,[6] and from the commutators between **q** and **M**, dipole selection rules are obtained. Here, for the first time, are identified the operators $M_{\pm} = \mathrm{M}_x \pm iM_y$, the raising and lowering ("ladder") operators for the *z*-component of the angular momentum.[7] The angular momentum *states* themselves are only chimeras in the BHJ theory, that is, they play a totally subsidiary role because they are not observables, but the matrix elements of **M** and its components do play an important role. The paper of Heisenberg and Jordan, received by *Zeitschrift für Physik* exactly 4 months after BJH's paper,[8] which focused on fine structure and the Zeeman effect, developed almost all the other necessary angular momentum algebra, at least for the case $j = \ell \pm 1/2$. Pauli's treatment of the hydrogen atom had used the same development.[9]

The subsequent development of the theory of angular momentum followed two somewhat distinct tracks, first by BHJ, as well as by Dirac and others, without the help of group-theoretic concepts; and then by Weyl and Wigner, especially, using the powerful tools of group theory.[10] In Dirac's case, the first treatment of angular momentum was in a paper communicated in March 1926,[11] 4 months after that of BHJ and only 10 days after the paper of Heisenberg and Jordan previously mentioned. Dirac noted that his results were obtained "independently" by BHJ. Be that as it may, he derived all of the commutation relations among the components of the angular momentum vector **M**, including the spherical components M_+ and M_-, as had BHJ, and found the Landé *g*-factor for the weak-field anomalous Zeeman effect.[12]

Schrödinger attacked the Kepler problem on the second page of the paper that introduced wave mechanics in 1926.[13] His separation of the differential equation immediately led to an angular solution in terms of surface (or spherical) harmonics. On the other hand, he did not carry through the solution far enough to explicitly make the identification of the surface harmonics as angular momentum eigenfunctions labeled by integral ℓ.

When in 1930 Born and Jordan published their *Elementare Quantenmechanik* and Dirac his *Principles of Quantum Mechanics*, the theory of angular momentum, including spin, was developed further, including vector angular momentum coupling, selection rules, etc. By the time Condon and Shortley's book was published 5 years later, the theory of angular momentum coupling had been substantially completed. Their book would become the standard source on angular momentum coupling and atomic spectra for a full generation of physicists, being reprinted six times over the next 29 years.[14]

GROUP THEORY IN QUANTUM MECHANICS

Angular momentum, whether classically or in quantum theory, can obviously be treated without the use of group theory.[15] The same is true of almost any symmetry of the Hamiltonian or Lagrangian. That being said, the efficacy of the group-theoretic approach pioneered by Weyl and Wigner gradually became evident and eventually was widely used. We will expand on group theory and its connection to symmetries below, but for the present concentrate on rotational symmetry, angular momentum, and applied group theory.

The initial applications of group theory to the new physics were those of Wigner, Weyl, and von Neumann in 1927–1928,[16] with the first *thorough* treatments of angular momentum, founded on the theory of continuous or infinitesimal groups, being in the books by Weyl and Wigner in 1928–1931, based on earlier lectures.[17]

In a 1927 paper Wigner, then at Göttingen,[18] was making his first foray into group theory, and it is in this paper that he introduced the "Wigner D-matrices" that were crucial to transforming angular momentum eigenfunctions.[19] He had benefited from the important work that Weyl had done on continuous groups as early as 1924, as well as from advice and urging by von Neumann. Soon Wigner's fellow Hungarian Leo Szilard[20] prevailed upon him to make his ideas about group theory and physics available to the larger physics community in book form. The result, Wigner's monumental *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra,* based on his articles in *Zeitschrift für Physik* in 1926–1927, was published in 1931.

Weyl himself followed Wigner's early work with a massive 46-page paper in 1927 titled "Quantenmechanik und gruppentheorie," opening vol. 46 of *Zeitschrift fur Physik*,[21] and he published his book (reversing the title) *Gruppentheorie und Quantenmechanik*[22] the next year, laying out the application of Lie groups to quantum mechanics.[23] The book, originally based on lectures given in Zurich in 1927–1928, had an importance beyond its group-theory arguments, as we have already seen. Two years later a second, somewhat more accessible, edition appeared, as well as an English translation partially based on lectures Weyl had given at Princeton during 1928–1929, appeared[24] as *The Theory of Groups and Quantum Mechanics*. There he offered a thorough treatment of angular momentum, based on the theory of continuous groups.

Wigner's book was ultimately more influential than Weyl's, probably because it was more accessible and focused on applications to atomic spectra. This despite the fact that it was not translated into English until 1959. Some of Wigner's most important further results were obtained in 1938–1940 as world conflict approached and he was safe in Princeton. A major paper, "On the matrices which reduce the Kronecker products of representations of simply reducible groups," written in 1940, found its way into print only in 1965 in Biedenharn and van Dam's *Quantum Theory of Angular Momentum*. Many of the same results were obtained by the Italian Giulio Racah in 1942–1943 by algebraic means.[25]

During WWII Wigner's attention was diverted to the war effort, and in particular attempts to produce a nuclear chain reaction and to generate plutonium for a nuclear weapon, activities that likely inhibited publication and distracted him from the mathematics of quantum theory as well. His Nobel award in 1963 was primarily for his contributions to nuclear physics, but mentioned his "discovery and application of fundamental symmetry principles."[26]

In the 1930s, not everyone was happy to see group theory introduced into the problem of understanding atomic spectra. Of the theory of groups, Condon and Shortley wrote succinctly that "We manage to get along without it."[27] Dirac and Slater were actively hostile to the dependence on group theory as a way of understanding quantum behavior. They made a point of the fact that they could obtain all of the relevant results without group theory, and Slater, in particular, tried to show that the

"group pest" [*Gruppenpest*] was unnecessary, by deriving all of the significant results without it.[28] However, Weyl wryly observed that, in effect, group theory, albeit disguised, had actually been used in each case.

Despite the works of Weyl and increasingly that of Wigner as the former's interests turned elsewhere, the importance of Lie groups, symmetries, and invariance was neglected throughout much of the 1930s. Pauli's classic 1933 article in *Handbuch der Physik*, in which group theory is applied not only to the rotation group and angular momentum but to the permutation group in the context of the statistics of two-particle states,[29] is a notable exception to the indifference to group theory (his chapter VII is entirely devoted to the subject). Born and Jordan had earlier adopted the group-theoretic viewpoint in their *Elementary Quantum Mechanics* (1930),[30] without, however, making much use of it. And textbooks of the time, including those of Condon and Morse, Pauling and Goudsmit, Ruark and Urey, and Sommerfeld, take almost no notice of these ideas at all; Rojansky, in 1938, mentions group theory only in passing.

Although the theory of continuous groups played an important role in classical mechanics, as quantum mechanics came to be formulated in Hilbert space, it was very natural that group theory would become an important tool. Notwithstanding this fact, the group-theoretic approach and its attendant language were by no means immediately embraced. By the time Wigner's book appeared one would have thought that the power of group-theoretic methods would have been fully acknowledged, but such was obviously not the case. Even today, most modern quantum-mechanics texts give at most lip service to group theory, although Messiah is a happy exception, and, more recently, Greiner and Müller is another.[31] The problem, one assumes, is with the "overhead" associated with learning group theory.

The angular momentum algebra that emerged grew out of the theory of Lie groups, in particular the orthogonal group in three dimensions (the "rotation group") $SO(3)$, and $SU(2)$, the unitary unimodular (or special unitary) group in two dimensions, which shares a Lie algebra with $SO(3)$.[32] The theory was elaborated in terms of the commutators of components of the angular momentum operator, L_i, which are the generators of the Lie algebra, that is, $[L_i, L_j] = i\hbar\,\varepsilon^{ijk}L_k$, leading to "ladder operators" of the form $L_+ = L_x \pm iL_y$, which cycled through the eigenvalue spectrum of L_z. Born and Jordan present this development with only minimal reference to group theory.[33] The 2×2 Pauli spin matrices, σ_i, or $S_i = \hbar/2\,\sigma_i$, the generators of the fundamental representation of $SU(2)$, first appeared in Pauli's 1927 paper, again without the explicit use of group theory.[34]

ANGULAR MOMENTUM COUPLING

In wave mechanics in three dimensions, with or without group theory, the operator corresponding to the square of the orbital angular momentum, that is, L^2, is a differential operator on the wave function $\psi(\mathbf{x})$ in a position representation, as are the Cartesian or spherical components of $\mathbf{L}$. All of this follows from the usual separation of the second-order partial-differential equation, which is the wave equation

in spherical coordinates (in terms of the variables r, θ, and φ). The only difference between this and Laplace's or Poisson's equations, say, being the presence of $\hbar^2$ in L^2 so that $\nabla^2 = 1/r^2\partial/\partial r\,(r^2\partial/\partial r) - L^2/\hbar^2 r^2$. The angular momentum eigenfunctions (eigenfunctions of L^2 and L_z) are then just the spherical harmonics Y_{lm}.[35] In Schrödinger's papers, as we noted, all or most of this apparatus is present, but without clear identification of the solutions as angular momentum eigenfunctions. Weyl's book of 1928–1930, on the other hand, gives very clear discussion of Lie groups and angular momentum.[36]

The problem of angular momentum coupling arises in even the simplest atom, as in coupling **L** and **S** for the single electron in the hydrogen atom. But the justification of the commutation relations for the components of the intrinsic spin, which have no classical counterparts, was a major conceptual leap, first accomplished by von Neumann and Wigner, using group theory, in 1928, and by van der Waerden.[37] Prior to this, the commutators were obtained by simple analogy with orbital angular momentum, which was at best a leap of faith.[38]

When coupling vector angular momenta $\mathbf{j}_1$ and $\mathbf{j}_2$ to a resultant $\mathbf{j}$, that is, $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2$, the construction of eigenstates of total angular momentum involves decomposing the direct tensor product space $\mathbf{j}_1 \otimes \mathbf{j}_2$ into irreducible representations of the rotation group, corresponding to $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2,\ \mathbf{j}_1 + \mathbf{j}_2 - 1, \ldots |\mathbf{j}_1 - \mathbf{j}_2|$. This is straightforward group theory, though of course it can be done without it. Another way to look at this is as a change in basis, involving a unitary transformation, whose matrix elements are the Clebsch–Gordan (C-G) coefficients. For example, in the case of $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$, the result is

$$|j,\ m,\ j_1,\ j_2\rangle = \Sigma_{m1,m2} \langle j_1, m_1, j_2, m_2 | j, m, j_1, j_2\rangle |j_1, m_1, j_2, m_2\rangle$$

where the expansion coefficients $\langle j_1, m_1, j_2, m_2 | j, m, j_1, j_2\rangle$ are the (real) C-G coefficients[39] or *vector coupling coefficients*. The sum is over the values of m_1 and m_2 consistent with $m_1 + m_2 = m$. The C-G coefficients are essentially the same as the 3-*j* symbols of Wigner, the "Wigner coefficients," for which he gave the first general, closed-form formula in 1931. Their properties were worked out by Wigner, Racah, and others.[40] Generalization to the addition of three or four angular momenta in the form of 6-*j* (Racah coefficients) and 9-*j* symbols ($3n - j$ symbols, in general) was carried out by Wigner in 1940–1941.[41]

In 1925 Henry Norris Russell and Frederick Saunders pioneered the treatment of two-electron atoms, i.e., the alkaline earths and especially calcium, that had direct astrophysical significance.[42] Analysis of the spectra of these atoms required the angular momentum coupling scheme that bears their names, i.e. Russell–Saunders, or "**L** – **S**" coupling, which is particularly appropriate in light atoms. In this scheme the individual orbital angular momenta $\mathbf{L}_i$ are coupled together to get a resultant **L**, the spins $\mathbf{S}_i$ are coupled to a resultant **S**, and then **L** and **S** are coupled to give $\mathbf{J} = \mathbf{L} + \mathbf{S}$. This approach is favored when there is negligible coupling between the spin and orbital angular momentum of individual electrons or nucleons; rather the coupling between

individual spins is stronger (and the same for the orbital case). This vector coupling scheme would be appropriate when ℓ and s are good quantum numbers, that is, when $\mathbf{L}^2$ and $\mathbf{S}^2$ are diagonal, before a perturbation is applied. Such would be the case without an applied magnetic field and with a weak $\mathbf{L} \cdot \mathbf{S}$ spin–orbit interaction treated as a perturbation, so that the unperturbed Hamiltonian is diagonal in $|j, m, \ell, s\rangle$ basis; it is an eigenstate of $\mathbf{J}^2$, $\mathbf{L}^2$, and $\mathbf{S}^2$ (and $\mathbf{J}_z$).

Alternatively, in "*jj* coupling," the individual spin and orbital vectors are strongly coupled, so that $\mathbf{L}_i$ and $\mathbf{S}_i$ are coupled to $\mathbf{J}_i$ and the latter are coupled to $\mathbf{J} = \sum \mathbf{J}_i$. This scheme would be appropriate when, as in the nuclear-shell model,[43] there is a strong spin–orbit force $\Sigma_i \mathbf{l}_i \cdot \mathbf{s}_i$, which couples the individual spin and orbital angular momenta into a total angular momentum $\mathbf{j}$. Then the J_i are good quantum numbers, but not the total orbital or spin angular momenta. In the case of two particles, J_1^2 and J_2^2 are diagonal, but not $\mathbf{L}^2$ or $\mathbf{S}^2$. The appropriate basis would be $|j, m, j_1 j_2\rangle$ or $|j_1, m_1, j_2, m_2\rangle$.[44] Both coupling schemes are described in the 1930 works of Pauling and Goudsmitand in Sommerfeld and, of course, in the later work by Condon and Shortley (1935).[45] These are not the only possible coupling schemes, especially when more than two angular momenta are coupled. In the case of two electrons, say, the spatial and spin symmetries of the states are straightforward, but with $n > 2$ the situation quickly gets complicated and group-theoretic methods become very important, notably the permutation group.[46]

I mention in passing the very powerful Wigner–Eckart theorem that originated in papers by Eugene Wigner in 1927 and Carl Eckart in 1930,[47] as well as in Wigner's book, *Gruppentheorie*, of 1931. The theorem provides a way of expressing matrix elements of an irreducible tensor operator of rank k, say T^k_q, between states $|jm\rangle$, in terms of the "reduced matrix element" of T^k that is independent of m, that is, the orientation of **j,** multiplied by a C-G coefficient. Thus,

$$\langle j'm' | T^k_q | jm \rangle = \langle j' \| T^k \| j \rangle \langle j'm'\ k\ q | j\ m \rangle.$$

The term $\langle j' \| T^k \| j \rangle$ is the "reduced matrix element," and it is popular to say that the Wigner–Eckart theorem separates the physical aspects of a problem (reduced matrix elements) from the geometric aspects.[48] This modern form of the Wigner–Eckart theorem, writing the reduced matrix element as $\langle \| \| \rangle$, is first found in a famous paper by Racah, in which the notation of Condon and Shortley[49] is modified. A reasonably current source is Fano and Racah, *Irreducible Tensorial Sets*,[50] of 1959, and most quantum texts demonstrate the utility of the Wigner–Eckart theorem.

GROUP THEORY, SYMMETRIES AND CONSERVATION LAWS

In the process of tracing the development of the theory of angular momentum, we have touched on the way in which group-theoretic arguments contributed to the understanding of angular momentum and angular momentum coupling. Here we

consider the application of group theory to the larger issue of general symmetries of the Lagrangian or Hamiltonian and how they are related to conservations laws. The invariance under rotations that is expressed in the form of angular momentum conservation is a special case of the general problem of symmetries in quantum mechanics and Noether's theorem, which we subsequently explore.[51]

As was the case with angular momentum, it is possible to attack many of these issues without group theory, and that was certainly done, but that means discarding what is clearly the most powerful tool available. But as we proceed, our discussion will have to be quite general, because, except for space–time symmetries, internal symmetries that arise in a specific context are usually quite problem dependent.

The discovery or identification of symmetries in nature is often difficult, because the data frequently do not readily reveal the symmetries of the Hamiltonian in a simple or direct way, and frequently they are only approximate or broken. Often the symmetries are *identified* a priori, that is, they are imposed from first principles, are assumed or postulated, with, again, the understanding that they may be broken. One of the earliest applications of symmetry arguments in modern physics was to Lorentz invariance in special relativity by Poincaré and Minkowski.[52]

The essential discovery was that the solutions to the dynamical equations of a physical system are restricted by, or can be classified in terms of, the symmetries of the system. This came about through the work of Lie, Cartan, Weyl, and others in the first quarter of the 20th century. Violation, or breaking, of those symmetries is no less important, as, for example, in modern particle physics, where broken $U(1) \times SU(2)$ and $U(1) \times SU(2) \times SU(3)$ symmetries are at the heart of the unification that is represented by the Standard Model. In any case, the mathematical foundations for exploring the importance of symmetry in quantum mechanics had already been laid before the advent of the new quantum theory in 1925.[53]

Of course, symmetry or invariance arguments were already an important part of classical Lagrangian mechanics, in which Noether's theorem, dating from 1915–1918, established the existence of a conservation law associated with each continuous symmetry of the Lagrangian.[54] Whether we see the symmetries or the conservation laws as primary, Noether's theorem is a generalization of the well-known result from classical mechanics that if a coordinate is cyclic or ignorable, that is, does not appear in the Lagrangian, then there is a conserved momentum associated with it. Quantum mechanically, there is a conserved current (charge) and a gauge field associated with every gauge symmetry, something we briefly discuss below.

While the founders of quantum theory—Heisenberg, Schrödinger, Jordan, Pauli, and Dirac—were occupied with establishing the validity of the theory and extending its reach, Wigner and Weyl were concentrating on the role of symmetries of physical systems and how they could be employed to classify or restrict the states of a quantum-mechanical system. The vehicle for this work was the theory of continuous groups. As we saw earlier, von Neumann played the role of midwife to Wigner's entry into the application of group theory to quantum mechanics,[55] and it was Born who

interested Weyl—who had previously been investigating the use of group theory in general relativity—in applying these techniques to quantum theory.[56]

Group theory became an integral part of quantum theory primarily because of the transformations that were at the heart of the problem of finding a set of "good" quantum numbers used to describe a quantum-mechanical state. Initially, a good quantum number, e.g., the angular momentum quantum number ℓ, meant that the appropriate Hermitian operator, in this case L^2, was diagonal,[57] which in turn meant that the system was invariant under rotations, that is, under the transformations of the rotation group SO_3.[58] The complexities of atomic spectra meant that group-theoretic techniques were directly applicable.

As noted, much of this effort involved continuous groups, derivable from infinitesimal transformations, such as rotations, translations, time displacements, etc. But discrete symmetries such as space and time inversions, crystal symmetries, etc., were also important.[59] In the case of spatial reflection, if the Hamiltonian is invariant under reflections, it commutes with the parity operator so that the eigenvalues of the parity operator are constants of the motion, and hence matrix elements of this Hamiltonian between states of different parity are zero, and so on.[60]

The extensive use of symmetry arguments in quantum mechanics, as we have seen, had its tentative beginnings at the hands of Wigner, Weyl, and others, and can include van der Waerden, in 1927–1928, just as the theory itself was emerging.[61].

The most obvious space–time symmetries that a physical system might possess are (1) rotational invariance, (2) invariance under translations, (3) invariance under time displacements, and (4) invariance under spatial and temporal reflections. Among the conservation laws these symmetries generate are conservation of angular momentum and linear momentum, which are examples of continuous space–time symmetries. But there are other important symmetries, some involving finite groups, such as crystal symmetries, chiral (left–right) symmetry, invariance under charge conjugation, CPT invariance (charge, parity, and time reversal symmetry), permutation symmetries, and so on, but also internal gauge symmetries such as those of the Standard Model of particle physics.

The fact that translational invariance implies conservation of linear momentum and that rotational invariance implies conservation of angular momentum are well-known results from classical mechanics. In classical mechanics, if the Hamiltonian does not explicitly contain the time, it is a constant of the motion, and under fairly general conditions the energy is conserved.[62] This is expressed in quantum mechanics through the result that invariance under time displacement (a unitary transformation of the form $U = \exp\{iH\ t/\hbar\}$) yields energy conservation because the time-displacement operator then commutes with H. These results are worked out in detail in the first edition of Dirac's *Physical Principles of Quantum Mechanics* of 1930.[63]

The simple nonrelativistic hydrogen atom without spin and with only a Coulomb interaction between the electron and the proton (having no structure) is invariant under rotations because its Hamiltonian is spherically symmetric. Thus its angular

momentum (along with its energy, because it is isolated) is conserved. This does not mean that the wave function is spherically symmetric, however, which is true only for zero angular momentum ($\ell = 0$, *s* states). But then it can be shown that the $\ell \neq 0$ (unsymmetrical) states with a given principle quantum number are degenerate. This is a general result,[64] but in the case of the hydrogen atom it means that the energies of the stationary states depend only on the principle quantum number *n*, and the $n - 1$ states labeled by ℓ are degenerate.[65] This symmetry is broken in various ways, so that the degeneracy is removed by, among other things, the spin–orbit interaction. In a similar way, degeneracies imply symmetries, so that mass multiplets, such as the charged and neutral π-mesons or the neutron–proton nucleon pair, and the charge independence of nuclear forces, imply an isospin symmetry (see Chapter 15) weakly broken by electromagnetic interactions.

Symmetry principles were soon widely applied to the physics of nuclei, as well as atoms, starting with Wigner's introduction of $SU(4)$ spin–isospin symmetry into nuclear physics in 1937.[66] Racah explored the $SU(2)$ symmetry of the pairing force between nucleons, but important work on applications to atomic spectra was published by him during WWII as well. Elliott[67] and others concentrated on the $SU(3)$ symmetry of the nuclear-shell model in the early 1950s. We look at the rise of nuclear physics in the 1930s in Chapter 15.[68]

GAUGE SYMMETRIES

Gauge theories (*eichtheorie, eichinvarianz*) could be thought to have their origin in Maxwell's electromagnetic theory, whose gauge symmetry is the familiar invariance under the gauge transformation $\mathbf{A} \rightarrow \mathbf{A} + \nabla f$ and $\varphi \rightarrow \varphi - 1/c\, \partial f/\partial t$, where f is an arbitrary scalar. A broader interest in gauge theories arguably stems from a 1929 paper by Weyl and some work by Oskar Klein in 1938.[69] Thus the power of gauge invariance was really recognized only in the years leading up to 1940, and in quantum textbooks of the 1950s and 1960s, typically electromagnetism is the only example of a gauge transformation. Davydov (1965)[70] shows that the Klein–Gordon equation (see Chapter 13) for a spinless particle interacting with an electromagnetic field is invariant under this gauge transformation so long as the wave function ψ undergoes a unitary transformation to $\psi e^{ief/\hbar c}$, a result Pauli gave in his 1933 article on wave mechanics, crediting Fock.[71] This is the origin of the $U(1)$ Abelian unitary gauge group under which electromagnetism (Maxwell theory) is invariant, although this group-theoretic language was not generally used—indeed was unnecessary—until the discovery of electroweak $U(1) \times SU(2)$ gauge symmetry in the 1960s.[72] This symmetry is an example of an *internal* symmetry, which in this case is related to the conservation of charge (as opposed to external symmetries like space and time displacements or Lorentz transformations). Non-Abelian[73] gauge fields, now known as Yang–Mills[74] fields, originally arose in the 1950s in the theory of isospin and now are at the heart of the Standard Model, building on the quark model of the 1960s in which the $SU(3)$ color symmetry first appeared. Quantization of a gauge field yields a gauge boson, which in

the case of electromagnetism is the photon. O"Raifeartaigh's *The Dawning of Gauge Theory* is a wonderful introduction to the evolution of these theories.[75]

CONCLUSION

It was in the problem of angular momentum, particularly spin with its special properties, that the relevance of transformation groups came into their own. The tools of group theory proved to be especially powerful in the understanding of atomic spectra, in which angular momentum coupling issues were often predominant. The work of Wigner and Racah is especially to be noted. By 1935, when Condon and Shortley's book on atomic spectra was published, the major issues surrounding angular momentum in multielectron systems had been solved, often with the aid of group theory. Attention then turned to many-body techniques and to the approximations that would make numerical treatment of complex atoms possible. Some of the early results are sketched in Chapter 17.

It was at about the same time that the neutron was discovered (1932), and it quickly became clear that the atomic nucleus was made up of protons and neutrons, that is, nucleons, rather than of protons and electrons. This made it possible to begin to tackle the problem of nuclear structure in a way similar to that which took place in atomic and molecular spectroscopy. Most of the same techniques were applied in the nascent nuclear physics and, in particular, the *jj*-coupled nuclear-shell model. The theory of angular momentum developed in the atomic context could be carried over directly to the case of the nucleus, in which one had the intrinsic spin of all nucleons to consider, and a strong spin–orbit force. The introduction of the isotopic-spin formalism, with the nucleons forming an isospin doublet, and Wigner's exploration of an $SU(4)$ spin–isospin description of light nuclei, are examples of the introduction of group-theoretic ideas into nuclear physics. The development of the quark model of nucleons and the introduction of the electroweak and color gauge symmetries, although relatively recent, represent the most ambitious application of the ideas discussed in this chapter.

In short, symmetry and its formal implementation through group-theoretic arguments is an important tool of theoretical physics that has been widely applied from high-energy physics to the study of the structure of solids. It has functioned at the level of metatheory, providing generalizations which profoundly affected frontier areas of modern physics, and also at the rather mundane level of crystal symmetries. No one would today regard the introduction of group theory into quantum mechanics as a *pest*.

NOTES

1. The reader might want to look at Sommerfeld's semiclassical analysis of hydrogen in his chapter IV in which the radial and azimuthal motion is quantized using the Bohr–Wilson–Sommerfeld "quantum phase integral" (Sommerfeld (1923).

2. In German, *richtungsquantelung*. Gerlach and Stern (1922a, 1922b, 1922c).
3. See, for example Weinert (1995), "Wrong theory—right experiment: The significance of the Stern–Gerlach experiments"; Scully, Lamb, and Barut (1987), "On the theory of the Stern–Gerlach apparatus"; Bernstein (2010), "The Stern Gerlach Experiment."
4. BHJ; Born, Heisenberg, and Jordan (1926).
5. As an aside, Condon and Morse (1929) followed BHJ in using **M**, as did Weyl, Dirac (even through 1958), Taylor and Glasstone. Rojansky in 1938 used **L**. Schiff changed from **M** to **L** between his second and third editions.
6. Although the [,] notation for commutators was not used until Dirac noticed the analogy with Poisson brackets. This result contained the uncertainty principle no less than that $[p, q]$ was nonzero, but in neither case was it recognized in 1925–1926. For a while, e.g., in Dirac, the German term *Vertauschungs* was used for commutators.
7. In physical applications. According to Biedenharn and van Dam (1965, p.3), this was first done in E. Cartan's 1894 thesis.
8. Heisenberg and Jordan (1926).
9. Pauli (1926a).
10. Jordan, however, did not shun group theory, as Dirac did. He wrote an important paper with Wigner in 1928 (Jordan and Wigner, 1928), which Weyl (1928) cites, though the citation is defective.
11. Dirac (1926b). The same month Schrodinger's first paper reached print.
12. Dirac (1926b); p. 301. He adopts $gs = 2$ for the electron, without citing Uhlenbeck and Goudsmit or Thomas. The paper was submitted a month after Thomas's and about 10 days after HJ's.
13. Schrödinger (1926a).
14. Condon and Shortley (1935). As noted elsewhere, the best source on the development of the theory of angular momentum is the reprint volume by Biedenharn and van Dam (1965). Edward Condon was the highest-profile victim of the Cold War "red scare" before Oppenheimer. See Wang (1992). Also Wheeler (1998), p. 113.
15. Group theory was founded by Evariste Galois in the mid-nineteenth century, although he was anticipated in some of the ideas by Carl Gauss. Galois died at age 20 as the result of a duel, apparently over a love affair. For a modern treatment of group theory in physics, see especially Tinkham (1964) or Hammermesh (1989, Dover reprint).
16. Wigner (1927b); Weyl (1927). Wigner's paper is reprinted in Biedenharn and van Dam (1965) in German, They also give a paper of Pauli's on spin-1/2 matrices that immediately preceded Wigner's in vol. 43 of *Zeitschrift für Physik* (Pauli, 1927b).
17. Weyl (1928); Wigner (1931). Weyl provided a substantial introduction to group theory, per se, in addition to applications to quantum symmetries.
18. Having gone there to work with Hilbert, who Wigner found was no longer active. Hilbert would retire in 1930.Wigner (1927b). In this paper Wigner referenced the book by Speiser on group theory as well as papers by Schur.
19. Wigner (1927b). Deriving from *Drehgruppe* or rotation group. The Wigner D-matrices form a double-valued representation of the rotation group, that is, $SU(2)$. To be precise, the Wigner D-matrix notation employed the old German typeface, 𝔇, known in various periods as "blackletter," "fraktur," "sütterlin," or just "Gothic." Wigner used **D** for representations of the symmetric group, probably based on the German *Darstellung*, meaning representational.

20. Who, with Einstein and Wigner, wrote the fateful letter to President Roosevelt concerning the practicality of a nuclear weapon.
21. Weyl (1927). Note that Wigner's paper was in vol. 40 and Weyl's was in vol. 46, yet both were published in 1927. The journal was clearly the dominant modern physics journal of its day, with six volumes appearing in 1926 and seven the next year. Of this paper of Weyl's, Erhard Scholz (2007) has written that it had a "long and difficult reception history for several decades."
22. Weyl (1928).
23. Lie groups and their associated algebra sprang from the work of Sophus Lie (and Felix Klein) in the 1870s. See Hawkins (2000).
24. The translation by the general relativitist H. P. Robertson, who was then 27, was of the second German edition of 1930.
25. Reprinted in Biedenharn and van Dam (1965)
26. His name is rather ironically enshrined in what is known as "Wigner's disease," because of neutron damage in reactor cores.
27. Condon and Shortley (1935), p. 10. Their curt dismissal of group theory was undoubtedly influential, despite their concession that "Many things which are done here could be done more simply if the theory of groups were part of the ordinary mathematical equipment of physicists." Dirac wanted to eliminate the language of group theory (Dirac, 1929, especially p. 716).
28. Slater (1929). If anyone believes that fashions do not ebb and flow in physics, this is a wonderful example of that very thing. Even Weyl grudgingly acknowledged those who deplored the "group pest" in the preface to his second edition of 1930–1931.
29. Pauli (1933).
30. Born and Jordan (1930). In particular in secs. 21 and 22.
31. Messiah (1961); Greiner and Müller (1994).
32. $SU(2)$ is the universal covering group for $SO(3)$. Either may reasonably be called the rotation group. This glosses over the fact that the representations of $SO(3)$ are the odd-dimensional representations of $SU(2)$. See Gottfried (1966), chapter VI, especially sec. 34; Greiner and Müller (1994), chapters 3 and 4.
33. Born and Jordan (1930).
34. Pauli (1927b), reprinted in Biedenharn and van Dam (1965). Actually, the history of what, in the case of angular momentum, are the raising and lowering operators for the z-component of $\mathbf{J}$, is interesting. BHJ had introduced them into quantum mechanics in 1926, and Schwinger, much later, was awarded credit for this algebraic method as well. Note their presence in the Heisenberg and Jordan (1926) paper as well. See Mehra and Rechenberg (1982–2000), vol. 6, part 1, pp. 504–10.
35. Otherwise known as surface harmonics. They form a basis for a representation of the rotation group.
36. Weyl (1928).
37. Von Neumann and Wigner (1928); van der Waerden (1932). See the discussion in Biedenharn and van Damm (1965).
38. The problem of adding orbital angular momentum and spin vectorially was made easier by the lack of full understanding that spin was intrinsic, that is, not associated with a classical rotating particle in which the angular momentum would result, somehow, from $\mathbf{r} \times \mathbf{p}$.

In their 1926 paper treating fine structure and the Zeeman effect using spin, Heisenberg and Jordan write $(\mathbf{L}+2\mathbf{S})$ and $\mathbf{L}\cdot\mathbf{S}$ without any evident misgivings (pp. 264, 265, 268).

39. From the theory of binary invariants. Clebsch and Gordan were mostly 19th-century figures who encountered these problems in classical mathematics. See J. H. Grace and A. Young, *The Algebra of Invariants* (1903). Original sources are Clebsch, *Binaren Formen,* and Gordan, *Invariantentheorie.* Although the term "Clebsch-Gordan" does not appear in Grace and Young, both Clebsch and Gordan are frequently referenced in the work. The author has not been able to find where the term "Clebsch-Gordan" was first used. Weyl (1930) not only uses it, but refers to the work of Clebsch and Gordan on the theory of invariants (Weyl, p. 128). It does not appear in Wigner (1931), and in the translation (1959) it appears only in the index. It can be found in a modified version of Wigner (1940), but it is not clear that it appears in the original. See Wigner (1940) in Biedenharn and van Dam (1965), p. 87. Condon and Shortley (1935) do not use it. In 1959 Gregory Breit (1959, p. 115) specifically addressed the issue and simply argued for the name Wigner coefficients.
40. Wigner (1931). See, for example, Messiah (1962), p. 1056, Fano and Racah (1959). See also Wigner (1931); van der Waerden (1932); Condon and Shortley (1935); chapter III, Biedenharn and van Dam (1965); and Edmonds (1957). The latter gives, among other papers, famous ones by Wigner (1940) and Schwinger (1952) that were never published, partly because of wartime restrictions. The Wigner or 3-*j* coefficients are related to the Clebsch–Gordon coefficients as follows:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \equiv \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} \left\langle j_1 m_1 j_2 m_2 \,|\, j_3 - m_3 \right\rangle.$$

41. Wigner (1940).
42. Russell and Saunders (1925). See Sommerfeld, 5th German edition (1931), English translation (1934), pp. 441–4. Sommerfeld also called it "normal coupling." Condon and Shortley (1935) devote three chapters to Russell-Saunders, or alternatively, "**L**–**S**" coupling.
43. On applications to nuclei, see Roy and Nigam (1967), chapter 7; Elliott and Lane (1957); de-Shalit and Talmi (1963), p. 248. Typcially, **L**–**S** coupling is appropriate in light atoms, *jj*-coupling in heavier. See also Mizushima (1970), p. 285.
44. These could be written as $\left|(l_1 s_1) j_1 (l_2 s_2) j_2 JM\right\rangle$, etc.
45. Pauling and Goudsmidt (1930), chapter VIII; Sommerfeld (1930), Condon and Shortley (1935). After receiving his doctorate from Cal Tech, Pauling went to Europe and studied with Sommerfeld, Bohr, and Schrödinger. Goudsmit founded the journal *Physical Review Letter*s in 1958. Figure 110 in Richtmyer and Kennard (1942) shows the transition from atomic **L**–**S** coupling to *jj*-coupling in going from carbon to lead.
46. For nuclei, see Elliott (1963). Also Elliott and Lane (1957), one of the most important early postwar review articles on the nuclear-shell model.
47. Wigner (1927), of which Biedenharn and van Dam (1965) say that "We can discern, in retrospect, the beginnings of the 'Wigner-Eckart theorem.'" Eckart (1930). Eckart, who received his PhD from Princeton in 1925, ranks with John Slater and Ralph Kronig as the most important early American quantum theorists. Among other things, he independently established the equivalence of matrix and wave mechanics at almost the same time as

Schrödinger (and Pauli), apparently being prompted by a visit of Born to Pasadena, California, in the winter of 1925. See Jammer (1966), p. 275. Eckart made fundamental contributions to physical oceanography and ocean acoustics.

48. Biedenharn and van Dam (1965), p. 8, supposedly quoting Racah. In a modern text, see Merzbacher (1998), chapter 17.
49. Racah (1942), p. 442; reprinted in Biedenharn and van Damm (1965), p. 134; the definition is on p. 150. In Condon and Shortley's very idiosyncratic numbering system, sec. 9^3, meaning sec. 3 of chapter 9.
50. Fano and Racah (1959).
51. Aside from the books on group theory and quantum mechanics by Weyl, Wigner, and van der Waerden (1928), the reprint volume of Biedenharn and van Dam, and several books devoted specifically to angular momentum (Edmonds, etc), good contemporary general textbook sources on angular momentum and representations of the rotation group are Merzbacher (sec. 17.4), Roman (chapter 6), and Gottfried (sec. 34); Greiner and Müller is especially notable. The book by Rose (1957) is especially is heavy on nuclear applications.
52. Obviously the crucial step was made by Einstein, but general Lorentz covariance of Maxwell's equations was carried out by Poincaré, who rejected the four-dimensional geometry of spacetime as too cumbersome, and Minkowski, who did not.
53. For a succinct summary of the various ways in which symmetries contribute to the understanding and simplification of physical theory, see Roman (1965), pp. 498–9.
54. Noether (1918). Also the Ward–Takahashi identity of quantum-field theory (Ward, 1950; Takahashi, 1957). See, for example, V. I. Arnold (1978), chapter 4, or José and Saletan (1998), sec. 3.2. Arnold expresses it this way: "to every one-parameter group of diffeomorphisms of the configuration manifold of a Lagrangian system that preserves the Lagrangian function, there corresponds a first integral of the equations of motion" (p. 88). More simply, every continuous symmetry generates a conservation law. Emmy Noether was recruited to Göttingen in 1915 by Hilbert and Klein. See Ne'eman (1999).
55. By introducing him to a paper by Frobenius and Schur. Eventually, Von Neumann suggested to Princeton University that he and Wigner share one full-time position, something that took place in 1930. His position was not renewed in 1936. Wigner said that he learned more mathematics from von Neumann than from anyone else, despite his own renowned teachers, Ratz and Polyani. Received the Nobel Prize in physics in 1963 for his contributions to nuclear physics, mostly nuclear theory. On Wigner and his collaboration with von Neumann, see the Biographical Memoir of Wigner published by the National Academy of Sciences (1998), vol. 74. For what it is worth, Wigner's sister married Dirac and, Eckart married von Neumann's widow after the latter's untimely death.
56. See Scholz (2007).
57. Which in stationary states meant that L^2 commuted with the Hamiltonian.
58. The relevant coordinate transformations in three dimensions are those of $SO(3)$; the orthogonal group in three dimensions, the corresponding unitary transformations in state space are those of $SU(2)$. See Gottfried (1966), sec. 27 and chapter VI, especially pp. 32–4.
59. Finite groups, with a finite number of elements, describe these discrete symmetries, which include the symmetric, permutation, cyclic, and dihedral groups, etc.
60. See, for example, Condon and Shortley (1935), p. 186. Also an online paper by Otavio Bueno, "Weyl and von Neumann: symmetry, group theory, and quantum mechanics," PhilSci-Archive, 2001. Parity conservation is violated by the weak interaction, a fact that

was discovered in 1957 by Wu et al., in experiments proposed by Lee and Yang, who were awarded the Nobel Prize in 1957.

61. Some "modern" discussions are Roman (1965), chapters 5–6; Gottfried (1966), chapter 6; and Kursunoglu (1962), chapters 6–8.
62. If the potential is not velocity dependent and if the transformation between Cartesian and generalized coordinates is time independent.
63. Dirac (1930), sec. 33, pp. 107–13. For modern works, see Gottfried (1966) or almost any other text.
64. For example, see Gottfried (1966), sec. 9.2, or Sakurai (1985), pp. 250–1. Weyl in effect demonstrates this in his chapter 2, sec. 5 (Weyl, 1928).
65. Or $[H, L^2] = 0$.
66. Wigner (1937a). Racah's major work on atomic spectra began to come out in 1942 (Racah, 1942), though the four parts were completed only in 1949. He saw it, in some sense, as an updating by group-theoretic methods of Condon and Shortley (1935).
67. Elliott (1958a, 1958b, 1963). For a history of these developments, see Elliott (1999).
68. The first chapter of Bohr and Mottleson's *Nuclear Structure*, I (1998) is an excellent introduction to these topics.
69. Weyl (1929a, 1929b); Klein (1938).
70. Davydov (1965), pp. 209–10. See also José and Saletan (1998), p. 580.
71. Pauli (1933), p. 31; Fock (1926b).
72. For example, Glashow (1961); Weinberg (1967).
73. Non-Abelian means that the elements of the group do not commute, "Abelian" meaning the opposite.
74. First conceived by Pauli in 1953, according to Straumann (2009).
75. O'Raifeartaigh's book (1997) reprints 14 seminal papers in the history of gauge theories. O'Raifeaartaigh made major contributions of his own to the field. See the references in Pauli (1933, 1958, 1980), p. 31. See also "Historical roots of gauge invariance" (Jackson and Okun, 2001).

12

SCATTERING AND REACTION THEORY

INTRODUCTION

With few exceptions, the data that form the basis for constructing a theory of matter, whether liquid, solid, gaseous; atomic, or nuclear, have come from scattering experiments in which radiation is scattered from or absorbed by the object or objects under study. The same is true even in astrophysics, although in that case the data are observational rather than experimental.

Before about 1900, only the scattering of electromagnetic waves, restricted to visible light, was possible. The classical theory of light scattering that typically involved electric dipole scattering in liquids and gases was a 19th-century development, the incoherent scattering of electromagnetic waves by a collection of small scatterers having been treated by Lord Rayleigh (John William Strutt) in 1871 in the process that bears his name.[1] In 1907 J. J. Thomson studied the nonrelativistic elastic scattering of an electromagnetic wave by a free electron, which is essentially the low-energy (low-frequency) limit of Compton scattering, that in its fully quantum-mechanical (lowest-order Quantum Electrodynamics) version is given by the Klein–Nishina formula.[2] It has important applications from energy transport in the Sun to the origin of the cosmic microwave background.

The photon as the quantum of electromagnetic energy was born in 1905 in Einstein's explanation of the photoelectric effect for which he received the 1921 Nobel Prize in physics. The name photon did not appear until over 20 years after the light quantum was proposed,[3] but the by the time of the Fifth Solvay Conference in October 1927 its focus could be on "Electrons and Photons."

By 1916 Einstein[4] had concluded that the photon had to have a linear momentum $p = E/c = h/\lambda$. But it took Arthur Holly Compton's interpretation of the inelastic scattering of x-rays by electrons,[5] which actually involved only kinematics, that is, conservation of momentum and energy, to convince most physicists. Thus, by 1923 wave–particle duality, the imperatives of which began to become clear in the Compton effect and in de Broglie's application of the idea to particles, demanded a nonclassical approach to scattering. Compton's discovery and its explanation, which virtually demanded a particle picture of light ("radiation quantum," in Compton's words), with $p = \hbar k$ and $E = h\nu$, has an honored place in the history of quantum mechanics because for many it was what clinched the argument for the photon. It earned Compton the Nobel Prize in physics for 1927. The story is told in detail in Bruce Wheaton's *The Tiger and the Shark*, whose title (referring to wave–particle duality) comes from a quote from J. J. Thomson: "It is like a struggle

between a tiger and a shark, each is supreme in his own element, but helpless in that of the other."[6]

By the turn of the century, electrons could be "boiled" from a heated cathode—thus known as "cathode rays"—and then accelerated in an electric field to produce a beam that, if sufficiently energetic and scattered from a metal surface, led to the production of x-rays and to their discovery by Röntgen in 1895.[7] Once identified as particles in the experiments of J. J. Thomson (1897) and others,[8] electrons could also be scattered from an atomic target (gaseous or thin film) at energies of up to kilovolts, though usually lower, as in Lenard's experiments and the decisive Franck–Hertz inelastic-scattering experiment of 1913–1914.[9] In these cases it was the loss in energy of the electron or the ionization produced that was of interest. X-ray scattering from solids, especially crystalline solids, became an important tool for studying the structure of solid matter, beginning with Max von Laue, followed by the observation of x-ray diffraction by Walter Friedrich and Paul Knipping, who, on von Laue's suggestion, showed that x-rays demonstrate interference (see following discussion).

As is recounted in more detail in Chapter 15, Henri Becquerel discovered natural or spontaneous radioactivity in 1896,[10] and 3 years later Ernest Rutherford identified the two types of particle radiation, "α-rays" and "β-rays," the latter being much more penetrating than the former.[11] This discovery of radioactivity in the form of α- and β-emitters provided particle sources with energies in the 100-keV to 10-MeV range[12] and led to their scattering from atomic nuclei, though of course the structure of the nuclear atom had to be worked out before there was any hope of understanding the results. Finally, in 1900, Paul Villard discovered a third kind of radiation from radium salts that was not deflected by a magnetic field as α-rays and β-rays were, and the rays were eventually given the name "gamma rays" by Rutherford in 1903.[13]

In the first decade of the century, then, a variety of sources of radiation, particle and electromagnetic, were available to be used in scattering experiments. In particular, Rutherford's discovery of α-decay made radioactive sources available that could furnish an approximately collimated beam of α-particles. The resulting scattering experiments carried out by his collaborators, especially Hans Geiger and Ernest Marsden,[14] prompted Rutherford to give a description of the angular distribution of Coulomb-scattered α-particles from positively charged nuclei in 1911,[15] the familiar Rutherford-scattering formula, taught to every undergraduate physics student.

This analysis of α-particle scattering from atomic (i.e., nuclear) targets was purely classical, and the development of a quantum theory of scattering had to await the creation of the new quantum theory in 1925–1926 by Heisenberg, Born, Jordan, and Schrödinger. The experiments in Rutherford's laboratory showed the *existence* of the atomic nucleus, and further experiments in the 1920s and 1930s began to reveal the *structure* of the nucleus.

Thus, until 1930–1932, the main source of particles for scattering from various kinds of targets was radioactive decay (α- and β-decay)[16] and limited in energy and intensity by the processes that produced them, though electrons could be generated through thermionic emission and accelerated to tens or hundreds of electron volts But after E. O. Lawrence and Stanley Livingston invented the cyclotron in 1930–1931,[17]

combined with the nearly simultaneous development of the linear electrostatic accelerator by Robert Van de Graaf in 1929 and John Cockroft and Thomas Walton in 1932, it became possible to accelerate electrons up to 1 MeV, and soon protons with enough energy to probe the structure of the nucleus, despite the Coulomb barrier. Accelerators quickly replaced radioactive sources as the means of providing particle beams.

In this context, it is worth recalling that a number of assumptions had to be made in interpreting scattering data from bulk samples, including neglecting the effect of atomic electrons, and it was important to evaluate the validity of single-scattering approximations. This motivated the use of gas targets of low density or very thin films, as in the Geiger–Marsden experiment with gold foil.

As the usefulness of scattering experiments became apparent, there were several distinct scenarios to be addressed. Already the scattering of electrons from atoms was of interest as a way of producing atomic excitations, and after the discovery of the nucleus, particle scattering from nuclei provided the means for probing its structure. But understanding such scattering processes required, first, the new quantum theory, and second, the theory of collisions originated by Born in 1926.[18]

EARLY HISTORY: X-RAY SCATTERING

Following Röntgen's discovery of x-rays in 1895, the first pressing question concerned the nature of the radiation, that is, whether it was electromagnetic, and if so, whether a high-frequency form of electromagnetic wave, some kind of "discontinuous impulse in an electromagnetic continuum," or an unknown disturbance in the ether, including longitudinal (compression) waves, as advocated by Röntgen and Lord Kelvin. G. G. Stokes, following George Green,[19] rejected the longitudinal-wave hypothesis in favor of the idea that they were aperiodic transverse electromagnetic impulses. When x-ray diffraction was observed in 1899 by Cornelis Wind and Herman Haga,[20] the issue might seem to have been settled, but Sommerfeld's ingenuity was equal to the task.[21] Similarly, the discovery of x-ray polarization by Barkla in 1903 did not decide between the aperiodic impulse theory and periodic, light-like waves. The identification of α- and β-rays by Rutherford confused the issue until it was found that both were deflected by magnetic fields. Gamma-rays were another complication, but their identification with x-rays (that is, as high-frequency x-rays) was fairly rapid, being accomplished by 1905.

Classical scattering of electromagnetic waves by amorphous substances on the one hand and crystralline solids on the other provided different kinds of information about the media. The problem took on a new dimension when it became possible to scatter x-rays from solids, in particular crystalline solids, that is, Bragg scattering or diffraction, discovered by von Laue in 1912 (see next paragraph). In this case the wavelengths turned out to be comparable to the distances between atoms, making it very different from the light-scattering case, where wavelengths were 1000 times the interatomic spacing. The fact, discovered in these scattering experiments, that crystalline substances had a regular lattice structure mean that coherent scattering would

reveal much about the crystal structure at the same time that it was being learned that these waves could interfere.[22] If these early experiments could be understood classically, in due course the **scattering of electrons from similar materials, showing that an electron beam could be diffracted,** as in the classic experiment by Davisson and Germer of 1927, were thoroughly revolutionary, showing once and for all that particles possessed wave properties.[23]

At the urging of von Laue, who thought that the regularly spaced atoms in a crystal would be the key, Friedrich and Knipping were able to demonstrate interference of x-rays in 1912 at Munich.[24] At the same time, William Henry Bragg, who was to play an important role in understanding x-ray scattering, but had clung to the idea that γ-rays were corpuscular, began to adopt a dualistic theory of x-rays, as possessing both wave and particle properties. By analogy with diffraction of light from a grating, his son William Lawrence Bragg offered a theory of x-ray scattering and interference that we now know as Bragg scattering.[25] For this work, von Laue was awarded the Nobel Prize in physics in 1914, and the Braggs, father and son, received it the next year.

It was soon found that x-rays scattered from matter were of two kinds, one primary, continuous, and polarizable, and the other secondary, characteristic of the material doing the scattering. But a *theory* of x-ray scattering was another matter entirely. Moreover, Einstein's photon description of light, although not influential until almost 1920, nonetheless confused the situation.[26] According to Wheaton, Stark was the first physicist to take the theory of the light quantum seriously,[27] a view that brought him into direct conflict with Sommerfeld, whose pulse theory was incompatible with the idea.

This discovery of the diffraction and interference of x-rays led W. L. Bragg to scatter them from a mica crystal and then a wide range of crystalline substances, showing on the one hand that x-rays were periodic waves much like light, so that crystalline structure could act as a grating, as we have seen, but also suggesting that the scattered x-rays, exhibiting something like a line spectrum, might reveal something about the structure of the material.[28] This led to the study of characteristic x-rays by Henry Moselely and George Darwin[29] who collaborated at Manchester, just prior to WWI in which Moseley lost his life, at the same time Bohr was there. These studies provided the data, from characteristic x-ray scattering, that would ultimately require a full-blown quantum theory to explain. Eventually Rutherford and Andrade showed that γ-rays also exhibited interference behavior.[30]

THEORY OF SCATTERING

Initially scattering processes revealed as much about the incident radiation or projectile as the target, x-ray scattering being a case in point. Generally, however, the goal in scattering has been to learn about the structure of the target, something that was dramatically realized in the case of Rutherford scattering, which revealed the existence of the atomic nucleus. Scattering theory for its own sake was a natural outgrowth of the creation of quantum mechanics, and when Max Born wrote the first paper on

the subject in the summer of 1926,[31] there were at best a few hints of what structure might be lurking in the data obtained from the scattering of electrons or α-particles (and eventually protons and even neutrons) from gaseous or thin, amorphous targets, or crystals for that matter. The existence of the nucleus had been accepted for nearly 15 years, but nothing was known of its possible structure.

Born's description of the scattering of a beam of incident particles from a localized target is very close to what is found in modern quantum textbooks, involving asymptotic solutions to the Schrödinger equation with the assumption that the particle detector could be considered to be outside the range of the potential causing the scattering. This was not possible for the Coulomb force or at least was very problematical, and in nuclei, except for the later use of neutrons as projectiles, the Coulomb interaction had to be taken into account, even when one was probing nuclear structure and the nuclear force.[32] It is a little ironic that Born's paper, which formed the basis for future descriptions of the scattering problem, is far better known for what was almost tossed off, as it were, in a footnote, namely the probabilistic interpretation of the wave function. This, the famous "Born Rule" for which he was awarded the Nobel Prize in 1954, appears briefly in this initial five-page paper but was elaborated on in the much longer one that followed in the next volume of *Zeitschrift für Physik*.[33]

It had been known since about 1919, when the proton was identified (and over a decade later for the neutron), that the nucleon mass was nearly 2000 times that of the electron; hence the interaction with atomic electrons could be neglected in scattering protons or α-particles from nuclei. The result was that electrons (or x-rays) were better suited to probing atoms, whereas α-particles, and eventually protons, were better for studying nuclei.[34] With the discovery of the neutron in 1932, it was not long before neutron-scattering and especially neutron-capture reactions could be studied.

CHARACTERIZING SCATTERING: THE "CROSS SECTION"

The result of scattering a beam of particles from a target had to be expressed in terms of the fraction of scattered particles as a function of direction (into a small angular range). From almost the very beginning, the result of such a scattering process in which a particle is detected in the final state was expressed as a "cross section" or its equivalent, and typically a differential cross section, that would give the probability as a function of scattering angle, which is precisely what Born did.[35]

Over a decade earlier, in 1911, Rutherford had obtained a result that gave the number of α-particles scattered into a unit area in a direction **n**, divided by the incident flux (particles per square centimeter per second),[36] but in his first paper on the emission and absorption of light[37] of 1927, Dirac treated the scattering of an electron by an atom in passing, elaborated on Born's formulation, and obtained an "effective area" for the process,[38] which became the standard way to express the effectiveness of a scattering center. Oppenheimer, in a work on electron scattering from hydrogen atoms

the next year, used the term cross section without any fuss or apology,[39] and in a note in 1933, Rabi referred to the x-ray cross section per atom.[40] Breit and Wheeler first spoke of the "collision area" and then settled on the "collision cross section" $\sigma(\cos\theta)$ a year later.[41] So this English usage was fairly well established by the mid-1930s, despite alternative terms such as "relative target area,"[42] "scattering function," and so on. The German term used by Holtsmark in 1928, *Wirkungsquerschnitt*, was almost literally cross section. A review article by McMillan in 1939[43] was more conservative, giving results in terms of $I(\theta)$, which was a similar normalized intensity as a function of scattering angle, but Turner explicitly used cross section in a paper the following year,[44] and Richtmyer and Kennard, in their book of 1942,[45] presented results of x-ray scattering in terms of a "scattering coefficient," or cross section, evidence that the terminology was well established by the start of WWII.[46]

COLLISION THEORY

In what follows, we consider only collision theory, that is, the scattering of a projectile from an atomic or nuclear target, and initially, following Born, elastic potential scattering, without spin, the theory of which is conceptually quite straightforward. Born's development follows later. The starting point is the separated radial Schrödinger equation containing the scattering potential $V(r)$, for which there is an appropriate Green's function $G(\mathbf{r},\mathbf{r}')$. If $V(r)\psi(r)$ is seen as a source term, the Green's function is the solution to the radial part of the Schrödinger equation with a delta-function source, and so the solution for $\psi(r)$ can be written down implicitly as an integral equation of the form:

$$\Psi(r) = \Psi_o(r) + \int G(\mathbf{r},\mathbf{r}')\, V(r')\Psi(r')\, r'^2 d^3r'. \tag{12.1}$$

Here we have added a solution to the homogeneous (potential-free) problem, $\psi_o(r)$. The Green's function is just that for the Helmholtz equation (the outgoing solution).[47] This integral form of the Schrödinger equation is the starting point for most treatments of scattering theory, and in slightly modified operator form is known as the Lippmann–Schwinger (L-S) equation, from a paper written in 1950,[48] but at least implicit in applications the 1930s. With the Green's function given by

$$G(\mathbf{r},\mathbf{r}') = \exp(ik|r-r'|)/|r-r'|, \quad \text{for} \quad r >> r', \ldots \tag{12.2}$$

and the approximation for $r >> r'$ that $|r-r'| \approx r - \mathbf{r}\cdot\mathbf{r}'/r$, then

$$\Psi(r') = \exp(ikz) - \exp(ikr)/4\pi r \int \exp(-ikr')V(r')\Psi(r')\, d^3r', \tag{12.3}$$

where $\Psi_0 = \exp(ikz)$ is the incoming plane wave. This equation appears (slightly more generally) at least as early as 1930, in a paper by Mott.[49]

If we call the term multiplying the outgoing spherical wave the scattering amplitude $f(\theta)$, then

$$f(\theta) = \frac{1}{4\pi}\int \exp(-ikr')V(r')\Psi(r')\, \mathrm{d}^3r'. \tag{12.4}$$

This obviously is only an implicit solution, as the full wave function appears in the integral for $f(\theta)$, and some approximation has to be made, such as replacing $\psi(r')$ by the incoming wave $\psi_0 = \exp(ikz)$, which would be the first term in an iterative solution known as the *Born series*. We will see that Born introduced the series expansion from the outset in his 1926 paper, and, as a bonus, interpreted the wave function as a probability amplitude for the first time.

Finally, with the notion that dN, the number of particles per unit time per unit solid angle scattered into the direction $\mathbf{n} = \mathbf{r}/r$, is given in terms of the differential cross section $\mathrm{d}\sigma$ (thus defining σ) by the expression $\mathrm{d}N = N\ \mathrm{d}\sigma$, N being the incident flux, then it is easy to show that

$$\mathrm{d}\sigma / \mathrm{d}\Omega = |f(\theta)|^2.$$

This is all very familiar and can be found in every quantum textbook, e.g., Merzbacher,[50] but what is its relation to the initial treatments of scattering theory? In fact, the original development by Born[51] is very similar, culminating in his Eq. 11 under sec. 6 on "elastic collisions," giving "the probability that an electron is deflected into a solid angle [*Raumwinkelement*] dω in the (average) direction **n** . . . " is

$$\Phi \mathrm{d}\omega = \pi^2 k^2 \sum |f_n^{\infty}|^2\, \mathrm{d}\omega,^{52} \tag{12.5}$$

where, in modern terms, f_n^{∞} (the ∞ indicating "asymptotically") would be the scattering amplitude for the nth term in the *Born series*. This is, in part, the result for which Born finally received the Nobel Prize 28 years later.[53] The main departure from the typical modern development is that Born introduced the Born series from the outset, through a series of successive approximations.[54] In the lowest-order approximation, the general driving term $V\psi_n$ would be replaced by $V\psi_0 = V\exp(ikz)$. Thus, in the expression for the scattering amplitude in Eq. (12.4), this gives what is known as the "first Born approximation," or sometimes just the "Born approximation." In Born's approach, this is obtained from just the first term in the sum in (12.5), involving f_0^{∞}. For details, the reader is referred to the original paper, which is, of course, in German, to the translation in Ludwig, or to Weyl's *The Theory of Groups and Quantum Mechanics*,[55] which summarizes a portion of Born's argument. The literature on the Born series, including its convergence, and on the Born approximation, is vast.[56] Inescapably, Born's development utilized Schrödinger's method, something that Heisenberg saw as very much a betrayal.

In the next section of his paper, Born treated inelastic scattering, which may occur if the target or projectile has internal degrees of freedom that can be excited or if there

is particle creation or absorption.[57] The most interesting case occurs when the scattering process results in excitation in the target, as in electron scattering from a hydrogen atom, in which energy is absorbed or emitted by the bound electron, which is the case Born was considering. But of course the incident and scattered electrons, being identical fermions, can be exchanged, adding a new layer of complexity,[58] and ultimately complex projectiles would be used, which themselves could be excited or involved in rearrangements.

Again Born set out to solve the problem by means of successive approximation, that is, by generating the Born series, as in the elastic case. By writing the total wave function as a product of the electron wave function and that of the atom, he eventually arrived at a wave equation of the same *form* as the one he obtained in the elastic case, albeit for a somewhat different function u_{nm}, which represented the overlap between the final atomic state and the initial total wave function, including the initial atomic state. The interaction potential U_{nm} appeared in the form of the matrix element of the interaction between the initial and final atomic wave functions.[59] Although the details are beyond the scope of this narrative, the development is fairly transparent and remarkable for having been obtained less than a year after Born's seminal paper with Jordan laying out the formal structure of matrix mechanics. The basis for this paper of Born, however, was wave mechanics and represented a recognition that matrix mechanics as then understood could not readily deal with such problems. In that sense, as well, the paper was of major importance. Thus, as we have noted, when Born was eventually rewarded with the Nobel Prize, which he shared with Walher Bothe in 1954, it was not for scattering theory, per se, but for the probabilistic interpretation.

Born followed this paper with one at the end of 1926[60] in which he discussed both electron and α-particle scattering from hydrogen in much greater detail than in the earlier paper, employing the H-atom wave functions and a screened Coulomb interaction between the electron and the nucleus, and he gave expressions for the cross section for elastic and inelastic scattering. The theory was developed further by Wentzel[61] and Elsasser[62] and then, much more generally in 1928 by the young Robert Oppenheimer,[63] who was about to return to the United States but had gotten his doctorate under Born in 1927, at age 23.

THE NINETEEN THIRTIES

Well before Born's first paper on scattering, it had become clear that scattering processes provided *the* essential tool for probing the structure of atoms and even nuclei.[64] One can thus understand the remark by Goldberger and Watson many years later (1964) in the preface to their important book, *Collision Theory* that "what is surprising is that there are so few books on collision theory," a comment that was followed by a tribute to the classic book by Mott and Massey,[65] "which educated several generations of physicists." When their first edition was published in 1933, it was the first, and for years essentially the only, book devoted to this important topic.[66]

By 1930, collision theory, describing the scattering of electrons or α-particles and eventually protons and neutrons, from atoms, was still in its infancy. But as the structure of the nucleus began to be investigated, targets became more complex, and inelastic scattering could result in an unstable final nucleus that might then decay, and rearrangements could occur, exchanging particles between the projectile and target. Moreover, the strong nuclear force—which fortunately was of short range—was involved as well as the Coulomb interaction. In any case, the description had to include the initial and final states (wave functions) of the target system (assuming, as is often the case, that internal degrees of freedom of the projectile are not excited), which means that the problem is immediately very complicated, because, as noted, ordinarily the goal of the scattering process is to *determine* the structure of the target system.

So it was that on the heels of Born's work, quantum-scattering theory soon came to focus separately on atomic scattering on the one hand and nuclear scattering and reaction theory on the other. In the first case it was mostly x-ray and electron scattering from atoms, the latter becoming especially important as electron accelerators came on line around 1930. For the most part the discussion of nuclear scattering is deferred to Chapter 15, but suffice it to say that after the initial work with α- and β-particles from radioactive sources, nuclear applications also mushroomed as accelerators generated proton beams, eventually allowing the production of neutrons, which themselves were very effective in initiating neutron-capture reactions because of the lack of a Coulomb barrier.

As scattering theory rapidly matured in the early 1930s and emerged as a powerful tool for understanding atomic, molecular, and nuclear structure, the important technique of partial-wave analysis, which emphasized the contribution to the scattering process of the angular momentum components of the relative motion in the initial state became widely used. Although it was introduced by Faxen and Holtsmark[67] in 1927 and then by Gordon[68] the following year, is not clear that the implications of such a representation of the scattering "amplitude" were fully appreciated at the time. This expansion in partial waves was initially little more than the classical device of expressing a general solution to the angular part of the wave equation as an infinite series of terms labeled by an integral separation constant n, that is to say $\psi(r,\theta) = \sum \chi_n(r)\, P_n(\cos\theta)$. Faxen and Holtsmark cite Rayleigh's *Theory of Sound*,[69] in which a similar, classical development, appears, as support for their development. The now-standard parameterization of the scattered intensity or scattering amplitude in terms of the "phase shift" [*Phasensprung*] was introduced by Holtsmark in 1928.[70] Thus the total cross section could be given as $Q = \sum \frac{4\pi}{[k]2}(2l+1)\sin^2\delta_l(\infty)$, but there was still no explicit identification of l with the angular momentum[71] quantum number, even though Schrödinger had done that in his first paper (speaking of the "azimuthal quantum number") and Sommerfeld had done something similar in his "wave mechanics supplement" of 1929.[72] Of course in both these earlier cases, the issue was a bound-state problem, not one of scattering. A flurry of papers emerged in 1928–1931 by Mott and Massey separately, based on Born's work and on the partial-wave formalism of

Faxen and Holtsmark, in which they explored elastic and inelastic electron scattering from atoms, the scattering of neutrons from nuclei, and many other topics.[73]

The collaboration by Mott and Massey, beginning in 1933, on what would become the standard source on collision theory, eventually went through three editions, the last being published in 1965, the year after Goldberger and Watson's book. In the first edition they went to some lengths to establish the connection between the sum over partial waves and angular momenta.[74] The relative maturity of the theory presented in the first edition is reflected in the fact that when the second edition appeared 16 years later, in 1949, mostly by Massey, the principal change involved a much-revised and elaborated discussion of *nuclear* collision phenomena. Of course, the almost decade-long impact of the war delayed progress and at the same time produced the nuclear reactor with its ability to generate intense beams of neutrons, while nuclear weapons research prompted theoretical advances. The final edition, at over 800 pages, was more than twice as large as the previous one.

Interestingly, when Gregory Breit reviewed the first edition of Mott and Massey for the *Bulletin of the American Mathematical Society* in 1934, he expressed skepticism that the theory was applicable to nuclear collisions,[75] which the authors discussed in chapter XV. Breit would go on to make some of the most important contributions to nuclear scattering, himself.

REACTION THEORY; REARRANGEMENT COLLISIONS

This subject arose for the first time in the problem of electron exchange scattering from atoms, but Mott and Massey, in their first edition, also considered the general case of rearrangement collisions (chapter VIII), using as an example the stripping of an electron from an atom by an incident α-particle. This development, based on the Green's function for the problem, and repeated in the second edition, is very similar to that given in Davydov[76] over 30 years later (1965). Application to nuclear reaction theory came soon, as the first particle accelerators made beams of protons, α-particles, eventually neutrons, and of course electrons, of sufficient energy and intensity to produce reactions such as (α, n), (α, p), (p, n) and so on.[77]

S-MATRIX THEORY

In 1937, as the war approached, in a paper on light nuclei, John Wheeler introduced the idea of a scattering kernel or scattering matrix S that would prove to be a very fruitful way of formulating scattering theory.[78] It was picked up by Heisenberg in 1941–1943[79] in an attempt to resolve fundamental problems in quantum-field theory, and it became the dominant approach to particle interactions into the 1960s. The unitary scattering matrix or "*S*-matrix," can be defined as operating on the asymptotic initial state $|\psi_i(t=-\infty)\rangle$ to produce the asymptotic final state $|\psi_f(t=+\infty>)\colon S|\psi_i\rangle = |\psi_f\rangle$. Combined with the integral form of the Schrödinger equation, which is obtained by use of the Green's function along with Dirac's interaction picture, this elegant formulation of scattering theory quickly became an essential part of the development of

perturbative Lagrangian field theory and the mature theory of quantum electrodynamics (QED) in the 1940s and 1950s (see the next chapter).[80]

Nuclear reaction theory was reaching some degree of maturity at the hands of Bethe and Placzek, Wheeler, and others, just as WWII was about to begin, and then immediately afterward.[81] Although scattering and reaction theory naturally played an important role in the developments of the war years, it really came into its own only from about 1947 on. In any case, the proliferation of ideas and papers at this point and the specialization to nuclear physics makes further treatment of this subject impossible in these pages. Some aspects are explored further when we discuss applications to nuclear physics.

The so-called formal theory of scattering that describes the scattering process in general, fundamental terms, usually starting from the integral or operator form of the Schrödinger equation, i.e., the Lippmann–Schwinger equation, was pioneered by Møller, Lippmann, and Schwinger, and Gell-Mann and Goldberger in the immediate postwar era. The interested reader is referred to Goldberger and Watson's book.[82]

CONCLUSION

Scattering theory developed rapidly after Schrödinger's introduction of wave mechanics and, as we have seen, actually elucidated some important issues surrounding the interpretation of the solutions of the wave equation. By 1933, as the formulation of quantum mechanics itself was being completed, scattering and reaction theory was already fairly mature. There were still issues in the formal theory of scattering to be resolved, and the problems of more than two particles in the initial or final states, that is, the few-body problem, had not been addressed—and indeed, were not solved until at least the 1960s. But as a tool, in studies of the structure of atoms and nuclei and even of the challenging problem of nuclear reaction rates in stars, collision theory was already well developed before the start of WWII.

NOTES

1. Rayleigh, (1871a, 1871b, 1899) See Jackson (1992), chapter 10. Also Born and Wolf (1980).
2. Klein and Nishina (1929).
3. "I therefore take the liberty of proposing for this hypothetical new atom, which is not light but plays an essential part in every process of radiation, the name *photon*" Lewis (1926). See Pais (1982), p. 407.
4. Einstein (1916c). His 1909 paper "The development of our views on the composition and essence of radiation" essentially made the point 7 years earlier. Einstein (1909).
5. Compton (1923). Compton also obtained an expression for the cross section in a development C. N. Yang called "half-baked," in an address given in October 2005 (Yang, 2008). The entire address is of interest.
6. Quoted in Wheaton (1983). J. J. Thomson was G. P. Thomson's father.

7. The "cathode rays" were identified as material particles in 1897 by J. J. Thomson and others [including Wiechert and Kaufmann; see Wheaton (1983)], and given the name "electrons" by Stoney.
8. Including Phillip Lenard. See the references on p. 338 in Sommerfeld (1923).
9. At 4.9 eV. Franck and Hertz (1914). Lenard received the Nobel Prize in physics in 1905, J. J. Thomson the following year, and Franck and Hertz in 1925.
10. Becquerel (1896).
11. E. Rutherford (1899). He was then at McGill University in Canada.
12. At the time, energies were expressed in terms of range or stopping distance in air, not electron volts.
13. Villard (1900a, 1900b).
14. Marsden was a 20-year-old undergraduate and Geiger, who received his PhD in Germany in 1907, was, as Rutherford's assistant, what we would call a "post-Doc" today. See Chapter 15.
15. Rutherford (1911).
16. The only other possibilities involved nuclear reactions, but even a source of neutrons such as the (α,n) reaction required an α-emitter.
17. Along with David Sloan. Both were graduate students. Electron energies of over 1 MeV were reached in early 1931. See Heilbron and Seidel (1989).
18. Though coulomb scattering could be treated classically, and eventually the quantum mechanical result turned out to be the same as the classical Rutherford scattering.
19. Who argued that the ether was incompressible, hence no compression waves. We might say "wrong argument, right result."
20. See Wheaton (1983).
21. Although his aperiodic impulse theory would not stand the test of time. Sommerfeld (1899). For details, see Wheaton (1983), chapter 2.
22. Robert Hooke (in his *Micrographia*) and Christiaan Huygens (Traité de la lumière) speculated about regular crystal structure in the 1660s–1690s, and it was commonly believed in the 19th century that certain substances had some kind of periodic structure, but it took x-ray scattering to demonstrate that these ideas had a basis in fact. One naturally hesitates to cite a web page, but in this case it may be worthwhile: http://www.scs.illinois.edu/xray_exhibit/Lecture/HistoryCrystalStructureTheoryshortened.pdf.
23. C. Davisson and L. H. Germer (1927a). Germer was Davisson's assistant at Bell Labs while a graduate student at Columbia. Davisson and G. P. Thomson (1928) (who independently carried out a related experiment) shared the Nobel Prize in physics in 1937 for this discovery. Walter Elsasser had suggested in 1925 that electron diffraction might have already been observed in earlier experiments of Davisson and Kunsman (1923), and in 1926 Born interpreted these earlier experiments as an indication of electron diffraction. See Gehrenbeck (1976, 1978).
24. Formally published in 1913 [Friedrich, Knipping, and Laue (1913)]. According to Wheaton, Sommerfeld apparently opposed doing the experiment that was performed at his institute (Wheaton, 1983, p. 200).
25. W. L. Bragg (1912).
26. Einstein (1905). According to Wheaton (1983), "a seldom cited source." In 1910, Lorentz wrote that he "does not want to deny the heuristic value of the [light quantum], hypothesis, [but] only to defend the [classical] theory as long as possible" Lorentz (1910), quoted in Wheaton (1983), p. 168.

27. Which is deeply ironic, given Stark's later rejection of "Jewish science, including, of course, Einstein's." Stark even offered Einstein a position as his assistant in 1909.
28. W. L. Bragg (1912); W. H. Bragg and W. L. Bragg (1913).
29. Moseley and Darwin (1913). Wheaton quotes Moseley from a letter to his mother that "[X-rays] are a kind of wave with properties no wave has any business to have." Wheaton (1983), p. 199.
30. Rutherford and Andrade (1914). Again, see Wheaton (1983), p. 224.
31. Born (1926a). This paper is translated in Wheeler and Zurek (1983). Born (1926b).
32. The problem was first solved in 1928 by Mott (1928), Gordon (1928), and Temple (1928).
33. Born (1926b). This second paper is translated in Ludwig (1968). See n. 51 of this chapter.
34. Although in the 1950s high-energy electrons proved valuable in probing the nuclear radii and the charge distribution in the nucleus
35. The cross section was an effective area that could be used to characterize the scattering, and thus had square centimeters as the units of area. Because nuclear cross sections are very small, the usual unit is the somewhat whimsical "barn," 10^{-24} cm^2.
36. Thus, in Rutherford's 1911 paper he gives the results of scattering in terms of a quantity y, which is the number of particles scattered into a unit area A at a distance r from the scatterer, whence $yr^2/Q = \mathrm{d}\sigma/\mathrm{d}\Omega$ in modern notation, where Q is the incident flux (Rutherford, 1911, p. 674). Interestingly, he gives precisely the same description in his 1930 book with Chadwick and Ellis (Rutherford, Chadwick, and Ellis, 1930, p. 194).
37. Dirac (1927b)
38. The discussion is on pp. 256–7 and 260.
39. Oppenheimer (1928a).
40. I. I. Rabi (1933).
41. Breit and Wheeler (1934).
42. T. A. Bonner (1934).
43. Millikan (1939).
44. Turner (1940).
45. Richtmyer and Kennard (1942).
46. In Bethe and Saltpeter (1957), the scattering amplitude $f(\theta)$ is defined, $|f(\theta)|^2$ is called the differential cross section, and $S^2(\theta)$ is called the scattering coefficient, and its definition is the same as $\mathrm{d}\sigma/\mathrm{d}\Omega = \sigma(\theta)$. This book had its origin in an article for the Handbuch der Physik in the early 1930s by Bethe.
47. A good source is chapter XI in Davydov (1965).
48. Lippmann and Schwinger (1950), Eq. 1.61 or 1.84. In slightly different notation, $\Psi_a(E) = \Phi_a(E) + \left(E - H_0 + i\varepsilon\right)^{-1} H_1 \Psi_a$, where Φ_a is an eigenfunction of H_0 and H_1 is an interaction Hamiltonian (potential). An advantage over the Schrödinger equation is that the Green's function automatically incorporates the boundary conditions appropriate to the problem (usually at ∞). The standard implicit integral equation solution to the Schrödinger equation for potential scattering, e.g., Mott and Massey, 2nd ed, Eq. VII.3,is essentially the same equation, in a coordinate representation and with an incident plane wave. Thus, the **L** – **S** equation is more general, and more abstract, but not so very different. It is a handy integral form of the Schrödinger equation.
49. Mott (1930).
50. Merzbacher (1998), chapter 13. Another good source is Davydov (1965), chapter XI.

51. Born (1926b). It was in the previous paper (Born, 1926a), translated in Wheeler and Zurek (1983), and titled "Quantum theory of scattering," that Born wrote the following: "Reflection shows that the probability is proportional to the square of the quantity Φ_{nm}"; Born (1926a)—a five-page paper. This comment (p. 865) was added by Born in a footnote as a correction [*korrectur*] to the text after reading the galley proofs. The paper ended with "An extended treatment will appear shortly in this journal." This was expanded in Born (1926b) in 25 pages, in which he referred to the first paper as a preliminary study. See Jammer (1966), p. 284. It is that Born was speaking of the probability that a scattered particle would be detected in a certain direction, an idea slightly removed from the understanding that $|\psi|^2\, dx$ is the probability of finding the particle in dx. He was apparently motivated to study collision because of experiments by the Göttingen professor of experimental physics, James Franck Leon Rosenfeld has said that Born's conclusion was not a new idea to those at Bohr's institute in Copenhagen (AIP Oral History, September 3, 1968). It should be noted that Dirac was at the same time approaching such scattering problems by calculating the probability of transitions per unit time in both the target and the state of the projectile.
52. It is here and in the previous paper that Φ is introduced as a probability (or probability density). The step from that assertion to the general idea that $|\psi|^2\, dx$ is the probability of finding a particle in ds, which is not ontologically trivial, was absorbed very quickly, e.g., Condon and Morse (1929).
53. "Especially for his statistical interpretation of the wave function." That is, not for his collision theory, per se.
54. Writing $\Psi = \Psi_1 + \Psi_2 + \Psi_3 + \ldots$, he arrived at $\nabla^2\Psi_n + k^2\Psi_n = V\Psi_{n-1}$, etc. Ruark and Urey (1930) reproduce much of Born's proof.
55. Weyl (1928). In the 1932 English translation, pp. 70–4. There is also a translation by David Brooks that might be found on the Internet.
56. See Mott and Massey (1965), Wu and Ohmura (1962), and Goldberger and Watson (1964).
57. The section is titled "unelastische Electronenstoss" (p. 819). Elastic scattering just means that the projectile is scattered from the target, which recoils, without loss of energy. All such processes can do is probe the force law and perhaps study polarization, which Born did not attempt.
58. Oppenheimer demonstrated that one had to take into account the exchange of the two electrons, bound or unbound (1928a).
59. Born (1926b), pp. 819–21 (translated in Ludwig (1968)), or Davydov (1965), Eq. 103.20.
60. Born (1926e).
61. G. Wentzel (1926b).
62. Elsasser (1927).
63. Oppenheimer (1928a, 1928b).
64. As a matter of fact, according to Leon Rosenfeld, he and George Gamow were astounded to find that Rutherford and his collaborators had discovered many nuclear excited states through γ-decay (AIP Oral History, September 3,1968).
65. Mott and Massey (1965). The three editions were published in 1933, 1948, and 1965. The paucity of books on scattering theory noted by Goldberger and Watson is no doubt largely due to the dominance of Mott and Massey. The book by Wu and Ohmura (1962) that

appeared 2 years before Goldberger and Watson (1964) was largely supplanted by their more formal and comprehensive work.

66. The book *Nuclear Scattering* by Mather and Swan (1958) was the first important postwar book on scattering, but it was devoted entirely to the nuclear context.
67. Faxen and Holtsmark (1927).
68. Gordon (1928).
69. Rayleigh (1877, 1894), *The Theory of Sound*.
70. Holtsmark (1928).
71. "moment of momentum."
72. Sommerfeldd (1930), the English translation of the 1929 work.
73. Massey (1927, 1932, 1933); Mott (1928, 1929a, 1929b, 1930, 1931, 1932). Massey got his doctorate at Cambridge under Ralph Fowler, who also advised Dirac. It is said (Wikipedia) that he introduced Francis Crick to Maurice Wilkins; a critical event in the search for the structure of DNA.
74. Goldberger and Watson (1964), chapter II, sec. 2.
75. Breit (1934). Referring to results that seemed to show that the derived nuclear radius was a function of the velocity of the projectile, Breit commented that "the interpretation of the results seems to be largely a matter of faith."
76. Section105.
77. The notation (α,n) is shorthand for $\alpha + X \rightarrow Y + n$. See Chapter 15.
78. Wheeler (1937).
79. Heisenberg (1943a, 1943b).
80. For details, see books on scattering theory, e.g., Goldberger and Watson (1964), or on field theory, e.g., Mandl and Shaw (1993). Treatments of historical interest include those of Schweber, Bethe, and de Hoffmann (1955), and Muirhead (1965), chapter 7.
81. Bethe and Placzek (1937), Wheeler (1937). Wigner (1946), Wigner and Eisenbud (1947), Breit (1959), Briet and Wigner (1936), to mention only a few of the developments.
82. Lippmann and Schwinger (1950). Gell-Mann and Goldberger (1953), Goldberger and Watson (1964).

13

RELATIVISTIC QUANTUM MECHANICS AND QUANTUM-FIELD THEORY TO 1940

THE RISE OF PARTICLE PHYSICS

RELATIVISTIC QUANTUM MECHANICS

It is tempting to think of quantum electrodynamics (QED) as having had its origin in the late 1940s and early 1950s, highlighted by the Shelter Island Conference held June 2-4, 1947, and culminating in the awarding of the 1965 Nobel Prize awards to Feyman, Tomonaga, and Schwinger "for their fundamental work in quantum electrodynamics, with deep-ploughing consequences for the physics of elementary particles."[1] This work, mostly done between 1946 and 1949, represented the resolution of problems of divergences in the theory that had plagued it for more than a decade and had cast doubt on the entire enterprise. But it turns out that QED's history is much older and richer than that, reflected in the fact that the 1965 Nobel presentation speech mentioned took special note of Dirac, Heisenberg, and Pauli.

As soon as it was clear that the discoveries of 1925–1927 represented a robust theory of quantum phenomenon that had the possibility of wide application, the question of how it should be reconciled with special relativity became urgent. It was very clear that in the end a relativistic theory was required, though the path to that goal was far from obvious, and for many it was a matter of attacking one problem at a time. In fact, however, relativistic quantum mechanics had already had an abortive start when Schrödinger attempted to find a relativistic wave equation even before settling for the nonrelativistic theory.[2]

Attempts to use the new quantum theory to treat the interaction between particles (matter) and radiation soon made the new quantum theory something of a hybrid, because when the emission and absorption of light was considered, relativistic considerations accompanying the photon were inescapable; no nonrelativistic theory of the interaction between particles and light could really be considered fundamental. The emission and absorption of photons meant that ultimately a theory of how charged particles interact with the electromagnetic field had to involve the creation and annihilation of photons at least, but, by implication, of particles as well, e.g., electrons. It would eventually be necessary to view a process such as Compton scattering as one that involved annihilating an electron and a photon in an initial state, ending with the creation of an electron and a photon in the final state (with different energies and momenta), a process begun by Dirac and Jordan before 1930.

Although relativistic constraints had to be taken into account even in the old quantum theory, as when Sommerfeld showed that at least part of the fine structure could be explained thereby, it was another matter to construct a fully relativistic quantum theory, either in matrix or wave mechanics. The time-dependent Schrödinger equation, in the form in which we have previously discussed it, is clearly not Lorentz invariant, because time and space coordinates are treated differently.[3] It would not be enough merely to obtain an equation for the electron or for a spinless particle that was Lorentz invariant, but at least that much could be done, and was, by Gordon, Klein, and Dirac in 1926–1928, and we could say even Schrödinger.

The initial problem was essentially one of finding a relativistic Hamiltonian or Lagrangian that would lead to a Lorentz invariant equation of motion. Starting from the relativistic relationship between energy and momentum $E^2 = p^2c^2 - m^2c^4$, and Schrödinger's identifications[4]

$$E \rightarrow i\hbar\partial/\partial t \quad \text{and} \quad \mathbf{p} \rightarrow -i\hbar\nabla \quad (\text{operating on } \psi),$$

the relativistic equation $\nabla^2\psi - (m^2c^2/\hbar^2)\,\psi = (1/c^2)\,\partial^2\psi/\partial t^2$ immediately results.[5] It is convenient to write this in terms of the D'Alembertian operator $\Box = -\nabla^2 + (1/c^2)\partial^2/\partial t^2$: in which case, we obtain the elegant expression:

$$\Box\psi - \mu^2\psi = 0,$$

where $\mu = mc/\hbar$. This, the famous Klein–Gordon (K-G) equation, which is manifestly Lorentz invariant, was derived independently in 1926 by Oskar Klein and Walter Gordon,[6] but also by Schrödinger himself, and credit is also due Vladimir Fock.[7] This is, in fact, the equation satisfied by a scalar field in quantum-field theory (QFT). A Lagrangian can be constructed through the principle of least action,[8] which leads to the K-G equation as the equation of motion for a scalar field. As it happened, no scalar (spinless) particle was known at the time, so that it was unclear what the application of the K-G equation might be. An obvious candidate would later emerge in the form of the spin-0 pi meson (π, "pion") which was discovered in 1947, and especially the neutral pion (π^0), found 3 years later.[9]

The fact that the K-G equation was second order in time meant that giving ψ at a time t_0 did not determine its future behavior (alternatively, it is inconsistent with the time-dependent nonrelativistic Schrödinger equation), and also that nonphysical negative probability densities are possible, depending on the values of ψ and $\partial\psi/\partial t$ at a given time.[10] The latter problem was solved elegantly when Pauli and Weisskopf reinterpreted the wave function ψ as a *field variable* in 1934 and quantized the equation.[11] This quantization was carried out by requiring the wave function ψ to satisfy a commutation relation, that is, to become an operator, a process called second quantization.[12] But this idea effectively had been introduced as early as 1927 by Dirac and Jordan, as we shall soon see.

THE DIRAC EQUATION

At the end of 1927, Dirac began to show what a relativistic treatment of quantum mechanics might look like by deriving a relativistic equation for the electron in a paper titled "The quantum theory of the electron,"[13] which solved, for the moment, the problem of that fundamental particle, with the unexpected bonus that it showed how electron spin originated, or at least that the electron *had to have* an intrinsic angular momentum. But even before he developed what we know as the *Dirac equation*, in fact 11 months before, he was aware that such an approach would, in the end, not be sufficient.[14]

It was in the paper published on February 1, 1928, that Dirac boldly addressed the problem of an equation for the electron that was consistent with the requirements of special relativity by requiring that the wave equation for the electron be first order in time.[15] An important motivation was its consistency with the Dirac–Jordan transformation theory, in which, of course, the time evolution of the wave function is given by the time-dependent Schrödinger equation, which is also first order in time.[16] Dirac's argument was that the equation should involve only the first time derivative, $\partial/\partial t$, "so that the wave function at any time determines the wave function at any later time." But then Lorentz invariance demanded that the equation be first order in the spatial coordinates as well:[17] $a\,\partial\psi/\partial t + b\,\partial\psi/\partial x + c\psi = 0$. With the proper dimensional factors this can be written as

$$\left(1/c\right)\partial\psi/\partial t + \sum \alpha_k \partial\psi/\partial x_k + (imc/\hbar)\sum \beta\psi = 0, \quad \text{where } \psi = \psi(x,t).$$

Allowing for the fact that ψ might be a multicomponent function with components ψ_ℓ, then ψ is an n-dimensional vector, in which case α_k and β are $n \times n$ Hermitian matrices, and a term like $\beta\psi$ is a matrix product (matrix times a column vector). With a little manipulation, the Dirac equation can be put in covariant form, in which the coefficients turn out to be 4×4 matrices and the wave function ψ is a four-component column vector.[18]

As we saw earlier, aside from being the first relativistic equation describing the behavior of a real elementary particle, the electron, it also showed that the intrinsic angular momentum of the electron, that is, its spin, emerges naturally when one requires conservation of total angular momentum of a free electron.[19] Earlier, Pauli and Darwin separately had tried to incorporate spin into matrix mechanics or the Schrödinger equation, without much success.[20]

From the outset it was clear, somewhat ominously, that the Dirac equation had negative-energy solutions, causing its originator much consternation.[21] Dirac finessed this question in the 1928 paper, but in one published on New Year's Day, 1930, he observed that "an electron with negative energy moves in an external field as though it carries a positive charge."[22] This daring conjecture led him reluctantly to conclude that the negative-energy states were mostly filled and that the holes in this negative-energy "sea" appeared as positively charged particles. At this stage the only known elementary "particles" were the electron, proton, and the photon, so that the sole candidate

for the holes in the negative-energy sea seemed to be the proton, despite the incommensurability of the electron and proton masses. After Oppenheimer objected to this proposal,[23] Dirac suggested that the negative-energy states were "anti-electrons,"[24] but thought that they could not be detected because they would immediately annihilate with an electron. Very soon after, however, the anti-electron *was* discovered by Carl Anderson (in August 1932), and named the *positron*,[25] a label apparently suggested by a *Physical Review* editor and adopted by the discoverer. Unfortunately, subsequent attempts to apply Dirac's theory to the proton, which was then thought to be elementary, failed spectacularly, and we now know that it is a composite particle.

Dirac's development of the relativistic equation for the electron in 1927-8 created a sensation. It was this equation, with its unanticipated explanation of the electron's intrinsic spin and the prediction of negative-energy states, that focused attention on the problem of constructing a fundamental theory of the electron-photon interaction. Since it only described the electron, it was but a first step, and as it stood, it was not a field theory, per se. The solution was a wave function, not a field operator, but it provided the basis for a field-theoretic description of the electron and its interaction with the electromagnetic field, that would begin to emerge in the next four years.[26]

QUANTUM FIELD THEORY AND QUANTUM ELECTRODYNAMICS

Quantum electrodynamics (QED), the theory of the electron-photon interaction, is the clearest and most mature example of quantum field theory.[27] In the exciting early days of quantum electrodynamics and quantum field theory, 1927-33, a clear distinction was made between Dirac's particle-oriented theory on the one hand ("quantum electrodynamics"), and the field perspective of Jordan ("quantum field theory"),[28] on the other, both dating from 1927, though nearly a year apart. Jordan's view, a working out of wave-particle duality, emphasized that both matter and radiation were to be described by quantized fields.[29]

Of course in 1930 electromagnetism was the only known force other than the unique case of gravitation, and hence the only treatable field. Fermi's theory of the weak interaction was three years away, and there was no successful or satisfying theory of either the weak or strong force until the gauge theories of the 1960s. It remained to develop a quantum description of the electromagnetic field. Einstein's much earlier description of the field in terms of photons was the *sine qua non*, but it, like the Dirac equation, was not a quantized field theory per se.

The task of summarizing the origins of QED or quantum field theory is a challenging one, and we will have to be judicious and somewhat selective in choosing what to cover. Although its beginnings in the decade after 1927 are still manageable, as the 1930s wore on the number of important participants, especially in the United States (or at least writing in *Physical Review*) grew rapidly, and we lack the luxury that Schweber had in his *QED and the Men Who Made It*, where 250 pages are devoted just to covering developments through 1940. For the full story, I refer the interested reader to that work and to papers cited in it.[30] Another valuable resource is an article

"The quantum theory of fields (until 1947) "by Gregor Wentzel, who was a contributor to the early developments.[31] Especially useful, but very different, is Schwinger's *Selected Papers on Quantum Electrodynamics*, which reprints nine of the early papers before going on to those of 1947-52 when the difficulties with infinities were for the most part worked out, by Schwinger, Feynman, Tomonaga, Dyson, Wick, Bethe, and others.[32] Finally, a nice 25-page summary of developments in the mid-1930s is given by Pais in his *Inward Bound*.[33]

It was ultimately necessary, following Jordan, to formulate QED in terms of the quantized free Dirac field, the quantized free electromagnetic field, followed by the adoption of a Lagrangian formalism with appropriate interaction term, coupling the free fields, the $\mathbf{j} \cdot \mathbf{A}$ or $(j_\mu A^\mu)$ electron-photon interaction.[34] The coupling between the fields involves the fine-structure constant, $\alpha = e^2/\hbar c$,[35] and since it is small, perturbation theory, with certain qualifications, should work well. This made it possible, in principle, to obtain a cross section for a real process, though even for the simplest processes, such as Compton scattering, the computation challenges were monumental, and for the mostpart, the necessary techniques would reach maturity only in the late 1940s.

The first classical field theory, Maxwell's theory of the electromagnetic field, was put in covariant form by Einstein, Minkowski, Lorentz, and Poincare' in the first decade of the 20th century. While Lorentz and Einstein showed how the fields transformed under Lorentz transformation, it was Minkowski in 1908, who after introducing a four-dimensional pseudo-Euclidean flat spacetime, defined the electromagnetic field tensor $F^{\mu\nu}$,[36] in terms of which Maxwell's equations and the expressions for the potentials could be written in a manifestly covariant form. This made it possible to find a Lagrangian density that would lead to Maxwell's equations, as equations of motion. The formulation of fully relativistic *classical* electromagnetic theory was all but complete. The next step was the quantization of the Maxwell field.

SECOND QUANTIZATION

It soon became apparent that relativistic wave equations like the Klein-Gordon and Dirac equations fell far short of a final solution to the problem of charged particles and their interaction with the electromagnetic field. In a paper titled "The quantum theory of the emission and absorption of radiation," submitted in February 1927, Dirac made the first attempt to construct a quantum theory of the electron-photon interaction, that is *quantum electrodynamics,* a term that he made part of the literature in that paper, one that Schweber said "marks the birth of quantum electrodynamics.[37] Because such a theory involved absorbing or emitting photons, he was forced to introduce creation and annihilation operators for photons. Furthermore, in this, one of his most original papers, he introduced the procedure, now known as "second (or "hyper") quantization, writing that "The development of the theory that naturally suggests itself is to make these canonical variables q-numbers satisfying the usual quantum conditions. . . ."[38] The subsequent development of quantum electrodynamics follows from this step Dirac took in the winter of 1926–7. As he remembered

it over three decades later, he was "seeing what happens when you make the wave functions themselves into a set of noncommuting quantities."[39] And still later, "One simply supposes that all the $\psi(q)$'s for different values of q are made into operators."[40] While this is implied in Dirac's paper, it was made much more explicit in Jordan's work which followed it (see below).

As noted, inherent in Dirac's development of second quantization--indeed motivating it – is the non-conservation of photon number, as photons in a given state are created or destroyed in the emission and absorption processes.[41] This resulted in the introduction of states which were eigenstates of the number operator (an "occupation number" representation) whose eigenvalues were the number of photons in a given state, along with a definition of the photon *vacuum*. These creation and annihilation operators were analogues of the "ladder operators" first used to create and annihilate quanta of angular momentum or of vibrational energy in *BHJ*.[42] Dirac noted that the theory was not fully relativistic because space and time coordinates were still treated differently.[43]

In this ground-breaking paper, Dirac employed what we know as the interaction picture (sometimes the "Dirac picture", see Chapter 7), that he had introduced the year before[44] to obtain the time-dependence of the coefficients a_r and a_r^* that appear in the expansion of the total wave function in terms of eigenstates of the unperturbed Hamiltonian.

Dirac's theory was only the first step, but it was a bold step.[45] Ultimately quantiztizing the EM field would mean writing the 4-vector potential A_μ as an operator on a set of states in an occupation number representation, obeying Bose-Einstein (BE) statistics, represented as an infinite sum of Fourier amplitudes, each with a creation or annihilation operator which created or destroyed a photon in that particular state (specified wave number, polarization state).[46]

But Dirac only quantized the electromagnetic field,[47] and the process of making the wave function itself an operator, that is, actually quantizing "matter waves" by Jordan was an immediate response to Dirac.[48] Eventually these quantities become operators ("q-numbers" in Dirac's language) and the theory was quantized by requiring that they satisfy commutation relations.[49]

Thus, as Dirac was emphasizing quantization of the EM field, and treating particles separately, Jordan was concentrating on the matter field.[50] Wentzel has observed that when Jordan set out to quantize the electron field (that we would now call the "Dirac field") in 1927, it would not have been apparent to many why that needed to be done, since the nonrelativistic wave mechanics of many-electron systems was apparently understood.[51] Pauli in particular was a skeptic. And while a representation in which photons were created and destroyed may have been necessary when describing emission and absorption of EM radiation, it was not immediately obvious that the same needed to be done with electrons. Nonetheless, Jordan's approach was to quantize the matter waves or matter fields as well as the EM field, which was consistent with both wave-particle duality and the uncertainty principle. This distinction raised once again the question of whether fields or particles are fundamental, a modern view of which is that particles are just singularities in the fields.

It was in the 1927 paper with Oscar Klein,[52] that Jordan developed a Bose-Einstein description of the electromagnetic field in which the wave function $\psi(x,t)$ became an operator, satisfying (equal-time) commutation relations, and that represented full second quantization. And in the subsequent Jordan-Wigner paper, the anti-commutation relations that yield Fermi-Dirac statistics were derived. These were two of five papers Jordan published on the subject in 1927–28, including the work with Wigner and one with Pauli, both in 1928.[53] These papers firmly established second quantization of the matter waves, and laid the foundations for complete theory of quantum electrodynamics. The Jordan-Pauli paper obtained the first covariant commutation relations and introduced the invariant Δ-function that would play a central role in QED.[54] In Jordan's papers, the modern form of quantum field theory begins to slowly evolve, so that he was very nearly the most important figure in the creation of quantum field theory.

Heisenberg quickly became convinced that Jordan's approach was the right one, and eventually persuaded Pauli, the result being two important papers in *Zeitschrift für Physik* (the first running 61 pages) in 1929-30, both titled "On the quantum dynamics of wave fields."[55] In this period, especially the years 1929-32, development of the theory was taken over by Heisenberg and Pauli and then by Enrico Fermi, culminating in an influential paper of his in *Review of Modern Physics*.[56] This state of affairs, especially as given in the Jordan-Pauli and Heisenberg-Pauli papers is reflected in Pauli's *General Principles of Quantum Mechanics* of 1933.[57]

When Heisenberg and Pauli insisted that the equations of motion of field theory should be derivable from an action principle as in classical field theory, this necessitated a Lagrangian for the free electromagnetic and Dirac fields.[58] The classical form of the Lagrangian density for the free electromagnetic field, used by Heisenberg and Pauli,

$$L = -\frac{1}{4}F_{\mu\nu}(x)F^{\mu n}(x)$$

turned out to be unsatisfactory, because it led to a vanishing conjugate momentum $\pi^0(x)$.[59] Fermi's solution[60] was a Lagrangian density of the form $L = \frac{1}{2}(\partial_\nu A_\mu(x))(\partial^\nu A^\mu(x))$. Thus while Dirac's theory had been formulated in terms of the Hamiltonian, as indeed had quantum mechanics, Heisenberg and Pauli had adopted a fully covariant Lagrangian—least action formalism, and again obtained the covariant commutation relations and the invariant delta function $\Delta(x-x')$.[61] In Schweber's view ". . . quantum field theory came into being with Heisenberg and Pauli's papers . . . ",[62] though by 1932 Rosenfeld had shown that the theories of Dirac and Jordan-Heisenberg-Pauli were equivalent.[63]

We have seen that in 1930 Dirac had proposed that the negative energy states appearing in his theory were usually completely filled and that holes in that negative-energy sea would appear as positively charged particles, and so was born the "anti-electron" or "positron,"[64] which was important not only because of the immediate

problem of the negative-energy solutions, but because the developing theory of QED actually required it.[65] In the same year Victor Ambartsumian and Dmitri Ivanenko proposed that particles could be created and destroyed in elementary processes involving other particles as well as photons,[66] making the Dirac–Jordan second-quantized theory symmetric in electrons and photons.

In 1932 Hans Bethe and Fermi[67] interpreted the interaction between charged particles as being mediated by photon exchange, a revolutionary idea that would lead to Hideki Yukawa's theory of meson exchange as the source of the nuclear force 3 years later,[68] and when the muon (μ^-; "mu meson") was discovered by Carl Anderson and Seth Neddermeyer in 1936, it was initially thought to be Yukawa's particle, but turned out to be a heavy electron, not related to the force-binding nuclei. The relevant particle, the pion or pi-meson (π), would not be found until 1947. Both particles were found in cosmic-ray studies.

It was in the years 1934–1936 that Pauli and Weisskopf showed how pair production, the creation of an electron–positron pair, could be understood in terms of the quantized charged K-G field.[69] The phenomenon of β-decay had defied any similar kind of theoretical description for nearly three decades, finally yielding to Fermi's theory of 1934.[70] This theory involved a zero-range "contact force," because no particle was then known that could mediate what came to be understood as the "weak force" (see Chapter 15).

INFINITIES

Despite major successes, including Dirac's relativistic equation for the electron, quantization of the wave and particle fields by Dirac and Jordan, and theoretical insights that hastened the time when computation of real processes could be carried out, the realization, as early as 1930, that there were numerous infinities or divergences in the theory, led to widespread pessimism over the state of the theory. These included vacuum polarization, the electron self-energy, and the zero-point energy of the vacuum, and so on. Of the infinities that appeared in higher-order terms in the perturbation expansion, Pais has written that "higher order contributions are small but infinite, small because of powers of α, infinite because of the integrations."[71] This situation prevailed from 1929 until at least 1933, when the Seventh Solvay Conference was held, and even 20 years later there were still open questions.

A defining moment came with the publication of a paper by Oppenheimer in 1930 in which he showed that the coupling of a Dirac electron to the electromagnetic field involved self-energy effects (interaction between the electron and the field it generates) that were infinite. The electron self-energy was just one of the increasingly ominous infinities that plagued the theory, and Dirac was ready to abandon QED "without regrets, " adding that "because of its extreme complexity, most physicists will be glad to see the end of it."[72] Pauli thought of resorting to writing fiction out of frustration over the divergences. As Schweber wrote, "the occurrence of the divergences pointed to a deep inconsistency in the conceptual structure of QFT."[73] But it soon became apparent that the electron self-energy was only weakly (logarithmically)

divergent, offering some encouragement. Dirac's hole theory immediately changed the nature of the vacuum, out of which electron–positron pairs could be created, a process that contributed to polarization of the vacuum, something he talked about at the 1933 Solvay Conference. A flurry of papers in 1934 addressed this "vacuum polarization" due to virtual electron–positron pairs being created from the energy of the electromagnetic field, which, however, proved to be infinite.[74] Ever since the *Dreimännerarbeit* paper of late 1925**,** such infinities had been dropped or wished away, and in 1933–1934 Dirac introduced a subtraction process that offered a means, albeit a debatable one, of dealing with some divergences.[75] Attempts such as these in the mid-1930s to address the various divergences in the theory prompted Pauli to call it "subtraction physics,"[76] despite which the theory seemed to be in a moderately satisfactory state. Schweber's chapter "The 1930s" gives a good summary of the turmoil in this period, characterized both by optimism and seemingly hopeless floundering.[77] Some of this despair was lessened when the positron was discovered in 1932.

In the early to middle 1930s, the theory, although incomplete, had advanced to the point that cross sections for a few real processes could be calculated, including *e*–*e* scattering (Moller scattering), electron–positron (Bhabba) scattering,[78]and even some calculational techniques that are still used in obtaining *S*-matrix elements.[79] But these calculations were exceptionally difficult and continued to be so before "Feynman diagrams" were introduced well after WWII. As for the fine details of the development of QFT during the 1930s that were characterized more by the discovery of the problems with QED than with its successes or triumphs, the reader is referred to the books by Schweber and Pais and papers by Wentzel, already cited.[80] A loss of confidence in the theory because of difficulties with infinities, plus the hiatus due to the war, resulted in QED being reborn after hostilities ceased. Again, one of the seminal events in the postwar development of QED was the Shelter Island Conference in 1947.[81]

CONCLUSION AND POSTWAR DEVELOPMENTS

It would be too much to say that the latter half of the decade of the 1930s was one of unproductive floundering, because some progress was made in renormalizing the theory (see Schweber's chapter 9). In the early stages of the postwar attack on these divergences, speaking of what is known as the Lamb shift in 1947, Bethe wrote somewhat sardonically that "this shift comes out infinite in all existing theories, and has therefore always been ignored."[82] But the successful calculation within QED of scattering amplitudes for some fundamental processes, such electron–electron and electron–positron scattering, and despite the lurking infinities, led most to believe that it was a fundamental theory whose problems, as serious as they were, would eventually yield to a concerted attack. Indeed, as Schweber argues, the problems of infinities were very nearly solved by 1939, just as the world descended again into violence. In the end, over a decade was spent with these infinities front and center, with the caveat that the problems of Nazism and then the war itself forestalled significant progress. The successes that were achieved begin to go beyond the detail that can be treated in this work, and the interested reader's recourse is to consult Schweber's book.

The displacements, distractions, and diversion to defense issues meant that little further progress was made until 1946 or 1947, when, so to speak, the gates opened again.[83] By 1949, in a paper promoting Feynman's formulation of QED, Freeman Dyson could write optimistically that "the divergence difficulties have been at least partly overcome," and later in the same year he wrote almost jubilantly of *S*-matrix theory in momentum space that "the surprising feature of the S-matrix theory outlined in this paper is its success in avoiding difficulties . . . the well-known divergences seem to have conspired to eliminate themselves."[84] Another of the founders, Julian Schwinger, was not so optimistic, concluding in 1958 that "a convergent theory cannot be formulated consistently within the framework of present space-time concepts."[85]

Just as Dirac and Jordon independently developed transformation theory, the abstract unification of wave and matrix mechanics, thereby for all practical purposes casting quantum mechanics in a canonical form, so they also independently established the basic ideas of QFT, QED, in particular. These fundamental contributions that Jordan made, in collaboration with Born, Heisenberg, Pauli, and others, but in which generally his contributions were among the most original, dramatize his role as one of the three or four founders of both quantum mechanics and QFT, and, of course, the least well known.[86] But the torch had been passed. Most of the difficult issues of divergences were dealt with, if not totally solved, through the renormalization of mass and charge during the exciting period 1946–1960, involving a younger generation.[87]

Many of the important developments that led to the final successes of QED in the 1950s were carried out by Dyson, Schwinger, Feynman, and Sin-Itiro Tomonaga. Starting from the Lippman–Schwinger equation, introducing Wheeler's *S*-matrix, pursuing a perturbative solution, and employing the *S*-matrix reduction techniques due to Wick and Dyson, one could obtain cross sections for any QED process.

Most of us today visualize the matrix elements that appear in QED in terms of Feynman rules and Feyman diagrams, which emerged in 1949.[88] As important as these techniques were, and are, there are many other important parts to the story of how QED emerged as something approaching a finished theory by about 1953. A measure of this is the 1955 book *Mesons and Fields* by Schweber, Bethe, and de Hoffmann, based substantially on lectures by Bethe. And enough progress had been made by 1961 that Schweber wrote an entirely new, nearly 1000-page book, devoted to QFT.[89]

The problem of divergences in QED was still an active area of research in the early 1960s when interest began to shift to Yang–Mills non-Abelian gauge theories that were thought to be renormalizable and offered the hope of unifying QED and the theory of weak interactions, both of which required force-carrying vector bosons. Along with a gauge theory of the strong interaction that depended on the hypothesis of quarks and the quark model of nucleons and mesons, this meant that QFT had fully absorbed the developments of the 1930s and 1940s, some of which have been described, and was on the verge of an imposing synthesis that became the standard model. Yet the message of this chapter is that the origins of QFT lie in the first tentative steps taken while quantum theory itself was still in its infancy, by Dirac and Jordan and then by Pauli, Heisenberg and others, starting before 1930.[90]

NOTES

1. Dyson probably would have shared the prize but for the Nobel committee's restriction to three recipients. On just a small part of his contribution, that of facilitating the use of Feynman diagrams by a generation of young theorists from his position at Princeton's Institute for Advanced Study, see the paper by Kaiser (2005). Schwinger's *Selected Papers on Quantum Electrodynamics* (1958) reprints most of the important papers from that era.
2. In his part I (Schrödinger, 1926a), he rather cryptically notes that if the Kepler problem is treated relativistically, it leads to half-integral radial and azimuthal quantum numbers. In part II (1926b) he has ψ satisfying the full elliptic wave equation (Eq. 18) and introduces it again in part IV (Schrödinger, 1926e, Eq. 1). Finally, in an appendix to that paper (sec. 6), Schrödinger essentially derives the Klein Gordon equation. The orbital motion of the electron in a hydrogen atom is, fortunately for Bohr and Schrödinger, nonrelativistic, because the energies are of the order of 1–10 eV, which is about 100,000 times less than the electron rest energy of 0.5 MeV. Which is not to say that there are no relativistic effects, as fine structure has a relativistic origin.
3. Which might explain Schrödinger's reluctance to give up on a wave equation with a second time derivative, as we saw in Chapter 6.
4. See, for example, Schrödinger's "equivalence" paper (1926c).
5. Or Klein–Gordon–Fock; see subsequent discussion. Here we speak of Oskar Klein and Walter Gordon. Also Kudar and others. See Schweber (1994), p. 57. Wentzel (1949) called it the Schrödinger–Gordon equation.
6. Klein (1926a); Gordon (1926).
7. Fock (1926a, 1926b).
8. See, for example, Schweber et al. (1955), sec. 10, Muirhead (1965), sec. 4.3, or a variety of current sources. On the Lagrangian and principle of least action, see a mechanics text such as Goldstein (1980).
9. In fact, because the pion is a composite particle (quark–antiquark pair), there is no spinless elementary particle, except for the Higgs. The Nobel Prize in physics was awarded for its prediction in 2013, a century after the Bohr theory.
10. See Schweber (1961).
11. Pauli and Weisskopf (1934).
12. A commutator involving ψ and a momentum variable conjugate to it. See Schweber et al. (1955).
13. Dirac (1928a). The paper was published just over 2 years after Uhlenbeck and Goudsmit's first paper. Had things gone differently, Dirac might have had the opportunity to announce, from theory, that the electron must have an intrinsic angular momentum.
14. Dirac (1927b).
15. Dirac (1928a). The paper was received January 2, 1928. Others, including Pauli, were not far behind.
16. That is, only involving $\partial/\partial t$. Dirac (1928), Schweber (1994), pp. 56–8.
17. Dirac (1928a). See Kragh (1990), pp. 54–5.
18. Dirac developed these ideas in three papers in the *Proceedings of the Royal Society*: Dirac (1928a, 1928b; 1930b). He also published two papers in German in 1928 in which the theory of the electron was developed: *Physik. Zeitschr.* **39**, 561, and *Leipsiger Verträge*

1928: Quantentheorie und Chemie, p. 85. These are translated in his collected works (Dalitz, 1995).

19. See Schweber (1961), Mandl and Shaw (1993), among many possible sources.
20. Pauli (1927b); C. G. Darwin (1927).
21. Dirac (1928a), p. 612.
22. Dirac (1930b). It was submitted on December 6, 1929. The title was "A theory of electrons and protons."
23. Oppenheimer (1930). See also Schweber (1994), p. 66, for additional skeptics.
24. Dirac (1931).
25. Anderson (1933). There were hints of a similar particle going back to 1929.
26. In fact, Dirac's initial relativistic treatment of the interaction between matter and radiation, in which, arguably, second quantization was introduced (Dirac, 1927b), came before the Dirac equation.
27. Schweber's 75-page first chapter (1961), "The birth of quantum field theory," is an excellent introduction to the subject. Also valuable are Wentzel's article "Quantum theory of fields" in the Pauli memorial volume by Fierz and Weisskopf (1960). Another work is the symposium volume *The Birth of Particle Physics* (Brown and Hoddeson, 1983), with contributions from Dirac, Weisskopf, Schwinger, and others.
28. Jordan and Klein (1927); Jordan and Wigner (1928).
29. Schweber (1994), p. 9.
30. Schweber, op. cit. Over 1000 works, mostly research papers, are listed in the bibliography. About, half, of course, refer to the postwar era.
31. Wentzel (1960). Wentzel's little book *Quantum Theory of Fields* (1949) is largely devoid of history.
32. Schwinger (1958); 34 important papers are reprinted in this volume.
33. Pais (1986), pp. 270–96. See also Brown and Hoddeson (1986). There are many other sources and the essay review by Schweber (1995) lists most of them.
34. Of course QED is now formulated as a gauge field with $U(1)$ symmetry, as a part of the $U(1) \times SU(2)$ electroweak gauge theory and finally of the local $U(1) \times SU(2) \times SU(3)$ gauge symmetry of the standard model.
35. It has a different form in SI or "natural units." Its value is about 1/137.
36. Minkowski, "Die Grundgleichungen für die elektromagnetischen Vorgänge in bewegten Körpern" in *Nachrichten von der Georg-Augusts-Universität und der Königl. Gesellschaft der Wissenschaften zu Göttingen*, 1908 ["Basic equations for electromagnetic processes"]. Einstein (1916a) provided a full development in his groundbreaking paper on general relativity as well, but cited no one: "The foundation of the general theory of relativity" [Die Grundlage der allgemeinen Relativitätstheorie].
37. Dirac (1927b); Schweber (1994).
38. Ibid., pp. 250–1. Second quantization, turning the wave function into an operator that could be subject to commutation relations, was necessary to deal with creation and annihilation of field quanta, i.e., particles. This was necessitated by the fact that one would have matrix elements between states with different particle numbers.
39. AHQP interview with Thomas Kuhn, May 14, 1963.
40. Dirac (1983). Passage quoted in Schweber (1994), p. 33.
41. Dirac (1927b). In this work, while quantizing the electromagnetic field, he obtained the Einstein A and B coefficients describing the emission and absorption of radiation

(Einstein,1917a). Lepton and baryon numbers are generally conserved, but the hypothetical proton decay would be an example of baryon nonconservation. At a QED vertex, there will always be two fermions and a photon.

42. Born, Heisenberg, and Jordan (1926). In the context of the harmonic oscillator they appear in a somewhat obscure form in secs. 29 and 41 in the first edition of Dirac's book, and the formalism is almost fully developed in sec. 24 of *Born and Jordan* from the same year (1930), except, of course, that whereas *eigenvalues* are discussed, *eigenstates* are not.
43. John Slater, a renegade in this matter, advised students to avoid second quantization altogether. Slater (1975), p. 141. He also wrote of a kind of theorist, with Dirac in mind, "who like a magician, waves his hand as if he were drawing a rabbit out of a hat, and who is not satisfied until he can mystify his readers or hearers" (p. 42).
44. Dirac (1927b). In the interaction picture (Dirac, 1926c), the time dependence of the wave function is determined by the (transformed) interaction H'.
45. Dirac published over 40 papers related to QFT in the decade following the first paper on QED and that of the Dirac equation.
46. A model for this approach was Heisenberg's original treatment in which observables were written down in terms of a sum of oscillator terms or Fourier components (Heisenberg, 1925). This was a standard technique, of course, and the essentially quantum part consisted in discretizing these relations.
47. And only the radiation field, resulting in a theory that was not Lorentz invariant. That is, the static Coulomb field was given a separate treatment. See Wentzel (1960), p. 50.
48. Jordan (1927d).
49. Involving transformed quantities b, b^*. See Dirac(1927b), pp. 248–51. Also Schweber (1994).
50. A point made by various authors, including Bert Schroer, arXiv:hep-th/0303241, May 2003. Schweber (1994). The quote is from Schweber (1994).
51. Wentzel (1960).
52. Jordan and Klein (1927). Schweber emphasizes that initially, while employing an occupation-number representation, Jordan and Klein were considering *transitions* rather than creation and annihilation of particles. Schweber (1994), p. 10.
53. Jordan and Wigner (1928), reprinted in Schwinger (1958); Jordan and Pauli (1928). Also, Jordan (1927d).
54. Which has been called the Pauli–Jordan function.
55. Heisenberg and Pauli (1929, 1930), which had their own problems. See Schwinger (1958), p. viii.
56. Ibid, Heisenberg and Pauli; Fermi (1932), based on lectures he gave at the University of Michigan in 1930 (Schweber, 1994, p. 73). In the latter, second quantization is not evident.
57. Pauli (1933).
58. Wentzel (1960.), p. 51.
59. Heisenberg and Pauli (1929), p. 24, Eq. 45. Ibid., p. 51; Mandl and Shaw (1993), p. 83.
60. Fermi, (1929, 1930). The first paper is reprinted in Schwinger (1958), in Italian.
61. Which, as we have seen, Jordan had worked out with Pauli as well. For details, see, for example, Schweber (1961) or Schweber, Bethe, and de Hoffman (1955).
62. Schweber (1994), p. 88.
63. Dirac (1932), Rosenfeld (1932).
64. Dirac (1931). See Chapter 15.

65. Schweber's discussion of the events surrounding Dirac's hole theory and the anti-electron are very interesting (Schweber, 1994, pp. 61–70). Time-reversal invariance and Feynman's idea that positrons were electrons moving backward in time add to the necessity that positrons must exist. Blackett and Occhialini (1933), examining cloud-chamber photographs of cosmic-ray showers, essentially discovered pair production.
66. Ambartsumian and Ivanenko (1930b).
67. Bethe and Fermi (1932).
68. Yukawa (1935). Anticipated by Ernst Stuckelberg, one of the 20th century's most important theorists, but largely forgotten. Schweber's bibliography lists 34 of his works (Schweber, 1994).
69. Pauli and Weisskopf (1934); Weisskopf (1936). See Schweber (1994), p. 78.
70. Fermi (1934a,b)
71. Pais (1986)
72. Dirac (1936). This view, given in the last sentence of the paper, which was on energy conservation in atomic processes, was based in part on an unjustified faith in an experimental result.
73. Schweber (1994), p. 88. Of course the electromagnetic self-energy of a point charged particle is infinite, even in classical EM theory.
74. E.g., Furry and Oppenheimer (1934), et al. See Schweber (1994), p. 86, and Wentzel (1960), p. 58.
75. Dirac (1933, 1934).
76. Pauli and Rose (1936).
77. Schweber (1994).
78. See Pais (1986), p. 376, for references.
79. Including the so-called Casimir trick, which in its modern form involves projection operators onto positive- and negative-energy states, as well as trace identities.
80. Wentzel (1949); Schweber (1994); Pais (1986).
81. Including a calculation carried out by Bethe on a train after the 1947 Shelter Island Conference. Schweber's chapter 4 is devoted entirely to this and other contemporaneous conferences. Robert Marshak's contribution to Brown and Hoddeson (1983) includes a photograph of the participants (Marshak, 1983).
82. Bethe (1947).
83. The interesting exception is Tomonaga, whose first seminal paper was published in Japanese in 1943 in the midst of the war. It was published in English in *Progress of Theoretical Physics* in 1946 (Tomonaga, 1946) and was reprinted in Schwinger (1958).
84. Dyson (1949a, 1949b). The latter quote is from p. 1754.
85. Schwinger (1958), p. xvi.
86. Schweber's bibliography cites 24 papers by Jordan and coauthors and 26 by Heisenberg (In Dirac's case, 114!). We have noted that Jordan, alone among the founders of quantum mechanics, would not be awarded the Nobel Prize, in large measure because of his Nazi sympathies, but, as Schweber emphasizes, also because of his stature, his stuttering, which led to insecurity, and probably the fact that by 1933 he had begun to turn away from physics toward other scientific questions, including cosmology and biology. See Schweber (1994). Jordan did try to defend what was known as "Jewish physics" as against the supporters of a strictly "German physics," but there is no ignoring his ardent support of the Nazi regime. On Heisenberg's role in the German uranium program and

the extent of his collaboration with the Nazis and continuing suspicions of his physics, see Cassidy (1991).

87. For example, Feynman and Schwinger were born in 1918 and Dyson in 1923. A less than exhaustive list of the developments that led to the mature theory of the 1950s would include (1) second quantization and quantization of the electromagnetic field by Dirac, (2) quantization of the matter field by Jordan et al. and eventually quantization of the spinor field, (3) scattering as mediated by exchange of virtual photons due to Bethe and Fermi, (4) *S*-matrix theory of Wheeler and then Heisenberg; reduction of *S*-matrix elements including time and normal ordering by Wick and Dyson in 1949–1951, (5) introduction of Feynman diagrams and perturbative *S*-matrix expansion (Pocono conference, 1948), and (6) the renomalization program. See, of course, Schweber (1994).
88. Introduced at the Pocono Manor Inn in 1948. See David Kaiser's article in *American Scientist* for an extensive and lively look at the history of Feynman diagrams and their application to QED and to nuclear physics (Kaiser, 2005). For modern applications, see Mandl and Shaw (1993). The matrix elements represented by Feyman diagrams can now be mechanically computed using *Mathematica* plug-ins.
89. Schweber (1961).
90. The situation in quantum mechanics and quantum-field theory in 1933, say, was not so different from the one that Peter Bergmann observed about general relativity, according to Abraham Pais: "Bergmann once said to me 'you only had to know what your six best friends were doing and you would know what was happening in general relativity.' " In quantum mechanics and quantum-field theory, the number was more like 15. With the expansion of funding of research by governments in the postwar era, that quickly ceased to be the case.

14

FOUNDATIONS AND PHILOSOPHY OF QUANTUM MECHANICS

INTERPRETATION AND THE MEASUREMENT PROBLEM

"No science can be safely abandoned to its own devotees"—John Venn

INTRODUCTION: WHAT DOES IT MEAN?

Richard Feynman is famously supposed to have said that the philosophy of science is about as useful to scientists as ornithology is to birds. Despite the obvious hyperbole that is perhaps forgiveable in a genius of Feynman's rank, we have to admit that this view has its adherents. Is, in fact, philosophy useful to science?[1] Is that even an important question? Are the two, philosophy and science, handmaidens in the search for scientific truth, or is philosophy of science simply a gloss on or at best a reformulation of discoveries already made? Dirac's view was clear: "I feel that philosophy will never lead to important discoveries, it is just a way of talking about discoveries that have already been made."[2] It is hardly news that physicists and philosophers might not see eye-to-eye on the matter,[3] but these skeptical comments by two of the giants of quantum theory, which may or may not accurately reflect the impact of philosophy on physics, miss the point entirely. The object of the philosophy of science is not to move the science forward, though that would certainly be a happy situation, but rather to deal with meta-questions of how knowledge is obtained, what the legitimate claims of scientific inquiry are, how a theory ought to be constructed, and so on. A philosophical perspective on the process of scientific discovery has its own intrinsic importance.[4]

The philosophy of science has a long and honored history that can be traced back to Aristotle and Occam, Bacon and Descartes, Kant and Wittgenstein. . . . Just that short list covers two millennia of thought (even though none of them were philosophers of science per se) and would seem to argue for taking the philosophy of science seriously. We are thus motivated to ask first, what *is* the philosophy of quantum mechanics or, more generally, of science, and second, what role does it play, if any, in deepening our understanding of the theory, or even, perhaps, in guiding its development?

Bastiaan van Fraassen's plausible view is that the task of a philosopher of science is to "describe how the world can be the way that scientific theories say that it is."[5]

Because the scientific enterprise by its nature rests on a foundation of empirical knowledge, that branch of philosophical thought known as *epistemology* is most immediately relevant. But the larger imperatives of metaphysics are often focused on issues that arise in scientific discourse as well. Ontological questions in particular arise, involving what is real and what is not, thus having direct relevance to theories of the microscopic world. Philosophy, standing outside physics, as it were looking in, is in a position to judge what is "scientific" and what is not, to evaluate the methods used to gain knowledge of the natural world, and to sort out the claims that the entities being "observed" are indeed "real." To take just one modern example: If, and I emphasize "if," string theory is intrinsically untestable, can it be said to be a scientific theory? And in the same vein, we may well ask what the *scientific* basis is for a theory that suggests that multiple universes may have originated just as did our own, but are inherently inaccessible to us. For the most part, scientists and philosophers would be equally quick to express skepticism about a physical theory that is by its nature untestable. Yet a certain caution is due here; atomism as a theory of the nature of matter arose in antiquity when there was no possibility of verifying or falsifying it.[6] Eventually, however, by the 19th century, the philosophical questions posed by the existence of hypothetical entities not directly accessible to sense experience took a different turn when they finally could be subjected to experimental scrutiny. And in what could be the ultimate triumph of *theory*, there are now those, theorists of course, who seriously argue that in evaluating fundamental theories about the nature and origin of the universe, testability should not be the ultimate criterion.

Although the philosophy of science deals in large measure with how we obtain knowledge of the natural world and what meaning is to be attached to that knowledge,[7] we have noted that its reach is much broader and includes such problems as the nature of a physical theory, the character of the interaction between theory and observation or experiment, the meaning of and distinction between logical and observational statements, the role of induction, and so on. Thus we may ask whether any theory can claim to describe reality or is merely a way of summarizing the results of observation. Are the elements of a theory, such as particles or fields, to be taken as real or mere names?[8] These question have been lurking in the background since the time of the Greeks, who, in their description of planetary motion, were often content merely to "save the appearances"; that is, reproduce the observations.[9] This view was echoed in modern times by Pierre Duhem in the conclusion to his *To Save The Phenomena,* who wrote that "we believe today . . . that the hypotheses of physics are mere mathematical contrivances devised for the purpose of saving the phenomena."[10] Are we then entitled to ask of quantum mechanics that it do more than describe the results of measurement?[11] Although we can be sure of the answer to this question a practicing scientist would give, from the philosopher we might anticipate a more complex or nuanced answer. Einstein's very clear view, expressed in 1946 in his "Autobiographical

Notes," was that "physics is an attempt conceptually to grasp reality as it is thought independently of its being observed."[12]

The question of the reality of atoms, the ether, and even electromagnetic waves arose as debates over the nature of scientific truth were waged, led by philosopher–scientists like Ernst Mach—a positivist who denied the existence of atoms—and Duhem,[13] who separated physics from the other sciences in his analysis of how hypotheses are empirically tested. But within physics itself, quantum theory would soon raise epistemological and ontological issues that were entirely new to the philosophy of science, issues that have been debated vigorously ever since and that form the core of this chapter. In the United States, when the journal *Philosophy of Science*[14] first appeared in 1934 in the wake of the invention of quantum theory, its very first issue addressed the philosophy of quantum mechanics, reflecting the new issues raised by the theory.

The philosophical stances known as positivism, logical positivism, postpositivism, and logical empiricism, popular in the late 19th and early 20th centuries, represent different ways of evaluating the truth claims of science, in both its empirical and theoretical aspects. "Logical empiricism," dominated by notables like Rudolf Carnap, Hans Reichenbach, Karl Popper, Richard von Mises, W. V. O. Quine, and Phillip Frank (even Kurt Gödel and Ludwig Wittgenstein, who were mainly philosophers of mathematics),[15] was especially important in the first half of the 20th century, initially in Europe and then in the United States. All of these figures, like most of the founders of quantum mechanics, were born around the turn of the century (and lived at least into the 1950s) and, of course, were succeeded by their intellectual offspring. The creators of quantum mechanics, some of whom were philosophically sensitive, cannot have failed to be influenced by the intellectual ferment on the other side of the philosophy–science divide.

Although there was no real consensus among the logical empiricists or positivists, they generally agreed on the importance of sensory experience as the way to obtain knowledge of the natural world. Of special relevance to this question of the relation between experiment and theory was the influence of the late British philosopher Karl Popper, who emphasized that a scientific theory can only be falsified, not verified, by observation, essentially a rejection of simple induction.[16] Indeed, induction has always been a target for philosophers of science, as it clearly plays an important role in scientific discovery, and yet it is difficult, if not impossible, to establish a logical, inductive link between observation and theory.[17] In the face of the obvious role of induction, this seems to demonstrate that the discovery process is often more intuitive than logical. Indeed, most physicists would probably subscribe to the views of Paul Feyerabend, who in *Against Method* argued that scientific discovery is anarchic, not the result of any method and not susceptible to being reduced to a formal system.[18] What is clear, however, is that theories are not the product of observation or experiment alone. Observations are always guided by theory.

The problem of describing a physical theory might be formulated in terms of a formal mathematical structure, and a program or set of rules ("rules of correspondence") that, as it were, map the theory onto the real world. In the case of quantum mechanics since von Neumann, the canonical formalism or mathematical structure has been that

of the algebra of a Hilbert space of abstract state vectors. The rules of correspondence describe how the Hilbert-space vectors are to be interpreted as corresponding to states of the physical system, the stationary states of which system are states of definite energy, associated with eigenvalues of an Hermitian Hamiltonian operator on the space. On this point, the reader is referred to the first chapter in Jammer's *The Philosophy of Quantum Mechanics* for elaboration.[19] The formalism, what we might think of as the bare bones of quantum theory, has been relatively mature since about 1932, as was shown in previous chapters. In that sense, and with only the slightest caveat, the theory is not in question. There are, however, very deep philosophical questions that do arise, some of which we explore here. Finally, it would be folly to absolutely dismiss the possibility that these questions might at some point force fundamental changes in how the theory is viewed. Very unlikely, we might say, but not out of the question. All this being said, however, many of these issues are not peculiar to quantum theory and are not pursued further.[20]

Given the aims of the book, we adopt an historical perspective on the philosophical issues that grew up around quantum theory and do our best to confine the discussion to the period before WWII. As has been the case in the earlier chapters, we take note of the important published works on this question, mostly in the period between the wars, and as we proceed historically, such issues as the nature of scientific transformation and how theories come into being, how they are replaced, and how "revolutions" occur, that is, in Kuhnian language, "paradigm shifts,"[21] will hover over our discussions, including how such transformations are shaped or conditioned by the broader cultural context. If one likes this language, the transformation represented by the advent of quantum theory is surely as dislocating a paradigm or gestalt shift as the adoption of the heliocentric theory nearly 400 years earlier. Fortunately, or unfortunately, in many cases the resolution or at least elaboration of problems raised in the 1930s will have taken place after the war or even into the 1990s. The result will be that on several occasions, with apology, we will pursue some of these threads up to the present if it seems to shed light on questions that haunted the founders not quite a century ago.

Sociologists will sometimes argue that science can claim no more truth value than other human endeavors and that verities of science are no more than social constructs. Although scientists will no doubt reject this view—no scientist could believe that the scientific enterprise in which he or she is engaged is only a social construction—it is nonetheless clearly the case that the course of science is influenced in important ways by the culture in which it is embedded, both scientifically and in the large.[22] The reorganizing of Europe after about 1870, *fin de siècle* enthusiasms, collapse of the Weimar Republic, two world wars, and German anti-Semitism, make the influence of the broader culture especially clear in the present case. An example, albeit a unique one, of the intersection between philosophy and science, and at least potentially the impact of the former on the latter, can be found in the reaction of Soviet authorities against the Copenhagen Interpretation (CI) of quantum mechanics and even complementarity. On this, see the interesting paper of Loren Graham.[23] In the end, however, this important question is clearly outside our present remit.

In quantum mechanics, questions of the sort "what is an electron?" arise because we cannot *see* an electron with our own senses. Should we place the direct evidence of our senses above other kinds of knowledge of the natural world? When deciding whether something is or is not real, is that an important distinction? Are electrons, the most commonplace of all elements of the microscopic world, "observable?" And if not, can we nonetheless claim that such unobservable entities are *real*, because experiments involving electrons yield reproducible results?[24] These issues, which turn on how we obtain knowledge and what it means, bring together epistemology and ontology, as we have already seen.

This question of *realism* is an important and complex one, because in many fields of science—mechanics, for example, or geology—the existence of the objects being described is not in question. That this is obviously not true of studies of the world on the smallest scales prompts a division, as Duhem suggested, between the fields of science for which this is not an issue, and those in which the objects of study are not directly accessible or visualizable, and hence actually or potentially controversial. It has been argued since at least the time of Plato, and we think of Galileo's problem of convincing the church that what he saw through the telescope was real, that sense evidence does not a priori reveal reality. Although this is not an idea that appeals much to physicists, it does have adherents. But that physicists are almost universally "naive realists" is hardly surprising; a physicist who became converted to the thesis of Duhem or Quine that one cannot logically argue from empirical evidence to theoretical truth, that any experimental result could be explained in a great many ways, might well abandon physics for something more profitable.[25] In the end, the question of whether something is real—an electron or a wave function—ends up being a matter of defining "real." For something to be real it would seem that it must have an existence independent of our conception or perception of it, and scientific realists would argue that our claims about the microscopic world refer to existing, even if unobservable, entities. But there is probably no deeper philosophical question than the nature of reality, nor one more widely debated, and we do not possess the hubris (or an editor's forbearance) to try to capture the nuances of these debates here.[26]

PHILOSOPHY OF QUANTUM MECHANICS: FOUNDATIONS

As was suggested, it is not immediately clear what should be understood by "the philosophy of quantum mechanics," or what its boundaries might be. The implication is that there is a metatheory that stands above and beyond the formalism. There is no doubt that quantum theory has implications for philosophy, and surely the converse is true, if a bit harder to show,[27] but only the severest skeptic would try to argue that philosophy, and the philosophy of science in particular, has nothing important to tell us about quantum mechanics. The grumblings of Feynman and Dirac aside, we can reasonably conclude that each contributes fruitfully to the other; quantum mechanics because of the unique character of its claims and methods, philosophy because of what it has to say about its implications: ontology, epistemology and empiricism,

causality, the formal structure of theories, the relation between theory and observation, the nature of reality, the "demarcation problem," dealing with what is "scientific" and what is not, and so on.[28] It is worth noting that what counts as "philosophy of quantum mechanics" is itself far from monolithic; it might mean an exploration of quantum mechanics as a formal logical system, or perhaps the mathematical structure and its mapping onto reality, essentially the "measurement problem,"[29] which raises most clearly the fundamental implications of the theory, and so on.

From the outset, quantum mechanics has had to deal with the demands of special relativity as a theory of space and time. And an important heritage of relativity is the strongly operationalist approach to knowledge that Einstein (see Figure 14.1) offered there. In special relativity, one speaks only about the results of measurement or observation, and no meaning is to be attached to unmeasureable quantities. This is not so obviously the case with general relativity, in which concepts such as curvature of space and time, although perhaps measureable in principle, have no immediacy. But Einstein's insistence on understanding how something could be measured came to have a very strong impact on the evolving quantum theory. It was certainly a strong influence on Bohr, despite his frequent disagreements with Einstein, and it was the basis of Heisenberg's original concept of matrix mechanics, which, as we have seen, he attempted to formulate strictly in terms of observable quantities.[30] This view was

Figure 14.1. Albert Einstein (1879–1955), by permission of ETH Bibliothek Image Archive.

shaken to its core by Schrödinger's introduction of a complex wave function ("field scalar"), which was certainly not observable, though the question of the "reality" of the wave function is another issue that was debated for some time, and perhaps still is.[31] And as quantum states came to be identified with eigenfunctions of Hermitian operators on a Hilbert space, Heisenberg's goal was effectively abandoned, without rejection of its spirit. This, of course, raises the very deeply philosophical issue concerning the way the theory can be formulated in terms of an abstract mathematical structure that at best can be *mapped* onto reality, but is not "real" itself (see subsequent discussion). Again, that issue is not unique to quantum mechanics, but is much more pressing here.[32]

The role of measurement, the interaction between the observer and the system, has always been central to quantum theory for fairly obvious and practical reasons, but also because of the deep philosophical questions that arise that make it very different from measurement in classical physics. But although the problem of measurement raises these profound practical and philosophical issues, it is generally true that the practice of gathering empirical data on quantum systems is unaffected by this controversy, although it has motivated experiments specifically designed to elucidate them. Only in quantum mechanics does this question have so much resonance, as we will shortly see.

So, what "philosophical" questions *are* peculiar to quantum mechanics? We have already asked whether invisible objects such as electrons, quarks, and gluons are "real," mere names, or perhaps simply elements of an elaborate theory that could have been formulated in an entirely different way.[33] Do, or would, minds on another planet construct or deconstruct nature in the same way? The 18th- and 19th-century subjective idealists had already asked the question "does the world exist?," but quantum mechanics makes that question more urgent. It has been seriously argued that quantum theory excludes the possibility of an objective world. Such questions of interpretation hound quantum mechanics, and it would be rash to say that they have been answered, but if we accept the current consensus that the state of a quantum system is undetermined until a measurement is made upon it, then in what sense can we believe in an objective external world? If we cannot easily abandon the existence of an objective reality, it is certainly not clear how we are to retain it. In his Como lecture in 1927, Bohr said that "an independent reality in the ordinary physical sense can neither be ascribed to the phenomena nor to the agencies of observation."[34] But even in the face of these ominous questions, physicists make observations of what they believe, with at least some justification, is a real and objective microscopic world. A partial answer may be that the role of measurement in creating an external world has been exaggerated (see subsequent discussion). If we do believe that there is an objective reality independent of our observations, then quantum mechanics would seem to be incomplete, as Roger Penrose has argued.[35]

We will be exploring the evolving understanding of the meaning of the theory as we go along, but we note that much, even most, of what has been written on the philosophy of quantum mechanics, or more narrowly, its foundations and interpretation, dates from after WWII and is therefore properly outside the scope of this narrative.[36]

Finally, as we proceed we will do well to remember what Kant about epistemology: that it ought to be left to professional philosophers,[37] and adopt the humility expressed by Wigner in 1970 when he noted that "since most of us are not philosophers, we may say things that are dilettantish to true philosophers."[38]

BOHR AND THE PHILOSOPHY OF QUANTUM MECHANICS; THE "COPENHAGEN INTERPRETATION"

For nearly a half-century Niels Bohr's writings defined the philosophy of quantum mechanics; no one thought more deeply about the fundamental problems of the theory than he, and although he was not a trained philosopher and his writings can be maddeningly obtuse, for all that, they were the fundamental guide to the development of quantum mechanics during the two decades beginning in about 1918.[39] His direct influence really ended only with his death in 1962. Farmelo has somewhat gushingly described him as "the Socrates of atomic physics," who "made Copenhagen his Athens."[40]

As we proceed, we will have to confront the loose consensus known as the Copenhagen Interpretation (CI), which owes much to Bohr,[41] and to grapple again with his principle of complementarity, which was understood at the time as having important philosophical implications. And the importance of his correspondence principle was emphasized in previous chapters. So it is that, although not a formal philosopher, Bohr was as much of one as the subject had in its first two or three decades.[42] His thinking went well beyond the latest discoveries—or lack thereof—to what a theory of the microscopic world *should* be. And so the correspondence principle and complementarity, Bohr's most enduring ideas, are philosophical overlays onto the theory, just as much as they emerged from within it. The correspondence principle provided a scheme for arguing from a classical theory to its quantum counterpart (or vice versa), or at least judging whether a theory could be valid by looking at its classical limit. For that reason its significance was mainly practical, though not less important because of that. Complementarity, on the other hand, attempted to establish the general outlines of quantum mechanics as a global theory of the physical world and continues to have some currency.

But above all, it was the problem of measurement and what measurement could reveal that occupied not only Bohr, but Einstein, von Neumann, Wigner, and others during the decade or so after the formulation of the theory. It is in the measurement problem that the essentially probabilistic nature of quantum mechanics is most dramatically revealed. If it was von Neumann who in 1932 most clearly stated the problem, a crisis was reached shortly thereafter (1935) with the appearance of the paper of Einstein, Podolsky, and Rosen (EPR; see subsequent discussion)—the first serious challenge to orthodox quantum theory. But despite the sensation created by that controversy, Nazism and the war intervened, and there was new excitement from the early 1930s over nuclear physics and quantum-field theory that seems to have drawn attention away from problems of interpretation well into the 1950s. Eventually, after a

hiatus of two decades, there was a resurgence of interest, marking the start of the modern era of studies of the philosophy and foundations of quantum mechanics. In recent years philosophers of science have joined the conversation in major ways[43] at the same time that much of the writing on the subject continues to be by physicists themselves. The fact that many physicists have turned to philosophy, especially in their later years, surely shows its relevance to physics.

It is hard to dispute the point, often made about quantum mechanics, that there is no other example of a theory that is so successful and seems to be mathematically complete and internally consistent, but that no one understands.[44] There is no small amount of hyperbole here, but it is painfully obvious that this most beautiful[45] and efficacious theory of physics is built upon shaky philosophical foundations and suffers from serious controversy over its "meaning." Roland Omnès has observed that studies of the implications of quantum measurement still quote Bohr on these matters in a way that would not happen in any other field, his reflections of 80–90 years ago still having some life to them.[46] The huge volume (or what Walter Elsasser 40 years ago called "the endless stream"[47]) of papers on the interpretation of quantum mechanics makes clear the unease that many physicists feel when contemplating it.[48] Not surprisingly, many choose to look the other way, ignore the problem, and move on, heading back to the laboratory.

We may well ask why quantum mechanics needs an interpretation. Although Peder Christiansen's answer, that the goal of an interpretation is to "provide a semantics for the symbols of the mathematical formalism,"[49] may satisfy some, for most, given the goals and claims of quantum mechanics as the ultimate theory of microscopic phenomena and its implications for causality, determinism, reality, and locality, a deeper level of understanding should be our goal. But the skeptical reader would not be the first to say that no interpretation is needed. After all, an interpretation *ipso facto* preserves the formalism and predictions of a theory, in this case the standard or orthodox quantum mechanics (OQM). Is more needed?

As we have already seen, no dimension of quantum mechanics is as fraught as its fundamentally probabilistic nature. This radical feature of quantum mechanics is enshrined in what is sometimes known as the Born Rule,[50] although, as we have seen, the result was given in a much clearer form by Pauli. To this writer, at least, this understanding, that quantum theory is inherently probabilistic and ultimately indeterministic—that can be said to be at the core of the CI that began to crystallize at the Fifth Solvay Conference in 1927—was first stated, clearly and in modern terms, by Dirac in his *Principles of Quantum Mechanics* of 1930.[51] There he wrote that "the eigenvalues of an observable are the possible results of a measurement of this observable, "and in general the measurement of an observable for a given state will lead to one or other of a number of possible results. . . ."[52] This raised the question of the value or even the existence of that observable before or after measurement. In due course, this caused the lines to be drawn between "realists" or "determinists," who believed that a system does possess definite but unknown values of the observable that are *revealed* by measurement,[53] against those who claimed that the observable cannot be said to have a value until it is measured, so that its value is *determined* by the measurement. In the

latter view, which is part of the CI, a system that was previously in a coherent superposition of eigenstates of some observable, is, upon measurement, instantaneously in a *single* eigenstate.[54] This is often called the projection postulate. The future evolution of the system is then governed by the Hamiltonian**.**

As a sort of philosophical compromise, the CI has been derisively called a "gentle pillow" by Einstein and a "horse and buggy conceptual scheme" by Elsasser,[55] and tens of thousands of pages have been devoted to trying to avoid what can be seen as a sort of conceptual "trap."

CAUSALITY

Nothing about the world as we experience it, which admittedly is at a classical level, suggests that causality has to be abandoned. Yet Heisenberg believed, at least in 1927, that indeterminacy ruled it out. If the present is indeterminate, then so must be the future; how then can there be a causal connection? Bohr wrote a few years after Heisenberg that ". . . the finite interaction between object and measuring agencies . . . entails the necessity of a final renunciation of the classical ideal of causality and a radical revision of our attitude toward the problem of physical reality."[56] Philosophers have disputed that conclusion,[57] and in any case it is only partially consistent with the theory itself. Born waffled on the matter, but in his large paper on collisions, shortly after introducing the probabilistic interpretation of the wave function, he wrote that "the motion of the particles follows laws of probability, but the probability itself propagates in harmony with the causal law,"[58] which is essentially the widely held modern view. We will examine Bohr's views on the matter in what follows, but we will also see that the measurement process is definitively acausal.

Although initial conditions cannot be precisely known, given the representation of a system by a wave function ψ that is an eigenfunction of a limited number of Hermitian operators, its evolution is governed causally by the time-dependent Schrödinger equation (TDSE), or, if one prefers, the Hamiltonian. By 1930 Heisenberg seems to have been converted to this view: "If at a certain time all [compatible] data are known for a given system, then it is possible to predict unambiguously the physical behavior of the system also for the future."[59] The implications for determinism and free will, of this conclusion in particular, or of indeterminism in general, are widely debated.

To be specific, it is a fundamental tenet of orthodox quantum mechanics that an arbitrary state of a system can be expressed as a superposition of eigenfunctions of some Hermitian operator corresponding to an observable. The result of a measurement is the eigenvalue of the corresponding Hermitian operator.[60] A system, initially in some arbitrary state $|\phi\rangle = \Sigma a_j |\psi_{Aj}\rangle$, is forced into an eigenstate $|\psi_{Ak}\rangle$ of the operator A corresponding to that measured observable, with eigenvalue λ_k and with a probability $|a_k|^2$ that is the absolute square of the overlap or inner product $\langle\psi_{Ak}|\phi\rangle$. In an arbitrary state, for example, a system does not have a definite value for the total energy, but if the energy is measured, then it does have a definite value, but only the *probability* of obtaining that result can be given a priori. The wave function has "collapsed" or has been "reduced" to a single energy eigenfunction.[61] Dirac spelled this

out in the first edition of his *Principles* without making a fuss about it, noting that "In classical mechanics an observable always has a particular value for any state. This is not so in quantum mechanics."[62] A few pages earlier he wrote that "When a state is formed by the superposition of two other states, it will have properties that are in a certain way intermediate between those of the two original states." In a sense, all of quantum mechanics is right there.[63] Still, many millions of words have been written, by philosophers and physicists alike, on the issue of interpretation, the main reason being that the measurement process, is, in von Neumann's words, "non-causal."

This understanding, that observables do not possess definite values between measurements (except in stationary states)[64] and that most would argue follows directly from the Dirac–Jordan–von Neumann formalism, was not, and is not, without controversy, however. It was first seriously debated (though not in those precise terms) at the 1927 Solvay Conference among Bohr, Heisenberg, Pauli, Dirac, and Born. As we saw in Chapter 7, this amounts to the CI, a historical consensus that was achieved long before it was named. But if we accept the consensus view, the argument shifts to how a particular eigenstate is selected by measurement; how the system "decoheres," in current language, a question we will examine later. Alternative views abound., but because these alternatives all date from the postwar period, and generally from the 1970s on, we mostly ignore them in what follows.[65] But if an observable property of a system cannot be said to have a definite value until it is measured, the notion of an objective reality is clearly in play. This problem actually first arose with the appearance of Schrödinger's wave mechanics in 1926. Because the Schrödinger equation is a linear partial-differential equation, a superposition of solutions is also a solution, and already Schrödinger had an inkling of the implications of this fact: "If we like paradoxes," he wrote, "we may say that the system exists, as it were, simultaneously in all the positions kinematically imaginable."[66] This startling suggestion, that rather than merely a mathematical possibility, the state of a system is *actually* a superposition, is remarkable. And in due course Dirac provided the abstract, logical structure for the theory that enshrined these ideas:[67] But if the outcome of an observation can be predicted only statistically, and observables are not simply unknown but do not possess definite values until they are measured, the philosophical question remains: Is an objective reality compatible with quantum mechanics? Again, there is an enormous amount of recent writing on the subject, to which the reader is referred.[68]

The canonical view is that the wave function (or "state vector") contains all the information that can be known about a system, and in that sense (only) it is complete. It represents our maximal knowledge of the system (or reality?). But in another sense, the information is *incomplete*, in that the wave function can give only the *possible* results of measurement, with certain probabilities.[69] Upon measurement, it can provide us only with simultaneous knowledge of compatible (commuting) observables. Further, if for no other reason than that it is in general complex, the wave function $\psi(x)$ is not measureable; not an observable. Of course $|\psi(x)|^2$ could be said to be measureable, in the rather artificial sense that repeated position measurements on identically prepared systems could determine it, but not $\psi(x)$, with its phase information. What that says about its ontological status is a matter for debate. In what sense,

if any, is the wave function "real?" Presumably the wave function is no more real than the Hamiltonian, or the Lagrangian, but also no less real. It does not describe a "real" wave and it cannot be measured, which for most physicists, at any rate, is the test of something being real. Clearly, the answer to these questions depends profoundly on one's definition of "real."[70]

The fundamental question of the meaning (as opposed to reality) of the wave function divided the quantum-mechanical community for decades and in some quarters still does.[71] Einstein, with his own agenda, asserted in 1936 that "The ψ function does not in any way describe a condition which could be that of a single system; it relates rather to many systems, to 'an ensemble of systems' in the sense of statistical mechanics."[72] In that sense, the description would certainly be incomplete. Although this is neither the consensus view nor the canonical CI, it is not without adherents, and is known as the "statistical interpretation" or "ensemble interpretation." "Meaning," however, is a loaded term and perhaps too vague and broad to guide our discussions. For that reason we explore this idea by looking at certain critical issues that illuminate our understanding of the theory. Most important of these is the problem of measurement, as we will see.

MEASUREMENT

Commenting in 1963 on the revival of interest in foundational questions after WWII in perhaps the most important paper ever written on the subject, Eugene Wigner noted that "after the subject had been dormant for over two decades, we again hear discussions on the basic principles of quantum theory."[73] In fact, London and Bauer had addressed the problem in a serious way in 1939, just as the war was beginning, and in that work assigned an essential role to the consciousness of the observer.[74] As one might suspect, it is impossible to do justice here to the literature on the subject of measurement in quantum mechanics, which in any case is still an open question and therefore somewhat beyond the scope of this work.[75] But as arguably the central problem in quantum theory, and despite the fact that much of the discussion has taken place in quite recent times, it is not possible to avoid it altogether. By now hundreds of books have been written on the subject, even though it is likely that few of the issues of interpretation will be resolved by experiment soon, if ever. One could say that measurement is unlikely to resolve the measurement question in quantum mechanics.[76]

Quantum mechanics is an enormously successful theory with the widest application, and nothing suggests that its formalism requires serious scrutiny.[77] What remains as almost the only open question is the important philosophical one of meaning or interpretation that turns largely, but not entirely, on the thorny question of measurement and what it reveals about the theory and about reality.[78] It is probable that the uncertainty that has prevailed for nearly a century in interpreting quantum mechanics had its origin in the very rapid development of the theory, in only about 7 years, beginning in 1925. In those heady days there was little time for contemplating epistemological or metaphysical questions, though, of course, Bohr was always an exception. Arguably it was he in 1929,[79] then Dirac in the first chapter of his famous book, and,

more formally, von Neumann in 1932, who showed that the process of reduction of the wave function upon measurement was an inescapable feature of the structure of quantum mechanics. And why is this important? Because it is at odds with the notion that the time evolution of a system is determined entirely by its Hamiltonian and the TDSE (as discussed previously and in Chapter 6), describing an evolution that is deterministic and causal. This problem broke into the open as the structure of quantum theory crystalized in those crucial years 1927–1932 and was an element in the famous Bohr–Einstein debates that occurred around the time of the Fifth and Sixth Solvay Conferences in 1927 and 1930. As Bohr made it clear in his 1935 response to the EPR paper, the understanding of measurement in quantum mechanics derived directly from the Dirac–Jordan transformation theory,[80] and von Neumann made it explicit.

Thus there are two fundamental aspects to the measurement problem. The first, which we are about to discuss, has to do with the two distinct types of measurement, causal and acausal (or noncausal), that occur in OQM. The second has to do with the indeterminate nature of the quantum state and how information is obtained from measurement, involving reduction of a superposition to form a unique quantum state (the acausal process), a question we previously examined. It does appear to be inherent in the measurement process that a coherent mixture of states "decoheres" or collapses into a unique state upon measurement of an observable. This appears naturally in the Dirac–Jordan–von Neumann formulation of quantum mechanics and is an essential element of the CI. The way in which this happens is, on the other hand, quite controversial, because it must be describable from within quantum theory itself. If von Neumann could be said to have been the first to attempt to *explain* this decoherence process, that has not kept it from being a continuing conundrum. Aside from the problem of how decoherence takes place, there is also a kind of nonlocality in this description, in that if a particle is represented by $\psi(x)$, it has a certain probability of being found, upon measurement at a position x_i (or in dx_i at x_i), using a particle detector, say, and this probability may be nonzero over a very large region of space. But if the particle is measured to be at x_0, its probability of being at $x_i \neq x_0$ is instantaneously zero. Remember that it is not merely a case of finding where the particle is, but "creating" its position, speaking loosely. Or at least that is the CI.[81]

But the central paradox afflicting quantum mechanics has to do with the evolution of quantum-mechanical systems in time, which is determined by their interactions with other systems. Formally, this evolution is described, nonrelativistically, by the TDSE. Almost all interactions among physical systems are of this kind. And even if the interaction consists of an observation being made on a system, that is, a *measurement*, it is not obvious why that interaction should not be described by the TDSE. A measurement is no more and no less than an interaction between one quantum system (the system under study) and another (the measuring device or observer). Why is an irreversible, noncausal, nonunitary process, the collapse of the wave function, necessary? This is the problem posed by von Neumann in chapter VI of his book in 1932.[82] There he highlighted "the peculiar dual nature of the quantum mechanical" measuring procedure, pointing out that one is thermodynamically reversible whereas

the other is not, and worse, is acausal. These two types of interaction are his *processes 1* and 2.[83] Clearly this problem of measurement could not really be stated precisely before von Neumann and others cast quantum mechanics in the form of linear operators on a Hilbert space of vectors that were the eigenstates of a system, hence superposition, in the years after 1927; the development of this formalism was described in Chapters 8 and 9. When von Neumann emphasized this conflict between the evolution of a quantum-mechanical system under the action of the TDSE, that is, a unitary time transformation, and the *acausal* process by which measurement causes the reduction of the wave function, he cited Bohr's paper of 1929 as the place where the problem was first clearly pointed out.[84]

Von Neumann wrote that "quantum mechanics describes the events that occur in the observed portion of the world, so long as they do not interact with the observing portion . . . but as soon as such an interaction occurs, i.e., a measurement, it requires the application of . . . the acausal process. The dual form is therefore justified."[85] This is the crux of the matter and raises the question, is there a fundamental distinction between the observer and the observed? The term "Heisenberg cut" (or "von Neumann cut") is sometimes used to describe the point at which that separation is made, which for some is the line between the quantum system and the *classical* measuring apparatus, a distinction that cannot really be sustained because, although macroscopic, the apparatus is still governed by the laws of quantum mechanics.[86] If the observer and observed are considered a single isolated system, there would seem to be no role for this acausal process at all. The states of the microscopic system and apparatus are *entangled*,[87] so that measurement changes both the system and the measuring device; the state of one portion of the system cannot be described independently of the other. This, obviously, is not a simple problem. Hugh Everett posed it in the following way in his doctoral dissertation of 1957: "Can the change with time of the total system be described by [von Neumann's] Process 2? If so, then it would appear that no discontinuous probabilistic process like Process 1 can take place. If not, we are forced to admit that systems that contain observers are not subject to the same kind of quantum mechanical description as we admit for all other physical systems."[88] Everett was motivated by his interest in quantum gravity, which would apply to the universe, certainly not an isolated system. As he remarked, "No way is evident to apply the conventional formulation of quantum mechanics to a system that is not subject to *external observation*."

There being no limit to human ingenuity, many attempts have been made over the last three-quarters of a century to resolve or reframe this issue, including treating the measuring device as entirely classical or arguing that quantum mechanics does not apply to macroscopic systems.[89] Some have assigned the critical role in measurement or observation to human consciousness, but Wigner at one point perversely suggested that quantum mechanics might not apply to living systems.[90] All of the many alternative approaches are ingenious, but most, if not all, appear not to be subject to empirical test. Internal consistency, it must be admitted, is a powerful, if not conclusive, argument. When Bohm noted in his *Quantum Theory* of 1951, as have thinkers since von Neumann, that the measurement process itself destroys the coherence of the components of the wave function, it was probably the first time that this argument appeared

in a textbook and one of the first considerations of the problem since the late 1930s.[91] This decoherence apparently—in the consensus view—comes about as the result of the interaction between the measuring apparatus and the system, which introduces random multiplicative phase factors that in the end destroy the coherence.[92] Because the measuring device is macroscopic, it is an enormously complicated mixed state,[93] each of whose elements interacts with the system on which the measurement is performed, producing a highly complicated product state in which the superposition represented by the subject system loses its coherence and is reduced, essentially, to a single state. Among many examples of treatments of decoherence are chapter 7 in Roland Omnès' book[94] or chapter 3 in Joos et al.[95] D' Espagnat's *Veiled Reality* is also recommended.[96]

Paradoxically, the most radical of all proposed solutions to the measurement problem is in a way the most straightforward, namely Everett's "many worlds interpretation (MWI)."[97] In the MWI there is no collapse because all possibilities represented by terms in a superposition exist *after* the measurement; the meta-system of observer plus the system on which the measurement is being made is split into multiple copies of itself. The MWI clearly offers a solution to this most fundamental problem in quantum mechanics (Hawking is supposed to have said that it is "trivially true"), but, one would have to say, at great cost. Everett's solution seems to this writer not to meet the imperatives of Occam's Razor, and Norsen has observed that "it is hard to imagine how anyone could consider it reasonable to give up so much for so (relatively) little."[98] It is tempting to label the MWI as implausible, though that is hardly an argument.[99] The MWI has stimulated an enormous amount of discussion (and gnashing of teeth), with only modest result, but in any case these debates are all post-1957, requiring us to move on.

DOES MEASUREMENT MATTER?

The role of measurement in quantum mechanics is somewhat paradoxical. From one point of view it is the central issue. Not only is it a major conundrum, but it is only through measurement that we gain information on quantum systems, that is, the natural world, providing the data that theory has to explain. Moreover, this evaluation of measurement is entirely consistent with the operationalist point of view of much of modern physics, which posits that if something is not measureable, it is not real.[100] It also comports well with the position that is of ancient lineage, that physical theories are merely ways of expressing the relations among measurements or observation. But given that measurement is undeniably a two-way process that changes both the system and the measuring device or observer, it is important to again distinguish between von Neumann's two processes. It is fairly clear that, although measurements may enlighten us, this rather paltry human activity has little impact on the physical world as a whole, that is, the universe, in which particles and systems go on endlessly interacting without any interference from measuring devices or conscious observers (despite some controversy, this seems a reasonable conclusion). That measurement is an important

human scientific activity is beyond question, but the idea that the universe is affected in any meaningful way by our measurements is the ultimate in anthropocentrism and clearly fallacious, deep thinkers like John Wheeler to the contrary notwithstanding.[101] Assigning to human beings or even consciousness a central role in the measurement process does not alter the fact that human beings themselves play an insignificant role in the behavior of the universe. In a universe in which *all* baryonic matter makes an almost negligible contribution—much less that infinitesimal part assembled into sentient matter—and in which, therefore, humans play a totally negligible role, these anthropocentric arguments would seem to be thoroughly misguided.[102] The universe evolves, endlessly (at least on the scale of human lifetimes) one might say, causally, obeying the TDSE, and it is very unlikely that life, intelligent or otherwise, is a factor. Surely very few people believe that the universe needs human observers and their observations in order for it to exist or evolve.[103]

It is still possible, of course, to accept the previous argument that human activity and measurement in particular are inconsequential on the large scale and still believe that consciousness plays an essential role in the reduction of the state vector. This view has had some important adherents, including von Neumann and Wigner at one time or another,[104] and clearly the final stage of a measurement is when it is registered by the mind. David Chalmers has noted that "the only way to distinguish between measurement and non-measurement is the presence of consciousness." Of course most experimental data are taken automatically, by computers, and unless one maintains that the result stored in a computer is fixed only when the data file is opened, the relevance of consciousness would seem to be ruled out. Still, it remains possible to believe that the process of decoherence or reduction is a mental process, not an external physical one, and thus involves consciousness in that sense. This is not an appealing prospect for most physicists, who believe that their investigations reveal an external reality, but something like this seems to have been Heisenberg's view.[105] In that case quantum mechanics would simply be about the knowledge of human observers, as Stapp has put it.[106] Wigner speculated that measurement only increases our knowledge of a system, rather than forcing a change in it.[107] Earlier, Heisenberg had some interesting things to say about this problem in the lectures he gave at the University of Chicago in the spring of 1929, to which the reader is referred.[108]

But in the absence of human observers, there would be no quantum theory and hence nothing to interpret, and in that sense, the measurement process is obviously important. Von Neumann once wrote that ". . . experience only makes statements of this type: an observer has made a certain . . . observation; and never any like this: a physical quantity has a certain value."[109] The observer is essential, epistemologically; essential for the acquisition of human knowledge. To validate the theory (insofar as is possible), there have to be observations. It is sometimes argued that decoherence is responsible for the appearance of a classical world, and we do indeed inhabit a classical world. In the end, it is not unlikely that our experience of the world is an *emergent* phenomenon, irrevocably tied to the laws of quantum mechanics, but not easily derived from them, and perhaps not at all.

Does measurement, then, deserve the lofty place it occupies? Some would say yes, among them Freeman Dyson, who said that "As we look out into the Universe and identify the many accidents of physics and astronomy that have worked together to our benefit, it almost seems as if the Universe must in some sense have known that we were coming." This goes well beyond the so-called anthropic principle (what is now known as the weak anthropic principle, or WAP[110]) and is fraught with teleological or blatantly theological implications. And of WAP, the idea that the constants of nature had to be fine-tuned so that life could ultimately evolve, Jesus Mosterin has argued that "in its weak version, the anthropic principle is a mere tautology, that does not allow us to explain anything or to predict anything that we did not already know. In its strong version [strong anthropic principle, or SAP], it is a gratuitous speculation".[111]

Fortunately, the conceptual subtleties of the measurement problem that we have been debating almost never arise in the laboratory. In making a measurement it is rarely, if ever, necessary to ask whether one is adopting the CI or another one, perhaps the MWI.[112] Be that as it may, measurement has played a crucial role in the history of quantum mechanics, and its complexities and paradoxes have stimulated much deep thinking about the meaning of the theory.[113]

INDETERMINACY REVISITED: EPR, BELL'S THEOREM, AND QUANTUM INTERPRETATION

By the early 1930s the formalism of quantum mechanics was mature, and, one might say, essentially complete. Quantum-field theory was only in its infancy, but that was not where the interpretive battleground lay. So it was that the theoretical stability that prevailed in the years after 1932 provided the space and motivation to think deeply about the foundations and meaning of the theory. The result was that at the same time that quantum mechanics was having its greatest successes in applications to atoms and nuclei, substantial doubts about its foundations were being expressed by some of its founders, notably Schrödinger and Einstein, each of whom, in very different ways, played an important role in introducing probabilistic ideas into the theory. As it became apparent in 1925–1927 that the new theory was inherently probabilistic, Einstein brought his objections into the open, saying that "I believe that this theory represents a profound level of truth, but I also believe that the restriction to laws of a statistical nature will turn out to be transitory." From that point on the question of quantum indeterminism occupied much of Einstein's attention, culminating in the now-famous EPR paper of 1935. Although Einstein's most notable offspring, special and general relativity, have shaped our ideas of space and time, not to mention our understanding of the universe, and his legacy as one of the founders of quantum theory is unchallenged, the EPR paper and the "industry" that has followed from it, continues to assault the foundations of the theory he helped create. Already unhappy with the statistical interpretation, in 1928 Schrödinger criticized it by arguing that the idea of measuring a property of an atom was flawed because an inherently classical picture of the atom was being employed.[114] A certain longing for a deterministic world

still persists in some quarters, and let us acknowledge that there is a hefty dose of Newtonianism in us all. As late as 1972, on the occasion of his 70th birthday, Dirac, whose formal developments probably displayed the statistical character of the theory more clearly than anything that preceded it, said that "personally I still have this prejudice against indeterminacy in basic physics." But he went on to say that "I have to accept it because we cannot do anything better at the present time."[115]

Einstein's view was more unrelenting, believing as a realist that quantum mechanics was incomplete and that some deterministic theory must underlie it in very much the same way that classical mechanics underlies thermodynamics or statistical mechanics.[116] David Bohm and others carried this view further in attempting to devise a "hidden-variable" theory that would provide an underlying deterministic basis for quantum mechanics and yet be consistent with it. These theories have a long and important history, but very little to show for it. In a sense Heisenberg tried to duck the question early on by insisting that quantum mechanics should be formulated entirely in terms of observable quantities:

> It is possible to ask whether there is still concealed behind the statistical universe of perception a "true" universe in which the law of causality would be valid. But such speculation seems to us to be without value and meaningless, for physics must confine itself to the description of the relationship between perceptions.[117]

Conflict over the nature and results of measurement was at the heart of the disagreement between Bohr and Einstein at the Fifth and Sixth Solvay Conferences in Brussels and lies behind the EPR paper, which was published in the *Physical Review* in 1935, a paper that changed the discussion forever. Einstein was not alone in believing that physical systems possess certain definite properties independently of observation of them, that is, that there is an objective physical reality, independent of measurement, but this paper crystallized the arguments as no previous one had.[118] And soon the Irish physicist John Bell published his seminal paper that has framed the discussion ever since (see subsequent discussion). What Bell did was to show that EPR's arguments could be put in a form that could be subject to experimental test.

In the EPR paper the authors considered two systems in what we would now call an entangled state, with wave functions $\psi_n(x_2)$ and $u_n(x_1)$, so that a general, total wave function is the superposition:

$$\Psi(x_1, x_2) = \sum \psi_n(x_2)\, u_n(x_1).$$

The $\psi_n(x_2)$ can be viewed as coefficients in the expansion of $\psi(x_1, x_2)$ in terms of $u_n(x_1)$, eigenfunctions of an operator A. If the entangled systems are allowed to separate indefinitely, so that they can be said to no longer be interacting, and if a measurement is made on system 1, involving the dynamical variable A, thereby causing its wave function to collapse to $u_k(x_1)$ with eigenvalue a_k, then the wave function of the two systems reduces to a single term: $\psi(x_1, x_2) = a_k \psi_k(x_2) u_k(x_1)$. This alone shows that

measurement on one of two entangled systems can change the state of the other one, arbitrarily far away. EPR went on to consider the measurement on system 1 of a dynamical variable associated with an operator B, with eigenfunction v_m: $\psi(x_1, x_2) = \Sigma\phi_s(x_2)\,\nu_s(x_1)$ causing the wave function $\psi(x_1, x_2)$ to collapse to $b_m\phi_m(x_2)\nu_m(x_1)$ They note that therefore two different measurements (A, B) on the first system can leave the second system in different states, even though it is not interacting with the first. Finally, they show that $\psi_m(x_2)$ and $\phi_m(x_1)$ could be eigenfunctions of P and Q (momentum and position), respectively. Then the measurement of either A or B on system 1 will "predict with certainty" either the eigenvalue of P or the eigenvalue of Q for system 2. As they say, "This makes the reality of P and Q depend on the process of measurement carried out on the first system, which does not disturb the second system in any way. No reasonable definition of reality could be expected to permit this."[119]

In simple terms, given a pair of entangled particles moving apart in opposite directions until they could be said to be noninteracting, a measurement of the momentum of one would allow one to determine the momentum of the other without disturbing it, and the same for the position. Einstein then argued that if one could predict the value of the momentum of one particle with certainty without disturbing it, it must be that there was "an element of reality" associated with it: As it was put it in the paper, "If, without in any way disturbing the system, we can predict with certainty . . . the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity." That is, it had a definite value before measurement. The same is true of the position measurement. Even though simultaneous measurements are of course not made, the result, Einstein would say, means that the particle had a definite value of momentum and position before measurement, violating the uncertainty principle. This summary fails to capture the subtlety of the preceding development (though Einstein apparently objected to the mathematical complexity that Podolsky had introduced into the paper), but does capture its essence. The modern version of EPR, which we are about to discuss, highlights the fundamental problems much more clearly. Bohr responded to the EPR paper 4 months after it appeared in a very subtle paper based on his principle of complementarity that, however, barely addressed the experimental arrangement posed by EPR, and that, in retrospect, did not explain away the problem.[120]

A modern version of EPR was proposed by Bohm and Aharanov[121] employing two spin-1/2 particles coupled to a singlet ($s = 0$) state, that is, a linear combination of spin-up and spin-down states with equal probability: $\psi = 1/\sqrt{2}\left(\uparrow\downarrow - \downarrow\uparrow\right)$. If the two entangled particles are allowed to separate arbitrarily far (preferably a space-like separation[122]), a measurement of the spin of the first particle, say spin-up, will immediately "force" the second particle to be in a spin-down state. This is clearly a nonlocal process,[123] assuming conventional quantum mechanics is correct. This version of the EPR experiment is not only more straightforward than the original, it has now become much more than a *gedanken* experiment.

Einstein took the EPR paradox to mean that quantum mechanics was incomplete, and that there must be some underlying determinism (or hidden variables) that results in the apparent indeterminism of conventional quantum mechanics. For nearly three

decades—which take us well beyond our professed stopping point of WWII—EPR's claim that quantum mechanics was incomplete could not be falsified, though it was certainly controversial. The situation was clarified in 1964 when redundancy John Bell[124] showed that it would be possible, using a version of the EPR experiment, to decide empirically whether canonical quantum theory is correct, or at least that it would be possible to carry out an experiment that could rule out certain classes of local hidden-variable theories.[125] Henry Stapp, who has written extensively on foundational issues, has called Bell's theorem, "the most profound discovery in science."[126] In the event, Bell's theorem, or Bell's inequality, stimulated a series of experiments beginning in the 1970s[127] that appear to show that no local hidden-variable theory can provide an explanation. Elaborating on Bohm and Aharanov, Bell showed that in a local hidden-variable theory, involving spin components along *three* directions, an inequality could be derived that conventional quantum mechanics can violate. So either OQM is ruled out or a specific type of local hidden-variable theory is. Quantum indeterminism seems established, but at the rather high cost of nonlocality[128] or superluminal causality. The reader is referred to Weinberg's *Lectures on Quantum Mechanics* for details.[129] Put differently, quantum mechanics, and therefore (presumably) nature, violates locality. To emphasize: If for a long time either position, local or nonlocal, deterministic or indeterministic, was tenable, without any empirical constraints on speculation,[130] the situation has changed with these experiments, though there is still less than universal agreement over the implications of the evidence.[131] Not surprisingly, much attention is being given to the attempt to preserve locality, which seems increasingly difficult.[132] These attempts include accepting backward- or retro-causality, or a "superdeterminism" in which the free choice of the experimenter is eliminated. For the details of both the theoretical arguments and actual experiments, the reader must look elsewhere.[133]

COMPLEMENTARITY, A CONCEPTUAL FRAMEWORK

Complementarity appeared on the heels of the uncertainty principle, in late 1927. And although its historical importance is undeniable, it is rarely invoked today. This is not to say that it has disappeared from discussions of the philosophy of quantum mechanics, and Henry Folse's 1985 *The Philosophy of Niels Bohr*[134] is devoted entirely to "the framework of complementarity." Complementarity undoubtedly had a lengthy gestation period, culminating in the month-long skiing trip Bohr took to Norway in February 1927 (while Heisenberg was formulating the uncertainty principle). Bohr initially presented it to a Volta celebration in Como, Italy, in September of that year, and then at the Fifth Solvay Conference in Brussels in October. It found its way into print in April of the following year in the journal *Nature*.[135] As Jammer emphasizes, Bohr had been mulling over these issues for at least 2 years, perhaps even since de Broglie's dramatic claim of wave–particle duality 5 years before. He may have returned from skiing with complementarity substantially in hand, as he would claim, yet there is no doubt about the influence that Heisenberg's discovery of uncertainty, and especially the lengthy and sometimes heated discussions over his paper, had on Bohr's thinking.[136]

It would not be too much to say that more have been puzzled by complementarity than enlightened by it. Even in its heyday it was largely a commentary on or interpretation of an already-established theory. Bohr saw it as a fundamental overarching philosophical principle[137] that reconciled the demands of "space–time coordination" and causality, and it embodied the idea of mutually incompatible but complementary descriptions of nature. In Bohr's words, "we are not dealing with contradictory but with complementary pictures of the phenomena." He emphasized the impossibility of a sharp separation between the quantum system being observed and the observer or measurement apparatus, and that therefore all measurements on a system were *complementary*, not decisive in themselves. As Howard points out, here one can see the understanding that system and measuring device are "entangled."[138] Do systems have independent or intrinsic properties, independent of measurement? Bohr would say no.

Thus, for Bohr, complementarity functioned at multiple levels in the description of interacting systems in space and time, which makes it uncommonly difficult to state it succinctly.[139] At one level, it referred simply to wave–particle duality, exhibited by photons or fundamental particles. The two descriptions, wave or particle, are not mutually exclusive. It is possible to devise an experiment that demonstrates the particle properties of light, in the Compton effect, say, or one that exhibits its wave properties, but the particle and wave properties cannot be simultaneously observed. The same is true of what we ordinarily think of a particle.[140] At another level, the reference is to conjugate (or complementary) variables such as p and q that obey an uncertainty relation. More fundamentally, however, the imperatives of complementarity refer to the incompatibility of causality and a space–time description, which is how Bohr frequently put it.[141] As Folse says, for Bohr it was a rational generalization of the classical ideal of causality. Loren Graham has defined complementarity this way: "the quantum description of phenomena divides into two mutually exclusive classes that complement each other in the sense that one must combine them in order to have a complete description."[142] It is not clear that this helps much, but it carries a bit of the flavor of Bohr's thinking.

The ontological status of complementarity has always been in dispute, with some seeing it as no more than a philosophical gloss on quantum theory, and some, like Leon Rosenfeld picturing it as a "bedrock of the quantal description." And in the opinion of John Wheeler, who played a role similar to that of Bohr, but in the period after WWII, "Bohr's principle of complementarity is the most revolutionary scientific concept of this century and the heart of his fifty-year search for the full significance of the quantum idea." As we have noted, its meaning to Bohr was multidimensional, his expositions of it were deep and subtle, and the source of much confusion, so that much has been written on complementarity without elucidating it very much. Some commentators have essentially thrown up their hands in despair of ever pinning Bohr down on this principle. And yet it was clearly important to him.[143]

In the modern era, however, as Eugen Merzbacher has written, ". . . this epistemological view of the relationship between classical and quantal physics [i.e., complementarity] is no longer central to the interpretation of quantum mechanics . . .," and

most modern texts on quantum mechanics, such as Sakurai's or Weinberg's, do not even mention it.[144] If, however, one considers only one dimension of complementarity, that it is an expression of the fact that the complementary variables, such as the position and momentum of a particle, are defined only by measurement, that they are "potentialities" as Bohm called them,[145] and that they cannot be simultaneously measured with arbitrary precision, then it is an essential element of the metaphysics of quantum mechanics, containing the core of the Copenhagen interpretation.

Of the honored but perplexing place of wave–particle duality in quantum theory, Feynman has mused that "in reality it contains the only mystery."[146] The classic case is the two-slit experiment, in which an interference pattern is built up (at an arbitrarily low intensity, for example, one photon per day) only if it is not determined which slit the photon passes through. Beginning with a 1978 paper by Wheeler and further motivated by the possibility of carrying out actual experiments, there has been a resurgence of interest in interpretation of the double-slit experiment, particularly in its "delayed-choice" form.[147] These experiments, until recently in the form of *gedanken* experiments, highlight very clearly important issues of the interpretation of quantum mechanics, particularly indeterminism, wave–particle duality, and, if you like, complementarity.[148] They have a long history, dating back to the Bohr–Einstein debates. An example of a current experimental paper is that of Jacques et al. in 2007, and we leave this fascinating subject with the closing line of that paper: "we find that nature behaves in agreement with the predictions of quantum mechanics even in surprising situations where a tension with relativity seems to appear."[149]

For further exploration of the topic, the interested reader is referred to the paper by Scully et al., titled "Quantum optical tests of complementarity,"[150] and to the Nobel Prize–winning work of Haroche and Wineland involving experiments of this sort.[151] But as fascinating as this work is, and despite its relevance to an understanding of Bohr's complementarity, these issues are well beyond the scope of this chapter, both in their details and in chronology, and we must move on.

CONCLUSION

It is not too much to say that indeterminacy is the defining characteristic of quantum theory (see Chapter 7). Although it is clear how this came about theoretically, there continues to be a debate over the extent to which the ground may have been prepared, or the way in which the reception of indeterminacy may have been facilitated, by the larger culture. Even a cursory review of the way in which the standard or orthodox interpretation of quantum mechanics came about gives strong support for the view that it emerged entirely from within the theory: the linear nature of the Schrodinger equation, hence superposition, followed by transformation theory, and ultimately the uncertainty principle.[152] But one still may ask how it was that this radical idea, indeterminism, gained a foothold so quickly? Paul Forman, in what is known as the "Forman thesis,"[153] has argued that the reception of quantum mechanics was due in large part to the reactions against materialism, rationalism, and strict causality in the postwar Weimar Republic (1919–1933).[154] This is part of the old "internal versus

external" debate, in which, again, historians and sociologists will emphasize the social and cultural milieu that shaped the context for scientific progress, whereas the scientist often will see innovative ideas as springing from internal theoretical inconsistency or conflict between experiment and theory (see the first three chapters). It should go without saying that both factors will ordinarily be important in varying degrees.[155] In our case, we can argue that conditions that facilitated the reception of a radical theory had more to do with what was happening in European culture as a whole, from *fin de siècle* Vienna through the avant-garde movements in art, music, poetry, and fiction in the years leading up to, and immediately after, WWI.[156] If this argument fails to deal with the specific issue of indeterminism, it is not surprising that a cultural dislocation as large as that wrought by turn-of-the-century radicalism, as well as the war, would foster radical thinking, especially by a younger generation.[157] There is clearly room for serious contemplation of these influences, both on the internal side, where the completion of the program of 19th-century classical physics made it possible to address the annoying and lurking problems described in the first chapter, and on the cultural side, where an increasingly modern spirit generated an optimism that finally foundered on the rocks of WWI.

As I hope to have shown in this chapter, the most challenging philosophical issues facing quantum mechanics focus on the almost inseparable questions of interpretation and measurement. There is some irony here, of course, because there is essentially no argument about the empirical claims of quantum mechanics despite a great deal of controversy over the *meaning* of the theory. Measurement is the crux of the problem of interpreting quantum mechanics, something that was the case in the 1930s, and is no less true today. In classical physics the problem of measurement is a merely practical one, because in principle, at least, one can measure any physical quantity such as position or momentum with arbitrary precision. For example, the position of a particle could be determined by scattering light of vanishingly low energy from it, thus producing only an arbitrarily small disturbance in its position or momentum.[158] For this reason the role of measurement and the way in which it might interfere with a system has never been an issue in classical mechanics; it was a simple "registration of a fact."[159] Bohr seems to have been the first to recognize this as a problem in quantum mechanics resulting from the fact that light consisted of energy quanta, so that the minimum energy or momentum transferred to a particle in such a measurement was that of one photon.[160] The implication was that simultaneous knowledge of the position and momentum of a particle with arbitrary precision was impossible in principle, that there is a minimum size of phase-space cells.[161] This idea was codified only as part of quantum theory with the advent of Heisenberg's uncertainty principle of 1927, even though the connection between these two ideas, disturbance and uncertainty, is often misunderstood, as we saw in Chapter 7. Considerations of this kind led, as we have seen, to the famous debates between Einstein and Bohr, and the debate continues.

In contemplating the implications of quantum mechanics, we can explore further whether quantum mechanics eliminates determinism and or causality; but von Neumann's process 1 is clearly acausal.[162] Does quantum mechanics finally provide a convincing argument for that last great hope of mankind, free will? Arthur Eddington

thought so in 1929 when he wrote, speaking of the modern developments, that "science thereby withdraws its moral opposition to free-will."[163] Although these (and other) questions of interpretation have haunted quantum theory from almost the very beginning, it is not clear that a satisfying solution is nearer than it was 80 years ago. It is, however, possible to see these issues in a larger context. As we have noted, it takes an extraordinary amount of hubris to imagine that intervention by human—or for that matter, intelligent—observers, who represent a miniscule and irrelevant part of the universe as a whole, play any significant role in its nature and evolution. Furthermore, we—most of us at any rate—accept the existence of a real, objective universe that we have explored, in some sense, from the scale of the Planck length to that of the "known" universe (13.8 billion l.y.). Any other view makes the enterprise we have been discussing meaningless, little more than an exploration of the brain. Bernard d'Expagnat prefers a "veiled reality," or a "near reality," but this distinction has to do with how we *perceive* reality, rather than reality itself.

Of course we can maintain the existence of an objective external reality and still believe that we cannot know it, or that quantum theory cannot claim to be a description of it, but is only a way of connecting past and future observations, as d'Espagnat put it, calling the view "mathematical positivism."[164] In any case, it is extraordinarily unlikely that our view of reality, expressed in our theories, has anything but a very limited range of validity; Plato's cave comes to mind What we describe is real, but our description of it is a mere simulacrum, a "human point of view on reality."[165] If this is so, there is an objective reality, independent of human observation, but all we can know of it is what we learn from observation, and for several reasons, that is at best only an *element* of reality. In that limited sense, Wheeler was right in that we create the world as we observe it, but only in that sense.[166] These will always be profound questions.

Finally, in defense of the possibly dubious proposition that a look at current attempts to formulate a new orthodoxy that does away with indeterminism and collapse may actually shed some light on the problems the founders faced in the 1930s, I will so indulge myself, albeit briefly. It is probably true to say that almost no one who has thought about these issues is entirely satisfied with the answer provided by OQM, that is, essentially the CI.[167] Most rational people, including those who fully accept the formalism, will find it difficult to embrace the kind of ontological contingency that is part of OQM. It obviously conflicts with the world as we experience it on the macroscopic scale. There is, of course, precedent for this seeming disconnect between the microscopic and macroscopic worlds in in the time reversibility of the former[168] and the quite evident "arrow of time" in the latter, the fact that, at least statistically, entropy never decreases in real processes. An approach that effectively "ducks" the problem is to take the positivist approach of special relativity and say that we are not entitled to ask what happens before or between measurements. An easy way out, which is to assert that dynamical variables do have definite values and that a superposition is only a measure of our ignorance, an escape that was tried very early on, is one that is difficult to reconcile with the mathematical structure of quantum mechanics, and even experiments.[169] Of course the easiest escape of all is to suggest that the theory is wrong, and

so the interpretation is beside the point. Until experiment forces one to look in this direction this option can be put aside, but a reasonable historical perspective on the survivability, intact, of any theory, might give one pause.

These issues are mentioned here—even though they have been fruitfully addressed only in the last two decades and are therefore not properly part of the history being told in this volume—because they represent the possible resolution of a problem that has haunted quantum mechanics for 80 years. The origins of the current discussions of the process of decoherence can be found in von Neumann's 1932 classic, leading almost inexorably to the first serious attempts to treat this phenomenon in detail, beginning in the 1950s, with the vanguard being Bohm's 1951 book and Heisenberg's *Physics and Philosophy* of 1958.[170] Finally, in the conclusion to an unusually thorough discussion of the measurement problem in what is ostensibly a textbook, written not much over 3 years ago, Steven Weinberg concludes with the pessimistic view that "today there is no interpretation of quantum mechanics that does not have serious flaws, and . . . we ought to take seriously the possibility of finding some more satisfactory other theory, to which quantum mechanics is merely a good approximation."[171] Some of these issues arise with particular clarity and immediacy in analyses of simple quantum systems in quantum computing, but again these questions go far beyond our self-imposed limit of physics in the pre–WWII era. It remains the case, however, that despite modern developments, almost all of the important questions we have discussed had been raised in the decade or so before that war and thus naturally fit into this narrative. An important qualification to this statement comes from recent developments that have begun to move the discussion from the realm of philosophy to the practice of experimental physics.

One may well ask whether it is possible for a theory, however accurate its predictions may be, to long survive when its foundations are poorly understood. In this case, the answer seems to be "yes." At the dawn of the 21st century, there is no significant reason to doubt the validity of the consensus view of the structure of quantum theory, with only the qualification of historical contingency. It is an insight as much from history as from philosophy that one should view dreams of a final theory or "theories of everything" with a healthy dose of skepticism, and that applies to quantum theory as fully as to any other view of the physical world. It may be argued that the issues of interpretation are thereby made more salient and, in particular, the nature and implications of the measurement process, because it may be there that the limits of the validity of orthodox quantum theory may be revealed.

In short, our understanding of quantum mechanics continues to be in flux and the issues that have been raised are far from settled. It may be that as classical beings, we are just unable to accept the innate "wierdness" of quantum mechanics and what it says about the world. It remains possible that the inevitable confrontation of quantum theory with general relativity will be the event that, in reframing the theory, will answer these questions. The ironic thing is that the very success of quantum theory is what makes it impossible, at present at any rate, to imagine an *experimentum cruces* that could decide among the alternatives. To which the physicist may say, "so be it," whereas the philosopher merely shakes his head.

NOTES

1. This chapter is, of course, a history of the philosophical issues that arose in the period of interest, 1925–1940, or questions whose present importance have their origin in that period. That is, it is not in any sense a general survey of the philosophy of quantum mechanics.
2. Feynman's supposed quote is unsourced and may be apocryphal. On Dirac, the AHQP interview with Thomas Kuhn and Eugene Wigner, May 6, 1963. Hawking's statement that "philosophy is dead" cannot be taken seriously.
3. One might consider the example of Haag's Theorem, whose implications for QFT have been explored by philosophers but mostly ignored by physicists. See Roman (1969), sec. 8.4.
4. That is, philosophers and scientists ask different questions.
5. Van Fraassen (1981). More strongly, he asks, "Could the world be the way quantum theories say it is?" Finally: "The danger that spurs us on is that a theory we all love and cherish will turn out to admit of no reasonable interpretation at all." See his *The Scientific Image* (1980) on the reality of objects in the microscopic world.
6. Lucretius's *De Rerum Natura* of the first century BCE is a well-known example, as is Newton's atomism in the *Optiks* of 1703. But chemical atomism is an early 19th-century development (Davy and Dalton, for example). See Purrington, 1997.
7. There are larger questions, as Jammer points out, including what it means to interpret a theory. Jammer's 40-year-old book (*The Philosophy of Quantum Mechanics*, 1974) continues to be *the* best exploration of the philosophy of quantum mechanics.
8. There are, of course, disputes over what "reality" means. See, especially, Norsen (2007).
9. Need a theory be "true," or just "useful?" Dirac (1930, p. 7) wrote that "the object of quantum mechanics is to extend the domain of questions that can be answered and not to give more detailed answers than can be experimentally verified."
10. Duhem (1908, 1914).
11. Which indeed is a positivist view held by some, that quantum mechanics is merely a scheme for calculating the outcome of experiments. David Mermin had his own adivce: "shut up and calculate!" Mermin (1989). London and Bauer (1939) wrote, in somewhat the same vein, that "physicists are to some extent sleepwalkers."
12. "Die Physik ist eine Bemühung das Sciende als etwas begriflich zu erfassen, was unabhängig vp, Wahrgenommen-werden gedacht wird." In Schilpp (1949), p. 81, translated from the German by Schilpp.
13. They died in the same year, 1916.
14. The *Journal of the Philosophy of Science Association*.
15. Though it is difficult to summarize their disparate views on science.
16. Popper (1935). Hume was one of the first important critics of induction.
17. Laplace wrote that "it is difficult to estimate the probability of the results of induction," and in the same vein, John Maynard Keynes noted that "We know that the probability of a well-established induction is very great, but when we are asked to name its degree, we cannot." Both quoted in Polya (1954).
18. Feyerabend (1975). See the *Stanford Encyclopedia of Philosophy*, entry on PF.
19. Jammer (1974).
20. For some of these issues, chapter 1 in d'Espagnat (1995), titled "Philosophy and physics," is recommended. D'Espagnat was a student of de Broglie. At the textbook level, see

Couvalis (1997). It should be noted that the messy practice, or method, of discovery, is quite different from the context or crisis that may have given rise to it. This may be a faulty analogy, but it is like the difference between climate and weather.

21. Kuhn (1962).
22. As *New York Times* writer George Johnson recently put it, adherents of this postmodern view see science as "just another tool with which western colonialism extends its cultural hegemony;" and "science doesn't discover knowledge, it manufactures it." For an overview, see Giere (1999), especially the essay "Science wars in perspective," and also p. 43.
23. Graham (1985).
24. As for the separate question of what an electron *is*, what does it mean to say that the electron can be both a particle *and* a wave? Is it a singularity, nothing but the excitation of a field so that it is the field that is real, or is it perhaps the vibration of a *string*?
25. Duhem (1908,1914). On the other hand, Quine has spoken of the "tribunal of sense experience." I would not presume to try to summarize Quine's subtle arguments on these issues.
26. See Krips (1987) for example.
27. Imre Lakatos (1971) wrote that "without science, philosophy is null; without philosophy, science is blind." He was not the first to make this claim. He taught at London School of Economics with Popper, Agassi, and Feyerabend, and edited the *British Journal for the Philosophy of Science* in the early 1970s. Of philosophy, Adam Kirsch has recently written that "philosphers are people who . . . feel compelled to make the obvious strange."
28. I will not at this point cite any of the many books on the philosophy of science; the bibliography will have to suffice. On the other hand, I recommend an article by Phillip Frank on the philosophy of science and how it might be taught to physicists (Frank, 1947). In talking about "revisionist metaphysics" in a review of a book on quantum gravity, Michael Redhead says that "at this level of enquiry, physics rapidly merges with philosophy. Redhead (2002).
29. On quantum logic, see, for example, Beltrametti and van Fraassen (1981).
30. Although see the fascinating exchange between Heisenberg and Einstein that the former recounts in his *Der Teil und das Ganze Gespräche im Umkreis der Atomphysik* (1973) [*The Part and the Whole*]. When Einstein objected to the idea that a theory could be based only on observable quantities, Heisenberg, "astounded," asked "I thought that exactly this idea was essential for your theory of relativity?" Translated in Joos et al. (2003), where the full quotation is given as well as the original German. Einstein's answer was, as van der Waerden rendered it, ". . . maybe I have made use of this kind of philosophy, but still it is nonsense." In Mehra (1972), p. 262. See also Stapp (1990); the oft-repeated quote is originally from a 1974 lecture by Heisenberg.
31. Though of course the measurability of $|\psi|^2$, in some sense, mitigates this a bit. Does unmeasurability make it "unreal?" See "objective collapse theories."
32. Bueno and French (2012) is especially relevant here.
33. Gluons, and indeed quarks, being undetectable in even more profound ways than the electron.
34. Bohr (1928). This quote is actually from his *Nature* article published in April of the year following his Como lecture. On Bohr and reality, see Folse (1987).
35. In the preface to the 2005 re-issue of Pais's *Subtle is the Lord* (1982).

36. I will have to plead guilty to violating this commitment much more egregiously in the present chapter than in any other, and apologize for the indulgence. The justification, if there is one, is that although most of what has been written on this issues dates from the last four decades or so, all or most of the issues were first raised between 1932 and 1941 and seem to demand an answer of sorts.
37. Elsasser (1971), p. 200.
38. Opening an Enrico Fermi summer course on" The foundations of quantum mechanics" in July of that year. In d'Espagnat (1971), p. 1. A valuable collection that explores both the philosophical and historical context is Evans and Thorndike (2007). See also the important writing of B. C. van Fraassen and Michael Redhead.
39. Henry Folse (1993) demurs strongly from Pais's assertion that Bohr was "one of the major twentieth-century philosophers," undoubtedly a sound judgment, though if one considers impact or influence rather than contributions to philosophy per se, Pais's claim deserves serious consideration (Pais, 1991). There are other critics, as well, including Mara Beller, whose writing drips with sarcasm when discussing Bohr and the hero worship that was sometimes lavished on him (Beller, 1999). This historical revisionism fails, I think, to understand Bohr's demonstrable influence at the time.
40. Farmelo (2009).
41. Though, somewhat surprisingly, nearly as much to Heisenberg. An interesting take on this is Don Howard's "Who invented the Copenhagen interpretation? A study in mythology" (2004). That the literature on the CI is vast should come as no surprise.
42. On Bohr's philosophical education, see Christiansen (1987), who points out the influence on Bohr of Harald Høffding. Weisskopf (1985) quotes Bohr as observing that "physics in an honest trade; only after you have learned it have you the right to philosophize about it." See also Weisskopf's comment of Bohr, that "he suffers as he thinks."
43. At the risk of being superficial, a few important philosophers of science of our time, in addition to those mentioned in the text, include, Ian Hacking, Mary Hesse, Nancy Cartright, Imre Lakatos, John Norton, Michael Redhead; there are many others.
44. In 1970, at the Enrico Fermi International School of Physics on Foundations of Quantum Mechanics (d'Espagnat, 1971), Bryce de Witt (1971) said that although "forty-five years have elapsed since Heisenberg first unlocked the door to the riches of modern quantum theory, agreement has never been reached on the conceptual foundations of this theory." Jauch (in the same volume) argued that it had "no parallel in the history of science" (p. 20). Feynman said ". . . I don't understand it . . . nobody does" (Feynman, 1988).
45. Perhaps thermodynamics is more beautiful; Einstein would have thought so, as much for his distaste for quantum mechanics as for his love of thermodynamics.
46. Omnès (1994), p. 81.
47. Elsasser (1971), p. 199.
48. Because the theory can—with caution—be regarded as "complete," most writings on the formalism are in the form of textbooks, which are probably outnumbered by books on the interpretation of quantum mechanics by a factor of 10. There are, of course, many technical monographs on specialized topics such as quantum optics, quantum computing, and so on.
49. Christiansen (1987).
50. Many attempts have been made to remove it from the realm of a postulate (perhaps), to the status of a proof.

51. Dirac (1930), secs. 3 and 4, pp. 7–14. The Fifth Solvay Conference was held in October 1927, the sixth in 1930. The first conference was held in 1911, and there were physics conferences in 1913 and, following the war, in 1921, and thence every 3 years through 1933, all in Brussels. On the Solvay Conferences (*Conseils Solvay*), see Mehra (1975), and Bacciagaluppi and Valentini (2009). They continue to this day, having been resurrected in 1948 after a 15-year lapse.
52. Dirac (1930), chapter III, beginning on p. 35; and p.31.
53. See the following discussion of the famous EPR paper; but to anticipate: "If without in anyway disturbing a system, we can predict with certainty . . . the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity." Perhaps more has been written on realism than on any other issue in philosophy of science. See Leplin (1984), which includes a comment by Arthur Fine that "realism is dead." In the philosophical literature, there are "hard" and "soft" realists. See Krips (1987).
54. The philosopher of science Don Howard (2004) has argued that the standard CI, with collapse of the wave function or wave packet, owes more to Heisenberg than to Bohr and is to a significant degree a product of the 1950s. But whether the CI comports with Bohr's views or not, by 1930 in Dirac's hands, if not before, the essential ingredients are there.
55. On the other hand, von Weiszäcker (1987) has made the point that "as far as CI [Copenhagen interpretation] was successful in its purpose it *is* quantum theory. As far as it needs further semantical elucidation of its own terms nobody has so far understood quantum theory."
56. Bohr (1935), p. 697.
57. See Jammer (1974), sec. 3.4.
58. Born (1926b).
59. Quoted in Jammer (1974), p. 76.
60. There are as many such superpositions as there are observables. Usually the superposition of interest will involve eigenstates of the Hermitian operator corresponding to the observable one is interested in, e.g., the energy. The measurement process can represented mathematically by the operation of a projector onto that state. The details of the measurement complicate the matter enormously, e.g., it may involve counting particles absorbed in the experimental apparatus, the energy absorbed in a detector, etc.
61. The many-worlds interpretation sees the matter differently, and in any case the question is "how does that collapse or decoherence come about?
62. Dirac (1930), p. 31.
63. Ibid., p. 8. If that statement sounds a bit "heretical," one should read all of his p. 8. In his fourth edition, Dirac notes that "the intermediate character of a state formed by superposition thus expresses itself . . . , not through the result itself being intermediate between the corresponding results for the original states" (p. 13). Which is not to say that there is no controversy. Stay tuned.
64. So that immediately following an energy measurement, the system is in a superposition of position eigenstates, for example, such that the result of a position measurement can be predicted only statistically.
65. These include the so-called GRW or "spontaneous collapse" theory, modal interpretations in which there is a "value state" in which definite values of the relevant observables do exist before measurement, "objective collapse" theories, and, notably, the many-worlds interpretation (MWI). On the value state approach, see de Muynck (2002). For one modern perspective, see Adler (2014).

66. Schrödinger (1926e), p. 120 in the translation (Schrödinger, 1928). It is rather remarkable, is it not, that at this early stage, Schrödinger should take this seriously as a property of nature?
67. Clearly presented in the first edition of his *Principles* (1930).
68. Krips (1987), especially Chapter 6. Also Norsen (2007), and of course the books by d'Espagnat and Omnes, among others.
69. Some of which, of course, have probability unity, as in immediate, successive measurements of an observable. At this point the reader should be cautioned that the issue of probabilities, although seemingly transparent, is not. There is the question of probability as a measure of ignorance or frequency and whether a computed probability is a property of a single system or an ensemble. See Krips (1987), chapter 2, sec. 4, and p. 65, for an elaboration of these arguments that would carry us too far afield if we were to pursue them, though they do shed some light on the historical record. We adopt the "frequentist" interpretation, after von Neumann.
70. To the Platonist, it might be that nothing is more real than the wave function.
71. See, for example, Aharanov et al. (1993). Also "relational quantum mechanics" or the informational interpretation of the wave function, and so on.
72. See the statistical interpretation of Ballantine (1970). Also the arguments in Elsasser (1971), including those of Rosenfeld. Krips (1987), p. 60, discusses the problem, including the opposing view. See Einstein (1954), p. 290. Also Jammer (1974), chapter 6, n. 128. This view was echoed by Elsasser (ibid., p. 213): "a wave function does not refer to an individual object at all."
73. Wigner (1963). An early analysis is de Broglie's *The Theory of Measurement in Wave Mechanics* of 1957, in French. See, as well, Andrade and Silva (1982) and numerous de Broglie references therein.
74. London and Bauer (1939).
75. The literature is vast, but for a comprehensive treatment one might consult Omnès (1994). Other sources include d'Espagnat (1971, 2006).
76. The best source of original papers on the subject through the 1970s is Wheeler and Zurek (1983). John Bell argued against the use of the word "measurement" (as opposed to "experiment") in his book *Speakable and Unspeakable in Quantum Mechanics* (2004). See also Bell's profound "Against Measurement" (1990), and Lyre (1998).
77. What limits there are to its validity are obviously unknown, but reconciling quantum mechanics and gravitational theory may reveal those limits.
78. Although the first question must be, "what constitutes measurement?"
79. Bohr (1929) in *Naturwissenschaften. Naturwissenschaften*, like its English-language counterpart, *Nature*, published weekly.
80. Bohr (1935). The EPR paper is subsequently discussed at length, and, of course, Bohr's response.
81. For a skeptical view of decohence, see Adler (2003) and many references therein.
82. Von Neumann (1932), pp. 417–18. Evidently von Neumann was not yet aware of the issues posed by measurement when he wrote his important papers of 1927.
83. Von Neumann (1932), pp. 351, 418. These page numbers are in the 1955 English version. For a more formal analysis of the incompatibility of the two processes, see Jauch (1971), pp. 41–2.
84. Von Neumann (1932) pp. 417–20 in the 1955 translation. Also Bohr (1929). Dirac (1930) was the first to make the point in print. See also Wigner (1971), p. 8. There is also the thorny

question of the measurability of an arbitrary observable associated with an Hermitian operator. That is, can it really be done? An obvious example is position.

85. Von Neumann (1932), p. 420 in the 1955 translation. In turn, von Neumann cites Bohr (1929).
86. Bohr's position was somewhat equivocal, but he wrote in the published version of his Como lecture (Bohr, 1928) that "no independent reality in the ordinary physical sense can be ascribed to the phenomenon nor to the agencies of observation."
87. If two particles or systems are entangled, their state cannot be written as a simple product, and a measurement on one determines the state of the other.
88. Everett (1957). Everett died of a heart attack in 1982 at age 51, presumably the result of heavy smoking and obesity.
89. The first being a view apparently held by Bohr and perpetuated by Landau and Lifshitz in their *Quantum Mechanics* (1958), p. 22. On the question of quantum mechanics and macroscopic measuring devices, see Fock and Ludwig, cited in Wigner (1971), pp. 7, 14. See also Wigner (1963) in which the macroscopic character of the apparatus is crucial.
90. Wigner (1971), p. 17. I think we have moved beyond this. But on the role of consciousness, see Wigner (1962). See also the so-called "many-minds" interpretation of Dieter Zeh (Zeh, 2000).
91. Bohm (1951), pp. 585, 600.
92. This can be described as a transition from a product state $|\psi\rangle|\varphi\rangle$: (1) $|\psi\rangle|\varphi\rangle \rightarrow \Sigma\, c_n |\psi_n\rangle|\, \varphi_n\rangle$; (2) $\rightarrow \Sigma\, |c_n|^2 |\psi_n\rangle\langle\psi_n|$; (3) $\rightarrow |\psi_n\rangle$. Here $|\psi\rangle$ and $|\varphi\rangle$ are arbitrary states of the system and measuring apparatus before measurement, $|\psi_n\rangle$ and $|\varphi_n\rangle$ are the final ("collapsed") states. Step (2) gives the density operator for the system ("weak von Neumann projection"); the system in now in a mixed state. Step (3) is the collapse to the state $|\psi_n\rangle$. ("strong von Neumann projection"). Courtesy of an unknown Wikipedia author, but see Wigner (1983). As von Neumann (1932) wrote, "since the states go over into mixtures, the process is not causal" (p. 418). On decoherence, see Joos et al. (2003) and references therein. For a clear and incisive summary, see Weinberg (2013).
93. Which requires a density operator formalism, ultimately due to von Neumann. Density operators are discussed in most texts, including Gottfried (1966), sec. 20. See also d'Espagnat (1995), chapter 6, as well as our Chapter 8.
94. Omnès (1994).
95. Joos et al. (2003).
96. d'Espagnat (1995).
97. Or "relative state" interpretation. Sometimes known as Everett–Wheeler–Graham (Everett having been a student of John Wheeler at Princeton). Good sources are B. DeWitt (1971) and DeWitt and Graham (1973). Also a *Physics Today* article by DeWitt (1970). Current advocates include David Deutsch, who was a student of Wheeler. See Deutsch et al. (2005). The statement has been made that "this work will go down as one of the most important developments in the history of science" (Albrecht). There are, of course, other views. Everett's PhD thesis, which was published in its entirety in *Revews of Modern Physics* (Everett, 1957), was nine pages long. On Everett, see Byrne (2007, 2010). Everett spent all of his subsequent career in the defense industry.
98. Norsen (2007), p. 334.

99. In this connection, one might consider a comment by Gertrude Stein about modern art that Wheeler invoked in a discussion of quantum phenomena, which seem "implausible": "It looks strange and it looks strange and it looks very strange; and then suddenly it doesn't look strange at all and you can't understand what made it look strange in the first place" (Wheeler and Zurek, 1983, p. 185). Everett clearly believed that the other "branches" not realized in the measurement were equally real: "From the viewpoint of the theory all elements of a superposition (all 'branches') are 'actual,' none any more 'real' than the rest." A note added in proof, Everett (1957), p. 459. Testability is obviously an issue, but as already noted, atomism as promoted from Lucretius to Newton and beyond, was not testable, nor for that matter, was the Copernican theory. But the MWI is likely intrinsicially untestable. See also Osnaghi et al. (2009).
100. For example, Berkeley's "esse est percipi"; "to be is to be perceived."
101. Wheeler would have disagreed, of course. For example, "No elementary phenomenon is a phenomenon until it is a registered (observed) phenomenon." Wheeler in Wheeler and Zurek (1983), p. 192. This work, *Quantum Theory and Measurement*, reprints most of the important works on the subject, up to 1983, in its 800 pages. See the "strong anthropic principle." A source would be Barrow and Tipler (1988).
102. On this view, the MWI would seem particularly untenable.
103. Although, in fact, there are many who do, that seems to be more a matter of faith than science. Baryonic matter makes up about 4% of the mass energy in the universe, and in the solar system the ratio of the mass of brain matter to the total mass is on the order of 10^{-20} to 10^{-22}.
104. For example Wigner (1962) and "Are we machines?," Wigner (1969).
105. Heisenberg (1958). It also assigns to the human observer a status not shared by a detector or other measurement device that might be taking the data and hence, presumably, effecting the decoherence. We have earlier taken note of the "many-minds" interpretation (n. 86).
106. Stapp (2007). Then the wave function would, rather than describe a system, simply express our knowledge of it. Is there a difference?
107. Wigner (1963).
108. Heisenberg (1930). See also London and Bauer (1939).
109. Von Neumann (1932) p. 420 in the 1955 translation.
110. Whose pedigree can be traced to at least Dicke in 1961, Collins and Hawking (1973), and Carter (1974).
111. Mosterin (2005). If observers play a decisive role in the universe, does that mean only human observers? What about chimpanzees or dogs? What about life elsewhere in the universe? The SAP does have adherents. See Barrow and Tipler (1988). On the supposed anthropic prediction by Hoyle of a 7.65-MeV resonance in 12C, see Kragh's "When is a prediction anthropic?" in the PhilSci archive.
112. This statement is perhaps getting perilously close to being wrong in situations in which quantum bits are being manipulated. In a more positivist time, one might have argued that if the result of a measurement was independent of any question of interpretation, then the latter was outside physics.
113. It may seem a bit peculiar that the central controversy in quantum mechanics is over measurement at the same time that the theory is used to interpret measurements on quantum systems without a second thought.

114. In his lectures to the Royal Institution in London in March 1928 (Schrödinger, 1928, p. 206).
115. Dirac (1973).
116. At the microscopic level, collision processes are time reversible ; at the macroscopic level they are not. In the classical case it is understood how this seeming paradox comes about.
117. Heisenberg (1927b), p. 197.
118. Schrödinger's paper (Schrödinger, 1935) in which, quoting him, "the quite ridiculous case . . . of a cat held in a box with vial of cyanide and a radioactive source, giving rise to the paradox of "Schrödinger's cat," was published in the same year as EPR. See also the "Wigner's Friend" paradox (Wigner, 1962). I wonder if anyone seriously believes that the cat in question is neither alive nor dead until the observation is made. Otto Frisch once said that he thought this a "misuse of quantum theory," and that a cat should not be described by a wave function (Bastin, 1971). If nothing else, it would seem to violate the correspondence principle. But if we take that view of the macroscopic, but still quantum-mechanical world, what do we do with the microscopic world? The answers usually given are that decoherence, perhaps through interaction with the universe, makes the system a mixture rather than a pure state of superposition, or that the macroscopic alive and dead states are so complex and so different that there is essentially no interference between them, resulting in a statistical mixture, not a superposition.
119. Bohr's reply (Bohr, 1935) was received by *Physical Review* on July 13, 1935. EPR had been published on May 15. Weinberg (2013) gives a nice, brief summary of the EPR argument.
120. Bohr (1935). John Bell thought Bohr's reply was "totally obscure." See the reference in Christiansen (1987).
121. Bohm (1951); Bohm and Aharanov (1957). The first reference is to a part of chapter 22 in Bohm's *Quantum Theory* and is reproduced in Wheeler and Zurek (1983), which is the best collection of early papers on the interpretation of quantum mechanics.
122. So that a light ray would not have time to travel the distance between the particles in the time scale of the measurement.
123. Another way of putting it is that space-like separated events are correlated.
124. Who should be known to a generation of students for having translated, with J. B. Sykes and others, much of Landau and Lifshitz's *Course of Theoretical Physics* into English.
125. Bell (1964). See also "Hidden variables and the two theorems of John Bell" by David Mermin (1993). As tempting as it is to give Bell's argument, or one of the several alternatives, I forego that indulgence. A version can be found in undergraduate texts such as Griffiths's (2005), or in many of the works cited here. Also *Speakable and Unspeakable in Quantum Mechanics* by Bell himself (2nd ed., 2004). The idea of hidden variables originated, at least in a formal way, in chapter IV of von Neumann's *Mathematical Foundations of Quantum Mechanics* (1932).
126. Stapp (1975). Originally a quantum theorist concentrating on field theory and scattering, in recent years Stapp has written several books on the implications of quantum theory, including *The Mindful Universe* (2007) and *Mind, Matter, and Quantum Mechanics* (2009). Feyman, who independently derived what is in effect Bell's theorem, was dismissive of it, saying that "it is not a theorem that anybody thinks is of any particular importance . . . it is simply a statement of something we know is true." Quoted in Whitaker (1974).

127. For example, Aspect, Grangier, and Roger (1982), or G. Weihs et al., (1998).
128. As Joos (2003) put it, ". . . entangled quantum states have properties which defy any local statistical explanation" (p. 2). If Norsen (2007) is right, and he seems to be, only locality is ruled out, in which case faster-than-light influences are part of the natural world and special relativity is compromised, though perhaps nonlocality can be understood in some other way.
129. Weinberg (2013), sec. 12.2. Again, this elegant, historically sensitive text, is highly recommended.
130. To be precise, Bell's theorem has nothing to say about realism, per se, as John Bell himself emphasized. See Norsen (2007).
131. As proposed by Clauser et al. and carried out by Aspect, the experiments measured photon polarizations: Clauser et al. (1969); Clauser and Shimony (1978); Aspect et al. (1982). There are still those who feel that the experiments are not definitive and that increased counter efficiency, for example, will change the outcome.
132. Locality seems to require that in an EPR-type experiment, the particles possess definite values of the spin components that will be revealed by experiment. From Bell's inequality, this appears to be ruled out by experiment.
133. For example, d'Espagnat (1995), or on more general issues of physics and philosophy, but up to date, d'Espagnat (2006). See also the collection in Price and Corry (2007). A very recent paper is "Loophole-free Bell inequality violation using electron spins separated by 1.2 kilometers," Hensen et al. (2015). I would be remiss if I did not mention the so-called "pilot wave theory" introduced by de Broglie in 1927, which is an example of a hidden-variable theory and can be seen as rescuing quantum mechanics from the plague of indeterminism. This interpretation languished for a quarter-century before being resurrected by David Bohm, whose name is now also associated with pilot-wave theory. In the last decade the theory has undergone a vigorous resurgence as some classical experiments in fluid flow have exhibited properties of quantum-mechanical systems, particularly in a classical double-slit experiment. Does it pose a real "threat" to orthodox interpretations? We shall see.
134. Folse (1985).
135. Bohr (1928).
136. Thoroughly described in many places, e.g., Folse (1985) or Pais (1991), especially chapter 14.
137. Though Folse (1985) notes that Bohr never saw it as a "principle."
138. Howard (2004).
139. Rosenfeld (1963) wrote that "Complementarity is no system, no doctrine with ready-made precepts. There is no via regia to it; no formal definition of it can even be found in Bohr's writings, and this worries many people."
140. Nowadays, the distinction is quite blurred, as the known forces are mediated by vector bosons, including the massless photon, which clearly has wave properties, and the massive $W^{\pm}$ and Z particles that carry the weak force.
141. Spatial localization of a particle destroys knowledge of its momentum and hence any possibility of a causal description (von Neumann's process 1). See, for example, Bohm (1951), pp. 157–61, which, however, may not clarify the reader's understanding very much.

142. Graham (1985), in French, and Kennedy (1985). There are several speculative papers on complementarity in this volume.
143. See Faye and Folse (1998) and Bandyopadhyay (2000). Dirac had little use for complementarity, which he thought did not offer anything new. See Mehra (1972). The American theorist and philosopher Abner Shimony wrote that "I must confess that after 25 years of attentive—and even reverent—reading of Bohr, I have not found a consistent and comprehensive framework for the interpretation of quantum mechanics" (Shimony, 1985). Finally, I would perhaps be remiss if I did not apprise the reader of Beller's rather dismissive remarks on Bohr's thought, including on complementarity, even if I do not share them (Beller, 1999). In his wonderful memoir, Victor Weisskopf does take note of Bohr's "well-known unintelligibility" (Weisskopf, 1985).
144. Merzbacher (1998), p. 4. Messiah's classic text of 1961 devotes 10 pages to complentarity and causality, though the discussion concentrates on just two aspects of it, complementary variables and wave–particle duality.
145. Bohm (1951), p. 158.
146. Feynman, Leighton, and Sands (1965), p. I-1.
147. Or *welcher-weg* [which way; which path] experiments. Wheeler (1978). Also, Wheeler's paper, "Law without law" in Wheeler and Zurek (1983). See also Wooters and Zurek (1979) and Jacques et al. (2007) on experimental tests. Also the paper by Ma et al. (2013).
148. A discussion of the remarkable delayed-choice quantum erasure experiments of Kim et al. (2000), along with others, would enrich this chapter, but . . ..
149. Jacques et al. (2007), p. 968.
150. Scully, Englert, and Walther (1991). Also Ma et al. (2013).
151. The 2012 Nobel award. See Haroche (2013).
152. See Chapter 8 for details.
153. Forman (1971). Forman's thesis is developed over 115 pages, despite which my friend and Bohr scholar Henry Folse of the thesis says that there is "not a shred of evidence" for it. The idea should probably be called "Jammer's thesis," because it first appears, much more economically, in his *Conceptual Development of Quantum Mechanics* (1966). See also Schweber (1994), pp. 148–50.
154. Forman quotes Sidney Hook, having returned from Germany in 1929, as saying that "The attitude of the German philosopher to science is not always one of indifference. It is often an attitude of open hostility." Forman (1971), p. 21.
155. It doesn't suffice to say the Heisenberg was unpolitical, for example. Neither he, nor virtually any other scientist in any era, is free of the influence of the culture he grows up in. Elsasser (1971) was of the view that the reception of the statistical character of quantum mechanics resulted from the new understanding of statistical mechanics, due to Gibbs and Einstein.
156. There are many writers on this interesting subject.
157. Arthur Miller has argued that cubism was an influence on Bohr's thinking, especially on complemetarity (Miller, 2005). Many books have been written on the influence of the early 20th-century revolutions in physics on the arts, and the opposite argument is made as well. That avant-garde movements in physics and the arts took place almost simultaneously is a historical fact, but attempts to show how one affected the other have not born much fruit. It is probable that they were both products of a *fin de siècle* modernism that had its roots in the latter half of the previous century.

158. Alternatively, the disturbance produced by a measurement in classical physics can be calculated with arbitrary accuracy from the very laws of classical physics.
159. Born and Jordan (1930), pp. 322–6.
160. Bohr had a very equivocal position on the existence of the photon. See Slater (1985), p. 160. Kramers expressed his own skepticism as follows: "The theory of light quanta may thus be compared with medicine that will cause the disease to vanish but kill the patient." Kramers and Holst (1923), "The atom and the Bohr theory of its structure." See also Stachel (1986.), "Bohr and the photon." Until 1925 Bohr declined to accept the "reality" of the photon, instead preferring to adopt a skeptical attitude toward energy conservation (Bohr, Kramers, Slater, 1924). Folse (1985) describes the issue as Bohr saw it. See also Hendry (1984), p. 31.When Bothe and Geiger (1924) apparently showed that Bohr's skepticism was unwarranted, he was faced with wave–particle duality.
161. Zeh, in d'Espagnat (1971). See also the discussion in Chapter 7.
162. On this issue, see the important paper by London and Bauer (1939). This paper is one of the best and most accessible introductions to the measurement problem, certainly as understood at the end of the 1930s.
163. Eddington (1929), p. 295. Based on his Gifford Lectures delivered in 1927, but revised in 1928 after the uncertainty principle had been published.
164. D'Espagnat goes beyond where most physicists would go, I think, in saying that "there is something beyond the phenomena" (d'Espagnat, 1987, p. 159).
165. D'Espagnant, Ibid.
166. Among his writings in this vein, see his "Law without law" in Wheeler and Zurek (1983). Note especially the anecdote on p. 197.
167. Wigner (1963) used the term "uneasy" to describe the common reaction to orthodox quantum epistemology.
168. Nearly, at any rate.
169. This is the heart of the matter, of course: The debate turns on whether the superposition simply reflects our lack of knowledge of the state the system is in, or, in the consensus view, it really *is* the state of the system. For another view, see the "modal interpretations" of quantum theory (*Standford Enclycopedia of Philosophy* article that cites van Fraassen's papers of the 1970s onward). See also Krip (1987), which elaborates on several alternatives.
170. For a review, see Zurek (2003).
171. Weinberg (2013), p. 95. The textbook literature was virtually silent on the matter of interpreting quantum mechanics until the 1950s, something Jammer also pointed out in his *Philosophy of Quantum Mechanics* (1974). Books like those of Condon and Morse (1929), Pauling and Wilson (1935), or Rojansky (1938), to mention but three, fail to address the problem at all. Even when, as in Condon and Morse, some of the familiar pedagogical problems such as that of a particle in an infinite potential well are treated, the lurking measurement questions are not raised.

PART III

Applications: Atomic and Nuclear Physics

15

NUCLEAR THEORY
THE FIRST THREE DECADES

INTRODUCTION

In a departure from our strategy in studying the development of quantum theory itself, in relegating our discussion of experiments that would force a new way of thinking to an introductory chapter, our approach to the quantum theory of the nucleus will reflect the somewhat different relationship between experiment and theory in these two cases.[1] It had been generally agreed that atoms (whatever they were) existed ,since the early 19th century, and the origins of atomic spectroscopy go back almost as far. Much of the data that spawned the quantum revolution of the late 1920s had accumulated during the previous half-century or more and had long awaited a theoretical interpretation. The theory that then emerged dominated the next decade. In the case of nuclear physics, however, theory and experiment were much more strongly interconnected, in part because the very first experiments we want to discuss are those that *revealed* the existence of the nucleus itself and thus *created* nuclear physics. Despite these productive experiments, however, nuclear *theory* had to await the creat on of quantum mechanics in 1925.

The first hints of radioactivity came just before the turn of the 20th century, and Ernest Rutherford's discovery of the nucleus came not much more than a decade later. The experiments of the subsequent decade and a half, from 1911 until the years 1929–1932, revealed many of the phenomena that any theory would have to explain, but, as just noted, no real nuclear theory was possible before 1925. Ironically, it was the discovery of the nuclear atom by Rutherford and the Bohr theory that followed it that fostered the creation of quantum mechanics. Rutherford, the consummate experimentalist, aided by his assistants, dominated nuclear physics in its first two decades, as we will see. But just as with spectroscopy a decade or so earlier, theorists scrambled vainly to find a theoretical framework that could explain the empirical results, particularly radioactive decay, nuclear scattering and disintegration, and even the appearance of new particles when previously only the electron was known.

For the purposes of our discussion here, the first three decades of nuclear physics divide naturally into two halves centered on 1925. The earlier period, beginning with the discovery of the nucleus, was dominated by experiments that made it possible to sort out the constituents of the nucleus and the products of radioactive decay, and even discern the first hints of an intrinsic nuclear force. The second half, a period in which experiment and theory were remarkably and intimately intertwined, begins

with the formulation of quantum theory.[2] If nuclear physics peaked in the 1950s and 1960s, its heyday, when excitement of discovery was at a flood, began in the decade leading up to WWII. To proceed, the evolution of the theory of the nucleus is summarized from its modest beginnings not much before 1930 up to the beginning of the war, hardly more than a decade, but one that saw great progress in understanding the structure of the nucleus as a major application of quantum theory. Eventually, at the onset of WWII, the focus of nuclear physics, which increasingly occupied everyone's mind, changed dramatically, and nuclear physicists were at war. Finally, as the world began to emerge from the debilitating and distracting effects of the second global conflict in a generation, the modern era of the physics of the nucleus began, building on what had been learned in the previous decades.[3] But nuclear physics had become weaponized, something that still haunts the world three-quarters of a century later.

DISCOVERING THE NUCLEUS: 1895–1911

The birth of the physics of the atomic nucleus can be said to have occurred in late 1896 when Henri Becquerel discovered natural radioactivity,[4] although at the time its implications were a mystery. That discovery was followed in the next few years by the identification of a number of radioactive elements by Becquerel's student Marie Curie and her husband Pierre. In 1898 they discovered the elements they named polonium, after Marie's native country, and radium, after radioactivity, having separated them from raw pitchblende.[5] When Dmitri Mendeleev created the periodic table in 1869 there were 63 or 64 known elements, and 15–17 more were discovered or isolated during the next three decades, mostly chemically.[6] Following on the heels of the Curies' discoveries, the remaining naturally occurring elements were found or created, so that by 1940 all but one of them was known.[7] When the Curies isolated polonium in 1897, they were led to the discovery by the observation that purified uranium was less radioactive (from the ionization it produced in air) than the raw sample, from which they deduced that there must be another element present, eventually isolating a tiny amount of it. Becquerel and the Curies shared the Nobel Prize in physics in 1903,[8] and Marie was awarded the chemistry prize in 1911.

αβγ

Although cathode rays were discovered as early as 1869 by Johann Hittorf,[9] it was not until 1897 that J. J. Thomson identified them as due to a negatively charged particle, the "electron," that could be deflected by magnetic fields.[10] Two years later, Ernest Rutherford, newly arrived at McGill University in Canada, showed that the radiation from uranium included a component easily stopped by a sheet of paper, which he named α-rays, and a more penetrating component that he called β-rays.[11] The latter were easily deflected by a magnetic field and were found to have a charge of the same sign as the electron, but the α-rays could not be so deflected. It was not until Rutherford was able to employ much larger magnetic fields in 1903 that he was able to show that they could indeed be deflected and carried positive charge.[12] Becquerel's accidental discovery of radioactivity from uranium salts involved radiation that would

eventually turn out to be a mixture of α- and β-rays (see subsequent discussion), though the actual effect he observed was due to the β-rays.[13]

In fact, the situation is somewhat more complicated, though we have to get a bit ahead of ourselves to explain it. Pitchblende ore (uraninite) contains mostly uranium oxides and is about 99% ^{238}U, which has a half-life of 4.9 billion years and hence is only weakly radioactive. But it typically contains some thorium as well as trace amounts of the decay products polonium and radium, both of which were chemically separated from pitchblende by the Curies. The polonium, mostly ^{210}Po, is a decay product of ^{238}U through what is known as the *radium chain*, as a result of seven α-decays and six β-decays. ^{238}U has such a long half-life that the equilibrium concentration of ^{210}Po in pitchblende is very low, and because ^{210}Po has a half-life of 138 days, it meant that after the Curies had isolated it, it began rapidly disappearing. The radium that the Curies isolated in 1898 would have been mostly ^{226}Ra (half-life1602 years), a decay product of ^{238}U via three α-decays and two β-decays. The much greater activity of the polonium and radium sources made them attractive as alpha sources.

The year after Rutherford named the α- and β-rays, Paul Villard identified a highly penetrating radiation from radium that could not be deflected by a magnetic field, representing the discovery of γ-rays, a name also coined by Rutherford. At first thought to be merely high-energy x-rays[14] produced by atomic processes, it became clear that their energies meant that they had to have some other source, which, it became clear by the early 1920s, had to involve a nuclear origin. As early as 1914, Rutherford and Andrade[15] showed that they too exhibited interference. The proton was discovered in 1917 (see subsequent discussion), and it would be 15 years before another fundamental particle would be discovered.

By 1909 it was possible to collimate a beam of α-particles from a radioactive source and carry out scattering experiments with them. Cathode rays, that is, electrons, were useful in atomic scattering experiments, but α-particles, with their much greater mass (or mass-to-charge ratio), would be found to be far more effective in producing nuclear excitation and reactions at these energies. In 1903 Norman Ramsay and Frederick Soddy[16] identified helium in the spectrum of the gases emitted in the decay of radium (from radium bromide), although the situation was very much complicated by the fact that two gases were present, helium and what was known as "radium emanation," which turned out to be radon (^{222}Rn). In any case, there was no possibility of definitely tracing the helium to the emission of α-particles in this experiment, contrary to some claims, if for no other reason than that the atomic nucleus had not yet been conceived. When Rutherford and Royds wrote on radium emanation 5 years later,[17] they barely hinted at the presence of helium and made no reference to its presence in Ramsay and Soddy's experiment, but the following year they announced conclusively that the α-particle was indeed a helium nucleus: "We can conclude with certainty from these experiments that the α particle after losing its charge is a helium atom."[18] Surprisingly, as late as 1914 Rutherford continued to write cautiously that "it has been shown that the scattering of α particles in hydrogen and helium is in good agreement with the view that the hydrogen nucleus has one positive charge, while the α particle, or helium, has two,"[19] and even in 1919 he was still equivocating: "we have every reason to believe that the α particle has a complex structure consisting probably of four hydrogen nuclei and two negative

electrons."[20] Rutherford's excessive caution was not shared by James Chadwick and Etienne Bieler, who 2 years later treated this issue as settled.[21]

THE NUCLEAR ATOM: 1911–1930

The full import of the discoveries of radioactivity and radioactive elements could not be realized until Rutherford and his associates at the University of Manchester, notably Hans Geiger and Ernest Marsden,[22] discovered the atomic nucleus in experiments conducted in 1909–1911.[23] This revelation of the nuclear atom in turn made possible Bohr's 1913 quantization of the states of the hydrogen atom—Bohr having joined Rutherford at Manchester in 1912—and in a little over a decade led to the new quantum theory, a story that has already been told. The rapid acceptance of Rutherford's discovery meant that thereafter it was understood that the atom consisted of a small dense nucleus at the center of an atom whose extent was some 10^5 times larger in radius.[24]

Thus nuclear physics proper begins with the discovery of the nucleus in these experiments with thin metal (gold) foil targets carried out in Rutherford's laboratory, starting in 1907 and culminating in the decisive experiments of Geiger and Marsden in 1909.[25] It was found that a small fraction of α-particles from a ^{222}Rn source were scattered through angles up to 140°, which upon Rutherford's analysis[26] implied that there must be a small, massive, presumably positively charged core at the center of the atom, because it had been expected that at most α-particles would be scattered by a degree or two. In fact, a simple argument shows that if α-particles were scattered through angles greater than 90°, there had to be a small scattering center more massive than the incident particle. Of course the assumption had to be made that single scattering dominated in the thin foil, a situation that Rutherford discussed in detail.[27] This nuclear interpretation was completely at odds with the prevailing model, associated with the name of J. J. Thomson, of positive and negative charges smeared out over the volume of the atom, the so-called plum pudding model.[28] All Rutherford concluded was that the charge was concentrated in a very small ($< 10^{-12}$-cm) radius, and it was Bohr who, in print at least, first made the assumption that the mass was similarly concentrated.[29] The year after Rutherford published his paper on the results of Geiger and Marsden, C. T. R. Wilson graphically demonstrated the occasional backscattering of α-particles in his cloud chamber.[30] The atomic nucleus had been born.

In scattering experiments on heavy nuclei, as in the case of the gold foil, the results indicated, as expected, pure Coulomb scattering (until energies of over 25 MeV[31] became available in cyclotrons). But scattering from light nuclei was another matter. In 1919 Rutherford, who was in the process of moving from Manchester, where he had been for over a decade, to Cambridge as Cavendish professor,[32] showed that anomalous results were obtained with gaseous targets,[33] and in 1921 Chadwick and Bieler,[34] in Rutherford's laboratory, showed strong departures from inverse-square law scattering of α-particles from hydrogen. And 3 years on, Bieler studied the large-angle scattering of α-particles from heavier nuclei and again observed a dramatic departure from Coulomb scattering.[35]

From the outset Etienne Bieler made clear what was obvious to many, that on the assumption that the nucleus was composed of protons, which by this time had been discovered and named, it could not be in equilibrium without some additional, attractive force.[36] From his experiments he concluded that "we are . . . driven to expect that other forces intervene at these short distances, forces presumably of *attraction between like charges* that neutralize the electrostatic repulsion."[37] He went further to show, tentatively, that his results could be explained by the addition of an inverse fourth-power ($1/r^4$) attractive force. These experimental efforts, by Rutherford and then by Chadwick and Bieler, constitute the discovery of the strong nuclear force, the recognition for the first time that there exists in nature a force other than those of gravity and electromagnetism. Yet although Rutherford and Chadwick concluded in 1927 that "at large distances of collision the forces between the particles are given by Coulomb's law, but at closer distances very strong additional forces come into action,"[38] the cautious Rutherford hoped that the departures might be due to "magnetic fields in the nucleus" or to polarization of the nuclear charge distribution by the α-particle, as originally suggested by Debye and Hardmeier.[39] Chapter IX in the historically rich book by Rutherford, Chadwick, and Ellis summarizes all of these arguments as of 1930,[40] which was 2 years before the discovery of the neutron.

Rutherford had received the Nobel Prize in chemistry in 1908, well before his discovery of the nucleus, the proton, nuclear disintegration, and the strong force, "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances." If anyone deserved a second Nobel, it was he.[41]

DISCOVERY OF THE PROTON

Although it had been suggested nearly a century earlier (1814) by William Prout that all atoms were built out of units of hydrogen atoms, the first substantial hint of the structure of the atom came with Rutherford's 1911 announcement of the discovery of the nucleus itself. In his 1911 paper in *Philosophical Magazine* Rutherford suggested that the charge on the nucleus was the same as that of the extranuclear electrons ($Q_N = Q_e$), but of opposite sign ($+Ne$, where N was the number of electrons of charge e), and also that the nuclear charge was proportional to its atomic weight.[42] Although the first conclusion was correct, the second was only approximately true, and then only well below an atomic weight or mass number of about 100.[43] In a paper preceding Rutherford's, in the same issue of *Philosophical Magazine*, Charles Barkla showed that the intensity of scattered x-rays depended on the atomic mass, hence that the number of extranuclear electrons was proportional to the atomic mass (M or A)—which followed from Rutherford's conclusions as well—and finally that the number of extranuclear electrons was approximately equal to $A/2$.[44] The atomic number could not yet be identified with either the electronic or nuclear charge. But a month later in a letter to *Nature*, Antonius van den Broek concluded that the proper order of an atom in the periodic table, its atomic number, Z, was determined by e the charge on its nucleus. He wrote that "the number of possible elements is equal to the number of possible permanent charges of each sign per atom."[45] The proton, of course, was still

several years away, so that it could not be taken for granted that the positive charge came in integral multiples of $+e$, but the implication was that the atomic number represented both the number of positive and negative charges. These ideas were confirmed in 1913 by Henry Moseley (who we recall died at Gallipoli in 1915 at age 28) in his x-ray studies of 38 elements,[46] who showed that the elements should be ordered by their atomic number rather than weight, a subtle but important difference, and something Bohr had assumed, following van den Broek. This difference was fundamental, for in Mendeleev's periodic table the elements had been ordered by atomic weight, which was the relative atomic mass,[47] and *atomic numbers* were assigned on this basis, that is, were secondary,[48] and this sometimes resulted in the position in the table being inconsistent with chemical properties.

In 1914 Rutherford was writing that "from the data of scattering [by] α-particles previously given by Geiger, it was deduced that the value of the nucleus charge was equal to about half the atomic weight multiplied by the electronic charge," which was essentially Barkla's result.[49] By 1915, then, it was known that both the number of electrons and the nuclear charge varied by one unit in successive atoms, ordered by atomic number Z, and it became clear that the atomic number and the nuclear charge (in units of e) were the same and equal to about $A/2$. Frederick Soddy observed that α-decay moved a nucleus two places to the left in the periodic table (lower atomic number), whereas β-decay moved a nucleus one place to the right. And the result of one α-decay and two β-decays was to leave the nucleus in the same place (atomic number Z), but with four atomic mass units less mass. He called such nuclei, with the same atomic number but different weights, "isotopes."[50]

Then, in 1917, Rutherford showed that when he fired α-particles at a nitrogen target, some of the resultant radiation produced scintillations on a ZnS screen that resembled that caused by hydrogen atoms, primarily in the greater range of the particles in air ("long-range scintillations") compared with α-particles. Two years later he reported that they were deflected by a magnetic field and had positive charge.[51] Soon it became clear that these were hydrogen nuclei expelled from the nitrogen target,[52] and Rutherford named them "protons," from the Greek *protos*.[53] The name stuck, and the proton was born. Two years earlier Harkins and Wilson at the University of Chicago had called the hydrogen nucleus the "positive electron." The name "positron" might have been adopted, thereby foreclosing the later use of the term.[54]

Summarizing his results, Rutherford wrote that "we must conclude that the nitrogen atom is disintegrated under the intense forces developed in a close collision with a swift α-particle, and that the hydrogen atom that is liberated formed a constituent part of the nitrogen nucleus."[55] This $^{14}\mathrm{N}\ (\alpha, p)\ ^{17}\mathrm{O}$ process (to use modern notation) was the first identified *nuclear reaction*, and Rutherford had thus accomplished *artificial* nuclear transmutation for the first time.[56]

The final conclusion was that the positive charge on a nucleus was due to an integral number of protons, the nuclear charge was the same as the number of extranuclear electrons, which was the atomic number (Z), and the nuclear mass or atomic weight was about $2Z$. The lurking problem was that if the atomic number and the nuclear charge (divided by e) were the same, and the nucleus consisted only of protons and

electrons,[57] the fact that the atomic number was approximately *half* the atomic mass was difficult to explain, in view of the small electron mass.[58] That is, where did the extra mass come from? The growing appreciation of the fact that α-particles were helium nuclei (Rutherford and Royds, 1909), with a charge of 2 and a mass of 4, seemed to mean that the α-particle had to consist of four protons, with two electrons to neutralize two of the protons. Similarly, a nucleus like ^{238}U, with an atomic number of 92, would have 238 protons and 146 electrons, resulting in a net 92 positive nuclear charges to go with 92 extranuclear electrons, making the atom electrically neutral. This model required that the nucleus contain A protons and $A - Z$ electrons, resulting in a net positive charge of Ze and a neutral atom, but the stability of a nucleus with a net Z protons, hence a large Coulomb repulsion, clearly defied explanation. But without the nuclear electrons, the matter was worse.

NUCLEAR BINDING

As early as 1919 it was recognized that a solution to the binding problem was paramount, and among the proposals was that a neutral particle might exist with a mass similar to that of the proton, and the next year Rutherford aired that suggestion in his Bakerian lecture to the Royal Society.[59] William Harkins was another advocate,[60] and yet the proton–electron model of the nucleus would survive for another decade before evidence began to accumulate that this idea was simply untenable, capped eventually by Chadwick's discovery of the "neutron"—a neutral particle of mass 1 in—1932. This resolved the conundrum, with the result that nuclear electrons quickly disappeared (see subsequent discussion). The way was then open to the development of a real quantum theory of the nucleus that Heisenberg began to offer in the year of Chadwick's discovery.

In 1920 the neutron was over a decade away and quantum mechanics as we know it was still over the horizon, so that any hope of a quantum theory of the nucleus was also far in the future, despite the real achievements of 1911–1919 in understanding its structure. But the next major issue, nuclear binding, which had been lurking in the background, could be explored without any real theory. Ultimately a solution to this problem would be intertwined with the explanation of departures from Coulomb scattering observed by Chadwick and Bieler in 1921 and, of course, the eventual discovery of the neutron, but at the time, the only viable model of the nucleus seemed to be the proton–electron model.

The initial key to understanding nuclear binding came from accurate measurement of nuclear masses. As late as 1919 or 1920 it was still assumed, in the absence of evidence to the contrary, that atomic masses were simple integral multiples of the proton mass, that is, that atomic weights were integers, with hydrogen being unity. In 1915 Harkins and Wilson were more specific, writing that "to account for the closeness of the atomic weights to whole numbers, the simplest procedure is to consider that they are made up of hydrogen."[61] This speculation harkened back to Prout's hypothesis of a full century before. Then in 1920, Francis William Aston, having started out a decade earlier as assistant to J. J. Thomson[62] and delayed in his research by the war, began exploring this question, and by implication that of nuclear binding, at the Cavendish

in Cambridge. At the outset Aston himself was wedded to the "whole-number rule," but shortly after the war ended he built a prototype mass spectrometer, improving on Thomson's device that generated "positive ray parabolae."[63] One of the first discoveries was that chlorine had two isotopes of weights 35 and 37, providing an explanation of why the atomic weight of the gas had the anomalous value 35.46.[64] Aston also began to notice stability patterns, noting that isotopes[65] with even atomic number and even weight or mass number (what were to be called "even–even nuclei") were the most frequent, and that an odd atomic number was almost always accompanied by an odd weight.[66] These, of course, are manifestations of shell structure. Soon Aston found that there were slight systematic deviations from the integer rule that he described as "the failure of the additive law with respect to mass." And in a prescient passage in his Nobel Lecture, reflecting the insights Arthur Eddington (in 1919; see the next chapter) had gleaned from such measurements, Aston made the following remarkable statement:

> It has long been known that the chemical atomic weight of hydrogen was greater than one-quarter of that of helium, but so long as fractional weights were general there was no particular need to explain this fact, nor could any definite conclusions be drawn from it.
>
> The results obtained by means of the mass spectrograph remove all doubt on this point, and no matter whether the explanation is to be ascribed to packing or not, we may consider it absolutely certain that if hydrogen is transformed into helium a certain quantity of mass must be annihilated in the process. The cosmical importance of this conclusion is profound and the possibilities it opens for the future very remarkable, greater in fact than any suggested before by science in the whole history of the human race.[67]

As a way of quantifying these deviations from the whole-number rule, Aston used the term "packing fraction," which he borrowed from Harkins and Wilson, defining it to be $P = (M - A)/A$, where M is the atomic mass and A is the mass *number*. The alternative term "mass defect," also apparently coined by Aston, was commonly used well into the 1930s and survived into the 1960s. It was defined as $M - A$ or $A - M$ (mass excess, mass defect) (see Figure 15.1). Ultimately the term "binding energy," defined as $B = (Zm_p + Nm_n - M)c^2$, replaced the earlier terms once the neutron had been discovered.[68] Aston patiently measured the packing fraction for of the order of 70 isotopes, and he along with Harvard's Kenneth Bainbridge[69] measured nuclear masses well into the mid-1930s, slowly accumulating the information that would shed critical light on the problem of nuclear binding and eventually shell effects. The binding energy per *nucleon*,[70] B/A, turned out to be especially revealing, being essentially constant (beyond about $A = 16$). The significance of this was not immediately clear, but the binding energy per particle would have been expected to be proportional to A based on the number of pairwise interactions. Finally understood, these data represented the first indication of what is known as the "saturation" of nuclear forces.[71] Aston's attack on the problem of nuclear binding using mass spectrometry led to his being awarded the 1922 Nobel Prize in chemistry after just 3 years of study, for among other things, "his enunciation of the whole-number rule." This is ironic as his most important contribution was to show deviations from it.

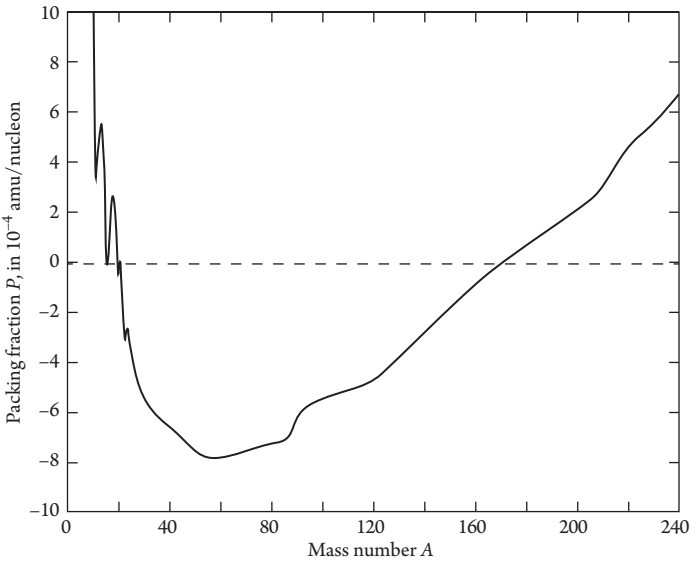

Figure 15.1. Packing fraction $(M - A)/A$ vs. mass number from mass spectrographic data of Aston and others. From Evans (1955). McGraw-Hill, by permission.

In the absence of the not yet discovered neutron, the problem was the binding of a nucleus with a net Z positive charges, making clear the need for some unknown force that would supply the necessary attractive energy, most likely a particle with the mass of a proton that did not contribute to the Coulomb repulsion. In the prevailing proton–electron model, the nucleus could not be bound.

By the mid-1920s, then, with quantum mechanics in the offing, it was becoming clear from early scattering experiments, the problem of Coulomb repulsion of the protons, and measurement of nuclear masses, that there must be some unknown attractive force inherent in nuclei. Further, the data showed that these forces saturated, even though that fact was not really understood. The implication of these results would become evident beginning in 1927–1928, and foreshadowed the development of a quantum theory of the nucleus.

THE DEMISE OF THE NUCLEAR ELECTRON

As long as the nucleus could be thought of as a uniform sphere of positive charge with no structure, one could finesse the problem of nuclear stability, but when it came to be understood that the positive nuclear charge was made up of discrete protons, it was necessary to imagine electrons in the nucleus providing the necessary attractive energy as there was no other known force (gravity being far too weak), nor any other known particle. When Chadwick and Bieler showed that there was a departure from the inverse-square Coulomb repulsion between the α-particle and the nucleus at short distances, it began to raise the possibility of finally understanding nuclear binding and stability through the existence of a new force. Either the electron had to

provide sufficient negative Coulomb energy, which was known to be impossible, or there had to be another fundamental particle besides the proton and the electron to provide the mass, but somehow contribute to binding the nucleus.

The now-familiar argument that an electron cannot not be confined to a volume the size of the atomic nucleus because of the uncertainty principle was not possible until after 1927,[72] but 3 years later, employing the Heisenberg principle, Ambartsumian and Ivanenko showed that the electron need not, and indeed could not, exist in the nucleus, essentially demolishing the proton–electron model and making the search for the neutron more urgent.[73] This was one of the very first applications of the new quantum theory to the nucleus, but a year earlier, in 1929, Oskar Klein had also shown, using the Dirac equation, that an electron could not be confined in the nucleus.[74]

If this were not enough, there were other very good reasons to be skeptical of the proton–electron model. As early as 1926 Ralph Kronig had noted that nuclear electrons, with their magnetic dipole moment of one Bohr magneton (see Chapter 10), would result in a hyperfine splitting in total disagreement with experiment.[75] The proton magnetic moment was not actually measured until 1933 (see subsequent discussion) and nuclear magnetic moments began to be obtained only after about 1931, but it was assumed to be nearly 2000 times smaller than a Bohr magneton because of the proton's mass. Furthermore, the nature of the N_2 rotational spectrum, which in 1928 led Kronig to conclude that its spin is 1 (despite the fact that it should have had an odd number of particles in the nucleus, $2A - Z$), and prompted him to write that "protons and electrons do not retain their identity to the extent they do outside the nucleus,"[76] a strong hint that something was wrong. Supporting this view, the following year Franco Rasetti, visiting Cal Tech, showed that the ^{14}N nucleus obeyed Bose–Einstein statistics (from Raman scattering and the N_2 rotational spectrum). This, again, was inexplicable, because in the electron–proton model it should have consisted of 14 protons and 7 electrons, that is, an odd number of spin-1/2 fermions (the proton spin had been known since 1927; see subsequent discussion).[77] It was also found in 1929 that the nuclear spin of the odd-A isotopes of cadmium ($Z = 48$, $A = 113, 115, 117$) was 1/2, rather than the integral value expected for a nucleus with even Z).[78] Even more convincing, perhaps, was the measurement of the proton magnetic moment in 1933 by Estermann, Frisch, and Stern.[79] Aside from its anomalous value of about 2.5 *nuclear* magnetons, the nuclear magneton (μ_N)[80] is of the order of 1000 times smaller than the Bohr magneton, μ_B (see Chapter 10), which is essentially the magnetic moment of the electron.

If, as in the case of ^{14}N, there were $A - Z$ electrons in the nucleus, with $A - Z$ odd, that is, at least one unpaired electron, the nuclear magnetic moments would be more than 1000 times the known value of less than 0.2 μ_N.[81] Nuclear magnetic moments had begun to be measured in this same period, 1931–1933, by Rabi and his collaborators,[82] but by 1933 the neutron had been discovered and the issue of nuclear electrons was largely settled, though there were certainly some holdouts. In their 1930 book on line spectra, Pauling and Goudsmit wrote, rather unhelpfully, that "the facts indicating that nuclei are themselves composed of electrons and protons . . . do not need to be discussed here.[83]

By the time of the neutron's actual discovery in 1932, its existence was generally assumed (somewhat like the Higgs before 2012), although attempts to find it had failed. In 1931, the year before it was discovered, Langer and Rosen[84] proposed from astrophysical considerations that a "neutron" might exist. Inconclusive experiments in 1931–1932 by Bothe and Becker[85] and by Irené Joliot-Curie and Frédérick Joliot[86] showed that energetic α-particles from polonium incident upon light elements (e.g., boron and beryllium) could produce a highly penetrating form of radiation, tentatively assumed to be electromagnetic, i.e., gamma rays. Then in 1932, in a series of superb experiments, James Chadwick, Rutherford's protégé and assistant at Cambridge, showed that the radiation could not be gamma radiation and suggested instead a neutral particle of about the same mass as a proton.[87] The reaction in question was $^{9}\mathrm{Be}(\alpha,n)^{12}\mathrm{C}$. Many have been inclined to credit Joliot-Curie and Joliot for the discovery, including Heisenberg, who wrote in his 1932 paper on exchange forces in nuclei that "Through the trials of Curie and Joliot and their interpretation by Chadwick . . .,"[88] which seems to be less than fair. Of his results, Chadwick wrote in *Nature* that they "are very difficult to explain on the assumption that the radiation from beryllium is a quantum radiation [i.e., γ-rays], if energy and momentum are to be conserved in the collisions. The difficulties disappear, however, if it be assumed that the radiation consists of particles of mass 1 and charge 0, or neutrons."[89] Chadwick was awarded the Nobel Prize in physics just 3 years later.[90] The discovery of the neutron provided a solution to the stability problem by contributing to the mass and nuclear binding but not to Coulomb repulsion. This came, however, at the price of requiring an attractive nuclear force somehow carried by the neutron, hints of which had come from the early experiments of Chadwick and Bieler.[91] Soon concern would shift from the question of what bound the nucleus to what stopped it from *collapsing*.[92] Almost immediately Bacher and Condon reported that the neutron spin must be 1/2.[93]

THEORIES OF RADIOACTIVE DECAY

The problem of nuclear binding and stability was intimately connected to that of radioactive decay. If a nucleus decayed, by α- or β-emission for example, it was evidently unstable before the decay, and perhaps more tightly bound after it (or not). And in late 1925, just as the new quantum mechanics was being born, Rutherford and Chadwick[94] noted that when they scattered α-particles of approximately 8 MeV energy from uranium, which they did precisely because this element emitted α-particles of about that energy, they got surprising results. Following Chadwick and Bieler's results from 1921–1924, they were expecting to see a departure from inverse-square Coulomb scattering by a point nucleus that would be a measure of the nuclear radius and would have indicated that the α-particle penetrated the nucleus itself. In the event, scattering experiments with several α-emitters, including thorium C′ (^{212}Po), were carried out to probe the height of the repulsive Coulomb barrier, and in each case it was found to be substantially higher (because of a lack of a departure from pure Coulomb scattering) than the energies of the emitted α-particles.

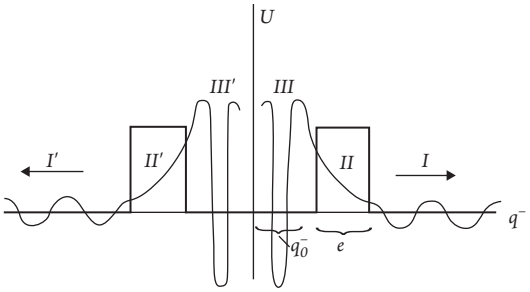

Figure 15.2. Gamow's illustration of tunneling through a rectangular barrier. (Gamow, 1928a). Springer, by permission.

The phenomenon of α-decay, then, seemed to imply that α-particles existed in the nucleus in some kind of attractive nuclear potential, but there was no way to understand how they could escape the potential well in which they were bound.[95] In 1927, on the heels of the quantum revolution of 1925–1927 and the uncertainty principle of the latter year, the quantum theory of the nucleus was necessarily in its infancy. But at that moment a few young physicists began to think of the application of the new theory to the nucleus, and in particular to the problem of radioactive decay. Among the most prominent was the young Russian émigré George Gamow, who had recently arrived in Göttingen from Leningrad.[96]

The entirely nonclassical phenomenon of quantum tunneling had been discovered theoretically, without much fanfare, by Friedrich Hund and Lothar Nordheim in 1927[97] in connection with molecular spectra and the emission of electrons from metal surfaces. Nordheim's work was directly relevant to the problem of nuclear decay because it involved barrier penetration into unbound states.[98] It took Gamow little time to treat the problem of α-decay as a barrier-penetration problem (see Figure 15.2),[99] though "beating" Gurney and Condon, who independently had the idea, to publication by only one day.[100] Gurney and Condon submitted a brief, qualitative letter to *Nature* and elaborated on it in the *Physical Review* the next year,[101] whereas Gamow published an earlier and much more substantial treatment in *Zeitschrift für Physik*.[102]

Essential to the solution of the problem was the assumption that the nuclear potential was attractive at short distances, creating a potential well through which the α-particle had to tunnel (see Figure 15.3). This 1928 application of the theory of quantum tunneling or barrier penetration represented the first time that the tools of quantum mechanics were applied to the specific problem of the structure of the nucleus. Gamow's triumph, using a method of complex eigenvalues, was to derive an approximate relationship between the decay constant λ and the α-particle energy, of the form $\log \lambda = a + bE_\alpha$, matching the empirical Geiger–Nuttal law, in which the decay constant increases rapidly with energy. Gamow demonstrated that this expression fit the data from a half-dozen radioactive nuclei (see figure 5 in Gamow, 1928a).[103] Although his solution shed little light on the detailed structure of nuclei, it clearly showed that tunneling was involved in at least α-decay and demonstrated, once and for all, that radioactivity was a fundamentally quantum-mechanical process.[104]

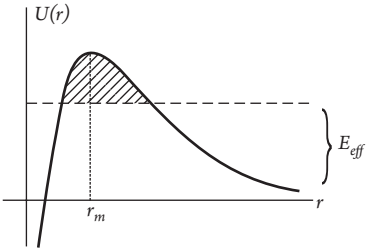

Figure 15.3. Tunneling. Nuclear potential well, describing a bound α-particle with energy E_{eff} inside the nucleus and at infinity, after decay. Gamow (1928b), by permission of Springer.

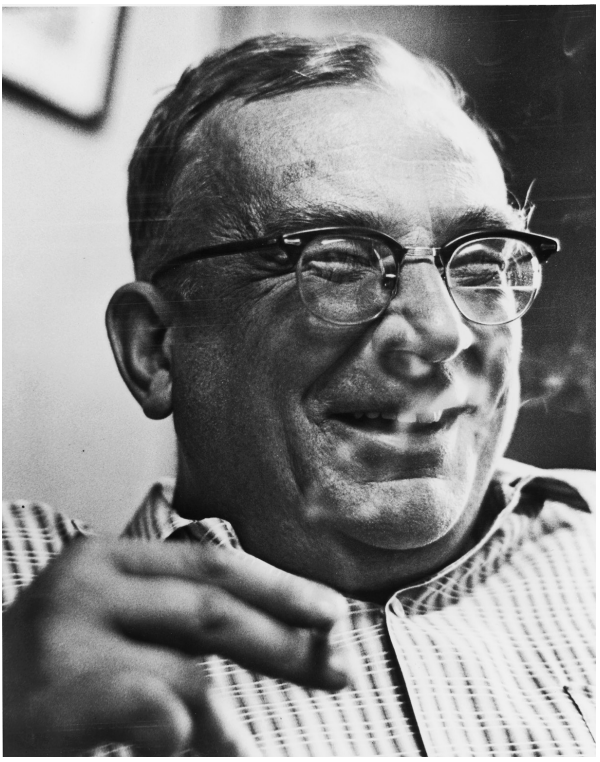

Figure 15.4. George Gamow (1904–1968). AIP Emilio Segrè Visual Archives.

It follows from the preceding discussion that cross sections (see Chapter 12) for nuclear reactions involving beams of α-particles or protons[105] also depend on penetration of the Coulomb barrier, and Gamow was able to show[106] that protons of less than 1-MeV energy could penetrate the nucleus, providing some of the stimulus for Cockroft and Walton to develop their electrostatic accelerator in 1932.[107] Soon Atkinson and Houtermans applied these barrier-penetration arguments to reactions initiated by protons in stars,[108] a subject Gamow was especially interested in because of the light it shed on the origin of the elements. We discuss the importance of nuclear reactions and nuclear structure in the problem of energy production in stars in the next chapter.

β-Decay; The Two Neutrons

Although β-decay, the emission of electrons from the nucleus, had been discovered in the first decade of the century, little progress could be made in understanding it before the neutron was found in 1932. The issues posed by β-decay were quite different from those of α-decay, especially once it was realized that electrons cannot exist inside the nucleus. Initially it was assumed that, like α-particles, the β-rays were monoenergetic, but evidence that this was not necessarily the case began to emerge as early as 1901 and by 1909 there were very strong hints, and in 1914 Chadwick clinched the case.[109] Many attempts were made to explain away the apparent violation of energy conservation as electrons were emitted with a continuous distribution of energy up to a maximum (Figure 15.5).[110] An excellent example of such studies was that by Ellis and Wooster in 1927, using as a source RaE (^{210}Bi) which has an almost pure β-decay spectrum. They showed, by using calorimetry, that no secondary process could be responsible for the apparent nonconservation of energy.[111]

Complicating matters, however, was the existence of characteristic β-rays, that is, discrete lines superimposed on the continuous β-spectrum. The cause, primarily the decay process known as *internal conversion*, was soon interpreted as an internal photo effect, in which γ-rays from an excited nucleus ejected atomic elections or secondary β-rays in the process of transitioning to its ground state. This process was discovered by C. D. Ellis in 1921, and a year later he published a remarkable paper on the β-ray spectra of RaB (^{214}Pb). Although internal conversion is now understood differently, it led Ellis to a very modern-looking energy-level diagram for RaB and the view that the results

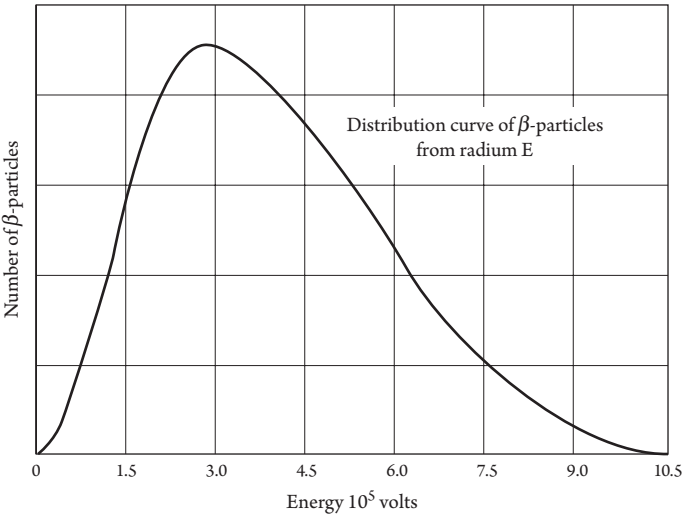

Figure 15.5. Continuous spectrum of β-rays from radium E (^{210}Bi) showing fixed endpoint energy (modern value 1.16 MeV). The average electron energy is about 0.39 MeV, and the remainder is the average neutrino energy. Ellis and Wooster (1927), by permission of the Royal Society of London.

"lend support to the view that quantum dynamics apply to the nucleus, and that part at least of the structure of the nucleus can be expressed in terms of stationary states."[112]

But to return to the continuous β-ray spectrum, clearly if only an electron was emitted in β-decay, it should be monoenergetic, as was the case in α-decay. It was found, despite the apparent nonconservation of energy, that the *maximum* energy of the β-spectrum did correspond to the available energy in the transformation. But linear momentum was found not be conserved either, as the electron and recoil nucleus did not in general depart in opposite directions.[113] In the face of this evidence, it fell to Pauli, in June of 1931, to make the remarkable proposal that there must be another particle involved, which would eventually become the *electron neutrino*. The initial announcement, which provided the key to understanding not only the continuous spectrum but also why spin angular momentum also appeared not to be conserved in β-decay (though that argument was not possible before the neutron's discovery), took place at an American Physical Society meeting in Pasadena, California, [114] and it was repeated at the Seventh Solvay Conference in Brussels 2 years later.

By 1927 the proton was known to have a spin of 1/2 from measurement of the specific heat of molecular hydrogen and the equilibrium ratio of orthohydrogen to parahydrogen spin isomers of 3:1 found necessary to explain it;[115] and by the time of the Solvay Conference the neutron also had been discovered. It was found in 1934 that the deuteron, the deuterium nucleus, was a boson with spin 1, virtually clinching the case that the neutron, like the proton, had spin-1/2.[116] And if this were true, angular momentum conservation required a new particle with spin-½, little or no rest energy (because electrons sometimes carried off *all* the energy), and no charge. Thus Pauli's 1931 announcement. Eventually, and slowly, it came to be recognized, first through Fermi's efforts, that a new interaction was involved in the emission of an electron and a neutrino, that is, β-decay. Physics was thus not far from the present understanding, however contingent that might be, that there are four forces of nature.

The understanding that the neutron did indeed have spin-1/2 came slowly. Shortly after its discovery, Ivanenko suggested that it might be elementary, that is, not a composite particle consisting of a proton and an electron,[117] and if that were the case, the earlier experiments of Kronig and Rasetti, which had shown that the proton–electron model of the nucleus was untenable (see previous discussion), were quite compatible with the idea of a neutron with spin-1/2 like the proton. The discovery that the deuteron was a spin-1 boson, as we noted, virtually decided the issue, but left open the possibility that the neutron spin was 3/2. Fermi's theory of β-decay from the same year assumed that it was ½, and ultimately Schwinger confirmed this 3 years later.[118]

THE TWO NEUTRONS

When Pauli proposed the existence of a neutral fermion in 1931[119] to conserve energy in β-decay, he called it the "neutron," a name that would have a very short life. Two years later he speculated that it might be massless but possessed of a magnetic moment, even though it carried no charge.[120] The discovery, or we might say

"invention," of what came to be called the "neutrino" represented the birth of the first new fundamental particle since that of the electron in 1897 and the proton in 1919, though it would remain very much hypothetical for over two decades.[121] The neutron followed the neutrino by one year, though the latter was hypothetical for over two decades.

With the neutron's discovery in 1932 and the knowledge that β-decay increased the atomic (proton) number by 1 (known for nearly two decades) without significantly changing the atomic weight (hence the neutron number must have decreased by 1) it began to be clear that a neutron had somehow to become a proton in the β-decay process. Buttressed by the discovery of Chadwick and Goldhaber[122] that the neutron mass is slightly greater than that of the proton (see subsequent discussion), and knowing that the neutron spin was evidently 1/2, it became clear that in the process $n \rightarrow p + e^-$, with the electron being emitted as a β-particle, angular momentum conservation was violated. Both particles in the final state are spin-1/2 fermions; hence their sum is 1 or 0, but the neutron spin is 1/2. There must be another particle of spin-1/2 or 3/2, Pauli's "neutron," which had originally been proposed only to conserve energy. Now, however, with the neutron's discovery, there were two neutral particles carrying the name neutron ("heavy neutron" and "light neutron") and so Pauli's hypothetical particle was renamed the (Italian) diminutive neutrino by Fermi (in a paper on β-decay rejected by *Nature*[123]). Fortuitously, the crucial discovery of the neutron came at the very moment that both Bohr and Heisenberg were on the verge of giving up on the seeming insoluble problem of the nucleus.[124]

Fermi's 1934 theory of β-decay[125] pictured a neutron decaying into a proton plus an electron and a neutrino $(n \rightarrow p + e^- + \nu_e)$,[126] which we take to be the basic weak-decay process, except that it is now understood as taking place at the level of *up* and *down* quarks: $d \rightarrow u + e^- + \nu_e$. The theory was a very early application of the Dirac–Jordan quantum-field theory, but it described β-decay as being a contact, zero-range interaction.[127] In the case of $p + e^- \rightarrow n + \nu_e$, a proton and electron are annihilated and a neutron and a neutrino created at the same space–time point, represented by an operator of the form $\phi_\nu \Psi_n \phi_e^\dagger \Psi_p^\dagger$[128] But in the standard model with a gauge theory of the weak interaction,[129] this process would be $u + e- \rightarrow d + \nu_e$, mediated by the W^- vector boson. When Fermi's theory was generalized by Gamow and Teller[130] in 1936, their more elaborate theory yielded selection rules for β-transitions more in line with experiment.

Pauli's new neutral particle, plus the unprecedented discoveries in 1932 of both the neutron, by Chadwick, and the positron, by Carl Anderson,[131] revolutionized nuclear physics. For a time opinion continued to be divided on the question of whether the proton was a bound state of a neutron and a positron, or the neutron a bound state of a proton and an electron; or neither, as it quickly became clear.[132] Once the spins were known (1927, 1932–1934) the earlier ideas became untenable and the idea of the neutron as a fundamental fermion immediately resolved the statistics and magnetic moment puzzles we discussed earlier.[133]

This important year of 1934 was also the one in which the Joliots discovered *artificial* radioactivity,[134] by bombarding an aluminum foil with α-particles. They were

awarded the Nobel Prize in chemistry the following year. The main reaction they studied was $^{27}\mathrm{Al}\,(\alpha, n)\,^{30}\mathrm{P}$, in which the excited phosphorous nucleus then decayed by positron emission, though the process of deducing all of this in 1934 was far from trivial.[135]

Fermi's theory was so successful that it survived almost unchanged for nearly three decades.[136] Eventually, beginning in about 1961, Glashow, Weinberg, and Salam developed a $SU(2) \times U(1)$ gauge theory of the electroweak force that unified electromagnetism and the weak interaction. It has been often noted that the weak interaction, that is, β-decay, is crucial to nuclear fusion in the Sun and therefore for life as we know it.

"THE HAPPY THIRTIES"

Nuclear physics had taken giant strides since the discovery of the proton in 1917–1919, culminating in the discovery of the other primary component of the nucleus in 1932, the neutron.[137] All of this progress had been accomplished by experiment, without major help from the rapidly evolving quantum theory, and consequently, without any real nuclear theory, per se.[138] With the constituents of the nucleus now understood, this left the problem of nuclear structure and nuclear forces to be addressed. The discovery of the neutron immediately meant that it must contribute to binding the nucleus (e.g., Ivanenko[139]), implying an entirely new force, and, in addition it enabled the birth of Fermi's theory of β-decay.

Not at all incidentally, as we have already seen, deuterium was discovered by Harold Urey (Urey et al.) in 1931, just before the neutron.[140] Thus the discovery of the simplest nontrivial nucleus, the deuteron.[141] In the old electron–proton model, it would have been assumed to consist of two protons and one electron, which led nowhere until Chadwick discovered the neutron the following year. Evidently the deuteron, which was found to have mass 2 and charge 1, must be a neutron–proton pair, and thus bound by an attractive $n - p$ force of an entirely unknown character.[142] Since Faraday in the 1830s and 1840s, there had been only two forces, gravity and electromagnetism, but by 1934 it could have been argued that there were four, which is our understanding 70 years later. That understanding did not emerge immediately, of course, even though the hints that there must be a non-Coulombic nuclear force were over a decade old. It also took some time to understand that β-decay involved a "weak force," expressed in the form of Fermi's zero-range weak interaction, and the strong force, suspected since at least 1921, posed entirely different problems.[143]

On the heels of the discovery of the neutron, and in the same wonderful year of 1932 in which it and the positron were discovered, Heisenberg quickly took the first giant step toward the modern theory of the nucleus, built of protons and neutrons in a classic three-part paper in *Zeitschrift für Physik*. Electrons had finally been banished from the nucleus, so that, as Heisenberg wrote, "the structure of nuclei . . . can be described, according to the laws of quantum mechanics, in terms of the interaction between protons and neutrons." He did raise the question of how a neutron can decay into a proton and electron in β-decay, but there were no more nuclear electrons.[144] He

also introduced the two-component *charge–spin* called "isotopic spin," in which the orthogonal basis vectors were the neutron and proton, thus emphasizing their deep similarity. Initially Heisenberg assumed that the only force between protons was the Coulomb repulsion, which seemed to dominate over any purely nuclear force between protons because no two-proton bound state existed. These papers by Heisenberg, all written in 1932–33 and totaling only 30 pages, represent the birth of nuclear theory as a fully quantum-mechanical discipline.[145] They came not long before the Solvay Conference in October of the next year, devoted entirely to nuclear physics.[146] As noted, it was there that Pauli presented his theory of what came to be called the neutrino, though his idea was 3 years old at the time. This year, 1933, was of course the year Adolph Hitler became chancellor of Germany.[147] Increasingly, the "happy thirties" were not.

Eugene Wigner's first paper on nuclear physics, in 1933,[148] which still entertained the possibility of nuclear electrons, followed Heisenberg in considering a nuclear force *only* between neutrons and protons: "the forces between two protons or two neutrons are always neglected."[149] But this paper represented the first real calculation of the structure of a nucleus, one in which the nuclear force was very much in the forefront, and from this point on, it was on everyone's mind. Heisenberg had effectively raised the question in his monumental 1932–1933 paper, but Ivanenko, Tamm, and Majorana, among others, were thinking about it at the same time.[150] For the next half-century, even as the structure of real nuclei were studied by use of phenomenological forces, the nature of the nucleon–nucleon interaction was a continuing problem, and even a solution to the problem in terms of the quark structure of nucleons and colored gluons as the carrier of the strong force in the 1980s and 1990s did not mean the end of phenomenological modeling of the nucleon–nucleon interaction.

As already noted, Heisenberg introduced the two-component charge–spin called *istopic spin (*or *isospin)* in 1932,[151] reflecting the obvious similarity between neutrons and protons. The name, isotopic spin, was coined by Wigner in 1937,[152] in a paper in which the powerful tools of group theory were applied to nuclear structure for essentially the first time. By analogy with intrinsic spin space, Heisenberg imagined that the proton and neutron form an isospin doublet, basis vectors in a two-dimensional isospin-1/2 space in which the proton would have a projection on the 3-axis of + 1/2 and the neutron had a 3-component of –1/2. A rotation by π about the 2-axis would turn a neutron into a proton, and charge symmetry would express the invariance of the nuclear force under such a rotation. The neutron and proton are thus seen as two states of the same particle, the *nucleon*. As with intrinsic spin, the symmetry group is $SU(2)$.[153] Isospin symmetry is broken, by a few percent, by the electromagnetic force, reflected in the difference between the neutron and proton masses. From the point of view of quantum chromodynamics (QCD), the theory of the strong force, charge symmetry expresses an invariance under a rotation that turns a *u* quark into a *d* quark, and vice versa. Isospin symmetry has played an important role in nuclear physics and in the development of the *standard model* of particle physics. Thus, although isospin had its origin in the early 1930s, its important applications took place mainly from

the late 1940s onward. In recent years, the broken charge–spin $SU(4)$ symmetry that Wigner proposed has played an important role.[154, 155]

NUCLEAR FORCES

As already noted, the existence of a previously unknown force essential to the binding of nuclei began to become apparent at an early date, beginning with Chadwick and Bieler in 1921 and Rutherford and Chadwick in 1927.[156] Alpha-decay, as interpreted by Gamow in 1928, showed that although there was a long-range Coulomb repulsion, there apparently was a shorter-range attractive potential well in which α-particles were confined, and then, perhaps, an even shorter-range repulsion or hard core. By the early 1920s, then, there was substantial evidence for the necessity of a new force binding nuclei, which in the early 1930s could be assumed to be a two-body force between (and among) protons and neutrons. Direct evidence came with the discovery of the deuteron, but it was unclear whether the force acted between only neutrons and protons or between like nucleons as well, so that charge symmetry or charge independence was still over the horizon.[157] Indeed, Bethe and Bacher wrote in 1936 that ". . . the forces between like particles, if they exist, must be smaller than the forces between proton and neutron."[158]

The saturation of nuclear forces and its implication were just beginning to be discussed, but it was known that the nuclear force was short ranged and strong enough to overcome the Coulomb force at those short distances. Little could be done with this knowledge, however, until quantum theory had reached a degree of maturity that allowed it to be confidently applied to the nucleus. The discovery of the neutron in 1932 made this possible, and as we have seen, it was Heisenberg who took the first major step.

The earlier measurements by Aston and others had shown that the "volume effect," or contribution of pair-wise interactions to the binding energy, was proportional only to A, not A^2 as one would expect.[159] This phenomenon was crucial in the attempt to understand nuclear forces as it could be seen to imply a short-range repulsion or an exchange force, that is, the effect of the Pauli principle.[160] In principle, the details of the short-range repulsion should be understood in the context of the standard model, in which nucleons are bound states of u and d quarks,[161]so that the net force between nucleons is ultimately due to the "color forces," but in practice, phenomenological theories have a long and honored history, involving the exchange of pseudoscalar and vector mesons, all of which are quark–antiquark bound states.

Two pieces of evidence revealed the saturation of nuclear forces. One came from the previous argument, that the measurement of nuclear masses and thus their binding energies were found to be proportional to A rather than to A^2. The other came from measurements of nuclear radii. Determining the nuclear radius, or for that matter even defining it, was difficult, though it could reasonably taken to be at the point that nuclear forces began to dominate over the Coulomb force; that is, indeed, how Bieler defined it in 1924.[162] Experimental results, by Bieler and others, plus theoretical arguments by Gamow, led to the expression $R = R_0 A^{1/3}$ for the nuclear radius,

which implied constant density.[163] But a density independent of the number of particles bound by attractive forces also implies a saturation of those forces, and hence a repulsive core or some other short-range correlations must be involved.

Although the nuclear force was known to be short-ranged, showed saturation, and was attractive between neutrons and protons, nothing was known of its origin. In his three papers of 1932–1933,[164] which we have argued represent the birth of nuclear theory, Heisenberg was concerned with the problem of constant density, but failed in his attempt to solve it. Papers in 1933 by Wigner and Landé[165] hardly address the saturation issue, although it is noted that mass defects are approximately proportional to A, so that divided by the number of nucleons, they are constant.[166] But the introduction, in 1932–1933 by Heisenberg, and then by Ettore Majorana, of their exchange forces was decisive, and for some time it was assumed that saturation *required* an exchange force. [167]

Heisenberg's charge-exchange mechanism (isospin exchange, equivalent to position and spin exchange) was motivated by a model of the resonance exchange of an electron between a proton and a neutron, which he soon discarded,[168] and was proposed purely by analogy with the hydrogen molecular ion. Saturation does not seem to have been a primary goal, and in fact with his exchange force the binding energy increased faster than A^2.[169] When he realized that his exchange mechanism did not produce saturation, however, he introduced a short-range repulsion that limited how close nucleons could approach each other.[170]

But in a paper received by *Zeitschrift für Physik* on March 3, 1933, Majorana tackled the problem of saturation head-on, and, following Heisenberg's lead, introduced a new exchange force, apparently using for the first time in print the term "saturation" [*Absättigung*] to describe the property of nuclear forces. He first considered an interaction between neutrons and protons that was repulsive at short range in order to achieve saturation, but rejected the idea in favor of the exchange force.[171] Majorana also assumed that the only force acting between protons was the Coulomb force, reflecting a skepticism about the existence of a nuclear force between like particles that was common at the time.[172] But it was he, at the time working with Heisenberg in Leipzig,[173] rather than Heisenberg himself, who clearly exhibited the connection between an exchange force and saturation and succeeded in devising such a force that actually did produce saturation.[174]

CHARGE INDEPENDENCE

As was said, little attention was given to the existence of a strong $p - p$ or $n - n$ force, largely because such bound two-body configurations do not exist in nature. In each of the exchange forces previously mentioned, the $n - p$ interaction was *spin dependent*, and its sign might depend on whether the particles were in a spin singlet or triplet state. Majorana's exchange force, which involved spatial-coordinate exchange, was attractive in even angular momentum states (notably S states), but otherwise repulsive**.** Bartlett subsequently proposed an exchange force that was a combination of Heisenberg and Majorana forces, and thus purely a spin-exchange force.[175]

So Eugene Wigner was not alone in assuming that the new force acted between only neutrons and protons or that the force between like nucleons must be weak.[176] In fact, the attractive nuclear $p - p$ force is stronger than the Coulomb force at short distances, one piece of evidence being the fact that protons do not collect on the surface of nuclei.[177]

These early assumptions about the weakness of the $p - p$ force are at odds with what would eventually become dogma, the *charge independence* of nuclear forces, but this is what could be inferred from the fact that, neglecting Coulomb repulsion, nuclei with the same numbers of protons and neutrons ($N = Z$ stability line) were the most stable. As early as 1935, Eugene Feenberg provided theoretical evidence that the $p - p$ and $n - n$ forces did exist,[178] and proton–proton scattering experiments by White and by Tuve et al. carried out the following year[179] made it clear, experimentally, that in addition to the Coulomb repulsion, there was a strong $p - p$ interaction. Furthermore, mirror nuclei, odd-A isospin doublets in which the numbers of neutrons and protons were interchanged, showed similar binding energies, e.g., ^{3}H and ^{3}He, again except for the Coulomb contribution.[180] After the experiments of Tuve et al. on $p - p$ scattering, Breit and Feenberg, along with colleagues Condon and Present, suggested the $n - n$, $p - p$, and $n - p$ forces might be precisely equal, that is, charge independence.[181] Although Breit et al. stated the case for charge independence in 1936, the actual demonstration of the equivalence of the $n - p$ force and that between like nucleons took place in the 1950s, in both low-energy s-wave $p - p$ and $n - p$ scattering, as well as in high-energy nucleon–nucleon scattering.[182] It was clear from the early α-scattering experiments that the two-body force must be short ranged, and in his work on the deuteron and on ^{4}He, Wigner showed that this had to be the case, examining various possible forms for such a potential and attempting to show that the properties of light nuclei were not very sensitive to their precise form.[183]

The surprising discovery of the nonzero ground state quadrupole moment of the deuteron in 1939 by Rabi's group[184] required the introduction of a noncentral term in the two-body interaction (specifically $n - p$), and indeed Yukawa and Kemmer had predicted such a force a year earlier.[185] The neutron and proton were supposed to be in a $^3S_1$ state, that is $L = 0$ and $S = 1$, the spin triplet state. But the $L = 0$ state would be spherically symmetric and have no quadrupole moment, so the $n - p$ interaction must mix states with the same J but different L: the $^3S_1$ and $^3D_1$ states, which have the same parity.[186] This would be caused by a *tensor force*, presumably of the form $3\boldsymbol{\sigma}_1 \cdot r\boldsymbol{\sigma}_2 \cdot r - \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2$, where $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are the spin operators for the two particles. With this information, Wigner and Eisenbud[187] gave the most general form of the two-body interaction in 1941, including a spin-dependent force, tensor force, and spin–orbit interaction. We will return to the problem of nuclear forces and their role in the first serious attempts to describe the structure of the nucleus. We will also briefly touch on the progress in understanding the two-nucleon force from a fundamental, field-theoretic point of view. Of the further struggles to understand the nuclear force, Marvin Goldberger, a student of Fermi's, summarized the situation in 1960 by asserting that "scarcely ever has the world of physics owed so little to so many."[188]

ANOMALOUS MAGNETIC MOMENT OF THE PROTON AND NEUTRON

Following the determination of the proton spin in 1927, it was expected that as an elementary point particle of spin-1/2, it would have a magnetic moment of 1 nuclear magneton,[189] the counterpart of 1 Bohr magneton for the electron. As it happened, when the proton magnetic moment was measured in 1933 by Estermann, Frisch, and Stern,[190] it was found to be approximately 2.5 nuclear magnetons, of which the authors themselves said, "this is a very striking result." Striking because the immediate implication was that the proton was not an elementary or point particle, and later experiments would show that both the neutron and the proton had spatial extension, unlike (presumably) the electron. As Fermi said in 1950 in lectures at Yale, ". . . we are led to the conclusion that the physical proton and neutron are in fact much more complicated objects than they seem when described in terms of Dirac theory."[191] Eventually, of course, this would be explained in terms of the quark model of nucleons,[192] but for the moment, and indeed for over a quarter-century, it was a major mystery. When the neutron magnetic moment was found to be nonzero, from the magnetic moment of the deuteron, it was not completely unexpected,[193] even though the neutron, unlike the proton, had no (net) charge. Its value was directly measured in 1940 by Alvarez and Bloch, and turned out to be about –1.9 nuclear magnetons.[194]

NUCLEAR REACTIONS

Almost the only way to obtain information about the structure of the nucleus was through scattering experiments, primarily nuclear reactions involving inelastic scattering and rearrangement collisions.[195] No theory of nuclear reactions existed before Born first formulated scattering theory in 1926 (Chapter 12) and specifically, the theory of inelastic scattering. But as quantum mechanics came to be applied to the atomic nucleus, it was obvious that reaction theory had to take into account the structure of the nucleus, if indeed there was any structure. Nuclear cross sections were found to be energy dependent, as one would expect from tunneling arguments, but also showed resonant-like behavior that implied the involvement of detailed structure. Before the discovery of the proton, of course, there was no hint that the nucleus had any structure at all, and into the late 1930s some, like Bohr, continued to argue against the existence of anything like stationary states in nuclei. In contrast to inelastic scattering in atomic physics, in which electronic excitations—even vibrations and rotations—were relatively simple, in the nuclear case very complicated rearrangement collisions were possible. Here the number of nucleons can be of the order of 100 or greater, raising the specter of enormous and very complex configurations, so that as calculations began to be attempted, severe truncation of the state space was inevitable. Furthermore, the discovery of collective excitations induced by nuclear reactions added another dimension to the problem.

Prior to 1930 nuclear scattering and reaction experiments were limited to α-particle sources obtained from radioactive decay, which were of fixed energies, corresponding

to the radionuclide emitting them. Protons and neutrons themselves, produced in nuclear reactions, could be used as sources, but the intensities were very low and their energies were constrained by the kinematics of the reactions that generated them. Radioactive decay experiments and nuclear reactions produced by collimated radioactive sources could probe the nuclear potential but provide little information on the details of nuclear structure.[196] The invention of the van de Graff electrostatic accelerator in 1929, Ernest Lawrence's construction of the first cyclotron in 1931 and the Cockroft and Walton accelerator of 1932[197] changed the situation dramatically, making possible experiments in the mid-1930s such as those by Tuve et al., using a van de Graff accelerator at the Department of Terrestrial Magnetism in Washington, DC, and by White with a small cyclotron at Berkeley, opening new horizons in experimental nuclear physics.[198] Soon protons could be accelerated to energies of hundreds of keV, and what is often considered the first entirely manmade nuclear reaction employing an accelerated projectile was the $^{7}\mathrm{Li}(p, \alpha)^{8}\mathrm{Be} \rightarrow 2\ ^{4}\mathrm{He}$ reaction, observed by Walton in the early Cockroft–Walton voltage multiplier at Cambridge in 1932,[199] thus edging out Lawrence and Livingston.

Neutron-induced reactions, which had the advantage of being free from the Coulomb barrier, depended on the availability of convenient neutron sources, but began to be explored by 1937.[200] Neutrons could not be readily produced or collimated, but a neutron source could be placed in close proximity to the target, to initiate neutron-induced reactions, including neutron capture. Despite the low flux, without a Coulomb barrier, low-energy neutron-induced reactions immediately became possible. Early neutron sources involved (α, n) reactions, for example on beryllium ($^{9}\mathrm{Be} + \alpha \rightarrow {}^{12}\mathrm{C} + n$), as used by Chadwick in discovering the neutron with α-particles from radioactive polonium.[201] Other examples were (p, n) reactions on lithium, for example, with the protons from an ion source using molecular hydrogen and radio frequency excitation to ionize the hydrogen; also (d, n) reactions employing an accelerated deuteron beam. Eventually in the 1940s, high fluxes of thermal neutrons from nuclear reactors revolutionized neutron physics, and today, spontaneous neutron sources such as $^{252}\mathrm{Cf}$ are also used.

The goal of nuclear reaction theory was obviously to gain information about nuclear structure. In one form or another such reactions had been observed since 1911, but in 1932, when particle accelerators were becoming available, the theory of nuclear reactions was still a very young art. But the description of the reaction process had to include the structure of the target nucleus itself; hence it was very much a bootstrap process. It was important to try to understand how the incident energy was shared among nucleons, how the incident particle was incorporated into the existing structure, and the nature of the final state. This process of deducing structure from nuclear reactions was an ongoing one well into the 1960s and beyond.

Such considerations led, at one extreme, to Bohr's 1936 theory of the compound nucleus[202], in which the energy of the incident particle is assumed to be essentially "thermalized," shared among the particles of the nucleus, so that to a good approximation the excited compound state, and thus the final state, is independent of the mode of formation.[203] At the other extreme, some reactions could be considered "direct

reactions," involving only one or a few particles of the target nucleus, often near the nuclear surface.[204] Such was the case in "stripping" or "pick-up" reactions. Important and representative papers of the period are by Breit and co-workers, Bohr and Kalckar, Bethe, and others, perhaps most especially Weisskopf,[205] who diligently attempted to find a potential energy function that would make it possible to fit experiment. Especially influential was a paper by Breit and Wigner on the capture of slow neutrons, which gave the famous Breit-Wigner resonance formula.[206] This issue of discrete nuclear structure, as against the liquid drop and compound nucleus models, caused a huge schism in the nuclear physics community in the late 1930s, a schism that was not really resolved until after the war.[207]

NUCLEAR STRUCTURE: THE SHELL MODEL

When it was found in the early 1930s that nuclear reaction cross sections were not featureless functions of energy but showed resonance-like behavior, this was understood as revealing something of the structure of the nucleus itself, that is, nuclear energy levels or stationary states.[208] As we have noted, the initial and final states of a nuclear reaction involve the nuclear states themselves,[209] so that some understanding had to be developed about the nuclear wave functions just to proceed. Even after WWII it was a difficult challenge to separate those parts of a description of nuclear reactions that depend on the details of the states involved and those that do not. Wigner's ***R***-matrix theory,[210] which formulated the theory of resonance reactions in a way that separated exterior and interior regions defined by the rather sharp nuclear radius, along with Wheeler and Heisenberg's more abstract *S*-matrix, were attempts to do this.

In a heavy nucleus with 50 to 100 or more nucleons, the number of possible microscopic states is enormous, so that even light nuclei posed an intractable computational problem in the 1930s. In addition, the strong nuclear force, that is, the nucleon–nucleon interaction, was poorly known. Unfortunately, in contrast to the atomic case in which the electrons all moved in the Coulomb potential of the nucleus, the nuclear Hamiltonian contained only the particle kinetic energies and the two-body (nucleon–nucleon) interaction and there was no natural force center. It was immediately clear that no progress was possible unless the nucleus, to a first approximation, could be treated as a system in which individual nucleons moved more or less independently in an average spherically symmetric potential due to all of the interparticle interactions. This would be an independent-particle "mean-field" approximation in which the "residual" interparticle forces could then be taken into account as a perturbation or by some other means. It was hoped that only certain "valence" nucleons, outside closed shells, might determine the low-energy properties of a nucleus or enter into a typical reaction, something that seemed to be justified by the magnetic moments and ground state spins of odd-*A* nuclei.

In the atomic case there was a distinct shell structure (see Chapter 17), and it was conjectured that the same might be true of nuclei. Evidence of "magic numbers" in

nuclear stability tables began to accumulate in the early 1930s, so that although the nuclear-shell model is considered a postwar discovery, its roots definitely lie in the prewar period as these data were being amassed and mulled over. Although the success of the compound nucleus model of nuclear reactions seemed to many to argue against shell structure, as did the related liquid-drop nuclear model (see subsequent discussion),[211] nuclear systematics made quite clear the importance of odd nucleons outside nearly inert shells. The evidence included the fact that all even–even nuclei had zero ground state spins and generally were stable, the fact that virtually all odd–odd nuclei were unstable (four stable cases were known), and that the spins and magnetic moments of the ground states of odd-*A* nuclei at least approximately result from only a single unpaired nucleon. This argument produces what are known as the "Schmidt limits" between which the magnetic moments of almost all odd-*A* nuclei lie (see subsequent discussion).[212]

The successful shell model of the *atom* was a consequence of the Pauli principle and Bohr's *aufbau*—or "building-up" principle. Even without detailed calculations, it was fairly clear from the exclusion principle how electronic states in light atoms should be constructed. Then, as an *n*-body problem with no analytical solution, the details of the shell structure emerged from calculations in which, initially, the interactions between electrons were neglected, and eventually in Hartree-type calculations[213] in which an electron moved in a mean field due to the other electrons. It was apparent that the same approach might work in nuclei, but the immediate problems in the nuclear case were that there still was no detailed knowledge of the two-body force and still less of the process by which this interaction resulted in an average nuclear potential that all particles felt. Because the two-body force was known to be of short range, it was difficult to see how it could give rise to an overall average central potential felt by all nucleons. In fact, it did turn out to be possible.

The parentage (no pun intended[214]) of the nuclear-shell model, like so many issues of priority, is in dispute. It may very well be true that Guido Beck, who received his doctorate under Hans Thiring in 1925 and served as an assistant to Heisenberg, was the first to suggest, as early as 1927, that the nucleus, by analogy to the structure of the atom, was "built up of shells,"[215] but the first detailed model was developed in 1932 by the Russians Ivanenko and Gapon.[216] By 1934 Elsasser and Guggenheimer,[217] separately, had noticed that nuclei with 2, 8, 20, 50, and 82 neutrons or protons were unusually stable, which made the analogy with closed atomic shells much more convincing. A year earlier 1933 Alfred Landé wrote of "complete outer shells" in an α-particle model of the nucleus, and in 1937 Wigner commented that in the "one particle picture, after the 2p shell is completed at O^{16}, the 3d and 2s shells begin to be built up simultaneously."[218] Further progress was made in understanding the shell structure of nuclei by Schmidt and Schüler,[219] when they demonstrated the importance of unpaired nucleons in determining nuclear magnetic moments. In 1940 Wheeler and Barshall[220] almost completed the picture by showing the benefits of adding a spin–orbit interaction in treating the scattering of neutrons from helium, and not long after the war, Fermi casually nudged Maria Goeppert-Meyer toward the crucial step of

incorporating a spin–orbit force in nuclei (see subsequent discussion). Because this would turn out to be the key to a successful shell model, we can see that the ingredients were there just as progress was suspended by the war.

Ultimately, the success of the independent-particle model in predicting low-lying nuclear energy levels, ground state spins, and nuclear magnetic moments, convinced most skeptics that shell structure played at least a role in nuclei, and perhaps an important one. The imperatives of the exclusion principle were paramount, but as we have already noted there was much skepticism about a shell model because of the lack of a force center in nuclei, coupled with the completely unknown internucleon potential that had to be introduced phenomenologically. Bohr, in particular, adamantly rejected *any* independent-particle model. The result was that the shell model had a hard time gaining traction in the late 1930s, when the liquid-drop model was popular. As Elliott and Lane[221] have pointed out, the incipient shell (or independent-particle) model had some success in explaining some of the accumulating data, but failed notably in other cases, especially in predicting binding energies. And most important, it seemed to lack theoretical justification. The solution, essentially, was that nuclei are nearly degenerate Fermi gases and that because of the Pauli principle the states available to nucleons are restricted, resulting in a large mean free path between collisions.[222] A full understanding of why such a model of nuclear structure works was slowly achieved, though for the most part only after its great successes of 1947–1949.[223]

The best guide to the state of understanding of the nucleus in the late 1930s is a monumental trio of papers in *Reviews of Modern Physics* in 1936–1937 by Hans Bethe, along with R. F. Bacher and M. Stanley Livingston, totaling 467 pages, and colloquially known as the "Bethe bible."[224] Although nuclear theory was only about 5 years old at this point, the knowledge that had accumulated during the previous two decades, on nuclear systematics in particular, is impressively displayed there.[225] The sizes, binding energies, spins, stabilities, and so on, are discussed at length. The striking fact that although stable even–even (Z, N) nuclei are common, odd–odd stability, is very rare (noted by Aston many years before), is a product of shell structure. Also treated are the magnetic moments of the neutron and proton, including the fact that they are not pure Dirac particles, as well as the forces among neutrons and protons. David Hill noted in 1957, 20 years after the Bethe trilogy appeared, that "These definitive treatments of nuclear physics were for years the standard reference and still retain great utility."[226] One ought to note that the quantity of applied quantum mechanics in this review paper is enormous, despite no important new additions to quantum theory per se. The thorny puzzle of the nature of the purely nuclear force, including its saturation in nuclei, is explored at length. This situation, opposite to that found in atoms but similar to the situation in condensed matter, led, as we have seen, to the proposal that nuclear forces are exchange forces.[227] The authors (Bethe et al.) present the familiar arguments to approximately explain nuclear binding energies, due principally to von Weizsacker,[228] but deriving in some sense from Gamow's liquid-drop model of 1928–1929,[229] with a surface effect proportional to the radius squared.[230] This is essentially the famous "semi-empirical mass formula."

Figure 15.6. Hans Bethe (1906–2005). Courtesy of Cornell University Library.

In discussing stability, Bethe and Bacher (BB) noted that nuclei apparently show the phenomena of closed shells similar to those in atoms,[231] something that, as we have seen, was becoming well known, as well as, in effect, the phenomenon of pairing, or a pairing force. In treating the deuteron the authors observed that "the forces between neutron and proton are an entirely new phenomenon,"[232] and in general it is concluded that the internucleon forces are of very short range, which was of course evident from Rutherford's work of 20 years before.

Perhaps the most interesting parts of the work of BB are secs. 32–34, in which the filling of neutron and proton states is discussed, basically the building-up principle for nuclei. As noted, it was motivated by the empirical data on the fluctuations in the abundance of nuclei and the fact that nuclei with 2, 8, 20, 50, 82 neutrons or protons are especially strongly bound, the magic numbers. The shell model clearly had strong advocates, but important ingredients, notably the spin–orbit force, were still lacking. Thus it was becoming clear that the simple and tractable choice of a central square well or harmonic oscillator potential failed to reproduce the observed shell closures at N or Z equal 50 and 82. As it would turn out, a simple spherically symmetric potential will not, by itself, reproduce the magic numbers. It worked for the 1*s*, 2*s*, 2*p*, and 3*d* shells (the "s–*d*" shell), but higher shell closures were problematic and the very highest (e.g., $N = 126$) were yet to be indentified.[233] Bethe's verdict was that ". . . the naïve theory of neutron and proton shells fails for higher atomic numbers." But although it was clear to him that the theory of neutron and proton shells "certainly cannot claim more than moderate success as regards the calculation of nuclear binding energies . . ."

it is, nonetheless "the basis for a prediction of certain periodicities in nuclear structure for which there is considerable experimental evidence." Furthermore, "the individual-particle-approximation seems to offer some hope for the development of a rational theory of nuclear spins in the future."[234]

For a variety of reasons, including the war and the lack of data, success in reproducing the magic numbers and at least approximately the ground state properties of nuclei was not achieved until the introduction of the $j - j$ coupling shell model with a spin–orbit force in 1947–1949. This despite the fact that all of the ingredients were present as the war turned attention and resources elsewhere by 1939. The details are found in many places, notably Elliott and Lane (1957). As tempting as it is to elaborate, I have already overstayed the reader's welcome by straying into the late 1940s. Some historical details are given in in Mladjenvoic's book[235] as well as in Mehra and Rechenberg's vol. 6 in which the letters of Hans Seuss in 1947, papers by Maria Goeppert-Mayer in 1948 and 1949, and the joint paper of Hans Jensen, Otto Haxel, and Seuss are described.[236] The two groups published letters in the same volume (**75**) of *Physical Review* in 1949 explaining how the spin–orbit interaction allowed the magic numbers to be reproduced,[237] and Jensen and Goeppert-Mayer shared the 1963 Nobel Prize with Eugene Wigner, with half going to Wigner. Goeppert-Mayer ended her letter with the comment "Thanks are due to Enrico Fermi for the question, "Is there any indication of spin-orbit coupling?" which was the origin of this paper."[238] (see Figure 15.8) The resulting independent-particle shell model in which nucleons moved in a potential intermediate between a harmonic oscillator well and a square well, with the addition of a spin–orbit force, was found to be spectacularly successful, especially near closed shells.

Nonetheless, as late as 1957 Elliott and Lane wrote of the nuclear-shell model that "until recently, arguments why the model would *not* be valid were more numerous and convincing than those in favor of the model."[239] And in 1952 Blatt and Weisskopf, in their monumental book on nuclear theory, devoted only 13 pages to the independent-particle model, and two of those were critical of it.[240]

THE COMPOUND NUCLEUS AND THE COLLECTIVE MODEL

As mentioned earlier, in 1936 Niels Bohr introduced the idea that in certain nuclear reactions, the time scale over which the reaction took place (perhaps 10^{-19} s) was very much longer than the transit time of a neutron across the nucleus, which allowed for the incident energy to be shared among many, or all, nucleons, so that the resulting nuclear state was at least approximately independent of how it was formed, and the same for the reaction products.[241] This was the compound nucleus model, which proved to have a substantial range of validity, especially in treating nuclear reactions, and was soon elaborated on at length by Bohr in a paper with Fritz Kalckar.[242] Bohr was especially interested in neutron-capture reactions in which a γ-ray was emitted by the excited "compound nucleus," noting specifically that the lifetime of such states, as measured by the width of the γ-ray spectrum, was long compared with the neutron

transit time. It suggests, or rather requires, *collective* behavior, cooperative phenomena involving many nucleons, implying long-range correlations. A major implication of such a model of nuclear reactions is that the shell model, which emphasizes short-range correlations, can be only part of the picture, with the result that the decade leading up to 1947 was one of confrontation between the dominant liquid-drop or collective model, championed especially by Bohr and Wheeler, and some kind of shell model. In his first paper on the compound nucleus, Bohr wrote that "In the atom and in the nucleus we have . . . to do with two extreme cases of . . . many-body problems for which a procedure of approximation resting on a combination of one-body problems, so effective in the former case, loses any validity in the latter." And in the paper with Kalckar he was particularly adamant on the matter: ". . . any attempt of accounting for the spin values by attributing orbital moments to the individual nuclear particles seems quite unjustifiable."[243] In this paper there is considerable discussion of the thermodynamics of excited nuclei and subsequent emission of a neutron or proton as an evaporation, citing papers by Bethe.[244]

Although the first use of what amounts to a *collective model* was implicit in George Gamow's introduction of the "liquid-drop model" of the nucleus, conceived in Copenhagen in 1928 and first appearing in print the next year,[245] the liquid-drop model has come to be associated with Bohr's name partly as the result of the joint paper with Kalckar, because there Bohr neglected to cite Gamow's work, and as Stuewer[246] notes, Bethe perpetuated the omission in his massive 1936–1937 project. Of course the compound nucleus model was originally a model of nuclear reactions, not a nuclear model per se, but it and the liquid-drop model soon became conflated.

The fission of the atomic nucleus, a prototypical collective phenomenon, was observed for the first time in 1938 by Hahn and Strassmann,[247] who found that they detected barium in thermal neutron-capture reactions on uranium, a result that Lisa Meitner and her nephew Otto Frisch[248] explained, coining the term "fission" and invoking the liquid-drop model in attempting to explain the results.[249] Soon thereafter Bohr and Wheeler developed the liquid-drop model of fission in detail in an important paper titled "The mechanism of nuclear fission,"[250] exploring the stability of the liquid drop against deformations and how that led to fission, without, again, acknowledging Gamow. They concluded, among other things,[251] that the uranium isotope involved must be ^{235}U. The further implications of the possible existence of nuclear vibrational excitations were overlooked at the time[252] and would be discovered only when there were enough data on the spectra of even–even nuclei near closed shells to show the characteristic harmonic spacing of levels.[253]

The earliest information on permanent nuclear deformations came from spectroscopic hyperfine structure. Hyperfine splitting had been observed by Michelson before 1900, but its explanation, in terms of the interaction between nuclear and electronic magnetic moments, was not possible until spin was discovered. But it turns out that the nuclear electric quadrupole moment also contributes to hyperfine structure, as was suggested by Schüler and Schmidt in 1935 and demonstrated by Casimir the same year.[254] The deuteron electric quadrupole moment was first measured in this fashion by Kellogg et al. in 1939.[255] As nuclear quadrupole moments came to be

routinely measured, beginning with Schmidt[256] but most of it after the war, it was realized that they were small near magic numbers of neutrons or protons but large away from them, indicating large nuclear deformations in the latter situation. Such behavior is obviously collective, involving correlations among many nucleons, so that application of the collective model, or at least a unified model, is demanded. The fact that such deformed nuclei rotated was discovered when nuclear systematics showed that the spectra of deformed even–even nuclei away from closed shells showed a typical $I(I+1)$ rotational pattern (Figure 15. 7). This culminated in Aage Bohr's dissertation and his work with Ben Mottleson, beginning in 1953. As one reads papers in *Physical Review* from that year by Ken Ford and by David Hill and John Wheeler,[257] it is quite clear that the appreciation of the existence of nuclear vibrations and rotations is still in its infancy.

Although it was expected that a model of the nucleus built from nucleons interacting through some kind of two-body force should ultimately explain all nuclear properties, including those that were clearly collective, it was also clear that the size of the state space required was prohibitively large and that such a microscopic description would obscure rather than illuminate many obvious features of nuclear spectra, such as rotations and vibrations and their coupling to single-particle states. The result was two or three decades of attempts to adequately merge the two descriptions, the shell (or independent particle) and collective, in various "unified models," including, to single out one, the strong-coupling model of Sven Gösta Nilsson.[258] All of these attempts posed problems of redundancy, since the collective degrees of freedom were obviously built in some complicated way from single-particle degrees of freedom. The final unification of the collective and shell model descriptions was carried out by James Rainwater[259] and by Aage Bohr and Mottleson, beginning in 1950, in what came to be known as the "unified model," and the three shared the 1975 Nobel Prize in physics.[260]

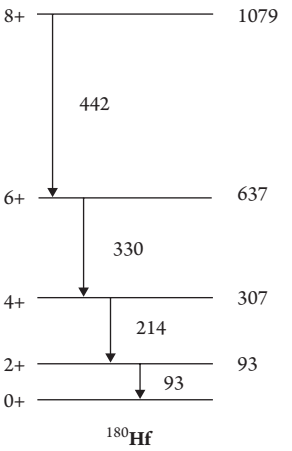

Figure 15.7 Ground-state rotational band in ^{180} Hf, showing typical $I(I+1)$ level spacing. Bohr and Mottleson (1953), courtesy of American Physical Society.

Further treatments were offered by Rowe and others, but this, is in any case, beyond our charge here. [261]

This modern era that with apology we have touched on could be said to have begun in 1947 with the initial successes of the shell model, and the subsequent decade was perhaps the golden decade of nuclear physics, as understanding of shell effects grew right along with concentration on collective motion. If this process of building upon the nascent collective model of Bohr and others seems desultory, the cause is twofold. Obviously the war took a major toll, as nuclear physicists were displaced by politics and assigned to war efforts, but the data just were not there in 1939–1940 and really weren't available until nearly a decade after cessation of hostilities. What was lacking were data on nuclear charge distributions that gave information about nuclear shapes, electric quadrupole moments, which provided such information even more directly, and nuclear energy levels or spectra obtained from γ-emission and β-decay by excited nuclei—especially electric quadrupole transitions—that would ultimately reveal rotational and vibration band structures.

FIELD THEORY OF NUCLEAR FORCES

By about 1936, much of the basic phenomenology of the two-body force was understood, that is, charge independence,[262] spin dependence, as well as the existence of exchange forces and a hard core that kept the nucleus from collapsing. Only lacking, as we have seen, was the spin–orbit force. A microscopic theory was not possible, but the initial work on exchange forces[263] in 1932–1933 along with parallel developments in quantum-field theory in the same period, pushed things in the direction of a field theory of nuclear forces, and that theory grew out of the Fermi field theory of β-decay, offered at the end of 1933.[264]

The issue was that if, as seemed to be the case, the electron and neutrino in β-decay did not exist in the nucleus but were created at the moment the neutron changed into a proton, $n \rightarrow p + e^{-} + \nu$, then one had to introduce creation operators for the two particles, that is, invoke something like the field theory of Dirac and Jordan and Klein of 1927–1928.[265] The 1934 theory of Tamm and Ivanenko[266] that pictured the $n - p$ force as being due to the exchange of a virtual neutrino–electron pair, though a conceptual leap forward and actually pioneered by Heisenberg, was superseded by Yukawa's proposal in 1935,[267] based on the short range of nuclear forces, that the interaction between neutrons and protons must be carried by a medium-mass particle, the "meson."[268] This theory represented the birth of the modern theory of nuclear forces as due to the exchange of a force-carrying particle. When the muon, with a mass of 106 MeV, was discovered in cosmic rays by Anderson and Neddermeyer in 1936[269] at about the predicted mass, it was initially assumed that this was Yukawa's particle, responsible for the strong force.[270] It was not until 1946 that the pion ($\pi^{\pm}, \pi^{0}$), the basis for the one-pion-exchange potential (OPEP), which preceded the quark–gluon model and continues to be useful, was discovered.[271] Issues of phenomenology would occupy the decade or so leading up to 1946–1949, when as quantum electrodynamics (QED) matured, it became possible to think of a fundamental theory of the strong

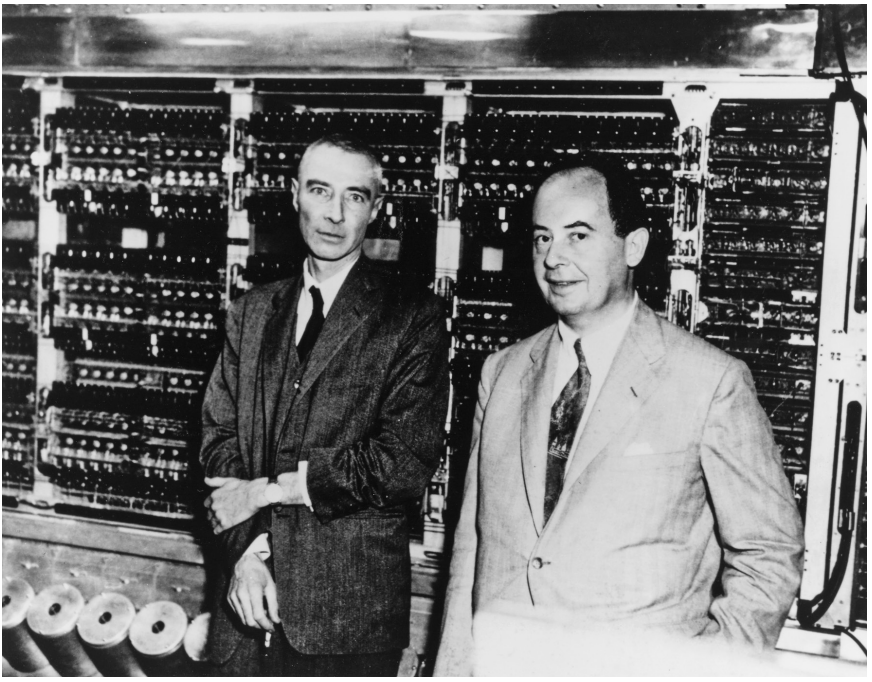

Figure 15.8. Robert Oppenheimer (1904–1967) and Enrico Fermi (1901–1954). AIP Emilio Segrè Visual Archives.

force, and the Pauli–Yang–Mills non-Abelian gauge theories came on the scene in 1953–4.[272]

The further development of the theory of nuclear forces is told elsewhere,[273] but with the discovery of the pion, emphasis was placed on the relatively long-range OPEP and phenomenological potentials involving ρ, η, φ mesons, and so on. It became clear in the 1960s that the full character of the two-body force could be studied in only at least three-body systems.

The discovery of $SU(3)$ flavor symmetry by Gell-Mann and Ne'eman in 1961 and the quark theory of hadrons by Gell-Mann and Zweig in 1964 changed all that, and led to the gauge theory of strong interactions, QCD, as part of the standard model.[274] Thus the "nuclear force" or nucleon–nucleon force, first conceived in the 1920s, was replaced by the "strong force," one of the four fundamental forces of nature, carried by a gauge boson, the "gluon." The other ingredient of the standard model, the theory of the weak interaction, mediated by the $W^{\pm}$ and Z vector bosons, and ultimately the gauge theory of the electroweak force, had its origin in 1967–1968 in the hands of Glashow, Weinberg, and Salam.

It is interesting, nonetheless, that it was found that enormous progress could be made in treating the structure of nuclei without a detailed and fundamental knowledge of the two-body force, so that the nascent state of knowledge of that force did not

appreciably inhibit progress in understanding real nuclei, as argued by Wigner over 70 years ago.

MANY-BODY THEORY OF NUCLEAR MATTER AND FINITE NUCLEI

Even had the nucleon–nucleon interaction been fully understood, the problem of the nucleus as a many-body system would have remained**.** Strongly correlated systems, which include magnetic materials, superconductors, nuclei and nuclear matter, and so on, are commonly approached using very similar theoretical techniques. Thus many-body theory is not just a branch of nuclear physics, or for that matter, of solid-state physics, but rather a field of its own, with extensive applications, specialized techniques, and formalism. The fact that solids and liquids are many-body systems was inescapable almost from the moment the atomic theory of matter was accepted near the end of the 19th century. The knowledge that atomic nuclei are many particle systems was known by the second decade of the century, and by the early 1930s the basic properties of nuclei were known. What was not known was how a system of many interacting fermions should be treated theoretically. In theory, the many-particle Schrödinger equation could be written with two-body interactions coupling the particles, but no simple solution was possible. The typical progression began with a model in which the particles, atoms, electrons, or nucleons moved independently in an average central force field, with the possibility of including two-particle interactions as a perturbation. The final result might be a model of noninteracting quasi-particles (particle–hole excitations) that at least partially included the effects of interactions. The problem of nuclear matter (no boundaries) was treated in the Brueckner–Goldstone theory, using the full apparatus of many-body theory, in the 1950s.[275] The story of these and subsequent developments must be left for another time and place.

CONCLUSION

We have learned that although nuclear physics had its experimental origins in 1911 with Rutherford's nuclear atom, no theoretical description was possible before quantum mechanics was created in 1925–1926. The result was that nuclear theory had a new beginning in the years around 1930, with the first attempts to understand α- and β-decay, the discovery of the neutron, and Heisenberg's early attempts to understand the nuclear force. Although much was accomplished in the decade that followed, the war soon halted progress or pushed it underground, so that nuclear physics had a further beginning as it burst its wartime constraints in the late 1940s. The nuclear-shell model, including the crucial spin–orbit interaction, emerged after 1947, and if for a while there was vigorous competition between the proponents of collective models and those of the shell or independent-particle models, the unification that resulted from their merger became dominant.

Thus the 1950s and 1960s were the real decades of nuclear physics, before the excitement in fundamental physics moved to such high energies that the nucleus was no longer on the cutting edge, and particle physics came to the fore. Portions of the story of how nuclear physics, building on the foundations laid down in the 1930s, became the frontier field of physics in the 1950s can be found elsewhere, though there is room for a more comprehensive account.[276] It does seem worthwhile, however, to take notice of two applications of the maturing science of nuclear physics (and therefor of quantum mechanics), which evolved right along with the physics of the nucleus itself and are inseparable from it: nuclear energy generation in stars and cosmic nucleosynthesis. This we will do in the next chapter.

NOTES

1. I have chosen in this chapter and the next three to trace the history of four fields that, as applications of the quantum mechanics, have had the greatest impact on the development of quantum theory itself. One may choose to argue the point, but certainly there is a case to be made that these fields have been the most fertile sources of problems that required innovative and revolutionary developments in quantum mechanics itself. And lest I be accused of personal bias based on the length of this chapter, it is clear that the application of quantum mechanics to nuclear physics in the decade after 1930 led to more fundamental discoveries in fundamental physics than in any other field of applied quantum theory. As for "The First Three Decades," we take nuclear physics to have had its origin in 1911. There is no better guide to these developments than the first 18 chapters of Pais's 1986 *Inward Bound*.
2. If we wanted to carry this slicing of history still further, the decade and a half between the discovery of natural radioactivity in 1895 and that of the atomic nucleus in 1911 was very similar to the period leading up to the Bohr atom, one in which there was essentially no theory at all.
3. One of the very best sources of personal recollections by the founders of nuclear physics is *Nuclear Physics in Retrospect* (Stuewer, 1979) based on a conference held in 1977 when many of the early figures were still with us. A useful reprint volume is Beyer (1949), though there are no translations. Brink's *Nuclear Forces* (1965) reprints 14 early papers, all rendered into English.
4. Becquerel (1896). The *becquerel* (Bq) is the SI unit of radioactivity, replacing the older *curie*. The history of radioactivity is there.
5. The term radioactivity having been coined by Marie Curie. The chemist Wilhelm Ostwald described the facility in which they carried out the separation as "a cross between a stable and a potato shed" (Reid, 1974, p. 95). Although Marie died in 1934 at age 77 from the effects of working with radioactive sources, Pierre was spared that end, having been killed in a street accident 28 years earlier. On the scandal involving Marie's relationship with her former student Paul Langevin, see Quinn (1995).
6. Including five of the noble gases. In some cases the date of discovery is a judgment call. Promethium was only discovered in 1945 as a fission product of uranium.
7. Or so it was thought. It is now known that 98 elements occur naturally, up to californium. Ten elements were first synthesized and later found in nature, including four below uranium (Z = 43, 61, 85, and 87). All the elements from Z = 93 to 98 occur naturally in very small

amounts. Californium is commonly used as a neutron source, ^{251}Cf having a half-life of 898 years. ^{254}Cf was once thought to determine the decay of the light curves of type Ia supernova. Technitium ($Z = 43$) is especially interesting, because it has no stable isotopes and thus does not occur naturally, except in minute amounts. But it has recently been found in cool stars.

8. Röntgen having been awarded the first Nobel Prize, in 1901.
9. And named by Eugen Goldstein [*Kathodestrahlen*]. Canal rays [*Kanalstrahlen*], as opposed to cathode rays, had positive charge (positive ions) but some were what came to be called protons.
10. He wrote "I can see no escape from the conclusion that they are charges of negative electricity carried by particles of matter" (Thomson, 1897b). George Johnstone Stoney had named the "atom" of electricity the "electron" by 1891 (Stoney, 1894). One could therefore argue the question of the "discovery" of the electron. While Stoney taught at Queen's College, Galway, Thomson held the prestigious post of Cavendish professor at Cambridge. Thomson, however, carefully measured the charge-to-mass ratio of the "corpuscles" using electrostatic and magnetic fields. His assistant H. A. Wilson eventually became the first professor of physics at the newly founded Rice Institute, in 1912, retiring from Rice in 1947. It is a bit surprising to find Blatt and Weisskopf saying as late as 1952 that "The evidence that beta-rays are identical with ordinary electrons and positrons is overwhelming" (p. 670).
11. Rutherford (1899). There he wrote, "These experiments show that the uranium radiation is complex, and that there are present at least two distinct types of radiation—one that is very readily absorbed, which will be termed for convenience the α radiation, and the other of a more penetrative character, which will be termed the β radiation." In 1903 he said this: "It is known that uranium, thorium, and radium emit two types of radiation. One is not appreciably deviable by a magnetic or an electric field and is and is very easily absorbed in matter. These will be called the α rays. The others are deviable and of a more penetrating in character, and will be called the β rays" Rutherford (1903a). It is said that Mach renounced his skepticism about the existence of atoms after viewing α-particle scintillations in 1900.
12. Rutherford (1903b). The radius of curvature is proportional to the mass-to-charge ratio, and the α-particle is over 7000 times more massive than an electron or β-particle, with only twice the charge.
13. Because the α-particles would have been absorbed by the paper in which the photographic material was placed.
14. Which is, of course, technically true, and it is essentially a matter of the source of the radiation. Gamma rays from nuclear decay are called γ-rays regardless of energy, but usually are above 100 keV of energy (Villard, 1900a, 1900b). Nuclear γ -rays rarely exceed 10 MeV, and so astrophysical γ-rays of TeV energy have other sources.
15. Rutherford and Andrade (1914). See Wheaton (1983), pp. 222–4.
16. Ramsay and Soddy (1903). Soddy received the Nobel Prize in chemistry in 1921. Ramsay was awarded the 1904 Nobel Prize in chemistry.
17. Rutherford and Royds (1908a, 1908b).
18. Rutherford and Royds (1909).
19. Rutherford (1914). In the paper that followed this one, communicated by Rutherford, C. G. Darwin assumed without comment that the α-particle was of mass 4 (Darwin, 1914). C. G. Darwin was the grandson of Charles Darwin and the son of George Darwin, mathematician and astronomer.

20. Rutherford (1919a), speaking here of the helium nucleus, not the atom.
21. Chadwick and Bieler (1921). In his book *Radiations from Radioactive Substances*, written in 1930 with Chadwick and Ellis (Rutherford et al., 1930, p. 48), Rutherford wrote that "The evidence of the identity of the α particle with the helium nucleus is thus very strong," though he does make stronger statements elsewhere in the book.
22. Geiger (1909, 1910); Geiger and Marsden (1909, 1913). Geiger was a new PhD working with Rutherford and Marsden was still a 20-year-old undergraduate at Manchester in 1909.
23. Rutherford (1911).
24. Immediately making it clear that the nucleus had an enormous density, something like 10^{14} g/cm^3. It also hinted, or at least would eventually reveal, that there might be some kind of short-range force, perhaps repulsive in some situations and attractive in others, that eventually would have to be understood in terms of an intrinsic nuclear force (what we know now as the "strong force").
25. Geiger and Marsden (1909). The α-particles from radium C' (^{214}Po) had an energy of 7.68 MeV. In a paper immediately preceding the joint paper, Geiger described in detail how their radioactive sources were calibrated (Geiger, 1909). Evans's volume on the nucleus (Evans, 1955) describes in detail the state of nuclear physics a decade after the war ended, but is full of historical detail.
26. Rutherford (1911). Rutherford famously recalled that it was "as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you" (Andrade, 1964, p. 111). Geiger and Marsden only remarked that "it seems surprising that some of the α-particles, as the experiment shows, can be turned within a layer of 6×10^{-5} cm. of gold through an angle of 90° and even more." The experiments themselves did not determine the sign of the charge on the nucleus. It is worth adding that the uncertainty principle places limits on the validity of a classical treatment of Coulomb scattering; ultimately the scattering has to be treated quantum mechanically, which began to be possible only after 1926.
27. Op. cit. Rutherford (1911). That is, the possibility that the large-angle scattering was due to numerous successive scatterings had to be ruled out.
28. Thomson (1904). Due originally to Kelvin (see Rutherford, 1914). A model that was quickly abandoned by its creator in favor of one with electrons circulating in rings. See Brown and Rechenberg (1996), p. 6. The model was motivated by the stability problem.
29. In his paper on the hydrogen atom (Bohr, 1913a). To a considerable degree the success of the Bohr theory was what convinced many that Rutherford was right.
30. Wilson (1912). Wilson invented the cloud chamber in 1911 and shared the 1927 Nobel Prize.
31. Although energies were expressed in terms of the range of the particles in air early on, by 1933 (at least), energies were often expressed in volts. By 1942 MeV had become standard.
32. Thomson was apparently forced out in favor of Rutherford by being asked to become master of Trinity College, an offer he couldn't very well refuse.
33. Rutherford (1919a).
34. Chadwick and Bieler (1921). In Chadwick's case, after having been interned by the Germans during the war.
35. Bieler (1924). This paper gives a very lucid description of the theoretical and experimental situation in Rutherford's laboratory in the 1920s. Bieler died in Australia in 1929 of pneumonia at the age of 35. He had spent 3 years in Rutherford's laboratory at Cambridge before returning to McGill University, from which he was on leave in 1929. It is conceivable that he might have been awarded the Nobel Prize in physics with Chadwick, who received

it in 1935. The story of Chadwick's involvement with the Manhattan Project is one that should not be missed.

36. Although the proton was named only in 1920, it had been produced in 1917, and of course it was the nucleus of the hydrogen atom.
37. My italics. A revolutionary idea. Bieler (1924).
38. Rutherford and Chadwick (1927), p. 620. By the time this paper was written, both matrix and wave mechanics had appeared. Rutherford pointed out that Oppenheimer (1927) had shown that the quantum-mechanical treatment of Coulomb scattering did not differ from the classical result.
39. Debye and Hardmeier (1926).
40. Rutherford et al. (1930). Maurice Goldhaber has characterized Rutherford as a "cryptotheoritician," for his interest and indulgence in theory, despite his role as one of the premier experimentalists (Shea, 1983). For some reminisces see Pais (1986), pp. 436–8. Rutherford died of a strangulated hernia in 1937.
41. The same could be said, of course, of Einstein and perhaps others, e.g., Pauli, Heisenberg Only two people have received two Nobels in a scientific field, Marie Curie and John Bardeen, both of whose prizes were in physics. Bardeen did his doctoral work under Wigner (as did Seitz, Shimony . . .).
42. Rutherford (1911).
43. Because the nuclear stability line rather strongly departs from $N = Z$, or $Z \propto A$ at large Z, indeed for A not much greater than 40.
44. "The theory of scattering as given by Sir J. J. Thomson leads to the conclusion that the number of scattering electrons per atom is about half the atomic weight . . ." Barkla (1911).
45. Van den Broek (1911). In 180 words.
46. Moseley (1913).
47. First by Dalton and Berzelius. In 1811 Avogadro concluded that equal volumes of gases contained equal numbers of particles (a story in itself); hence simple weighing could determine relative atomic weights. In 1819 duLong and Petit concluded that the product of the specific heat of an element and its atomic weight was equal to 6.4, providing another means for determining the latter. Eventually atomic weights were defined in terms of a standard such as ^{16}O or ^{12}C. From the time of Aston, they could be determined by mass spectrometry.
48. See Darwin (1955), "The discovery of atomic number." Also Kragh (1985), "The theory of the periodic system," p. 50.
49. Rutherford (1914). Rutherford argued that the experiments of Geiger in 1910 (Geiger, 1910) and Geiger and Marsden in 1913 (Geiger and Marsden, 1913) had established this fact.
50. Literally meaning "same place." Soddy (1913).
51. Rutherford (1919b).
52. Verified in cloud-chamber photographs. This would be an (α, p) reaction.
53. Meaning "first." He also apparently suggested "prouton" in honor of Prout. In a summary of the BAAS meeting in Cardiff, Wales, in 1920, we find "proton, as Sir Ernest Rutherford would have us call them." *Nature* **106** (1920), 357.
54. Harkins and Wilson (1915b). More than a decade before Dirac's theory of the electron that eventually predicted positive electrons, though with the same mass as the electron.
55. Rutherford (1919b), p. 586. Rutherford had four papers, titled "Collision of α particles with light nuclei," parts I–IV in issue 222 of the *Philosophical Magazine* in 1919; this was part IV.

56. Soddy later recalled that in 1901 when he and Rutherford discovered that α-decay converted thorium into radium, he had exclaimed "Rutherford, this is transmutation!" Rutherford snapped back, "For Christ's sake, Soddy, don't call it *transmutation*. They'll have our heads off as alchemists." Blackett obtained cloud-chamber photographs of this process in 1924, working for Rutherford (Blackett, 1925).
57. Which was assumed to be the case, to provide stability.
58. The electron charge-to-mass ratio $[e/m]$ had been determined by J. J. Thomson and its charge by Millikan and Fletcher in 1909–1913. The measurement of even relative atomic masses was very difficult before mass spectrometry, beginning in 1912 and widely utilized by Aston (see subsequent discussion).
59. Rutherford (1920). The neutral particle, "an atom of mass 1 which has 0 nucleus charge," was supposed to be formed from a proton and an electron.(p. 396).
60. Ibid., Harkins (1920).
61. Harkins and Wilson (1915b).
62. Aston was also mentored by J. H. Poynting.
63. A mass spectrometer utilizes the curved path of a charged particle in a magnetic field to separate particles with slightly differing mass. Mass spectrometry was one of the methods used to separate ^{235}U from ^{238}U in the early 1940s.
64. See Aston's Nobel Lecture. He describes detecting 6 isotopes of Kr and 9 of Xe, and says that the weights of all the elements are "whole numbers to the accuracy of experiment," then qualifies this by saying that "the whole number rule is not supposed as mathematically exact . . ." and even mentions the "packing effect." Ironically, Aston's award was in part for "his enunciation of the whole-number rule." J. J. Thomson had discovered two isotopes of neon with weights of 20 and 22 in 1912.
65. Although the term "isotope" was first used in print by Soddy in 1913, it has an interesting history. See Soddy's biographical memoir by Fleck (1957), p. 208.
66. These are, of course, special cases of the well-known fact that even–even (Z, N) nuclides are the most stable, with even–odd and odd–even being on average less stable, and odd–odd almost never stable. Aston's observation that isotopes with odd Z usually had odd A is an example of the odd–even case. The neutron was, of course, a decade away. Aston's understanding of nuclear structure was based entirely on the prevailing proton–electron model, which he endorsed. See his Nobel Lecture.
67. Nobel Lecture, delivered December 12, 1922. He also commented that "Should the research worker of the future discover some means of releasing this energy . . . the human race will have at its command powers beyond the dreams of science fiction; but the remote possibility must always be considered that the energy once liberated will be completely uncontrollable. . . . In this event the whole of the hydrogen on the earth might be transformed at once and the successs of the experiment published at large to the universe as a new star." In 1933 Rutherford commented at a BAAS meeting that "the energy produced by the breaking down of the atom is a very poor kind of thing. Anyone who expects a source of power from the transformation of these atoms is talking moonshine." (Pais, 1986, p. 436).
68. Harkins and Wilson (1915a). They were just as interested in the departure of the atomic weights from whole numbers as was Aston, several years later. For details see Evans (1955), pp. 294–5. Writing $M = A(1+P)$, where P is the packing fraction, makes it clear that P is

a small correction term of less than 1 part in 1000 (positive or negative) to the integer rule. Pais (1995) has described it as "one of the least transparent ways of representing data I know of." The binding energy, $B = (Z\, m_p + N\, m_n - M)c^2$, is very approximately the mass of A nucleons minus the atomic mass M, multiplied by c^2, in appropriate units (1 amu translates to 931 MeV). Then

$$B = \left[A - M + Z\left(m_p - m_n\right) + A\left(m_n - 1\right)\right]c^2,$$

or

$$B/A = [-P - Z/A\,(\Delta m) + (m_n - 1)]c^2,$$

where P is the packing fraction, and Δm is the n–p mass difference, about 782 keV. The Z/A Δm term amounts to ~~nearly~~ less than 1 MeV/nucleon and B/A averages about 8 MeV/ per nucleon. The final term (mn–1) also amounts to about 8 MeV per nucleon. Thus, in MeV/nucleon, the packing fraction averages close to zero, and because the were defined to be zerod of ^{16}O, they can be positive or negative. [see Evans (1955), p. 295]. The addition of the Z/A term, which decreases with A, means that the B/A curve is flatter than the packing fraction. Because of the similarity of the proton and neutron masses, B is very nearly equal to $(A - M)c^2$. The mass defects and binding energies are positive, averaging about 8 MeV per nucleon.

69. Aston (1933, 1935, 1936a, 1936b); Bainbridge (1932–~~1932d~~, 1933a, 1933b, 1933c, 1933d, 1933e. ~~1933c~~). Bainbridge, who died at age 92 in 1996, directed the first nuclear test at the Trinity site in 1945. His is reported to have said to Oppenheimer that "we are all sons of bitches now."
70. We use the term anachronistically; it appears that the first use of "nucleon" was in a letter by C. Møller to *Physical Review* dated December12, 1940 and titled "Nomenclature of nuclear particles." Møller acknowledged that an unnamed person persuaded him that nucleon was philologically more appropriate than "nuclon."
71. *Absättigung* in German. Because the number of pairwise interactions is $A(A-1)/2 \approx A^2$, then B/A ought to be proportional to A for A sufficiently large. For example, see Evans (1955), p. 299. Evidently, a nucleon interacts only with nearest neighbors, because of the short range of the force and/or the Pauli principle. Thus the nucleus is fairly dilute.
72. See the discussion in Evans (1955), pp. 276–7, in which all of the evidence against nuclear electrons is summarized; Chadwick, Constable, and Pollard (1931), p. 482.
73. Ambartsumian and Ivanenko (1930a). More properly, Iwanenko. See also Pais (1986) for the contribution of Y. G. Dorfman. Wheeler admitted that as late as 1939, he was still trying to find a way of understanding the nuclear force through the electron–positron interaction. Weiner (1972), p. 147–8.
74. Klein (1929).
75. Kronig (1926).
76. Kronig (1928b).
77. Rasetti (1929a, 1929b, 1929c). The interpretation of Rasetti's experiments was due largely to Heitler and Herzberg (Heitler and Herzberg, 1929). Also Ornstein and van Wijk (1928). See Pais in Brown et al. (1995), but especially Pais (1986), pp.300–1. Recall that the proton was found to have spin-1/2 in 1927 (Dennison, 1927). See Stuewer (1983), p. 19: See also

the *Cal Tech Oral Histories* interview with Rasetti by Judith Goodstein, February 2, 1982, in the *Archives of the California Institute of Technology*. The term "fermion" was coined by Dirac much later.

78. Schüler and Brück (1929). The number of fermions would be $N_f = 2A - Z$, an even number if Z is even. The reference is faulty in Pais (1986).
79. Frisch and Stern (1933); Estermann and Stern (1933). The value was soon improved by Rabi and collaborators to about 2.8 nuclear magnetons.
80. $e\hbar/2m_p$ in SI units.
81. A value obtained by Bacher (1933) from the lack of hyperfine splitting. A more precise value of $0.4\,\mu_N$ was obtained in 1938–1939 by Rabi et al. (Kusch, Millman, and Rabi, 1939).
82. See papers in *Physical Review* beginning in 1931 by Breit and Rabi, Rabi and Cohen, etc. Nuclear magnetic moments could be measured by a variety of means, including atomic hyperfine structure, Larmor precession, molecular beam experiments, etc. Rabi was awarded the 1944 Nobel Prize in physics for nuclear magnetic resonance. For what it is worth, he was reputedly a notoriously bad teacher.
83. Pauling and Goudsmit (1930).
84. Langer and Rosen (1931). This remarkable paper in *Physical Review* in 1931, a year before the discovery of the neutron, examined the possible role of a hypothetical "neutron" in stellar nucleosynthesis!
85. Bothe and Becker (1930).
86. Joliot-Curie and Joliot (1932a, 1932b).
87. Chadwick (1932a, 1932b). The first paper is reprinted in Beyer (1949). It is said that Majorana had the idea before Chadwick but declined to publish it.
88. According to Segrè in 1972, Majorana was convinced that the Curie-Joliots had discovered the "neutral proton," and "they don't even recognize it. They are stupid as usual." Segrè commented that "this was Majorana's style." (Weiner, 1972, p. 125.) The usual cautions apply when evaluating a 40-year-old recollection.
89. He noted that "If it be supposed that the radiation consists of quanta, then the capture of the α-particle by the Be^9 nucleus will form a C^{13} nucleus." The $^9Be\ (\alpha, n)^{12}C$ reaction has an especially high cross section.
90. An example of the typically short gap between experimental discoveries and the Nobel award, in contrast to awards to theorists, for fairly obvious reasons. The award of the 2013 prize for the discovery of the Higgs the year before is less typical. Probably not hasty, but who knows? The three of them, Rutherford, Chadwick, and Ellis, wrote the definitive book on radioactivity in 1930. It is worth noting that while Ellis and Chadwick were making these discoveries in Rutherford's laboratory in Cambridge, Lisa Meitner, along with Hahn and others, was exploring similar problems in Vienna and Berlin. Meitner, who was called by Einstein "Germany's Marie Curie," as a woman and a Jew, suffered discrimination throughout her career, finally being passed over when the 1944 Nobel Prize in chemistry was awarded solely to Otto Hahn for the discovery of fission. Meitner, it could be said, got the last word, for element 109 bears her name: Meitnerium. In recent years seven chemical elements in the $A = 99$–112 range have been named for 20th-century scientists, and two others after Mendeleev and Copernicus. Element 102 is nobelium. Six others are named after geographical locations, usually laboratories
91. Chadwick and Bieler (1921). See n. 35, 36.

92. Paraphrasing a statement of Peierls (1979, p. 185). Peierls says that "it had been known for a long time that the binding energies of nuclei rose only proportionally with the mass number" (ibid., p. 186). As we proceed, we will try to trace the evolution of this awareness.
93. Bacher and Condon (1932). Some of their assumptions were untenable, however. See Ward Whaling's 2009 biographical memoir of Bacher.
94. Rutherford and Chadwick (1925).
95. See the argument in Evans (1955), pp. 47–8. There is also an excellent discussion in Gurney and Condon (1929), p. 139: "That is to say, the uranium alpha-particle appeared to emerge from a region where its kinetic energy was negative." Also Chadresekhar (1939), pp. 458–60.
96. He studied with Alexander Friedmann of Friedmann-Lemaître fame, before the latter's death, and student friends included Lev Landau and Dimitri Ivanenko.
97. Hund, (1927); Nordheim (1927). Also Fowler and Nordheim (1928) and Oppenheimer (1928c). For details, see Merzbacher (2002).
98. This idea worked its way into Slater and Frank's book on theoretical physics of 1933 in the form of a one-dimensional rectangular barrier (sec. 212).
99. Gamow (1928a, 1928b). Also Gamow and Houtermans (1928). See Stuewer's 40-page paper on Gamow's discovery (Stuewer, 1986). Wigner, *Recollections* published in 1992 tells an interesting story about Houtermans and his warnings about the German nuclear weapons program. See also *Physics in a Mad World* (Shifman, 2015) on Houterman's imprisonment both in the Soviet Union and in Germany. This is clearly not the place to explore Heisenberg's vigorous prosecution of the German nuclear weapon program, but see Bernstein (2002), for example.
100. Acccording to Stuewer (1986) or Merzbacher (2002), Gamow submitted his paper on July 29, 1928, and Gurney and Condon the next day, which is the date on their letter to *Nature*. Gamow's was received by *Zeitschrift für Physik* on August 2. Gurney and Condon beat Gamow into print by 20 days, when their letter appeared on September 22, 1928 (official dates). A more expansive paper was published the following February (Gurney and Condon, 1929). Mehra and Rechenberg (1982–2000; vol. 6, part 1, p. 639) provide an extensive discussion of the physics and the timing of the affair, but the most thorough discussion is in Stuewer (1986), who notes that Condon said that the idea was Gurney's. In a thoroughly fascinating and poignant retrospective, Condon described their collaboration in a paper published posthumously in 1978 (Condon, 1978). He also recounted the further career of Gurney and how Gurney and eventually he, Condon, became victims of Cold War hysteria. Gurney died in 1954, Condon 20 years later. In Condon's view, it was the greater exposure that Gamow enjoyed in late 1928 in Europe, which was a hotbed of frontier physics, that led to his getting most of the credit for the discovery of nuclear tunneling or "barrier leakage." In Condon's words, "In those days American physics did not amount to much."
101. Gurney and Condon (1928, 1929), the latter employing the Wentzel–Kramers–Brillouin approximation.
102. Gamow (1928a). He first examined penetration of a rectangular barrier, then introduced a more realistic radial dependence.
103. His actual result was more complicated and depended on the nuclear potential. The empirical Geiger–Nuttall rule (1911, 1912) was of the form $\log \lambda = a + b \ln r$, where r is the range in air and λ is the "transformation constant." The range in air is roughly

proportional to the energy. The Geiger–Nuttall law is now usually stated in terms of the half-life as $\log \tau_{1/2} = a + bZ\, E^{-1/2}$. In either form this means that the half-life decreases very rapidly with increasing energy; for example, see Halliday (1955), p. 74. Preston and Bhaduri (1975) provide a derivation.

104. Another approach was soon given by Born (1929), again showing his command of wave mechanics.
105. Obtaining a proton beam was not at all easy, of course. Electrons could be generated by thermionic emission and α-particles from radioactive decay; protons were another matter, and of course neutrons were even harder. Practical acceleration of protons had to wait until electrostatic machines like the van de Graaf accelerator appeared, no earlier than 1930.
106. Gamow (1928b). Also Breit (1929).
107. Cockroft and Walton (1932).
108. Atkinson and Houtermans (1929).
109. Chadwick (1914).
110. Including Bohr, ca. 1928–1929, who again toyed with the idea of giving up energy conservation, an idea that he never published but was widely circulated. The initial and final states of the two nuclei seemed to always have the same energies, but the electron did not. In the neutrino model, the energy of the decay process is shared among the recoiling nucleus, the electron, and the neutrino.
111. Ellis and Wooster (1927).
112. Ellis (1922). See Pais's delightful discussion as well (Pais, 1986, p. 160). Charles Drummond Ellis had been interned by the Germans during WWI with Chadwick, who inspired him, and he joined Chadwick in Rutherford's laboratory at the Cavendish.
113. Leipunski (1936); Crane and Halpern (1938). Although conclusive experiments were not possible until about 1949. See Fermi (1950), p. 84.
114. American Physical Society, June 15–20, 1931. Mladjinovic (1998) makes the point that the idea was so controversial that Pauli only presented it at conferences in 1931–1933, rather than trying to publish it. He had been mulling the idea over since some time in 1930.
115. Dennison (1927). See also Dennison (1974) for his recollections, nearly a half-century later, of this theoretical discovery.
116. Murphy and Johnston (1934); Raether (1934). Note that Bacher and Condon had earlier come to the same conclusion about the neutron. See n. 93 in this chapter. As early as 1920, Rutherford had spoken of "the possible existence of an atom of mass nearly 2 carrying one charge, which is to be regarded as an isotope of hydrogen." Such a nucleus, later to be the deuteron or deuton, could have been seen as having two protons and one electron. Rutherford (1920), his Bakerian Lecture to the Royal Society. The lecture has been given yearly since 1775, except for 11 years in the 19th century.
117. Ivanenko (1932a, 1932b).
118. The neutron spin was known to be 1/2 or 3/2, and assumed to be 1/2, but in 1937 Schwinger showed that it was the former (Schwinger, 1937).
119. The capitalization problem here is a bit annoying. Units such as the coulomb or the becquerel are not capitalized, but in Coulomb scattering, for example, uppercase is used. Similarly, fermion or boson is not capitalized. The rule is that names used as adjectives are capitalized; when used as nouns they are not.

120. In extensions of the standard model, the neutrino magnetic moment is tied to a nonzero mass.
121. Finally dectected in 1956 by Reines and Cowan (Cowen, Reines et al., 1956; Reines and Cowan, 1956). To be precise, the effect or signature of neutrino capture was detected. Reines was awarded the Nobel Prize in 1995. Of course we now know that although the neutrino is elementary, the proton is not.
122. Chadwick and Goldhaber (1934). The neutron magnetic moment was measured in the late 1940s, of which Robley Evans (1955) wrote that it "possesses an unknown inner constitution . . ." to explain the nonzero moment of a neutral particle. And indeed it does. The greater neutron mass means that a free neutron can decay into a proton, with a half-life of 886 s. Proton decay is another matter entirely, bound up in fundamental questions about the standard model. On Goldhaber, see the *NAS Biographical Memoir* by Crease and Alfred Goldhaber (2012).
123. ". . . speculations too remote from reality to be of interest to the reader." See Pais (1986).
124. See, for example, Cassidy (1992), chapter 14.
125. Fermi (1934a, 1934b). English translation in Wilson (1968). Also Gamow and Teller (1936). Fermi died in 1954 at age 53, of stomach cancer, the same disease that killed Maxwell at age 48. Von Neumann died of cancer at age 54.
126. An anti-neutrino in today's parlance. Pais (1986) says that "anti-particle" and "anti-neutrino" were introduced by de Broglie in 1934. Also positron (β^+-) decay, or positron emission from the nucleus, in which a proton decays into a neutron plus a neutrino, which cannot happen in free space. At this point (1934) it was slowly beginning to become clear that what we now call baryon and lepton numbers were conserved.
127. Pais (1986) notes that "Fermi was the first to use second-quantized spin-1/2 fields in particle physics."
128. Here $\psi_p\dagger$ annihilates a proton, and $\phi_e\dagger$ destroys an electron. Similarly, ψ_n creates a neutron and ϕ_ν creates an electron neutrino. Conventions differ. Some details are given in Pais (1986), pp. 417–23 or DeBenedetti (1964), pp. 534–40.
129. The use of the term weak interaction was not common before the mid-1950s. It was usually referred to as the "Fermi interaction" or perhaps the "β-interaction."
130. Gamow and Teller (1936).
131. Anderson (1933). The positron was discovered by Anderson, who received the Nobel Prize in 1936, and gave the particle its name. Several scientists had had glimpses of the positron as early as 1929 in cloud-chamber photographs, especially ~~by~~ Dmitri Skobeltsyn, without recognizing what they were seeing. Patrick (P. M. S.) Blackett was essentially a codiscoverer of the positron, using a cloud chamber in early 1933 (Blackett and Occhiallini, 1933). Blackett was awarded the Nobel Prize in physics in 1948 for the development of the Wilson cloud chamber and the discoveries he made with it. Until the positron was discovered, Dirac believed that in some sense the negative-energy states he discovered were protons (see Chapter 13).
132. An interesting discussion is in Millikan (1935), pp. 375–9. Chadwick himself was noncommittal on the question of whether the neutron was elementary: "It is, of course, possible that the neutron may be an elementary particle. This view has little to recommend itself at present, except the possibility of explaining the statistics of nuclei like N^{14}" (Chadwick, 1932a, 1932b). And there was, of course, the magnetic moment problem, discussed above.

133. Although the "spin–statistics theorem" dates from 1939, even in 1928–1929 it was assumed that particles with odd half-integral spin were fermions (again, the name coined by Dirac in 1945), and with integral spin were bosons.
134. Joliot-Curie and Joliot (1934a, 1934b). (Also Frédérick Joliot's Nobel Lecture, December 12, 1935, and the article by their collaborator Pierre Savel at *springer.com/article/10.1007%2FBF01115678*.
135. For details, see Guerra et al. (2012).
136. The state of weak interaction theory as of about 1960 is exhibited in Kabir's compilation of papers (Kabir, 1963).
137. Borrowed from Hans Bethe (Bethe, 1979). This was the title of his contribution to Stuewer's symposium proceedings, *Nuclear Physics in Retrospect* (Stuewer, 1979). Bethe was one of Sommerfeld's students at Munich, and Sommerfeld tried to help find the 27-year-old Bethe a job in the face of Nazi anti-Semitism. Or "The Age of Innocence," the decade of nuclear physics before the discovery of fission and its use in making bombs. See Crease and Goldhaber (2012).
138. The main exceptions being Dirac's hole theory of the positron and the use of tunneling arguments in α-decay.
139. "is it not possible to admit that neutrons play also an important role in the binding of nuclei?," Ivanenko (1932a, 1932 b). As well as in Fornier (1932) and Perrin (1932).
140. Urey et al. (1932). For that discovery he was awarded the 1934 Nobel Prize in chemistry. The work was prompted by a suggestion by Birge and Menzel (1931), who are unjustly forgotten. They wrote "It [the discrepancy in atomic weights] could be removed by postulating the existence of an isotope of hydrogen of mass 2."
141. Once known as the "diplon" (Goldhaber, 1979). Also, the "deuton" (Rabi et al. 1934).
142. Because as an isotope of hydrogen, it had $Z = 1$, that is, 1 proton, but mass 2. Its total angular momentum ($J = 1$) could be determined from the band spectra of the D_2 molecule. See Evans (1955), pp. 189–90. The deuteron, whose ground state is primarily $^3S_1$, has no bound $^1S_0$ excited state. This has implications, under the assumption of charge independence, for the existence of the di-neutron or di-proton, both of which must be in a ^1S state by the Pauli principle.
143. According to Robert Serber, some thought that the weak interaction at short distances might become strong. In Weiner (1972), p. 124.
144. "The neutron will be taken as an independent fundamental particle that, however, can split, under favorable conditions, into a proton and an electron, violating the conservation of energy and momentum." Translated in Brink (1965), p. 145. Heisenberg seems to have been equivocating at the Seventh Solvay Conference held in October 1933, where he was still entertaining the idea of nuclear electrons. When Rudolf Peierls asked him why he thought the neutron was elementary, he replied that "this was just an impression." Mehra (1975), p. 226.
145. Heisenberg (1932, 1933a, 1933b). The first and third of these are translated in Brink (1965). It was in the first of these papers that Heisenberg introduced his ρ-spin, which we now call isotopic spin. Bethe commented in 1977, "So 1932 was the beginning of the theory of nuclear physics as we know it" Bethe (1979). On this theory, one would expect the $n - n$ nucleus to be very stable, but Heisenberg assumes that the neutrons would decay into protons by β-decay. Because Heisenberg did not allow a non-Coulombic *pp* force, the *nn* force had to be weak as well, because the approximate equality of the number of

nuclear neutrons and protons ($N = Z$) implied that the *nn* and *pp* forces were comparable, though perhaps weak compared with [to] the *np* force. Further, the fact that the difference in the ^{3}He and ^{3}H binding energies was due to the Coulomb force alone also suggested the equality of the *nn* and *pp* forces. See Pais (1986), p. 423.

146. It was also at this Seventh Solvay Conference that initial results from the new charged particle accelerators were presented. The next conference was held 15 years later, by which time much had changed. See Bacciagaluppi and Valentini (2009).
147. It was also in the depths of the great economic depression, which had a major impact the support of science.
148. Wigner (1933). Wigner was still speaking of "heavy neutrons" and " light neutrons." By this point, the American Physical Society's *Physical Review* was becoming the most important physics journal in the world, just as Jewish scientists were fleeing Germany.
149. This was shown not to be justified by Tuve in 1936 by studying $p - p$ scattering [Tuve et al. (1936); see also Bethe (1979)]. The arguments of Guggenheimer, Young, and Feenberg in 1934–1935 were influential. See references in Peierls (1979). Wigner was not being fair to Heisenberg in saying that in the first two parts of his trilogy (Heisenberg, 1932, 1933a) he allowed only protons and electrons in the nucleus. As noted earlier, n part I, Heisenberg wrote that "The structure of nuclei . . . can be described, according to the laws of quantum mechanics, in terms of the interaction between protons and neutrons." Heisenberg even cites Ivaneko's conclusion that there are no nuclear electrons. Wigner, by the way, briefly entertained the idea that there was a three-body *ppn* force in helium, which, in fact, there is.
150. See the discussion in Wiener (1972), pp. 14–15.
151. Heisenberg (1932).
152. Wigner (1937a). In this paper, Wigner notes that it had been shown that the Pauli principle required the nuclear wave function to be antisymmetric with respect to the exchange of space, spin, and isotopic spin coordinates of pairs of nucleons. See references in Wigner's paper.
153. The pions, consisting of a quark–antiquark pair, form an isospin triplet (π^+, π^0, π^-).
154. Wigner (1937a).
155. For much more detail, see Brink (1965), and especially Brown and Rechenberg (1996). It is perhaps worth pointing out that the very idea of "nuclear forces" is nonrelativistic. Ultimately, the nuclear force is a residual interaction resulting from the exchange of colored gluons by *u* and *d* quarks.
156. Chadwick and Bieler (1921); Rutherford and Chadwick (1927)
157. Charge independence expresses invariance of the nucleon–nucleon interaction under rotations in isospin space, charge symmetry represents invariance under rotations by π about the I_3 axis. Or, the first expresses the fact that the *nn, pp,* and *np* interactions are the same, the latter that *nn* = *pp*.
158. Bethe and Bacher (1936), p. 99.
159. As in n. 71, the number of pairwise interactions would be $A(A-1)/2$ or approximately A^2, for A not too small.
160. See the discussion in Fermi's classic *Nuclear Physics* (1950), pp. 111–13.
161. Possibly explained by one-gluon-exchange forces. See the review by Valcarce et al. (2005).
162. Bieler (1924). Evans (1955), chapter 2, gives an excellent discussion of the determination of nuclear radii.

163. If $R = R_0 A^{1/3}$, then V, the nuclear volume, is proportional to A, and the density $\rho = M/V$, is a constant. Gamow (1928a, 1930).
164. Heisenberg (1932, 1933a, 1933b).
165. Wigner (1933); Landé (1933). Wigner is already publishing in *Physical Review*, having gone to Princeton in 1930. The term "saturation" first appears in *Physical Review* (in a nuclear context) in 1935–1936 in papers by Lloyd, Feenberg, and Wheeler.
166. A few years later, Wigner was focusing on "kinks" in the mass-defect curve, that is, departure from the proportionality to A (Wigner, 1937b).
167. Exchange forces arise because of the requirements of the Pauli principle and the requirement that a wave function for a fermion be antisymmetric under exchange of space, spin, and, in the case of nucleons, isospin coordinates. See Peierls (1979), pp. 187–8 on the rejection of a repulsive core.
168. Because it was unrealistic, requiring a spinless electron devoid of a magnetic moment. Heisenberg's model was analogous to the treatement of H_2^-. See Brink (1965).
169. Heisenberg (1932), pp. 591–2. See Brink (1965), p. 17. Brink did not translate the final five pages of the paper where, among other things, the nature of the neutron was discussed. Brown (1995) observes that this material is often ignored because it can be argued that Heisenberg slipped back into a nuclear proton–electron model. See chapter 6 in Mladjenovic (1992).
170. See Brink (1965), p. 23; Heisenberg, p. 159 in Brink. Although Heisenberg later abandoned the idea of a hard core, it was resurrected two decades later. Heisenberg's exchange force, for even ℓ was attractive in the triplet state and repulsive in the singlet; the reverse was true for odd ℓ. See Evans (1955), p. 312. Alternatively, the force was attractive in isosinglet states ($\tau = 0$, np), so that the deuteron would be bound, but repulsive in isotriplet ($\tau = 1$) S-states (like nucleons). So the spin-triplet $^3S_1$ [$^3(np)$] isosinglet state was bound, but no such $^3(nn)$ or $^3(pp)$ isotriplet states exist because this would violate the Pauli principle. With the Heisenberg exchange force, the $^1(nn)$ and $^1(pp)$ forces would be repulsive if we restrict ourselves to S-states, but that is not true of the Majorana or Wigner forces, which are attractive in both the singlet and triplet states. There are, of course, no bound (nn) or (pp) configurations.
171. Majorana (1933), p. 139. Much later (ca. 1952) it was found that in $p - p$ scattering the $^1S_0$ phase shift in the lab system became negative beyond 250 MeV, indicating a repulsive core.
172. See Peierls (1979), p. 189.
173. Majorana was 27 at time, working with Heisenberg in Leipzig. He became a virtual hermit after 1937. His life quickly deteriorated, and he died at sea under unexplained circumstances at age 32. Fermi called him a genius and compared him to Galileo and Newton.
174. See Heisenberg's and Majorana's (Majorana, 1933) papers in Brink (1965). The Bartlett exchange force was a spin-exchange force. Peierls has said of Heisenberg that "there is no indication in his three early papers that he saw the connection between exchange and saturation" (Peierls, 1979), which seems a little harsh.
175. Bartlett (1936).
176. As we saw in n. 170, the corresponding spin states would be singlets ($s = 0$) for even ℓ except in the np case, where both singlet and triplet states $^3(np)$ can exist. We have concentrated on even ℓ because the two-body forces are strongest in relative S-states. Again, see table 1.1, p. 312, in Evans (1955) and the related discussion. Or DeBenedetti

(1964), p. 65. It is the lack of an excited ^1S state of the deuteron that reveals that the $n - p$ force is spin dependent. The weakly bound deuteron is in a $J = 1$ state, hence $^3S_1$, though it was eventually found to have a small mixture of the ^3D state, resulting in a quadupole moment. Pairs of like nucleons [di-neutron $(n - n)$ or di-proton $(p - p)$] cannot be in a ^3S state because of the exclusion principle. Again, the two-nucleon force is strongest in relative *S*-states; hence for like nucleons, the spin state must be a singlet. The deuteron magnetic moment was measured in 1934 by Rabi et al.

177. Evans (1955). Chapter 10 will be helpful.
178. Feenberg (1935a, 1935b, 1935c). See also "The possibility of the same form of specific interaction for all nuclear particles" (Feenberg, 1936). In 1931 Feenberg studied with Sommerfeld, Pauli, and Fermi, and upon returning to the United States collaborated with Breit and then Wigner.
179. White (1935a, 1935b); Tuve et al. (1936). In a paper immediately following Tuve et al., Breit, Condon, and Present (1936) offered a detailed explanation of the implications of the experiment and of White's. The important paper by Breit and Feenberg (1936) appeared in the same November issue of *Physical Review*.
180. Pointed out by Fowler et al. (1936), p. 573. Charles Lauritsen was (Willie) Fowler's research advisor at Cal Tech. Both Charlie (Charles Christian) and his son Tommy Lauritsen were active in this period. We discuss Fowler's contributions to astrophysics in the next chapter. His obituary is in Woosley (1995). The similarity of neutron and proton separation energies was another piece of evidence for charge independence.
181. Breit and Feenberg (1936); Breit, Condon, and Present (1936). One of nine papers that Breit published in *Physical Review* in 1936. The authors wrote that "As a tentative hypothesis we may consider the interaction between heavy particles to be universally equal except for the Coulombian effects."
182. See DeBenedetti (1964), chapters 1 and 3.
183. Wigner (1933).
184. Kellogg, Rabi, Ramsey, and Zacharias (1939a, 1939b, 1940).
185. Yukawa et al. (1938a, 1938b); Kemmer (1938). See the discussion in Brink (1965), sec. 3.6.
186. Otto Laporte may have been the first to introduce parity into discussions of atomic spectroscopy in 1925 (Laporte and Meggers, 1925), leading to what is known as the "Laporte Rule," but considerations of the properties of classical systems under spatial inversion is much older.
187. Eisenbud and Wigner (1941).
188. Quoted in several places, including Moravcsik and Noyes (1961). In the same vein, Bethe wrote that "more time has been devoted to the problem of the nuclear force than to any other scientific problem in the history of mankind" (Bethe, 1953). By the 1980s enormous progress had been made in obtaining two-body forces that fit the $N - N$ scattering and bound-state data, and even used three-nucleon results to determine the off-shell parts of the two-body force.
189. The Bohr magneton is $e\,\hbar/2m_e$; the nuclear magneton is $e\,\hbar/2m_p$.
190. Frisch and Stern (1933); Estermann and Stern (1933). There is an interesting story told by Weisskopf about Stern taking bets on its value (all the while knowing it?), with everyone saying one nuclear magneton (Weiner, 1972).
191. Fermi (1951).

192. Although there are still mysteries hiding there, because it has been found that the proton spin is not simply the vector sum of the quark spins. Thus there is angular momentum associated with the motion of the quarks, and then there are "sea quarks," those other than the *u* and *d* quarks that are the principle constituents of nucleons.
193. Kellogg, Rabi, Ramsey, and Zacharias (1939b). Five years before, Tamm and Altshuler (1934) considered the possibility of a neutron magnetic moment. See also Tamm (1934a).
194. The negative sign meaning that the magnetic moment and spin point in opposite directions.
195. An exception would the measurement of nuclear moments, for example, from hyperfine splitting, as in the case of the quadrupole moment of the deuteron.
196. High-energy electrons would be used to measure the nuclear radius and charge distribution, leading to a Nobel Prize for Robert Hofstadter in 1961, sharing it with R. L. Mössbauer.
197. For example, Lawrence and Livingston (1932). Cockroft and Walton (1932). Livingston's life, including his relations with Lawrence, who alone received the Nobel Prize in 1939, is of interest. See his biography in Courant (1997). Livingston was co-author with Bethe of part C of the "Bethe bible" (Bethe and Livingston (1937).
198. Tuve et al. (1936); White (1935a, 1935b).
199. Cockroft and Walton (1932).
200. Bonner (1937). In this case, a deuteron beam incident upon hydrogen was used to create a neutron beam that was scattered from a hydrogen target. Before this, the $n - p$ force could be studied only through the deuteron. And even there off-shell effects were not accessible.
201. The same source of neutrons used in early nuclear weapons.
202. Bohr (1936). Also, Breit and Wigner (1936).
203. Bohr and Kalckar (1937).Bohr's papers on nuclear physics are in vol. 9 of his *Collected Works* (Bohr, 1972–2008). His role at this point is especially interesting, because for over a decade his contributions to quantum physics were mostly philosophical, or at least discursive. But with the burst of activity on his part in the late 1930s, he became one of the important founders of nuclear physics. His son, Aage, then assumed his mantle and made seminal contributions to the theory of nuclear collective motion, for which he received the Nobel Prize in in 1975 (shared with Rainwater and Mottleson).
204. On stripping, Oppenheimer and Phillips (1935). See Breit (1959), "Introductory survey," p. 1.
205. Bohr and Kalckar (1937); Bethe (1936, 1937); Livingston and Bethe (1937); Kalckar, Oppeheimer, and Seber (1937a, 1937b). See the summary and references in Breit (1959), sec. 1.
206. Breit and Wigner (1936). Four hundred pages of vol. 41 of the *Handbuch der Physik* (1959) were devoted to resonance reactions, all by Gregory Breit.
207. A very useful summary is that of Wigner (1955), which was the printed version of his Richtmyer Memorial Lecture of that year.
208. An excellent summary of developments in nuclear physics in the 1930s is Amaldi's 332-page paper in *Physics Reports* (1984). See also Johnson (1992).
209. At a fundamental level, the cross section is a function of the overlap between the initial and final asymptotic states, which include the initial and final nuclear wave functions.

210. Due to Kapur and Pierels as well as Wigner, in 1938–1941 to deal with resonance reactions, but developed during and after the war: Wigner (1946); Wigner and Eisenbud (1947). See Breit (1959), pp. 7–8.
211. And its progeny, the collective model, which described the collective or cooperative behavior of individual nucleons.
212. See Evans (1955), p. 157. The limits represent moments resulting from $j = \ell \pm 1/2$.
213. Hartree (1928).
214. Fractional parentage coefficients play a large role in constructing nuclear many-particle wave functions. See de-Shalit and Talmi (1963).
215. Beck (1927, 1928, 1931). Beck's AIP interview with Heilbron is very much worth reading. His analysis assumed the existence of electrons in the nucleus. Elliott and Lane (1957) give some other precursers. A useful survey is Johnson (1992).
216. Gapon and Ivanenko (1932). For other suggestions by Elsasser and Guggenheimer, see Moskowski (1957), p. 466.
217. Elsasser (1933); Guggenheimer (1934).
218. This statement has a modern ring to it for those who cut their teeth on the shell model in the 1960s.
219. Schmidt (1937, 1940). Also Schüler and Schmidt; see references in Evans (1955).
220. Wheeler and Barschall (1940).
221. Elliott and Lane (1957). This article give an excellent picture of the state of the shell model about a decade after its "birth." As they say, "few models in physics have had such a persistently violent and chequered history as the nuclear shell model."
222. See, for example, Povh and Rosina (2005), chapter 14.
223. Fermi (1950), perhaps the first nuclear physics "text" Weisskopf (1950), p. 194. Blatt and Weissskopf's 800+-page book of 1952 was on a different scale altogether.
224. Bethe and Bacher ("BB";1936), Bethe (1937), Livingston and Bethe (1937). Note that Bacher was involved in only the first. On the "Bethe bible," see Victor "Viki" Weisskopf in Weiner (1972), p. 40. Sommerfeld tried to persuade Bethe to return to his native Germany after the war. See Brown and Lee (2006).
225. Bethe, we recall, has called this period "the happy thirties" (Bethe, 1979).
226. Hill, op. cit. (1957), p. 178. The article was actually written in January 1956.
227. Heisenberg (1932). A good summary of the ingredients of a nucleon–nucleon interaction that produces saturation is given in Bethe (1971).
228. Von Weizsacker (1935); see also Bethe and Bacher (1936), p. 165. The asymmetry and pairing terms are sometimes ignored.
229. This idea first appeared in print in a "Discussion on the structure of atomic nuclei," involving Rutherford, Aston, Ellis, Chadwick, and Gamow, among others (Rutherford et al., 1929), on pp. 386–7.
230. Wick (1934).
231. BB, p. 102.
232. BB, p. 106.
233. De-Shalit and Talmi (1963), p. 5
234. BB (1936), pp. 171, 177. Another notable conclusion, from proton–proton scattering experiments (see previous discussion) was that "there must be a force between two protons besides the Coulomb force," and it must be attractive (BB, p. 133).

235. Mladjenovic (1998), chapter 15. This book is full of detail on both the experimental and theoretical sides. The first six chapters are organized historically. There is some prewar history in chapter VII in Blatt and Weisskopf (1952), which became the postwar "bible" of nuclear theory.
236. Seuss was at Hamburg, Jensen at Heidelberg, and Haxel at the Max Planck Institute in Göttingen, Germany.
237. Haxel, Jensen, and Seuss (1949a, 1949b); Goeppert-Mayer (1949). Mayer delayed her paper so that it could appear in the same issue, but it ended up in the issue following the paper of Haxel, Jensen, and Seuss. These brief letters were followed up by large papers in *Physical Review* and *Zeitschrift für Physik* the following year.
238. See Seuss's comments on how their team arrived at the importance of a strong spin–orbit force in Stuewer (1979), pp. 27–8.
239. Elliot and Lane (1957).
240. Blatt and Weisskopf (1952).
241. Bohr (1936). There is not an equation or table in the paper, which is no doubt due largely to the fact that it was based on an address given to the Copenhagen Academy on January 27, 1936.
242. Bohr and Kalckar (1937). Fritz Kalckar died the next year at age 27, another physicist who died young.
243. Ibid., p. 12. (Bohr and Kalckar, 1937).
244. Bethe (1936); BB (1936).
245. Gamow (1930). Especially Stuewer (1997), p.30.
246. Stuewer, op.cit.
247. Hahn and. Strassmann (1939).
248. Meitner and Frisch (1939). See the account that Frisch gave of this collaboration in Stuewer (1979), in which Meitner urged Hahn to more carefully examine his initial results, which had been interpreted as radium rather than barium (p. 71). Barium and radium are in the same group ($Xe6s^2$ and $Rn7s^2$) and hence chemically similar. In fact, the Curies discovered radium in a barium sample.
249. The German chemist Ida Noddack has been credited with first suggesting that the nucleus might break apart "into several large fragments" in 1934. See Wheeler (1998), p. 15.
250. Bohr and Wheeler (1939). Also Yakov Frenkel the same year (Frenkel, 1939), in which he wrote, as an explanation of fission, of the "capillary instability of a liquid drop."
251. Wheeler (1998) describes how this idea came to Bohr while talking to Leon Rosenfeld after the question had been raised by Placzek (pp. 27–8).
252. Though these were raised by Bohr and Kalckar (1937). The first self-sustaining nuclear fission reaction was accomplished by Fermi at the University of Chicago in December 1942. The slow neutron fission of ^{235}U is a consequence of the energy released in pairing the odd neutron ($N = 143$) with the captured one.
253. Some have wondered why nuclear fission was not discovered sooner, including a reviewer of this work. One thing is clear, however, and that is that if fission had been discovered 5 years before, there might have been a nuclear war in the 1940s.
254. Schüler and Schmidt (1935); Casimir (1935); Bethe (1936). To the extent that nuclear states have definite parity, the nucleus should have no electric dipole moment. Nuclear electric dipole moments would require both P and T violation.
255. They used a molecular beam magnetic resonance method. Kellogg et al. (1939a).

256. Schmidt (1940).
257. Hill and Wheeler (1953); Ford (1953)
258. Nilsson (1955), "Binding states of individual nucleons in strongly deformed nuclei."
259. Who received his PhD in 1946 after his dissertation was declassified. See Rainwater (1950).
260. See, for example, A. Bohr and Mottleson (1953) and Aage Bohr's Nobel Lecture (Bohr, 1976).
261. Rowe (1985). A good source illustrating the state of the art in the mid-1950s is Moskowski (1957).
262. And charge symmetry, which exchanges neutrons and protons, and is thereby studied in mirror nuclei. See previous discussion.
263. So when we speak of exchange forces, there are two meanings. As discussed here, an exchange force is the result of the exchange of a force-carrying quantum (vector boson) between two fermions.
264. Fermi (1933, 1934a, 1934b). See the discussion in Brown and Rechenberg (1996).
265. See Chapter 13.
266. Tamm and Ivanenko [in separate letters on the same page in *Nature*; Tamm (1934b), Ivanenko (1934)].
267. Yukawa (1935). For which he received the 1949 Nobel Prize. Reprinted in Brink (1965).
268. Because of the short range of the nuclear force. The term was not introduced by Yuakawa; see Pais (1986), p. 431.
269. Anderson and Neddermeyer (1937). Anderson was awarded the Nobel Prize for the positron in the year he discovered the muon. Neddermeyer, who was his student, was intimately involved in the plutonium bomb project.
270. When it was realized that it was a "heavy electron," the name "barytron" got some currency; its discoverer (Anderson) called it a "mesotron." The name "muon" was chosen after the discovery of the pion in 1947. See the discussion of prewar nuclear theory in Weiner (1972). When it became known that the muon was a heavy electron, Rabi is supposed to have said "who ordered that?"
271. Lattes, Muirhead, Occhialini, and Powell (1947).
272. A useful review is that of Machleidt, presented to the Nuclear Structure '98 conference in Gattlinburg, Tennessee, in August 1998, including the importance of "off-shell" effects.
273. See Brown and Rechenberg (1996); Brink (1965).
274. Which as of this writing is the accepted theory of particle interactions. Some regard it as the final theory, but as a caution one might recall a reminiscence by Rudolph Peierls in which he said "we thought, in the late twenties and early thirties that physics was almost finished" (Peierls, 1979). Recall, as well, Kelvin's confidence that discovery in physics was nearly complete.
275. Brueckner et al. (1954). The interested reader (with sufficient background) might consult the review article by Ben Day (Day, 1967), and the articles by Rajaraman and Bethe and by Baird Brandow that followed Day's in the same volume of *Reviews of Modern Physics*.
276. For reminiscences of the founders, I recommend Stuewer's *Nuclear Physics in Perspective* (Stuewer, 1979). Also Pais (1986), chapter 14, and Brown (1995).

16

QUANTUM THEORY AND THE BIRTH OF ASTROPHYSICS

INTRODUCTION

By 1913, on the heels of the discoveries by Planck, Einstein, Rutherford, and Bohr, it had to be clear, if one thought about it, that stellar burning must be in some sense a microscopic, hence quantum, phenomenon; the age of the Earth, and by implication the age of the Sun, effectively eliminated all classical alternatives. But the details would take over two decades to work out, mostly for the obvious reason that the new quantum theory was itself still more than a decade away. Furthermore, Aston's evidence on mass defects—discussed in the previous chapter—raising the possibility of energy release in what we now call fusion reactions, was also years away. But if quantum theory was not quite ready to tackle the problem, evidence about the nature of the Sun that provided at least hints about its interior had started accumulating nearly two centuries before.

Spectroscopy as a science could be said to date back to the 17th-century disputes between Hooke and Newton on the nature of light and color. In the absence of artificial sources, early optical spectroscopy primarily had to make do with sunlight. It would be more than a century before the discovery of discrete lines in the solar spectrum by Wollaston in 1802 and Fraunhofer in 1814 turned spectroscopy into an analytical tool.[1] Nearly a half-century more would pass before the implications of these discoveries became clear, and in the meantime, in 1835, the French positivist philosopher August Comte uttered his famous assertion that it was obvious that we would never be able to learn the composition of stars. In the decade 1849–1859, Foucault, as well as Kirchoff and Bunsen, showed that atomic absorption and emission lines appeared at the same wavelength. In particular, the German scientists, in experiments using flame and spark sources, found that the dark lines in the Sun's spectrum corresponded to the emission lines they were observing in terrestrial sources, thus identifying these lines as due to absorption by atoms in the outer layers of the Sun. Absorption lines in the spectra of other stars were first photographed by Henry Draper, using the star Vega in 1872,[2] the dominant lines seen in this hot star being due to hydrogen. This followed the studies of the spectra of excited gases by Anders Ångström in the 1850s, and his demonstration in 1861 that the solar spectrum contained lines of the Balmer series seen in terrestrial studies of hydrogen. In fairly short order, many of the chemical elements were identified in the spectrum of the Sun, and it was arguably the remarkable astronomer William Huggins (1824–1920) and his wife Margaret who achieved the

milestone of showing convincingly, through spectroscopy, that the Sun is made up of the same elements as the Earth.[3] The issue of the detailed composition of the Sun, that is, the relative abundance of the elements that make it up, was an entirely different matter, as we will see.

It is worth reminding ourselves that almost all information about stars, stellar energy production, and stellar evolution comes from astronomical spectroscopy, even today,[4] and prior to WWII, it was all optical spectroscopy. It was spectroscopy that moved astronomy from its long descriptive phase into what we now know it as, astrophysics. The emphasis on spectroscopy reminds us that the Sun's 6000 K surface temperature of[5] means that the radiation from the photosphere is predominantly in the visible part of the spectrum.[6] So the information on the composition of the Sun comes from the quantum theory of atoms, that is, atomic physics, not nuclear physics. Because the optical depth at the Sun's surface is of the order of 0.1% of its radius, it is clear that we cannot see into the interior of the Sun. This, in turn, raises the possibility that the elemental abundance in the center of the Sun might be very different from its surface, which is, of course, the case.

Determining the abundance of the elements in the Sun is complicated because the lines of the solar spectrum are due to absorption, generated in the so-called reversing layer, as in the Balmer series of hydrogen in the visible, where absorption raises electrons in the $n = 2$ level to higher energies. Thus the equilibrium population of the $n = 2$ level is a determinant of the intensity of the absorption lines. At a temperature of 6000 K, only a small fraction of hydrogen atoms are in the $n = 2$ state (Boltzmann factor).[7] Historically, the weakness of the Balmer series absorption lines in the Sun's spectrum, relative to iron, say, or sodium or calcium, was taken to mean that the Sun contained little hydrogen, which is certainly not the case. A breakthrough occurred in 1920 when Meghnad Saha derived the ionization formula that bears his name. It allowed Cecilia Payne,[8] in her PhD dissertation at Radcliffe College in 1925, to decipher stellar spectra, relate them to temperature, and to extract abundance information from them. She showed that in cool stars few electrons are in the $n = 2$ state of hydrogen and hence the Balmer series absorption spectrum would be very weak or absent, despite the abundance of hydrogen in the star. Ultraviolet spectroscopy of the Sun, which would have revealed the Lyman series spectra in hydrogen $1 \rightarrow 2$, $1 \rightarrow 3$, etc., was not possible until balloon flights could place spectrographs above most of the Earth's atmosphere. Ironically, and even cruelly, Henry Norris Russell is given credit for Payne's discovery, despite the fact that he actually discouraged her from publishing her results.[9]

The theory of stellar structure is also far more than just an application of quantum mechanics and atomic and nuclear physics in a very specific realm; it depends decisively on thermodynamics, statistical mechanics, hydrodynamics, gravitational potential theory, and so on. Stellar opacity, which controls energy transport from the center of a star to its surface, is due to the interaction between electrons and radiation, hence purely atomic. It goes without saying that radiative energy transport in a star requires a quantum-mechanical description, but at least a simple model of stellar structure can be constructed from these mostly classical building blocks without knowledge of the nature of the nuclear furnace in the center of the star. In fact, Arthur Eddington, in

his *The Internal Constitution of the Stars*,[10] leaves the question of the source of solar energy to chapter 11 out of 13. So again, the problem of stellar structure is much more than just the question of nuclear energy sources. This was important historically, since quantum mechanics was invented over a decade before nuclear physics made it possible to understand stellar nuclear burning.

The principle of hydrostatic equilibrium, along with knowledge of a star's mass (the luminosity should *emerge* from such a calculation), is sufficient to approximately determine what the central temperature must be. One does not expect such a calculation to be more than approximate, but knowledge of the central temperature provides the critical initial information on which to base a theory of nuclear reactions in stars. In the case of the Sun, it is some 15×10^6 K, or the equivalent of a little over 1 keV energy. Among other things, this tells us that generally speaking, atoms in the Sun's interior are fully ionized (a discovery due to James Jeans), as atomic ionization energies are in the range of 10s of electron volts, so that we are looking at purely nuclear reactions, however important electrons may be in other ways. Thus nuclear physics enters into the treatment of stellar structure and evolution in two ways: first, in the way in which nuclear reactions generate energy in the star's core, and second, how these and other nuclear reactions, which may be endothermic or exothermic, are involved in stellar (and even cosmic) nucleosynthesis, and ultimately stellar evolution.

STELLAR ASTROPHYSICS: NUCLEAR BURNING IN STARS

A simple calculation based on the luminosity of the Sun and its known age eliminates chemical reactions and gravitational contraction as primary energy sources.[11] Chemical reactions, that is, combustion, could be eliminated as soon as the Earth's age was known to be at least millions of years, an achievement grounded in Hutton and Lyell's geology and Darwin's theory of the evolution of species, among other things. Lord Kelvin's thermodynamic arguments, based on the cooling of the Earth, which suggested an age of 50 million years or more, raised the possibility that release of gravitational energy might power the Sun, but the growing appreciation of the much greater age of the Earth effectively eliminated gravitational contraction as a significant part of the energy budget of stars, leaving no physics on which to base a theory of stellar energy production. The first attempts at radiometric dating by Boltwood and Rutherford—even before the discovery of the nucleus—suggested an age of around a billion years,[12] and finally, between 1911 and 1921, Arthur Holmes was able to show from uranium–lead radiometric dating, building on the work of Boltwood and Rutherford, that the Earth was probably well over 10^9 years old.[13]

The answer to this conundrum would depend on nuclear physics, and nuclear theory could not exist before quantum mechanics was born. This has to be qualified slightly, however, as Einstein provided the essential ingredient that pointed toward where stellar luminosity originated, that is, in the conversion of mass to energy, even though there was not even a hint as to how this might take place. In 1919–1920 Aston,

using his mass spectrometer at Cambridge, showed that the mass of a helium atom was less than that of four hydrogen atoms,[14] confirming a conjecture of Planck's from 1906 about bound systems.[15] The implication of this measurement was not lost on Eddington, who became one of the first to suggest that somehow hydrogen was converted into helium in the Sun's core, with the release of energy.[16] Helium had been discovered in 1868 by Norman Lockyear and Pierre Jules Janssen, independently,[17] but was identified on the Earth only in 1895.

However, quantum mechanics had not yet been born in 1920 and nuclear physics was at best in its infancy, and as we saw in the last chapter there was certainly nothing like nuclear *theory*. It was not even absolutely clear that the α-particle was a helium nucleus (though most, including Rutherford, believed it),[18] the positron and, especially, the neutron had not been discovered, and it would be well over a decade before the combined forces of quantum theory and the growing knowledge of the nucleus could foster any sort of theory of how the elements were formed or precisely what the source of the Sun's energy might be, and more generally, what kinds of nuclear processes could occur in a star. Recall that the theory of nuclear reactions that grew out of Born's theory of inelastic scattering and the discovery of quantum tunneling (see previous discussion) emerged only in the late 1920s.

Nonetheless, with the discovery of the nuclear atom less than a decade after Einstein's special relativity, along with the tentative conclusion that the α-particle might consist of four hydrogen nuclei, the stage was set for the first intimations of a theory of energy production in stars. When Harkins and Wilson wrote on the formation of complex atoms in 1915, they commented that "when the evidence offered by stellar phenomena for the evolution of the elements is considered. . . .," suggesting something like widespread speculation on the topic. Although Karl Schwarzschild (who is better known for his work in general relativity) and his brother-in-law Robert Emden[19] had laid the groundwork for a theory of stellar structure at the beginning of the 20th century, the work of Eddington in the decade after 1916 could be said to represent the first serious attempt to deal with the problem of radiative equilibrium in the interior of a star. Among other things, he showed that radiation pressure was necessary to keep a star from collapsing**.** He derived, theoretically, the mass–luminosity relation[20] in work that culminated in *The Interior Constitution of the Stars* in 1926, revised in 1930, a book that became something of a bible for a generation of astrophysicists.[21] In it he wrote that "it is now generally agreed that the main source of a star's energy is subatomic." Of course, quantum mechanics had only just been born, and nuclear physics was still mostly a collection of experimental results, including Aston's. In 1926, Eddington seriously considered two possibilities, the annihilation of a proton and an electron to produce pure energy,[22] and fusion, which he thought most likely was the conversion of four protons to produce helium. He had made his suggestion as early as 1920, as had Jean Baptiste Perrin.[23]

By 1930, not only had the world seen the birth of quantum mechanics, but Gamow's work on tunneling had been published, making the subatomic nature of energy generation in the Sun ever more plausible.[24] Despite this, when Eddington reprinted his famous book in 1930, he wrote in the preface that "the advances made since this book

was first published [1926] are scarcely of sufficient importance to justify an extensive revision."[25] His chapter III, titled "Quantum theory," does invoke Einstein's radiation theory,[26] the photon hypothesis, and the Bohr theory of hydrogen. He rejected the popular notions that the source of energy was some form of radioactivity or his earlier suggestion of the annihilation of protons and electrons, in favor of fusion or "transmutation" of hydrogen to helium. Eddington's book is a testament to how far one could go in understanding stellar structure without detailed information on the source of the star's energy.

In 1929 Atkinson and Houtermans[27] made the first significant step toward the calculation of nuclear reaction rates and stellar nucleosynthesis, though the work had little impact, principally because it was still thought that the abundances of hydrogen and helium in the Sun were very low.[28] The success of such calculations depends on opacities and therefore on stellar composition, and this is still an active research topic.[29] The precise nature of the reactions involved was still in dispute nearly a decade later, in 1938, and in that year Chandresekhar imagined that the relevant nuclear reaction might be ${}^{7}\mathrm{Li} + {}^{1}\mathrm{H} \rightarrow 2\ {}^{4}\mathrm{He}$. But before the latter's book *An Introduction to the Study of Stellar Structure* [30] was published in 1939, first von Weizsäcker[31] and then Bethe and Critchfield[32] proposed that the fusion of hydrogen nuclei, involving tunneling through the Coulomb barrier, could provide some or all of the Sun's energy. Bethe and Critchfield used the the Gamow–Teller[33] version of Fermi's theory of β-decay to explain how two protons could form deuterium with emission of a positron, in what we know as the first step in the *p*–*p* chain: ${}^{1}\mathrm{H} + {}^{1}\mathrm{H} \rightarrow {}^{2}\mathrm{H} + e^{+} + \nu_{e}$. This was an implicit recognition that the weak force was crucially involved in nuclear burning in the Sun.[34] The calculation showed that at the 1-keV energies in the center of the Sun, this process (and the subsequent steps) could explain most of the Sun's energy output, though the reaction rate is below measurability at these energies. Bethe and Critchfield also found the second stage in the *p*–*p* chain, and also the three-step final stage in the "*pp* II" branch, that does indeed involve "lithium burning." About 86% of the Sun's energy is generated in the "*pp*-I" branch:[35]

Proton–proton Chain (*pp*-I)

${}^{1}\mathrm{H} + {}^{1}\mathrm{H} \rightarrow {}^{2}\mathrm{H} + e^{-} + \nu_{e}$

${}^{2}\mathrm{H} + {}^{1}\mathrm{H} \rightarrow {}^{3}\mathrm{He} + \gamma$

${}^{3}\mathrm{He} + {}^{3}\mathrm{He} \rightarrow {}^{4}\mathrm{He} + 2{}^{1}\mathrm{H}$

Von Weizsacher, in the 1938 paper previously noted and Bethe the next year[36] also discovered the "carbon" or CNO (CNO I) catalytic cycle, which also fuses hydrogen to produce ${}^{4}\mathrm{He}$. Bethe thought that this was the dominant energy-generating process in the Sun because of false estimates of the solar nitrogen abundance, as well as the Sun's central temperature, which he took to be about 19×10^{6} K. It turns out that the CNO cycle becomes dominant at about 17×10^{6} K, not much above the Sun's central temperature of about 15.7×10^{6} K.[37] When Bethe was awarded the 1967 Nobel Prize in physics, it was "for his contributions to the theory of nuclear reactions, especially his

discoveries concerning the energy production in stars." But the challenges to nuclear astrophysics do not end with discovery of the source of energy for the Sun and more massive stars; given the finite lifetime of a star, the question of stellar evolution immediately arises.

STELLAR NUCLEOSYNTHESIS

The problem of the origin of the elements is naturally of the greatest importance, but it has a great bearing on stellar evolution as well, because this evolution results as the elemental composition of the Sun (or star) changes as a consequence of nuclear reactions in its core. It is to von Weizsacker that we owe the conclusion that most of the chemical elements are manufactured in the interior of stars: "Apart from secondary effects of minor importance, the transmutation of elements is the entire cause of the presence of all elements in the stars; they are all being synthesized continually in the stars that are assumed to have started as pure masses of hydrogen; further, transmutations are the only source of stellar energy."[38] Now, of course, we known that the 25% helium abundance is also primordial. At about the same time, in the late 1930s, it became evident to Chandrasekhar that successive proton capture could not proceed very far up the periodic table (although α-capture reactions could, and do) because the nuclei would get progressively more unstable against positron ($\beta^+ -$) decay (because of increasing repulsive Coulomb energy), and that therefore neutron-capture processes must be important.[39] These considerations were the forerunner of the *s*- and *r*-neutron-capture processes[40] of modern nuclear astrophysics, hinted at in 1956 by Seuss and Urey[41] and given a prominent place in the classic B^2FH paper discussed in what follows.

The further exploration of nuclear burning in stars and its implication for stellar evolution is for the most part beyond the scope of this chapter, if for no other reason than that most of the work took place well after the first serious step was taken in 1938–1939 by von Weiszäcker, Bethe, and Critchfield. On the verge of WWII, there were still many unsettled issues, and Chandrasekhar discussed the difficulties with von Weiszäcker's theory in the final pages of his book, and even noted that von Weiszäcker himself had grave doubts about it.[42] At least some of the wartime work on nuclear fission, which involved among other things neutron-capture cross sections, had relevance for an understanding of stellar burning.[43]

In that important year of 1939 Bethe showed that apparently stellar nucleosynthesis could not proceed beyond the lightest elements because of the "bottleneck" due to the fact that no stable element exists with $A = 8$. ^{8}Be, consisting of two α-particles, has a half-life of the order of 10^{-16} s. Thus, the process $^4\mathrm{He} + {}^4\mathrm{He} \rightarrow {}^8\mathrm{Be}$ could not serve as a stepping stone to the synthesis of ^{12}C, ^{16}O, etc. It was apparent to Bethe that "*no elements heavier than He^4 can be built up in ordinary stars*." Consequently, Bethe argued, "the heavier elements found in stars must . . . have existed already when the star was formed."[44] This turned out to be fundamentally wrong (depending on the age of the star), and the resolution came only after nearly a decade when in 1953 Fred Hoyle suggested to W. A. ("Willy") Fowler that there should be a nuclear level in ^{12}C near 7.69

MeV, allowing a resonance capture reaction that would enable the "triple-α process" $^{34}\mathrm{He} \rightarrow {}^{12}\mathrm{C}$ to take place with nonnegligible probability at equilibrium.[45] Following Hoyle's prediction, such a level was found experimentally, though its properties are still under active study.[46] Thus the modern theory of stellar nucleosynthesis begins in the late 1940s with the collaboration of Hoyle, Geoffrey and Margaret Burbidge, and Willie Fowler, starting with Hoyle's groundbreaking paper in 1946[47] and culminating in the famous B^2FH paper in 1957.[48] The 1983 Nobel Prize in physics was awarded to Fowler and Chandresekhar, ignoring Hoyle and the Burbidges.[49] This story is provided only for the sake of completeness and continuity.

DEGENERATE STARS; APPLIED QUANTUM MECHANICS

From almost the beginning, quantum mechanics could have been expected to play an important role in understanding energy transport in stars, stellar opacities, etc., and perhaps even stellar energy production and nucleosynthesis. However, the discovery that some stars could be understood as essentially a degenerate quantum gas was quite unexpected. The first white dwarf star to be discovered was 40 Eridani B, in 1783 by William Herschel,[50] but it was not until its spectrum was examined over a century later, in 1910, by Russell, Pickering, and Fleming that the star was identified as extremely underluminous for its spectral type, *A*, and therefore was a new type of star.[51] In the meantime, Friedrich Bessel had discovered the companion of Sirius, "Sirius B," in 1844 from its gravitational effects,[52] and in 1915 it was also found to be a faint type-*A* star. The next year it became clear that the density of 40 Eridani B had to be something like 25,000 times that of the Sun—clearly not "normal" matter—and the term "white dwarf" seems to have been coined by William Luyten 6 years later.[53] At the same time, quantum mechanics was being born, and by 1926, the Pauli principle had been formulated, allowing Ralph Fowler, Dirac's mentor, to suggest that the interior of a white dwarf star should be a degenerate electron gas as early as 1926 [54] This fundamental insight made understanding these stars possible, and soon a finite maximum mass for a white dwarf star was derived by E. C. Stoner and Wilhelm Anderson[55] in 1929 (assuming constant density), and more accurately by Milne and by Chandrasekhar (using hydrostatic equilibrium) within 2 years[56]; hence the term "Chandrasekhar limit," of about 1.4 solar masses.

By 1935 it was already understood that white dwarfs, considered both theoretically and observationally, were examples of quantum degeneracy on an enormous scale, at least as far as the electrons were concerned. A number of people contributed to this realization, beginning with Fowler in 1926,[57] immediately after Dirac had formulated the theory of electron spin statistics. By the time of the publication of Chandresekhar's book in 1939, the theory of white dwarf stars had been fully developed, mostly by Chandrasekhar himself. He had been a student of Fowler's at Cambridge, having received his doctorate in 1933, and also felt Dirac's influence while there.[58]

In 1931, shortly before the discovery of the neutron, the Russian theorist Lev Landau suggested that there might exist a type of star that was essentially pure nuclear matter.[59] These objects would not yet have been *neutron stars*, of course, but immediately following the discovery of the neutron, Baade and Zwicky suggested, presciently, that neutron stars might exist and that they might be formed in a supernova process: "We have tentatively suggested that the super-nova process represents the transition of an ordinary star into a neutron star. We are fully aware that our suggestion carries with it grave implications regarding the ordinary views about the constitution of stars and therefore will require further careful studies."[60]

In 1939 Oppenheimer and Volkoff predicted that a neutron star with a mass greater than 3 solar masses (the "Tolman–Oppenheimer–Volkoff limit") would collapse, and concluded that no known physical process could halt that collapse.[61] It would be the 1950s before David Finkelstein, Charles Misner, and others would work out the implications of this proposal, including the existence of event horizons, by applying general relativity to the problem. John Wheeler is often giving credit for first applying the term "black hole" to these objects, though that attribution is controversial.[62] And although quantum mechanics mostly has to yield to general relativity in understanding these phenomena, it is not entirely irrelevant, especially in finding the equation of state of such objects, that is, quantum statistical mechanics.

BIG-BANG NUCLEOSYNTHESIS

The cosmological galactic redshifts were discovered mainly by V. M. Slipher beginning as early as 1912, and more data were gathered by Milton Humason, leading to the interpretation as radial velocities of recession.[63] The *expansion of the universe*, known as the "Hubble expansion," the understanding that the redshifts are proportional to distance and have cosmological implications, was announced by Edwin Hubble in 1929,[64] based on accumulating information on presumed radial velocities and distances of the "extra-galactic nebulae." Hubble obtained a very dramatic linear relationship between velocity and distance, the "Hubble Law," and commented somewhat cryptically that ". . . it is thought premature to discuss in detail the obvious consequences." He did invoke relativistic cosmology, and in particular, de Sitter's cosmology. Already the Belgian cleric and physicist Georges Lemaître had shown in 1927 not only that such an expansion could be obtained from Einstein's equations, but that Hubble's previously unpublished data were consistent with such an expansion.[65] A "Hubble constant" (slope of the v–d curve) of about 500 km/s/Mpc (megaparsecs) was obtained by Hubble, about seven times today's value.

The term big bang was a derisive one coined by Hoyle in a BBC broadcast in 1950, but the idea that the universe originated in a singularity or primeval atom, from which it has expanded to its present scale, had been advocated by Lemaître and even earlier, in 1922, by Alexander Friedmann[66] following Einstein's publication of the theory of general relativity in 1916 and his paper on general relativistic cosmology in 1917.[67]

This conclusion, that the universe expanded from a hot singular state, eventually led to the first attempts to determine how the elements were formed; hence its brief place in this narrative. As is well known, Einstein added a "cosmological constant" to ensure that the universe would be static, as he assumed it to be,[68] but Friedmann and Lemaître concluded otherwise. For the role of the cosmological constant in post-1998 cosmology the reader will have to look elsewhere.

Although quantum mechanics began to be applied to stars as early as 1926 while the theory was still in its infancy, big-bang nucleosynthesis, the theory of the origin of light nuclei in the early universe, had to wait for the growing awareness that its origin in a singular state, as proposed by Friemann and Lemaître, was plausible, combined, importantly, with the maturation of nuclear reaction theory and the discovery of the neutron, positron, and neutrino. This, as we know, was not possible before at least the mid-1930s, and even in the 1940s the meaning of the galactic redshifts was still the subject of some controversy. Then, as we have seen several times already in this work, WWII intervened at just the point that it was becoming possible to treat the early universe quantum mechanically. Big-bang nucleosynthesis effectively had its origins just after the war, in the work of Gamow and his students, most especially Ralph Alpher, who studied under Gamow at George Washington University, receiving his doctorate in 1948.[69] On April 1 of that year, *Physical Review* published the Alpher and Gamow letter, to which they added the name of Hans Bethe "because it seemed unfair to the Greek alphabet" otherwise.[70] The calculations incorrectly showed that all or most of the elements could have been created in the big bang, but as it turned out, the bottleneck mentioned earlier at $A = 5$ or 8, although later resolved by Hoyle in the case of nuclear burning in stars, halted the synthesis of elements in the big bang at beryllium because of the very low reaction rate of the triple-alpha ($3\,^4\mathrm{He} \rightarrow {}^{12}\mathrm{C}$) process in the face of the rapid expansion. The synthesis of helium, however, was essentially accurately predicted.

Alpher collaborated with Robert Herman in the late 1940s when both were doing applied physics and not only performed calculations of cosmic nucleosynthesis, but made the remarkable prediction that there would be relic radiation left over from the big bang that should be detectable, an idea that lay dormant for almost two decades, until the discovery of Penzias and Wilson of the cosmic microwave background (CMB).[71] Alpher and Herman's seminal paper[72] was published in November 1948 following that of Alpher, Bethe, and Gamow. Of course it is only since the 1950s that advances in nuclear and particle physics, improved knowledge of the weak and strong forces, the advent of particle accelerators that can reach at least 1 TeV in energy, and enormously improved calculational capacity have allowed a clear picture to emerge of the early universe, going back to when it was less than 10^{-12} s old. But big-bang nucleosynthesis took place only from about $T = 1$ s to a few minutes. Again, this is far outside our agreed-upon time period, but it does illustrate how quantum theory and its progeny, nuclear physics, began to make possible a theory of how the elements formed, both in the early universe and in the interior of stars, beginning in 1938–1939.

QUANTUM COSMOLOGY AND QUANTUM GRAVITY

The current state of studies of the early universe, which were just alluded to, and of quantum gravity largely derive from work begun in the late 1940s to the 1960s, but that is not entirely the case. In 1926 Oskar Klein applied the new quantum mechanics to an older idea of Theodor Kaluza, based on classical general relativity. The Kaluza–Klein theory,[73] which invoked extra dimensions that were compactified in some sense, was revived after the war and has relevance for the modern theory of strings, which hopes to unify quantum theory and the theory of gravity, presumably the general theory. As for the early universe, although the theory may have originated with George Gamow and Ralph Alpher,[74] including a prediction of what we now call the cosmic microwave background (CMB), between 1941 and 1948, modern developments involve vastly accumulated knowledge about elementary particles and the gauge theories of the electromagnetic, weak, and strong interactions, not to mention cosmic inflation. There lies another book.

CONCLUSION

This chapter on an application of quantum mechanics is not just about applied quantum theory, but about applied nuclear physics as well, which of course had to build on the structure of quantum mechanics itself, though it coevolved, as it were, alongside the development of the formalism of quantum theory. By about 1925, the ability to understand the nature of stars purely from the point of view of classical physics had reached a dead end, although special relativity had clearly pointed the way. Already the old quantum theory had been exploited as far as possible, but until the interaction between atoms and radiation could be treated in a fully quantum-mechanical fashion, no further progress was possible, and before the physics of nuclei began to mature in the mid-1930s, no understanding of the source of the Sun's energy could emerge, meaning that there was no chance to study how stars evolve. It was in the decade between the work of von Weizäcker, Bethe, and Critchfield and that of Gamow, Alpher, and Herman that the application of the quantum theory to astrophysics began to shine, so to speak.

NOTES

1. Wollaston (1802); Fraunhofer (1814).
2. Draper (1877).
3. Becker (2011). Huggins was the first to measure the radial velocity of stars using the Doppler effect. See the *DSB* article in vol. VI, p. 540, by Herbert Dingle.
4. The main exception would be cosmic rays and, perhaps increasingly, neutrinos.
5. That could not really be determined until Planck completed his analysis of the blackbody spectrum in 1900. Among the first to compare the continuous spectra of stars with those of a blackbody were Wilsing and Scheiner in the first decade of the century.
6. Which is no accident, of course.

7. 6000 K corresponds to a thermal energy of about 0.5 eV, but the difference in energy between the $n = 1$ and $n = 2$ levels in hydrogen is 10.4 eV.
8. To become Payne-Geposhkin. She had attended Cambridge University on a scholarship in the early 1920s, but was not allowed to take a degree because of her sex. This changed only in October 1948.
9. His results were published nearly a decade after Payne's dissertation. Russell (1934).
10. Eddington (1926).
11. For details, see Chandresekhar (1939), chapter 12, or Eddington (1926), chapter 11. Note that radioactivity, which generates energy in the interior of the Earth, was discovered just as Kelvin was doing his cooling calculations.
12. Boltwood (1905); Rutherford and Boltwood (1905). Boltwood's career was at Yale but he visited Rutherford in Manchester in the first decade of the century. He died at his own hand in 1927. See Boltwood's biography in Kovarik (1929).
13. Holmes (1911).
14. Aston (1920).
15. Pais, in Brown et al. (1995), p. 111.
16. Eddington (1919). He presented these ideas in his presidential address to the 1920 meeting of the British Association for the Advancement of Science (BAAS) in Cardiff, Wales, as well. In effect he argued that the helium had to come from somewhere, and that somewhere was from hydrogen nuclei.
17. As usual, the situation is a bit more complicated than that, but Lockyear first suggested that the yellow line seen in 1868 was due to a new element, which he named helium. Lockyear was the founder and first editor of *Nature*.
18. Certainly Boltwood in 1905 (Boltwood, 1905).
19. Schwarzschild (1906); Emden (1907).
20. The fact that the luminosity is proportional to the third or fourth power of the mass, for main sequence stars.
21. Eddington (1926). The revisions were quite minor. It is a testament to its staying power that it was reissued in its 1930 form in a Dover reprint in 1959, with a foreward by Lloyd Motz, who himself made contributions to the field.
22. As one might recall from Chapter 13, this was the state of things in 1930, before discovery of the positron and long before any suggestion that both baryon and lepton numbers were conserved.
23. Eddington (1920), p. 45; Perrin (1920).
24. Gamow's tunneling analysis, which initially emerged in the problem of radioactive decay, is important because it allowed calculation of the probability of overcoming the Coulomb barrier in nuclear reactions. See the previous chapter.
25. Although in the July 1926 preface to the first edition he wrote that "As we go to press a "new quantum theory" is arising which may have important reactions on the stellar problem when it is more fully developed." Evidently he was not impressed with the progress in the succeeding 3 years, which represent the crucial period in which quantum theory was formulated. In the concluding paragraph to the book he does speak of "two clouds obscuring the theory of the structure and mechanism of stars," and identifies one as "the failure of our efforts to reduce the behavior of subatomic energy to anything approaching a consistent scheme."
26. Einstein (1917a).

27. Atkinson and Houtermans (1929). Houtermans was imprisoned by both the Soviets and the Nazis.
28. Because Russell's intervention delayed the discovery of Payne by nearly a decade. See previous discussion.
29. Stellar opacities are a measure of the absorption of electromagnetic radiation in the star by atoms, and thus determine energy transport in a star. See any book on stellar structure, e.g., Motz (1970).
30. Chandrasekhar (1939).
31. Von Weiszäcker (1937, 1938).
32. Bethe and Critchfield (1938).
33. Gamow and Teller (1936).
34. Although Fermi proposed a contact or point theory of the weak interaction in 1933, little progress was made until 1958, when Gell-Mann and Feynman proposed that an intermediate vector boson might mediate the weak force. Eventually the problem would be solved by Weinberg, Salam, and Glashow around 1967, for which they all received the 1979 Nobel Prize. But we must return to the prewar period.
35. The *pp*-II and *pp*-III branches are generally more important in stars with higher central temperatures than the Sun. See Carroll and Ostlie (1996), p. 343. Also the CNO cycle. As an aside, it may be worth noting that the fifth edition of Baker's *Astronomy*, published in 1950, two decades after the first, still equivocates on the source of the Sun's energy and makes no mention of the *p*–*p* chain. Also Bethe, Phys. Rev. 55, 434 (1938).
36. Bethe (1939).
37. In general, rates for nuclear reactions driven by thermal energy represent a competition between the Maxwell–Boltzmann decaying exponential and the Gamow penetration factor that rises with increasing energy. The "solar neutrino problem," which raised questions about the *p*–*p* chain and the central temperature of the Sun in the 1960s, did not arise until Ray Davis's neutrino capture experiments, which yielded about 1/3 the predicted number of neutrinos. This conundrum was resolved only when it was verified that neutrinos have a small mass. Davis shared the 2002 Nobel Prize, and the discovery of neutrino oscillations was honored in 2015.
38. Quoted in Chandresekhar (1939), p. 469. See also von Weiszächer (1937).
39. Chandesekhar (1939), p. 478.
40. Respectively, *slow* compared with the subsequent β-decay rates, and *rapid*, on a much shorter time scale. The *r*-process is most important in stellar core collapse.
41. Seuss and Urey (1956). See, for example, Motz (1970). A more accessible introduction to the subject is Martin Schwarzschild's *Structure and Evolution of the Stars*, which, however, by virtue of having been published in 1958, is now somewhat more dated. In *s*- (or slow) processes, the excited nucleus decays by β-decay before a second neutron capture, and in the *r*-process the capture rate is high enough so that on the average another capture occurs before the decay. Seuss and Urey also arrived at elemental abundances, mostly from meteorite samples. A modern source is Prialnik (2010).
42. Chandrasekhar (1939), p. 485;Von Weiszäcker (1938).
43. It was in 1939 that von Weizäcker began work on the German nuclear weapon project, under the supervision of his mentor Heisenberg. There is still no consensus on the extent of their commitment to the bomb project.
44. Bethe (1939).

45. Hoyle (1954). The result was first published in Hoyle et al. (1953). See G. Burbidge "Hoyle's Role in B^2FH" (2008). Also Saltpeter (1952). Ward Whaling's account of this incident in the Cal Tech oral history project interviews is fascinating. Cal Tech Archives, April–May 1999. Interview with Shelley Erwin. After a search for the resonance failed, Hoyle is supposed to have said that no experiment can be believed until it is confirmed by theory.
46. This prediction has been portrayed an example of the predictive power of the anthropic principle. Whether that is merited is a matter of taste, it seems to me. The ^{8}Be resonance was also necessary, found by Fowler in 1952. See the interesting paper by Kragh, "When is a prediction anthropic? Fred Hoyle and the 7.65 MeV carbon resonance"(Kragh, 2010).
47. Hoyle (1946).
48. Burbidge et al. (1957).
49. By the time the prize was awarded to Fowler, Hoyle's advocacy of unpopular scientific positions and his role in a controversy over the awarding of the 1974 prize to Anthony Hewish had poisoned the waters. According to G. Burbidge, the Nobel Prize should have been awarded to Hoyle, who was the leader of the group, rather than to Fowler (Burbidge, op. cit.).
50. That is, he discovered the triple-star system 40 Eridani.
51. Holberg, J. B. (2005). 40 Eri B was about 100 times fainter than its K1 dwarf companion, but was white, and thus much hotter. The interpretation was due largely to Walter Sydney Adams (1914).
52. Bessel (1844).
53. Luyten, (1922), and others.
54. Fowler, R. H. (1926). With Dirac's help.
55. Stoner, C. (1929, 1930); W. Anderson (1929).
56. Milne (1930); Chandrasekhar (1931b).
57. Fowler (1926). Eddington noted that while he was writing his book, some 400 pages of papers on stellar structure had appeared in the *Monthly Notices of the Royal Astronomical Society*.
58. See the bibliography in Chandresekhar (1939), p. 451.
59. Landau (1931).
60. Baade and Zwicky (1934).
61. Oppenheimer and Volkoff (1939).
62. Apparently the journalist Ann Ewing used the term in 1964, 3 years before Wheeler.
63. Slipher (1917). In many cases the distances were based on Cepheid variable stars, which had been calibrated by Henretta Leavitt.
64. Hubble (1929).
65. Lemaitre (1927).
66. Friedmann (1922). Gamow and Vladimir Fock were two of his students, though he died (in 1925 at age 37) before Gamow could work under him.
67. Einstein(1916a, 1917b).
68. He wrote "In order to arrive at this consistent view [finite universe with positive curvature], we admittedly had to introduce an extension of the field equations which is not justified by our actual knowledge of gravitation" (Einstein, 1917b).
69. Alpher's wartime jobs were with the U.S. Navy, the Office of Scientific Research, and Johns Hopkins Applied Physics Lab. He met Robert Herman there, and in the late 1940s they did the first work on big-bang nucleosynthesis.

70. See Gamow's humorous explanation in his *The Creation of the Universe* (Gamow, 1957). The calculations were surely among the first non-war-related fundamental calculations carried out on an electronic computer. See also the article by Alpher's son in *Physics in Perspective* in 2012 (V. Alpher, 2012).
71. Penzias and Wilson, 1965.
72. Alpher and Herman (1948).
73. Kaluza (1921); Klein (1926a, 1926b).
74. Gamow (1946, 1948a, 1948b); Alpher and Herman (1948a, 1948b, 1949).

17

ATOMIC AND MOLECULAR PHYSICS

INTRODUCTION

If the reader has gotten this far, he or she will fully understand that the problem of atomic spectra and what was revealed there about the structure of the atom more than any other drove the quantum revolution. The data go back to the middle of the 19th century, and the first successful attempt at an explanation, Bohr's theory of hydrogen, dates from just over one century ago, 1913. Arnold Sommerfeld's authority in those years, coupled with Bohr's growing influence, shaped the direction that attempts to understand atomic structure took in the decade following the Bohr theory. Efforts to understand the complexities of many-electron atoms (essentially more than one!) made enormous progress in classifying the spectra, motivating the introduction of new quantum numbers, and even led to the discovery of selection rules governing atomic transitions. Theoretical insights were slow in coming, but even before the advent of the new mechanics (quantum theory), analyses of spectra led to the discovery of intrinsic spin and the Pauli principle,[1] both crucial to the understanding of atoms. But real progress in deciphering atomic structure had to await the creation of matrix and wave mechanics, in 1925–1926. Sommerfeld's authoritative *Atomic Structure and Spectral Lines* was the bible in the field for more than a decade after 1919, but perhaps no source does a better and more complete job of summarizing the state of atomic and molecular physics just as the revolution in quantum mechanics was taking place than Ruark and Urey's text, *Atoms, Molecules, and Quanta*, of 1930, which reveals on almost every page the transition in understanding that was taking place.[2]

Unlike nuclear physics, the problems of atomic and molecular structures did not raise issues of fundamentally new physics; new forces, new particles, new modes of decay. In the atom a natural force center exists, the nucleus, providing a starting point for an independent particle model or a mean-field approach to a description of complex atoms. And there was nothing unknown about the Coulomb interaction, at least before quantum electrodynamics (QED). These features made atomic and molecular physics less demanding theoretically but also made it much less likely to be the source of new fundamental insights into quantum theory.[3] By 1951, John Slater had observed that "that part of the quantum theory dealing with the structure of atoms, molecules, and solids . . . is in a sense a finished subject, in that we are quite sure that we know the theoretical framework on which it is built." But if *formulation* of a problem was relatively straightforward, any attempt at a detailed solution that could explain details of observed spectra, for example, was hardly less complicated than in nuclear physics.

This meant that fresh approximation and computational techniques did emerge from atomic and molecular physics, and of course applications in the real world were, and are, unlimited.

THE HYDROGEN ATOM

Because of its importance in the quantum revolution a chapter has already been devoted to Bohr's theory of hydrogen that explained the broad features of the hydrogen spectra. The first *quantum-mechanical* attack on hydrogen took place just months after the emergence of matrix mechanics, by Pauli, but Dirac and especially Schrödinger were not far behind. Schrödinger's was the most successful and dramatically showed the power of wave mechanics. These developments were discussed in earlier chapters. Although the Pauli–Dirac–Schrödinger treatments of the hydrogen atom did not attempt to deal with the fine details of the level structure, progress in the previous decade by Sommerfeld, Landé, and others, and of course the discovery of spin of both the electron and the proton, had shed light on fine structure and even hyperfine structure, again with few new theoretical insights. But close on the heels of the discovery of spin came the full quantum-mechanical explanation of fine structure and the Zeeman effect by Heisenberg and Jordan. Recall that the original papers on matrix and wave mechanics were published only 6 months apart, beginning in the summer of 1925, and that that spin was discovered in between them. And in that half-year, the Born–Jordan and BHJ papers also appeared, along with Dirac's first contribution. Heady times indeed! The finest details of the optical spectrum of hydrogen, including the "Lamb shift," would require QED, and indeed would provide a crucial test of it.[4]

THE HELIUM ATOM

It did not come as a complete surprise that the next simplest atom, neutral helium, posed an enormous theoretical challenge because of the Coulomb repulsion between the two electrons. This was, after all, a three-body problem, which has no general solution even in classical mechanics,[5] and Bohr's early naive model had the two electrons revolving at the ends of a diameter. In heavier atoms, simplification would result from the fact that the electron–electron interaction could be treated as a perturbation, but this was not the case with helium and other light atoms in which the e–e interaction is comparable in magnitude to that of each electron with the nucleus. This did not, however, deter attempts to use perturbation theory in the absence of a more fundamental approach. And with the discovery of spin, the problem became even more challenging. Of course the He^+ ion, with one electron, was immediately amenable to treatment within the Bohr theory, as Bohr himself showed in his original paper.[6]

If the problem of more complex atoms was already intractable in the old Bohr theory, it was now enormously more complicated, with relativistic effects, the spin–orbit interaction, a spin–spin interaction, and the two-electron Coulomb interaction, but at least one could write down the Schrödinger equation for helium, taking into account

the exclusion principle of 1924-1925 for the two electrons. The Pauli principle , along with the discovery by Dirac, Fermi, and others of the statistics of many-electron systems, provided important insights into how the electronic configuration of complex atoms (including helium) could be constructed. The degree of understanding of angular momentum coupling that is exhibited in Condon and Shortley's 1935 book[7] meant that this dimension of the problem (angular momentum decomposition) could be handled, even if the number of states to be considered was potentially very large in a complex atom. In such a case the state space might have to be seriously truncated by considering one, or a few, electrons outside closed shells. *Solving* the Schrödinger equation was another matter of course, because the $1/r_{12}$ electrostatic interaction between electrons makes the Schrödinger equation nonseparable.

It was not long before Heisenberg tackled the helium problem head-on using wave mechanics,[8] even before the last of Schrödinger's four papers was published in June 1926. Because the spin states of two electrons are either antisymmetric (singlet) or symmetric (triplet), the corresponding spatial solutions must be either symmetric or antisymmetric, respectively. The total two-electron wave functions are then antisymmetric with respect to interchange of the space and spin coordinates of the electrons, as required by the Pauli principle. These solutions, spatially symmetric or antisymmetric, were named by Heisenberg parahelium and orthohelium (Figure 17.1).[9]

Because the Schrödinger equation for helium is invariant under the interchange of the coordinates of the electrons r_1 and r_2, the spatial eigenfunctions $u(r_1, r_2)$ will be of the form $u(r_1)u(r_2) \pm u(r_2)u(r_1)$. And because the states of the helium atom, by assumption, have one electron in the ground state ψ_{100},[10] the spatial wave functions will all be

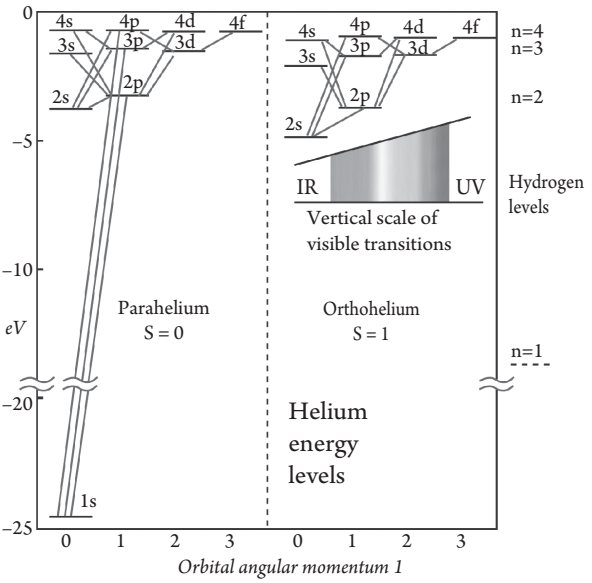

Figure 17.1. Low-lying levels in helium, showing the parahelium and orthohelium states. With permission of Rod Nave.

of the form $\psi_{100}(r_1)\psi_{nlm}(r_2) \pm \psi_{100}(r_2)\psi_{nlm}(r_1)$. In the lowest-order approximation the $1/r_{12}$ interaction between electrons would be neglected, or treated as a perturbation, or a variational method might be used. If the *e*–*e* interaction is neglected, the Schrödinger equation separates. If relativistic and spin–orbit contributions are also ignored, which is a reasonable approximation in light atoms, no transitions between the orthohelium (spin triplet, antisymmetric spatial wave function) and parahelium (spin singlet, symmetric spatial part) states can occur because of the orthogonality of the spin functions.

The orthohelium (triplet) states are more tightly bound, lower in energy (except for the ground state, which is parahelium), because in the spatially symmetric state (parahelium) the probability for the electrons being close together is large, the electrons can approach each other more closely on the average, increasing the repulsive energy, hence less binding (Figure 17.1). Formally, this results from an exchange integral[11] and is an example of Hund's Rule #1, dating from 1927.[12] Sommerfeld's wave-mechanical supplement to his *Atombau*, published in German in 1929 and in English the next year, is an excellent introduction to these early attempts to treat the helium problem.[13]

Quantitative treatment of the structure of neutral helium required the use of approximation techniques, that is, either perturbation or variational methods, especially that of Ritz.[14] By December of 1926, Albrecht Unsöld had prepared a 39-page paper for *Annalen der Physik* in which a perturbation calculation was carried out, showing promising results in the face of the knowledge that such a series would not converge rapidly (if at all).[15] Shortly thereafter, Kellner and Hylleraas performed multiple-step variational calculations that reproduced measured ionization potentials within a few percent,[16] and Slater offered a different variational method that gave more or less comparable results.[17] These were major achievements, both theoretical and numerical, especially for their time (pre-1930), showing the efficacy of the approaches to the many-electron problem.[18] A major paper by Pauling summarized and elaborated on this work, including in particular the hydrogen molecular ion, the hydrogen molecule, and the helium atom, and Pauling and Wilson, in their influential book on quantum mechanics, devote considerable space to these early approaches.[19]

In 1928 Douglas Hartree significantly advanced the process of doing realistic calculations by developing a variational method for finding energy eigenvalues and approximate eigenfunctions for an electron in a quasi-Coulombic field by deriving a mean field due to the charge distribution of the other electrons (*electron* in the case of helium), using an iterative or "self-consistent field" method.[20] This was later improved by Vladimir Fock,[21] who showed how to incorporate the Pauli principle in what became known as the Hartree–Fock method. With the advent of digital computers after WWII, these methods became very powerful computational tools, not only in atomic and molecular physics, but in nuclear physics as well (Hartree–Fock–Bogoliubov or HFB). But in the 1930s, with only manual or electromechanical calculators available,[22] computations were generally limited to a very small basis of single-electron states as the configuration space, that is, the very lowest levels, e.g., the *s* and *p* subshells[23] in the lightest atoms.

The initial application of Hartree's method was to the challenging case of helium. Given approximate neutral helium wave functions, problems involving the interaction of helium atoms with electromagnetic radiation, including the Stark effect, could be addressed, as indeed was done by Unsöld.[24] Ultimately, variational methods of one sort or another, including, for example, density-functional theory (DFT) of the 1960s, provide the most powerful techniques for obtaining numerical solutions to problems in atomic, molecular, and condensed-matter physics, as we will subsequently see.

COMPLEX (MULTIELECTRON) ATOMS

If the problem of the neutral helium atom was intractable, or very nearly so, then clearly the multielectron atom ($n > 2$) was that much more difficult, although in principle, as opposed to in practice or computationally,[25] there were no new issues. But approximations had to be resorted to from the very beginning, and for a long time empirical rules such as Hund's rules, were still employed.[26] As before, the Schrödinger equation is separable if the $1/r_{ij}$ interaction terms between electrons are neglected, and this provides a starting point for perturbative techniques, involving one or more valence electrons outside closed shells, that is, a restricted or truncated basis. Among the approaches tried in 1927–1928, that due to Slater was perhaps the most practical.[27] The details can be found in Slater's paper, which is a sort of primer for multielectron calculations, or in the accessible summary by Pauling and Wilson.[28]

It had been recognized very early on that optical spectra of the alkali metals, lithium, sodium, etc.,[29] could be approximately understood by assuming a single-valence electron outside an inert core with zero total angular momentum. Empirically one could identify the effects of shielding of the nuclear charge by this core as well as penetration of the core by electrons whose orbits do not have maximum symmetry.[30] The Hartree method could provide the central potential experienced by the valence electron. Atoms with nearly closed atomic shells could be treated in a very similar way to the alkali metals, as Heisenberg pointed out in 1931.[31] The alkaline earths, with two electrons outside a presumably inert core, would be expected to resemble helium.[32] And, to some level of approximation at least, one can carry this further, with electrons pairng to $S = 0$ in closed subshells. Condon and Shortley's book of 1935 not only represented the state of the art in that era, but had not been fully supplanted by the time it was reprinted in 1963. The key to computations that aimed to reproduce the optical spectra of these atoms was use of variational methods, and in particular Hartree–Fock, although as we have seen, the power of these methods could not be unleashed until the advent of digital computers in the 1950s. Ultimately the techniques of many-body theory using second quantization were applied to the structure of complex atoms and molecules.[33]

Bohr's building-up or "*aufbau*" principle, based on the exclusion principle, provided the starting point for any calculation, because it made clear what the basic multielectron configurations were. This was generalized by Charles Janet in 1929 and Erwin Madelung in 1936, who discovered that atomic subshells were filled in order of increasing $n + \ell$.[34] Even though in its simplest form the *aufbau* principle finally breaks

down, it represents the heart of the atomic shell model, especially when augmented with Hund's empirical rules, the Pauli principle, of course, and eventually real calculations. The required angular momentum coupling that is needed, in $L - S$- or jj-coupling, was, as noted, provided in detail in Condon and Shortley's book. Even the modern and robust *ab initio* calculations of the structure of complex atoms are not without dependence on ad hoc and empirically based rules at some level.[35]

In principle at least, the problem of many-electron atoms is addressed in the most straightforward way by writing down an unperturbed (noninteracting) wave function in terms of single-particle states, using perturbation theory to compute the matrix elements of the interaction among the coupled states and carrying out the appropriate diagonalization, thus obtaining the perturbed eigenfunctions, which are mixtures of the original basis states. The utility of such an approach is naturally limited by computational considerations and whether perturbation theory is appropriate. Alternatively, a linear variational technique such as the post–Hartree-Fock configuration interaction method, which takes into account electron correlations, is used in modern (postwar) quantum chemistry computations.[36]

MOLECULAR SPECTRA AND MOLECULAR STRUCTURE

Molecules, and even the simplest of all, molecular hydrogen, posed an entirely different set of problems, first successfully treated by Burrau,[37] that would eventually lead to an understanding of the chemical bond, as well as the additional degrees of freedom that can be excited. The fundamental question was, how is it that *neutral* atoms are bound into diatomic (and more complex) molecules with typical binding energies of a few electron volts?[38] The early spectroscopic evidence of molecular excitations came in the form of band spectra, observed in infrared absorption as well as in the emission spectrum of hydrogen, where electronic levels were seen to have rotational and vibrational structures superimposed upon them. Ad hoc and semiclassical attempts by Sommerfeld, Bohr, and others before the arrival of the new quantum theory met with little success. The case of H_2 is especially important, as it shows all the features of more complex molecules despite its simple structure.[39] Although first observed in the 1880s, the initial proposal that the observed bands were due to molecular structure, and in particular molecular rotation, was made in 1912 by Niels Bjerrum,[40] and by 1916, Karl Schwarzschild had provided some theoretical support.[41] Soon it was realized that molecular vibrations were involved as well, and some understanding of the rotation–vibration spectra, in which rotational structure was superimposed on vibrational excitations, was possible, even in the framework of the old Wilson–Sommerfeld quantization scheme.[42] In general, rotational and vibrational bands are found in the infrared (near and far), because the transition energies are very much smaller than for the electronic transitions, which are in the visible or even ultraviolet.

Molecular spectra were much more complicated than those of the most complex atoms because of these rotational, vibrational, and electronic degrees of freedom all interacting, so that, strictly speaking, there are no *pure* electronic transitions. Thus

it was apparent to Gerard Herzberg that "there is no hope of solving this problem rigorously . . ." And of the many approximations that must be made, he noted that "often [they] are very questionable, and in such cases the results obtained can only be called daring extrapolations."[43] In light atoms and molecules often the perturbation approach fails to converge rapidly enough to be very practical, something that does not plague the variational method, employed by Wang as early as 1929,[44] but the latter depends on the choice of a trial wave function, which is almost as much art as science.

Diatomic molecules obviously constitute the simplest case and were the first to be attacked. Much of the early work on molecular structure was confined to these diatomic molecules, and, for example, Herzberg's influential *Molecular Spectra and Molecular Structure* of 1939 was devoted entirely to that problem.[45] In diatomic molecules rotation about the symmetry axis does not contribute to the energy,[46] reducing the number of degrees of freedom. A special case occurs in homonuclear diatomic molecules, e.g., H_2, that do not possess a net electric dipole moment in the ground electronic state, and hence one does not see pure rotational spectra in the absence of a change in the electronic state. The same is true for pure vibrational spectra of these molecules, because the vibrations do not produce a charge separation, and hence there is no infrared emission or absorption.[47] In such cases Raman scattering provides another tool, in which photons are inelastically scattered, causing the excitation of vibrational or rotational modes. In general the vibrations will show anharmonicities, and the rotations will not be strictly those of a rigid rotor, because the molecule vibrates, essentially changing the moment of inertia.[48]

With the advent of the new mechanics, as in the case of complex atoms, it was easy to write down a Hamiltonian, and thus the Schrödinger equation, but not so easy to solve it. The heuristic Lennard–Jones "6–12" potential,[49] which was introduced to approximately describe the interaction of two neutral atoms, with a repulsive $1/r^{12}$ term and a $1/r^6$ attraction, had been proposed in 1924, and the first quantum-mechanical justification for it, by Fritz London, came in 1930,[50] by which time the full forces of quantum theory were being brought to the problem. These intermolecular "London forces" are more frequently called "van der Waals forces," without much justification.[51] In 1938 R. A. Buckingham offered a modified Lennard-Jones potential that replaced the short-range repulsion by an exponential.[52]

MICROSCOPIC THEORIES

Despite these efforts, both heuristic or phenomenological, and fundamental, a *microscopic* theory of intermolecular forces was lacking until Heitler and London, shortly after reading Schrödinger's papers, published the first quantum-mechanical description of covalent molecular binding in 1927, applied to the hydrogen molecule.[53] The first technical step toward understanding that problem was to treat the H_2^+ molecular ion, with a single electron interacting with two protons and including the *p–p* interaction. In this case, the Schrödinger equation for the motion of the electron in the Coulomb field of the two protons can be solved numerically, using perturbation

techniques. The neutral hydrogen molecule, H_2, is of course substantially more complicated because of the electron–electron interaction, as was the case in the neutral helium atom. This problem can be considered a prototype of the general problem of molecular binding, albeit obviously the simplest. Øyvind Burrau was the first to address it, in 1926,[54] by numerical integration of the Schrödinger equation, and soon after, Heitler and London published their treatment of the two-electron interaction (as well as the nuclear motion) as a perturbation.[55] This interaction is characterized by an exchange force[56] involving the electron spins that can be either attractive or repulsive depending on whether the spins are antiparallel (singlet) or parallel (triplet). This is considered the origin of "valence-bond" theory. The very different approach pioneered by Hund and Mulliken[57] led to today's molecular-orbital (MO) theory, the details of which would carry us too far afield (but see subsequent discussion).

Although the details of band structure even in *diatomic* molecules are beyond the scope of this work, it is worth elaborating on the first significant attempts to bring to bear on the problem the full resources of the quantum theory, beginning in 1927–1928, involving Friedrich Hund, Eugene Wigner, and others,[58] hardly more than a year after the creation of the new mechanics. In molecules the electronic and nuclear degrees of freedom, including rotations and vibrations, have very different time scales (typically of the order of the square root of the ratio of electron to nuclear mass) and operate in very different energy regimes. This is apparent from the fact that the band structure is superimposed on the electronic transitions. The spacing of vibrational levels is usually small compared to the electronic energies, and the rotational spacings are smaller still.[59] This makes it possible as a first approximation to neglect interactions between these modes of excitation, that is, to consider them to be independent of each other. This, for example, allowed Weizel, in his 1931 book on band spectra, to write the eigenfunction of the rotating oscillator in a simple product form $\Psi_{vib}\Psi_{rot}$.[60] It is also evident from the outset that because of the large nuclear mass, the nuclear motion is slow compared with that of the electrons, so that the nuclei can be considered stationary when treating the electronic motion, meaning that the total wave function can be approximately written as a product $\Psi_{nuc}\Psi_{elec}$ multiplied by a spin function. The electronic motion has a small effect on the state of the nuclei, slightly changing the potential that the protons feel, and thus the vibrational spectrum; the nuclear degrees of freedom include the rotations and vibrations. Thus the adiabatic principle plays a large role in the treatment of molecular structure, and in this context, the separation of electronic and nuclear degrees of freedom is known as the Born–Oppenheimer approximation.[61] The molecule is a nonrigid rotor (or symmetric top) and an anharmonic vibrator, which, combined with the electronic states (which already enter into the internuclear potential), makes for a very challenging problem, with the rotational and vibrational structure superimposed on the electronic transitions. Fortunately, because of the different energy regimes, all of the degrees of freedom can be at least approximately decoupled.[62]

It is perhaps worth mentioning here that in looking at the spectra of real gases, atomic or molecular, in thermal equilibrium, other considerations are involved, especially if the sources are astrophysical, as was often the case early on (mostly absorption

spectra). That is, the *population* of the electronic, rotational, and vibrational states is very important, hence the need for statistical mechanics. This also has a bearing on the contribution of various modes of excitation to the heat content of a gas, and therefore specific heats. As Herzberg wrote in his *Molecular Spectra and Molecular Structure*, "the variation of the intensity of the lines in a rotation-vibration band or in a pure rotation spectrum is given essentially by the thermal distribution of the rotational states."[63] This work is an excellent source for understanding the state of molecular structure physics at the beginning of WWII. Kronig's earlier *Band Spectral and Molecular Structure* of 1930[64] provides similar insights into the state of theoretical atomic and molecular physics as it was rapidly evolving following Schrödinger's introduction of wave mechanics.

When Friedrich Hund addressed the molecular problem in early 1927,[65] he focused on the rotational contribution to the specific heat of H_2, dividing the rotational states separately into those with even or odd J, which had even or odd parity, respectively.[66] In this homonuclear case, the wave function of two protons, by the Pauli principle, must be antisymmetric with respect to interchange of the coordinates of the particles, and the presence of both even- and odd-parity states means there must be a nuclear (proton) spin, with the spins coupling to symmetric and antisymmetric states.[67] Thus, in June of that same year (1927) David Dennison, a young American physicist visiting Cambridge, took the next step by suggesting that by analogy with the ortho- and para-states identified by Heisenberg in helium, a similar situation obtained in H_2, such that molecular hydrogen would be a combination of two independent gases, the spin isomers *orthohydrogen and parahydrogen*. Orthohydrogen, with the symmetric (triplet) spin state, would be spatially odd, and parahydrogen, having the antisymmetric (singlet) spin state, was spatially even. Because the spatially symmetric (anitsymmetric) states have even (odd) parity, transitions cannot occur between the two because of parity conservation. On the time scale of a measurement, then, the two gases would not mix, in the sense that energy input to the gas would be absorbed separately by them, because transitions between the two could not occur (or be weak). The result would be that the specific heat of the hydrogen molecule would result from the separate specific heats of the two components. In a note added in proof to a paper he submitted in early June 1927, Dennison showed that the results, which required an equilibrium ratio of orthohydrogen to parahydrogen at room temperature of 3:1 because of the threefold degeneracy of the triplet state, meant that the proton spin must be 1/2.[68] The paper was submitted to the *Proceedings* on June 3, but Bohr persuaded Dennison to add a hasty note to it on June 16, describing the implications of the 3:1 ratio. This was not the first time that atomic or molecular physics shed light on nuclear properties (see Chapter 15). Although the equilibrium ratio of orthohydrogen to parahydrogen at room temperatures is 3:1, at low temperatures, parahydrogen is favored, so that H_2 molecules will be in the $J = 0$ para-state (over 99% at 20 K).[69] The important experimental work on this complex was carried out by Bonhoeffer and Harteck and by Eucken and Hiller.[70] Similar symmetric and antisymmetric states occur in all homonuclear diatomic molecules.[71]

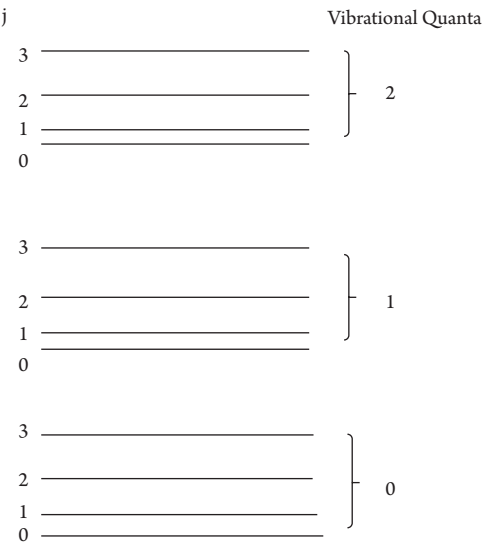

Figure 17.2. Rotational and vibrational levels in HCl. The equally spaced vibrational levels involve 0, 1, and 2 quanta. The rotational levels (expanded by a factor of 10 relative to the vibrational spacing) show an approximate $j(j+1)$ spacing. Ruark and Urey (1930), by permission of McGraw-Hill.

A well-studied example of a molecular spectrum is that of HCl, a heteronuclear diatomic molecule that shows clear rotation–vibration spectra in the near infrared (Figure 17.2).[72] Generally speaking, the band structure in the far infrared is rotational (involving smaller energy differences), and in the near infrared it is vibrational. As we noted earlier, because the rotating molecule is not a *rigid* rotor, the expected $J(J+1)$ spectrum is modified; the vibrational motion of the nuclei changes the moment of inertia of the rotating molecule. Taking into account anharmonicities, one sees rotational structure built on the vibrational states, and hence the observed spectrum (Figure 17.2).[73] Electronic transitions, which involve more energy, are typically found in the visible and the ultraviolet regimes.

MOLECULAR BINDING

The problems of molecular binding or stability and those of molecular spectra are quite distinct, though at a microscopic level they contain the same physics, with the former concentrating on the electronic configurations. Because the nuclei (protons in the case of H_2) repel each other, it is necessarily the electrons, interacting with the protons and through exchange forces, that modify the potential energy so that it is an attractive, "covalent bond." The elaborate and successful calculations on the H_2 molecule by Burrau in 1927 and by James and Coolidge in 1933 showed the power of computational methods in problems of molecular binding.[74] A good summary of the problem up to 1929 can be found in the early book on quantum mechanics by Condon and Morse as well as in Ruark and Urey of the following year.[75]

In 1930 John Slater introduced the one-electron wave functions that are now known as "Slater orbitals" as the building blocks or basis states,[76] and in 1931 studies by Slater[77] and Pauling[78] gave birth to the valence-bond method mentioned earlier, sometimes known as the Heitler–London–Slater–Pauling (HLSP) method using "hybridized atomic orbitals."[79] In 1929 Lennard-Jones, building on ideas of Hund, Mulliken, Wigner, and Witman, introduced what is known as the "linear combination of atomic orbitals" or LCAO (or LCAO-MO) method, which is a method of superposing atomic orbitals to obtain molecular orbitals.[80] As was the case with complex atoms, the most robust treatment of molecular structure involved using the adiabatic approximation to write down unperturbed product wave functions, which are the prototypes of what are known as molecular orbitals, the heart of the MO method of Hund and Mulliken,[81] and then finding the perturbed energies and eigenfunctions. (Indeed, Mulliken took "orbital" to be a translation of "eigenfunction.") When Mulliken met Hund in 1927, that encounter led to their collaboration on MO theory and to Mulliken's solo Nobel Prize in chemistry in 1966. In 1939 Pauling wrote what was the definitive book for its time on chemical binding, the classic *The Nature of the Chemical Bond*.[82]

FERMI–THOMAS THEORY

A very different approach to many-particle systems was proposed independently by Llewelyn Thomas and Enrico Fermi around 1927,[83] the so-called Thomas–Fermi method, in which the electron density, rather than the wave function, is the fundamental quantity. Thomas–Fermi theory was not a realistic theory of molecular binding,[84] but was the precursor to the now very popular and powerful DFT.[85] This approach has the virtue that because it deals only with electron densities, which are in principle observable, it is readily applied to real materials.

CONCLUSION

Atomic and molecular physics experienced a peak in the early to mid-1930s, as the theoretical tools it needed were developed by Heisenberg, London, Heitler, Slater, and others. In the later 1930s it became more the province of quantum chemists as it was overtaken as a frontier subject by the physics of the nucleus, so that it became common for those on the forefront of nuclear and particle physics to slight atomic and molecular physics because they involved only the well-understood Coulomb interaction. The discovery of fission and the war effort played important roles in this. In his book on the chemical bond Pauling emphasized that "only in a few cases . . . have results of direct chemical interest been obtained by the accurate solution of the Schrödinger wave equation . . . the advances which have been made have been in the main been the result of essentially chemical arguments."[86] Only a decade later, following the hiatus of 1939–1945, the introduction of digital electronic computers, beginning mostly in the early 1950s with their rapidly increasing

computational power, began to make robust calculations of the properties of complex atoms and molecules fairly routine, so that the severe approximations that had had to be employed up to that point could be dispensed with. Soon many of the techniques, both theoretical and commutational, found application to solids, which are, after all, collections of atoms. Mirroring the resurgence in nonmilitary science after 1945 that led to a flood of good quantum texts, especially between 1955 and 1965, John Slater published a two-volume *Quantum Theory of Atomic Structure* in 1960, which became the bible for a generation of atomic physicists.[87] Atomic and molecular physics have paid enormous dividends in the real world, and in the previous chapter we briefly saw how important these fields were in helping us understand energy transport in stars.

NOTES

1. That Ruark and Urey (1930) called the "Pauli equivalence principle." It is stated as "There are never two or more equivalent electrons in the atom, such that the values of all five of their quantum numbers will be identical when a strong magnetic field is applied (p. 214). See Chapter 10.
2. Ibid. The book is rather remarkable in that the first 14 chapters (515 pages) are devoted almost exclusively to experimental spectroscopy, based on the old Bohr–Sommerfeld "quantum condition," while the last 6 are devoted to wave and matrix mechanics.
3. See Kleppner's "A short history of atomic physics in the twentieth century," (1999).
4. See, for example, Bethe and Saltpeter (1957), secs. 20–2.
5. Mattuck (1967) makes the provocative argument, citing G. E. Brown, that "in eighteenth-century Newtonian mechanics, the three-body problem was insoluble. With the birth of general relativity around 1910 and quantum electrodynamics in 1930, the two- and one-body problems became insoluble. And within modern quantum field, 1927a theory, the problem of zero bodies (vacuum) is insoluble."
6. Bohr (1913a). The discussion is on pp. 10–11. The same thing would be true of the deuterium atom; only the reduced mass was different.
7. Condon and Shortley (1935).
8. Heisenberg (1926a,b).
9. Dirac demonstrated that the exclusion principle required the antisymmetry of the two-particle wave function in August 1926 (Dirac, 1926c), and Heisenberg did the same 2 months earlier (Heisenberg, 1926b), and there he introduced orthohelium and parahelium.
10. The argument being that if both electrons were in an excited state, one would drop to the ground state, ionizing the atom (Griffiths, 2005). This single-active-electron approximation ignores the complexities of so-called "doubly excited" states in helium.
11. See Merzbacher (1998), p. 479, for details.
12. Hund (1927a, 1927b, 1927c, 1927d). The rule is that the state of maximum multiplicity $(2s + 1)$ lies lowest in energy. Rule #2 states that for a given S, the term with the largest L has the lowest energy. Rule #3 says that in filling a valence subshell, the state with lowest J lies lowest until the subshell is half-filled, and thereafter the level with the highest J is lowest. Hund died in 1997 at age 101.

13. Sommerfeld (1930).
14. Ritz (1908b, 1908c). Numerical integration techniques as well, which were of course rather primitive.
15. Unsöld (1927). Both helium and lithium were treated. Unsöld, whose work was mostly in the astrophysical context, was one of Sommerfeld's students.
16. Kellner (1927); Hylleraas (1928). In 1929 Hylleras obtained an ionization energy within 0.003 V of the known value (Hylleras, 1929). For a discussion of the details and merits of this approach, and Hartree's, see Bethe and Saltpeter (1957), secs. 24–8.
17. Slater (1927, 1928).
18. See Condon and Morse (1929), pp. 131–5.
19. Pauling (1929); Pauling and Wilson (1935). Pauling's paper gives an excellent summary of the ways in which perturbation theory was employed in attacking these two-electron problems, including the numerical work of Burrau (1927).
20. Hartree (1928). After WWII, Hartree was a major figure in the development of large-scale computing in Britain and the United States. See Fisher (2003). Charlotte Froese Fisher herself, a student of Hartree's, developed the widely used multiconfiguration Hartree–Fock method for atomic calculations (Mike Wilson, personal communication).At one point, discussing the numerical integration of a modified Schrodinger equation, Hartree notes that "only one calculation in each interval requires a slide rule (or logs)." Have times not changed? Hartree's method actually predated quantum mechanics: Hartree (1923), and Fues (1922), etc. See Condon and Shortley (1935), p. 342.
21. Fock (1930). Independently by Slater.
22. Calculations began much earlier with Vanevar Bush's analog differential analyzer, which Hartree exploited as early as 1933.
23. Subshells have the same n and ℓ, e.g., the $2p$ subshell.
24. Unsöld (1927). An excellent source for the theory of one- and two-electron atoms is the classic work by Bethe and Saltpeter, published in 1957 but written in the late 1930s (Bethe and Saltpeter, 1957).
25. Notably the size of the configuration space; the size of matrices to be diagonalized in the days before digital computers.
26. See Herzberg (1944).
27. Slater (1929) cites earlier papers by Heisenberg, Wigner, Hund, and Heitler and Weyl's book, in making the point that group theory merely complicates matters. One suspects that Slater eventually changed his mind. . . . Pauling and Wilson (1935) comment that Slater "showed that this method was very much simpler and more powerful that the complicated group-theory methods previously used." (p. 233)
28. Pauling and Wilson (1935).
29. Also potassium, rubidium, and cesium. See Chapter 3.
30. See Pauling and Goudsmit (1930), chapter III.
31. Heisenberg (1931).
32. Pauling and Goudsmit (1930) discuss these problems in detail, including the angular momentum coupling involved.
33. Judd (1967).
34. Janet was an amazingly versatile scientist who never published his ideas on the periodic table. The rule is often known as the Madelung rule. Madelung (1936).
35. Scerri (2003).

36. The basis for much of the modern computational quantum chemistry is Boys (1950). See also Cramer (2002).
37. Burrau (1927). A representative modern text is Morrison et al. (1976). On the first page of the section on molecular structure the authors pass on the following advice from Benesh Hoffman (*The Strange Story of the Quantum*, 1947): "If you have read this far, there is no dignified way of escape left to you. You have paid your fare, and climbed to the highest peak of the roller-coaster. You have therefore let yourself in for the inevitable consequences. . . . The going will be rough, but I promise you excitement aplenty."
38. Such speculation dates back at least to Newton in his Opticks of 1704 (book 3, query 31). Early treatments of helium began by considering two noninteracting hydrogen atoms, with the interaction treated as a perturbation. See Pauling (1929).
39. Richardson (1934); Dieke (1958).
40. When he was working with Nernst in Berlin. DSB II, 169–71 (E. W. Hiebert).
41. Schwarzschild (1916). As Sommerfeld notes (1923, p. 276), this paper was published on the day he died, May 11. Molecular bands in cool stars were being studied in the early 1920s.
42. See Chapters 1–3. Also Sommerfeld (1934), pp. 80–4.
43. Herzberg (1939), p. 349. Pages 349–54 in the 1950 second edition give an excellent introduction to the theory of homopolar binding in H_2.
44. Wang (1929). Wang cites Heitler and London (1927), but also a paper by Sugiura.
45. Herzberg (1939). Herzberg (1904–1999) was awarded the Nobel Prize in chemistry in 1971. Subsequent volumes did treat polyatomic molecular spectra. Herzberg's life (1904–1999) spanned almost the entire 20th century.
46. This, too, is only an approximation, though a very good one. See Weizel (1931).
47. That is, no electric dipole radiation. See Herzberg (1939), pp. 84–6.
48. See Herzberg (1939) for details.
49. Lennard-Jones (1924).
50. Eisenschitz and London (1930); London (1930).
51. Van der Waals, who received the Nobel Prize for physics in 1910, did obtain an equation of state for real gases that attempted to take into account the intermolecular interaction—nearly 40 years earlier, in the 1870s.
52. R. A. Buckingham (1938).
53. Heitler and London (1927). Heitler studied with Sommerfeld, post-doc'd with Schrödinger, and was an assistant to Born. London was a doctoral student of von Laue. Both Heitler and London lost their jobs in 1933 as racial laws were imposed in Nazi Germany. In his archived interview with John Heilbron, Heitler describes how they came to add electron exchange to their calculation that led to the binding of the H_2 molecule. (AIP Center for the History of Physics, March 18, 1963, interview.)
54. Burrau (1927).
55. Heitler and London, op. cit.
56. Which is not, of course, a new force, but simply a result of the Coulomb interaction and the Pauli principle.
57. See the extensive bibliography in Herzberg (1939, 1950).
58. Hund (1927c); Wigner (1927a); Heisenberg (1927a). Also Guillemin and Zener (1929), as well as Hund's *Linienspektrum und Periodisches System der Elements* (1927d).
59. In the case of vibrations, approximately the square root of the ratio of the electron to the nuclear mass $(m/M)^{1/2}$, something like a factor of 100, of the order of 0.1 eV. For rotations,

it is about (m/M) or 100 times smaller, around 0.001 eV. See Bransden and Joachain (1989), chapter 10. Typical vibrational frequencies might be as high as $10^{14}\,s^{-1}$, while rotations are of the order of $10^{12}\,s^{-1}$.

60. Weizel (1931). Weizel was a prolific author and an opponent of the Nazi politization of science that affected his career from 1933 to 1936. See Beyerchen (1977).
61. Born and Oppenheimer (1927). In this paper, the authors treated helium in fourth-order perturbation theory.
62. Any purely nuclear excitations would involve MeV or a fraction thereof.
63. Herzberg (1939), p. 132. Also, pp. 139–44. A second edition of vol. 1 appeared in 1950, and two further volumes were added, in 1945 and 1966, on polyatomic molecules.
64. Kronig (1930).
65. Hund (1927b).
66. Symmetry under reflections. Even or odd, depending on whether the wave function does (–, odd) or does not (+, even) change sign under reflection through the origin. Here *J* is the angular momentum quantum number for the spatial (rotational) state.
67. Once the proton was shown to have spin 1/2 by Dennison (discussion below). See Herzberg (1950), pp. 124–34.
68. Dennison (1927). He described the thinking that led to this conclusion during his stay with Ralph Fowler at Cambridge. Dennison's interviews with Thomas Kuhn in 1964 with the AIP's Oral Histories project are extraordinarily interesting. Dennison taught at the University of Michigan for nearly a half-century, until his death in 1976.
69. The process by which orthohydrogen is converted to parahydrogen in liquid hydrogen at low temperatures is thermodynamically quite complicated.
70. Bonhoeffer and Harteck (1929); Eucken and Hiller (1929). Karl Friedrich Bonhoeffer was the older brother of Dietrich Bonhoeffer, the noted theologian who was hanged by the SS. See also Herzberg (1939), pp. 137–50.
71. Kronig (1928a, 1930). Also Ruark and Urey (1930), p. 429.
72. Imes (1919). Imes was the second African American PhD in physics awarded in the United States (fide APS).
73. See Herzberg (1939), chapter III. There is an approximate separation because the vibrational frequency is much higher than the rotational.
74. Burrau (1927); James and Coolidge (1933). The latter paper was in the initial volume of *The Journal of Chemical Physics* that began publishing in that year of 1933, with Harold C. Urey as its editor. It was, and is, an AIP journal.
75. Condon and Morse (1929); Ruark and Urey (1930).
76. Slater (1930b).
77. Slater (1931a, 1931b).
78. Pauling (1931).
79. As an aside, Slater chaired the MIT physics department for 20 years, beginning in 1930, and in the process played a seminal role in bringing American science to parity with European science in the years leading up to the war.
80. Lennard-Jones (1929). On previous work, see the references in this paper.
81. Which they developed together, but never published jointly. For a review, see Mulliken (1930). See also Mulliken (1975).
82. Pauling (1939). He was awarded the Nobel Prize in chemistry in 1954. He won the Peace Prize in 1962.

83. Thomas (1927a); Fermi (1927). In 1926, in Thomas's case. This was shortly after his critical paper on Thomas precession of the electron spin. Thomas taught at Ohio State University from 1929 to 1943.
84. Having been shown by Teller that it does not bind molecules.
85. Hohenberg and Kohn (1964). Walter Kohn died at age 93 in 2016.
86. Pauling (1939), p. ix.
87. Slater (1960). He had published *Quantum Theory of Matter* in 1951, one of the 14 books he wrote.

18

CONDENSED MATTER
QUANTUM SOLIDS AND LIQUIDS

INTRODUCTION

Although the early history of atomism is highlighted by speculations about atoms of the sort found in Lucretius, or in Newton's musings in his *Opticks,* it is a philosophical issue with an even longer and honored history. The questions that surround the nature of solids are ancient, prompted by the existence of lodestones with their magnetic properties, crystals with intriguing structure and often optical properties, minerals of varying density, and the variety of naturally occurring metallic ores that could be refined to yield pure metallic substances. The utility of alloys such as bronze led to questions about the nature of metals and why some alloys were possible. Issues of melting and freezing, properties like hardness, ductility, transparency, birefringence, and many others, prompted speculation about these largely impenetrable materials.

On the other hand, atomism as a testable hypothesis about the structure of matter only dates to the early 19th century, in the form of early chemistry of Davy, Dalton, and others. There it provided what little empirical evidence for atoms there was until Maxwell, Clausius, and Boltzmann founded kinetic theory and statistical mechanics, applied mostly to gases. By the end of the 19th century there was little doubt about the reality of atoms, and with the advent of atomic spectroscopy, it was demonstrated that atoms themselves have structure. Fortunately, the atomic nucleus turned out to have such unique properties that almost as soon as the possibility that the atom had some kind of structure was imagined, Rutherford and his team discovered its massive center. Thus atomic and nuclear physics evolved together as applications of quantum theory after 1925, though, as we have seen, atomic spectroscopy had the much longer history, being nearly a century old when nuclear physics was created by Rutherford. Atomic structure could be most easily studied in gases, but molecular structure exhibited itself in both gases and liquids, so it was not difficult to imagine a granular structure of some kind for solids as well. At the turn of the century, the generally held conviction that solid matter, rather than being some kind of elastic continuum, comprised atoms tightly bound together, which meant that the time was ripe for the development of a microscopic theory of solids.

Chemistry, with its widespread applications, was obviously built almost entirely upon a belief in atoms, but for a long time only bulk, essentially continuum properties of solids, such as elasticity, electrical and thermal conductivity, and thermal

expansion, were accessible to experimental investigation. Widespread industrial applications in the late 19th century shed relatively little light on the microscopic structure (if any) of solids, although there was some interest in atomistic theories of electrical conductivity.[1] Even the problems of the specific heats of solids, which were quantified in the law of Dulong and Petit as early as 1819, did not immediately reveal the atomic and molecular structure of solid matter. The story that Boltzmann took his life in 1906 as the result of depression over the negative reception of the atomic theory may be a romantic myth,[2] but it does show how tenuous a hold the atomic theory had at the turn of the century. But the dramatic explanation of Brownian motion by Einstein, along with the scattering experiments of von Laue, the Braggs, and others, beginning around 1912, left little room for doubt about the atomic structure of matter.

Serious attempts to understand the nature of condensed matter, emphasizing important problems such as specific heats and thermal and electrical conductivity, necessarily date from the early 20th century.[3] These applications of early quantum ideas followed close on the heels of the Planck–Einstein discoveries of 1900–1905, even though quantum mechanics, per se, could not be brought to bear on such problems before 1925–1926. But in less than 15 years after the creation of quantum mechanics, that is, at the start of the WWII, the theoretical and experimental study of the solid state had advanced to the point that it had become its own specialty—"solid-state physics," eventually to become "condensed-matter physics" as boundaries between solids and other strongly correlated systems became blurred.[4]

Much of the interest in the solid state was driven by applications that involved the optical, thermal, electrical, and magnetic properties of solids as well as the problems of defects, alloys, fatigue, and so on. The rapid specialization that took place in the immediate prewar and postwar years provides some motivation, or at least an excuse, for our looking at broad, major issues, such as the band theory of solids, Pauli paramagnetism, superconductivity, and so on, rather than details. The size and scope of Frederick Seitz's book, *Modern Theory of Solids*, written in 1940,[5] is a reflection of the rapid evolution of the subject in a little more than a decade. Seitz has extensive citations to the literature of the 1930s, to which it is a good guide.

Solids are intrinsically diverse, a fact that is reflected in Seitz's classification of them as metals, ionic crystals, valence crystals, semiconductors, and molecular crystals. Much of our attention here is devoted to crystals because their periodic structures invite theoretical description, and especially to the first category, metals, partly for historical reasons, as early attempts were made to understand their bulk properties. Amorphous solids such glass and polymers have interesting properties as well and have a history dating, in the case of glass, to antiquity, and for polymers to the early 19th century. And although specific heats of solids played an important role in the development of quantum mechanics, as we saw in the first chapter, solids possess many other interesting and important characteristics that have already been listed. In this chapter, we concentrate on those that represent fundamental applications of quantum theory.

SPECIFIC HEATS OF SOLIDS

One of the very first indications that something was amiss in classical physics was the problem of specific heats of solids (Chapter 1). Classically (after Maxwell and Clausius), taking into account the translational and vibrational degrees of freedom of a solid, with $1/2\,kT$ of energy per degree of freedom per atom (equipartition; k being Boltzmann's constant), the internal energy is $3NkT$, where N is the number of atoms, or $3nRT$, where n is the number of moles of the substance and R is the universal gas constant. Consequently the molar specific heat at constant volume should be $3R$, or about 6 cal/mole·K^{-1}, which is the Petit–Dulong law,[6] now nearly two centuries old. This turns out to be approximately valid for most solids at room temperature, especially metals, but, for example, diamond departs very strongly from it, something that had been known since the middle of the 19th century. In the 1870s it was discovered by Heinrich Weber that the specific heats of solids were strongly temperature dependent,[7] but it was only beginning around 1900 that measurements could be made at low temperatures, as Dewar did in 1905, when he found the specific heat of diamond to be a very low 0.004 cal/g·deg.[8]

Soon after, and on the heels of his first venture into quantum theory in treating the photoelectric effect, Einstein published the first quantum treatment of the specific heats of solids.[9] In this 1906 paper he started from a conventional statistical-mechanical calculation of the internal energy of a solid (he had independently invented post–Boltzmann statistical mechanics in 1902–4, but was anticipated by Gibbs): $\langle E\rangle = U = \dfrac{\int E\exp(-E/kT)\mathrm{d}E}{\int \exp(-E/kT)\mathrm{d}E}$. But if the energies of the oscillators were quantized, as in the case of cavity (blackbody) radiation, then the integrals really should be sums: $\dfrac{\Sigma nh\nu\exp(-nh\nu/kT)}{\Sigma\exp(-nh\nu/kT)}$. It is not difficult to carry out the sum: $\left[\sum\exp(-nh\nu/kT) = \dfrac{1}{1-\exp(-nh\nu/kT)}\right]$, yielding $U = \dfrac{h\nu}{\exp(h\nu/kT)-1}$. This results in $c_v = 3R\dfrac{(h\nu/kT)^2}{[\exp(h\nu/kT-1)]^2}\exp(h\nu/kT)$.

The only free parameter in Einstein's theory was the frequency of oscillation, ν, which could be obtained by fitting the measured specific heat. As the figure shows (Figure 18.1), the formula fit Weber's data quite well, and had the property that $c_v \to 0$ as $T \to 0$ as observed. This landmark paper signaled the beginning of the quantum theory of solids, but in the end the theory failed to accurately reproduce the measured specific heats at very low temperatures.[10] Nonetheless, this was the first application of the idea of the quantum to a problem not involving the electromagnetic field, anticipating Bohr's application to the hydrogen atom by 6 years.[11]

Five years after Einstein's paper, Pieter Debye approached the problem by quantizing the normal modes of vibration of the crystal lattice,[12] and although the solid was treated as a continuum, it was actually an improvement over Einstein's statistical treatment of a collection of independent atoms. The atomic nature of the crystalline solid

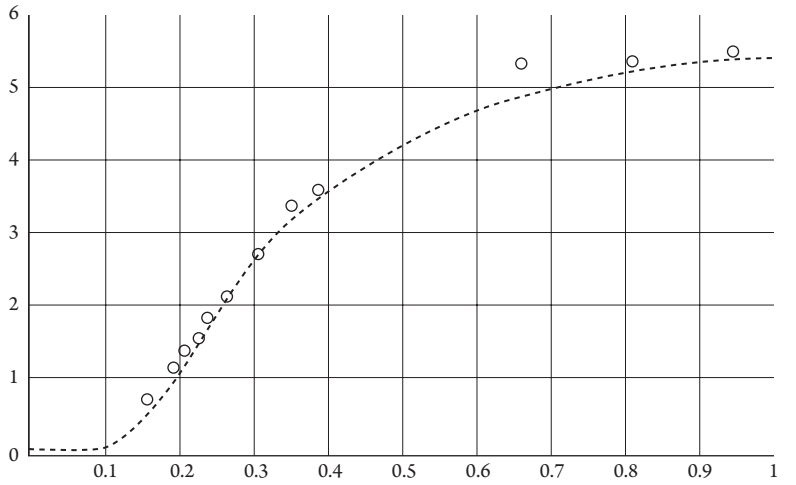

Figure 18.1. The specific heat C_v of a solid (vertical axis), plotted vs. $kT / h\nu$ from Einstein's theory with Weber's experimental data superimposed. Einstein's formula was $C=3R(\xi^2 e^{\xi} / (e^{\xi}-1)^2)$, which approaches $3R$ for large T (small ξ), and goes to 0 as $T \to 0$ (large ξ). From Pais (1982), in which the legend is in error. By permission.

was partially taken into account in Debye's continuum theory by limiting the number of modes to $3N$, where N is the number of atoms. Despite the theory's success,[13] discrepancies remained at low temperatures because of the neglect of the fundamentally discrete nature of the solid. A good summary of the state of studies of the specific heats of crystalline substances as WWII began can be found in Blackman.[14]

FREE ELECTRON THEORY OF METALS

The special and somewhat complex properties of nonmetallic solids such as semiconductors and insulators were not generally appreciated until a fairly mature theory of the band structure of solids was developed. But metals were of immediate interest because of their large electrical and thermal conductivity, which are, not surprisingly, related.[15] Nonetheless, an understanding of electrical conductivity in metals, and transport properties in general, required first, the identification of the electron as a fundamental unit of charge by J. J. Thomson in 1897, and then the realization that conductivity was due to electron mobility. This much had been largely accomplished by Drude and Lorentz between 1900 and 1905.[16] Their failed attempt to explain conductivity by coupling classical electromagnetic theory with the Boltzmann transport equation of statistical mechanics came just as the idea of the quantum was appearing, but in Drude's work, for the first time, the electrons were seen as "roaming" throughout the solid rather than being fixed to atomic sites.[17] Bohr's dissertation in 1911 dealt with the electron-gas model of metals and showed that the model would not yield the observed diamagnetism.[18] Bohr almost

immediately turned his attention to the problem of bound electrons, starting with hydrogen, and the rest is history, as they say.

In 1927, using essentially the same approach as Drude, Arnold Sommerfeld was the first to attack the problem by using quantum mechanics,[19] employing the new Fermi–Dirac statistics, which, as we have seen, came on the scene in 1926. The result is known as the Drude–Sommerfeld model.[20] The successes of the model included an explanation of why the electrons did not contribute as much to the specific heat as expected, namely that, owing to the Pauli principle (then 2 years old), only electrons near the *Fermi surface*[21]could be excited. At low temperatures, the electron contribution to the specific heat can dominate because it is proportional to the absolute temperature T, whereas that due to lattice vibrations is proportional to T^3.[22] The weak paramagnetism of metals (Pauli paramagnetism[23]) is similarly explained. The free electrons also exhibit what is known as Landau diamagnetism.[24] The essence of the free-electron model is that the interaction between electrons is replaced by some kind of average potential (periodic in crystals) that the electrons individually feel, and a major deficiency in the Sommerfeld theory was that it assumed that the potential felt by the conduction (valence) electrons was constant, whereas for a crystalline substance it clearly must be periodic**.**

PERIODIC LATTICES, BAND THEORY OF SOLIDS

The first attempt to treat a solid as a periodic array, that is, a lattice [*Raumgittern*] was the early one-dimensional model of Born and von Kármán from 1912 1913.[25] By the time the three-dimensional case was studied by Born and Maria Goeppert-Mayer[26] in 1933, giving the vibrational spectrum of a crystal lattice, the quantum-mechanical treatment of the harmonic oscillator was quite familiar. The modes of vibration of a crystal lattice are discrete, as they are in the classical case, but if the energy of a mode is written in the form $n\hbar\omega$, it can be thought of consisting of n quanta with the frequency ω. The name *phonon* was given to these quanta by Igor Tamm in 1932.

The vibrational spectrum of a linear diatomic lattice is, after the monatomic lattice, the simplest case, but already this reveals the presence of gaps in the frequency spectrum, a discovery made initially by Born and von Kármán.[27] Essentially, in a periodic potential, with periodic boundary conditions ("Born–von Karman boundary conditions"), the physics is the same in each "well," a simple kind of translation symmetry, and in a diatomic linear lattice there are separate modes, one in which the particles move together ("acoustical branch") and one in which they move in opposite directions ("optical branch"). Thus the $\omega(k)$ dispersion relation has two solutions with a gap in between (see subsequent discussion); the frequency is a periodic function of the wave number k. An integral part of these developments is the "Bloch theorem," which states that in a periodic lattice, $\psi(X+a)=\exp(\pm ika)\psi(X)$,[28] where a is the period (repeat distance) of the potential. This means that in an ideal periodic lattice, electrons propagate as they would if free, except for the exponential modulating factor. It follows that in a "perfect lattice," one with no thermal excitations, the conductivity

would be infinite.[29] Of course, no lattice is perfect, even at zero degrees, and thus the conductivity depends on the interaction between the electrons and the modes of vibration of the lattice. In three dimensions there are both transverse and longitudinal lattice vibrations, making the situation more complicated. An example would be a crystal such as NaCl, with a simple cubic structure, and similar atomic masses, in which, again, the spectrum divides into optical and acoustic branches, separated by an energy gap.[30]

In 1930 Ralph Kronig and William Penney applied the Schrödinger equation to the problem of an electron experiencing a one-dimensional periodic potential (Figure 18.2) consisting of square wells in the so-called Kronig–Penney model,[31] which reproduces some of the essential features of motion in a periodic lattice, including the existence of allowed energy *bands* separated by forbidden zones (Figure 18.3). Ultimately, of

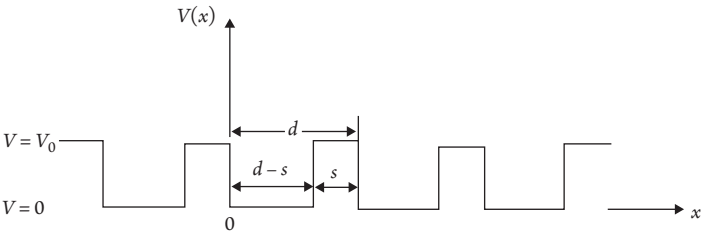

Figure 18.2. Periodic potential well of the Kronig–Penney model. From Morrison et al. (1976), by permission of Prentice-Hall.

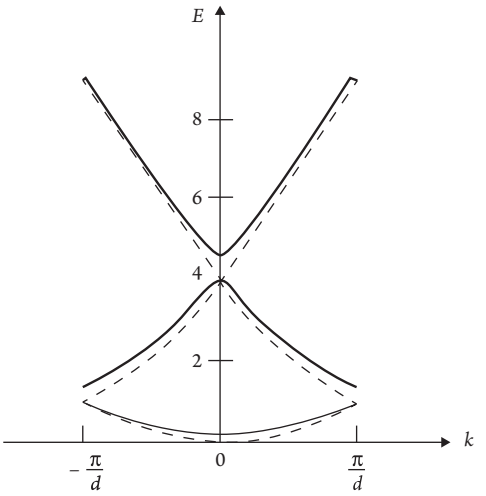

Figure 18.3. The three allowed energy bands (solid lines) in the Kronig–Penny model. Energy is plotted on the vertical axis and k on the horizontal axis. There are two gaps in which there are no solutions to the Schrödinger equation. The energies are given in units of $\pi^2 h^2 / 2m_e d^2$, where m_e is the particle (electron) mass and d is the repeat distance. From Morrison et al. (1976), by permission of Prentice-Hall.

course, a three-dimensional treatment is necessary for a realistic description of the electronic properties of solids, something that was accomplished by Wigner and Seitz in 1933[32] and Slater in 1934.[33]

Thus, in a periodic lattice, there appear a series of bands with gaps in between, though in three dimensions the bands may overlap. Within a band, the energy is a periodic function of the wave number k, which results in a series of zones, known as Brillouin zones. Because of the Pauli principle, the number of electrons occupying a particular band is restricted to $2N$, where N is the number of unit cells.[34] Considerations such as these lead to the classification of crystalline substances as metals, semiconductors, or insulators, depending on the filling of the uppermost (conduction) band by electrons. The band theory of conduction in solids is usually credited to Alan Herries Wilson in 1931–1932, published in a series of his papers beginning in 1932, and leading to the classic book *The Theory of Metals*, published in 1936.[35]

ELECTRICAL CONDUCTIVITY OF METALS

The conductivity of metals is limited by the interaction of free (conduction-band) electrons with the vibrations of the crystal lattice, that is, phonons. The corresponding theory has its origins in the work of Felix Bloch and Rudolph Peierls in 1928–1930.[36] Both Bloch and Peierls were students of Heisenberg, with Bloch having been the very first. Thermal conductivity depends both on lattice waves and conduction electrons, depending on whether the solid is an insulator or metal. Debye[37] found that nonlinearities led to an harmonic vibrations and hence interactions between modes of vibration of the lattice. In phonon terms, this could be represented by the phonon–phonon interaction (*umklapp* processes), first treated by Peierls in 1929.[38] It is interesting to note in this context what was being accomplished in the application of quantum theory, especially to solids, at the same time that quantum theory itself was still in flux and evolving, which provides the motivation for our talking about applications of quantum mechanics.

INSULATORS, SEMICONDUCTORS, AND CONDUCTORS

Given the division of the band structure of solids into a valence band and a conduction band, a metal is characterized by a valence band that is full or nearly full, a conduction band with many free electrons, and perhaps an overlap between the two. In an insulator, on the other hand, the conduction band is almost unoccupied, so that there are no electrons to conduct heat or electricity. In a semiconductor, there are few electrons in the conduction band, but the bandgap is small, so that thermal excitations can populate the conduction band. The size of the bandgap essentially determines whether a solid will be an insulator, and if it is greater than about 4 eV, it will function as an insulator. This recognition, that in addition to solids as conductors and insulators, there

were also "variable conductors" or semiconductors [*halbleiter*], is largely due to Johan Königsburger, in 1914, but it took nearly two decades to understand what was responsible for the division, that is, the band theory of solids, by Wilson, Blackmon, and others, in the early 1930s.

MAGNETIC PROPERTIES OF SOLIDS; MAGNETIC SUSCEPTIBILITY

The magnetic properties of solids are, if anything, more complicated than the transport properties. In large measure, this is because there are three types of magnetism, with very distinct causes: paramagnetism, diamagnetism, and ferromagnetism.[39] And these phenomena vary across the periodic table, so that, for example, metals can be any of the three or may transition from one to another as a function of temperature. Ferromagnetism, in particular, involves collective phenomena in ways that the others do not; its response to applied fields exhibits hysteresis effects, and its temperature dependence is characterized by important changes in the structure of the metal. Most insulators are diamagnetic and most metals are paramagnetic, including ferromagnetic materials at high temperatures.

The magnetic susceptibility of nonferromagnetic metals is small and independent of temperature, a fact that can be explained on the basis of the Pauli principle, that is, Fermi–Dirac statistics. In paramagnetic substances, in which the effect depends on partially filled electronic shells and specifically unpaired electrons, the net magnetic moments of the atoms or molecules are oriented randomly, but in the presence of an applied field will tend to orient along the field, producing a positive magnetic susceptibility. In some cases the effect of the orbital motion is "quenched."[40] In metals only the conduction electrons near the Fermi level will align, so that the susceptibility is small, in some cases so small that diamagnetic effects involving core electrons can overwhelm it, making a metal like gold diamagnetic.[41] Many of the transition metals[42] are strongly paramagnetic, in part because of strong electron exchange, a further effect of Fermi–Dirac statistics. On the diamagnetic side, with no unpaired electrons, is the purely quantum mechanical de Haas-van Alphen effect,[43] in which the diamagnetic susceptibility fluctuates with the field intensity. This phenomenon was discovered in 1930 at very low temperatures, given an explanation by Landau in 1930 and Peierls in 1933, and elaborated upon by Blackman in 1936–38.[44]

Ferromagnetism, known since antiquity, is an order–disorder phenomenon involving the familiar behavior of permanent magnetism in which the phase transition to the magnetized state is of second order with a decrease in entropy and a temperature dependence that causes it to go away at high temperatures. Early attempts to explain ferromagnetism before quantum mechanics were made by Lorentz and Weiss,[45] based on the idea of magnetic domains that possess their own long-range order and thus magnetization, but in general are randomly oriented, resulting in no overall magnetism. But ferromagnetism is a fundamentally quantum phenomenon.

In 1928 Heisenberg[46] was the first to provide microscopic quantum- and statistical-mechanical models of the internal molecular field in terms of the exchange interaction between electrons, rather than a simple dipole–dipole interaction. This model, based on the Heitler–London theory of molecular forces and that does not incorporate lattice periodicity, nonetheless continues to have pedagogical value.[47] Improvements were made immediately by Bloch, who developed a *spin–wave* theory,[48] which represent long-range, collective excitations in magnetically ordered materials (the details of which are beyond the scope of this chapter), and later by Slater, who elaborated upon it.[49] The earlier Ising model,[50] actually proposed by Ising's mentor William Lenz, has many advantages. The original Ising model was conceived before the new quantum theory, whereas, of course, Heisenberg's still simple model was not. The reader might consult Seitz's *The Modern Theory of Solids* for details of the situation when his book was written in 1940, but the key to ferromagnetism is an unfilled electronic subshell, which in the case of the transition metals, is the *d* subshell. According to Hund's Rule,[51] a subshell will fill with parallel spins until double occupancy would occur. Thus, as the result of the Pauli principle and the exchange interaction, the lowest-energy state of the several nearby spins may be one in which they are parallel, producing a region of net magnetic moment. This is a situation in which the exchange interaction, which favors parallel spins, dominates over the dipole–dipole interaction, which favors the antiparallel singlet state. Magnetic domains or "Weiss domains" dominate ferromagnetism in solids because the exchange interaction is of short range, and over a longer range the dipole–dipole interaction is stronger. Ferromagnetism is observed in some alloys that are not made of ferromagnetic materials, the lathanide and actinide elements, for example, and even lithium gas below 1 K.

SUPERCONDUCTIVITY

Superconductivity was discovered by the Dutch scientist Kamerlingh Onnes in 1911, when he found that the electrical resistance of mercury vanished at 4.2 K.[52] Three years before, he had become the first to liquefy helium, by reaching a temperature of 1.5 K.[53] Because superconductivity is a collective quantum phenomenon, no understanding at the microscopic level was possible until well after 1925. In 1933 Meissner and Ochsenfeld[54] discovered what is known as the Meissner effect, in which a magnetic field is expelled from a material as it undergoes the transition from the normal to the superconducting state. Brothers Fritz and Heinz London developed a phenomenological theory of the magnetic properties of superconductors in 1935,[55] which represented substantial progress but did not address the origin of the vanishing resistance. The theory dealt with the nature of the phase transition, which in "conventional" superconductivity is of second order. As happened elsewhere in physics and frequently in this narrative, little progress was made until after WWII. In 1950 Lev Landau and V.L. Ginzberg[56] offered their own phenomenological theory, but finally, in 1957, Bardeen, Cooper, and Schrieffer (BCS)[57] devised the microscopic theory that explained the effect in terms of an electron–electron interaction mediated by the

crystal lattice, that is, by the exchange of virtual phonons. Among further theoretical developments were those due to Nikolay Bogoliubov the following year.[58] The theory of collective many-body phenomena that produced superconductivity was very nearly the same as the microscopic theory of the nucleus, which came to be known as HFB or Hartree–Fock–Bogoliubov theory, and both, in turn, grew out of the formalism of quantum-field theory.[59]

Kamerlingh Onnes also observed the transition to the related phenomenon of *superfluidity* in liquid helium in an experiment performed in 1908, without recognizing it. The nominal discovery of superfluidity came in 1937 when Pyotr Kapitza in the Soviet Union and John Allen and Donald Meissner at Cambridge independently demonstrated it. Their papers were published, one after the other, in *Nature* on January 8, 1938.[60] Appallingly, when Kaptiza was awarded the Nobel Prize in 1978, no mention was made of Allen's simultaneous discovery, probably because of the dominance of Kapitza's group after the war. Superfluidity, which is a state of zero viscosity and zero entropy at low temperatures, is a collective phenomenon like superconductivity, but in the case of ^{4}He, the liquid undergoes a transition to a Bose–Einstein condensate (BEC) at about 2.2 K (its "lambda point"). Landau had proposed a phenomenological two-fluid model of the phenomenon in 1941, not long after its discovery, for which he was awarded the Nobel Prize in 1962.[61] Superfluidity in the Fermi liquid ^{3}He was seen only in the 1970s, and at a much lower temperature of about 2 mK, at which point the ^{3}He fermions couple to the singlet state, which has bosonic properties.

Finally, superfluidity plays a role in nuclear physics as well,[62] and by extension, in infinite (or semi-infinite) Fermi systems like the interior of neutron stars. In this case, the mechanism is the pairing correlation between nucleons.

CONCLUSION

If this brief survey of the application of quantum mechanics to condensed-matter physics in the 1930s has taken us rather far afield, solid-state physics clearly has the most direct application in the real world of all those we have discussed, having fostered many if not most of the industrial advances at the end of the 20th century, something that it is hardly necessary to belabor. Somewhat more exotic applications involving, for example, superconducting magnets with their importance in high-energy physics and possibly transportation, high-temperature superconductivity, nanotechnology, etc., continue to widen the horizons of applications of quantum mechanics. Needless to say, without the quantum revolution of 1925–1932, none of this would have been possible.

NOTES

1. See Eckert et al. (1992).
2. He had long been given to fits of depression.
3. And the first real attempt at a history of solid-state physics, a massive international project indeed, is Hoddeson et al. (1992).

4. See Walter Kohn's essay (Kohn, 1999), in which he says that the first course called "solid state physics" was taught in 1949. Kohn estimated that when he wrote the essay one-third of all physicists identified themselves as condensed-matter physicists.
5. Seitz (1940); over 600 pages long.
6. Petit and Dulong (1819). To avoid leaving the reader at the starting gate, the internal energy can be written as $U = 3NkT$, where N is the number of particles (atoms) and k is Boltzmann's constant. Then the specific heat at constant volume, C_v, is given by $C_v = (\partial U/\partial T)_v = 3nR = 3Nk$. Per mole, then, $C_v = 3R$. Thevalue of R is 1.99 cal $K^{-1}mole^{-1}$ or 8.314 J $K^{-1}mole^{-1}$. Thus $C_v \approx 6$ cal K^{-1} $mole^{-1}$. The calorie is now almost an archaic unit, and specific heats are now most commonly expressed in J/kg °C. Note that Petit and Dulong made their measurements long before the idea of equipartition had been conceived. See also Chapter 1. To elaborate, there are 3degrees of freedom, each containing two quadratic terms, the kinetic and potential energy (of vibration). Hence 6 quadratic terms per atom, or $3kT$.
7. Weber (1872, 1875).
8. In cal/g °C, at temperatures between –188 and –252 °C. Dewar (1905). $3R$ would correspond to 0.5 cal/g °C for carbon. Dewar liquefied hydrogen at the Royal Institution in London in 1898 and solidified hydrogen the next year. Diamond is an example of a low-mass tightly bound solid in which the vibrational levels are widely spaced and hence not highly populated at room temperature (Wikipedia author).
9. Einstein (1906). Again highlighting the fact that in a very real sense, Einstein led the quantum revolution.
10. This motivated Nernst and Lindemann (1911) to propose a modification of Einstein's formula for C_v by adding a term whose origin lay in "half-quanta." See Klein (1965).
11. See, for example, Pais (1982), p. 394.
12. Debye (1912). Debye's relationship to National Socialism has been controversial, based in part on a letter found in 2006 that ends with "Heil Hitler." The conclusion seems to be that he was an "opportunist" but not a collaborator or confirmed anti-Semite. A book in Dutch by Sybe Rispens, *Einstein in the Netherlands*, and an article in German by Helmut Rechenberg explore the issue. In the absence of translations, I refer the interested reader to the very informative *Wikipedia* article.
13. Decker (1957), Figure 2.7. See any text on solid-state physics, for example, Decker, chapter 2. Decker's book is more historically sensitive than most—if obviously dated.
14. Blackman (1941). Some very anomalous specific heats were known even in the early 1930s; see Seitz (1940), p. 14, or Cristescou and Simon (1934).
15. Recognized as early as 1853 in the Wiedemann–Franz law (Franz and Weidemann, 1853).
16. Drude (1900a, 1900b). See the historical introduction, chapter 1 in Wilson (1953). The focus of the book is electrical conductivity. Another source is Eckert et al. (1992).
17. Drude (1900a, 1900b).
18. All solids are at least weakly diamagnetic in their response to external fields. If paramagnetic or ferromagnetic, these properties dominate over the weak diamagnetism.
19. Sommerfeld (1928b). Also Sommerfeld and Bethe (1933); Sommerfeld and Franck (1931). Bethe completed his doctorate at Munich in July 1928 under Sommerfeld.
20. More generally, as Walter Kohn (1999) put it, ". . . by boldly proposing that, at least roughly, the forces on a given electron due to the other electrons cancelled those due to the nuclei, W. Pauli [1927a] and very extensively, A. Sommerfeld [1928b] were led to the . . . free-electron model of metals."

21. Often "the surface of the Fermi distribution" in the late 1920s and early 1930s. The paper by P.K. Hoch discusses the evolution of that term into the now common "Fermi surface." Hock (1983).
22. See chapter 6 in the second edition of Wilson's *Theory of Metals* (Wilson, 1953).
23. Pauli (1927a).
24. Landau (1930). See Seitz's classic *The Modern Theory of Solids* (1940).
25. Born and von Kármán (1912, 1913). The state of the theory as of the early 1920s is given in Born's *Atomtheorie des festen Zustandes* [*Atomic Theory of the Solid State*], 1923. Although Born received his Nobel Prize largely for his work on the probabilistic interpretation of the wave function, he had been nominated several times for his work on the theory of crystal lattices. On the influence of von Kármán on Born, see Greenspan (2005). Born credited von Kármán for rescuing him when he "threatened to sink in the formalisms of Relativity Theory" (quoted in Greenspan, 2005). For what it is worth, Born's daughter Irene married Brinley Newton-John, an MI5 agent who was involved with the Enigma machine at Bletchley Park, and a product of that marriage was the performer Olivia Newton-John.
26. Born and Goeppert-Mayer (1933). We recall that she shared the Nobel Prize in physics for 1963 with Jensen and Wigner, as the second female laureate. Von Kármán went on to become an important aerodynamicist and was a founder of the Jet Propulsion Laboratory.
27. Born and von Kármán (1912, 1913). In particular, fig. 2 in the 1912 paper.
28. F. Bloch (1928). Proved in most books on solid-state physics, e.g., Decker (1957). In mathematics, known as Floquet's theorem, dating from 1883.
29. Bloch (1928). See chapter II in Wilson (1953).
30. Blackman (1941).
31. Kronig and Penney (1931). Kronig's name, the reader will note, has appeared several times in this work, e.g., in connection with the discovery of spin.
32. Wigner and Seitz (1933). See Kohn (1999), p. S63. In an AHQP interview of Dirac on April 1, 1962, Wigner noted that when he first taught solid-state physics he knew nothing of the subject, and two of his students were Seitz and Bardeen.
33. Slater (1934).
34. The unit cell is the unit from which the entire lattice may be generated by certain translations. See Seitz (1940), p. 15. Or it is the "simplest repeating unit in a crystal" (Bodner Research Web), or "the least volume-consuming repeating structure in a solid" (UC Davis), or it is " The smallest building block of a crystal, consisting of atoms, ions, or molecules, whose geometric arrangement defines a crystal's characteristic symmetry and whose repetition in space produces a crystal lattice"(*The American Heritage Dictionary*).
35. Wilson (1932, 1936). Wilson had been a student of Heisenberg.
36. Bloch (1928, 1929, 1930); Peierls (1930). Peierls was an extraordinarily versatile theoretical physicist who made important contributions to both the theory of solids, especially electrical conductivity, and to that of the nucleus. On the latter, see Peierls (1979), and for an enchanting description of a career at the forefront of theoretical physics during the period in question, see his *Bird of Passage* (1985). He had also been a student of Sommerfeld's and an assistant to Pauli. And he was a major figure in the British nuclear bomb project. His obituary is in *Physics Today* **49** (1996), 74. See also the discussion in Decker (1957), chapter 11. Or Kittel's classic *Introduction to Solid State Physics* (1953), which was revised through 2005 (eight editions). His *Quantum Theory of Solids* (1987) is much more modern, of course.

37. Debye (1914).
38. Peierls (1929). Although, again, the "phonon" was named by Tamm in 1932.
39. Note that the names of the first two were coined by Faraday, with, however, the help of William Whewell. See Purrington (1997). One can say that diamagnets are repelled by a magnetic field and paramagnetic materials are attracted.
40. Van Vleck (1932). See also "Solid State Physics, Part III, Magnetic Properties of Solids," by Mildred Dresselhaus, available electronically.
41. See Decker (1957), chapter 18; Seitz (1940), chapter 16. The Fermi energy is the energy at which the occupation probability is 0.5.
42. The transition metals are those in groups 3 to 11 (12) in the periodic table. They are characterized by partially filled *d*-subshells, which actually are complete by group 11; they are known as the "*d*-block" elements. These are essentially $Z = 21 - 80$, with qualification.
43. De Haas and. van Alphen (1930a, 1930b). Van Alphen was de Haas's student.
44. Landau (1930); Peierls (1933); Blackman (1938). For a modern discussion, see Wasserman and Springford (1996).
45. Weiss (1906).
46. Heisenberg (1928). The original impetus was apparently a suggestion from WH that Peierls explore the effect of exchange forces on Bloch's theorem.
47. See statistical mechanics texts such as Pathria (1996).
48. Bloch (1931).
49. Slater (1937).
50. Ising (1925). On the statistical mechanics of both models see Wang (1963).
51. The state with maximum spin has the lowest energy. Sometimes known as the "bus seat rule." Also, the "box and arrow" pedagogical tool is used. For the three empirical rules, see Herzberg (1939).
52. Onnes (1911).
53. He was awarded the Nobel Prize in physics in 1913 for these accomplishments, after having been passed over for what appear to have been political reasons, despite a unanimous vote by the Physics Committee that was overturned by the Swedish Academy in 1912 in favor of one of their own. Superconductivity was not explicitly mentioned: "for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium." See Reif-Acherman (2013). He reportedly coined the term "enthalpy" $U + pV$.
54. Meissner and Ochsenfeld (1933).
55. London and London (1935).
56. Ginzburg and Landau (1950).
57. BCS (1957); John Bardeen, Leon Cooper, and Robert Schrieffer. For which Bardeen would share his second physics Nobel award, the only person to have been so honored.
58. Bogoliubov (1958).
59. Landau was awarded the Nobel Prize in 1962 for superfluidity in helium, BCS for superconductivity in 1972, and Ginzburg in 2003, with Abrikosov and Leggett. Landau was prevented from accepting the Nobel Prize in 1962 because of a car accident, from which he never fully recovered. He died in 1968.
60. Kapitza (1938). Allen and Meissner (1938a, 1938b). Pyotr (Peter) Kapitza worked for a decade with Rutherford and was the initial director of the Mond Laboratory in Cambridge in the 1930s. Returning to Soviet Russia, he was not permitted to travel to the West, but

eventually discovered superfluidity in Moscow in 1937, using equipment from the Mond Laboratory. Allen and Meissner independently discovered it at almost the same time at the Mond Laboratory, where Misener was working on his PhD. Kapitza apparently coined the term "superfluid." See Allen's obituary in *Nature*, **411** (2001), 436.

61. Landau (1941), based on some ideas of Laszio Tisza. Not all superfluids are BECs, nor are all BECs superfluids.
62. The formalism, involving excitations of a quasiparticle vacuum of a many-particle system, is remarkably similar in all of these cases. See, for example, Brink and Broglia (2005).

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EPILOGUE

A cynic might insist that this book should have been subtitled "The Creation of Quantum *Theory*," as opposed to "Quantum Mechanics," because of the heavy concentration on theory, which I think the reader understands was deliberate. This has, in fact, been unapologetically a book about the evolution of quantum *theory*, though perhaps this *is* the apology. As emphasized earlier, quantum theory was strongly motivated by experiment, and if much of that empirical evidence was accumulated in the later 19th century, the productive relationship between experiment and theory certainly did not stop there. We think particularly of the Franck–Hertz experiment, which confirmed the discrete nature of atomic levels, the Davisson–Germer experiment, which was a concrete manifestation of wave–particle duality, and the Stern–Gerlach experiment, which demonstrated space quantization, to merely scratch the surface. Nuclear physics has been an inescapably experiment-driven field from the very beginning, and Rutherford's long career was dominated by a lifelong skepticism about theory. Chapter 15 is full of recounts of experimental discoveries, by Rutherford, of course, but also by Aston, Bieler, Chadwick, Anderson, Neddermeyer, Lawrence, and many others. Nuclear and atomic physics have distinct histories, as we have already noted, because in the former, theory evolved right along with experiment, whereas in the case of atomic physics, many, if not most, of the challenging empirical results ("data") from experiments on atoms that quantum mechanics had to explain, came from before, or perhaps just after, 1900.[1] In any event, experiment has played a large role in this narrative even as the emphasis has been on theory. In acknowledgement of this fact, the particle theorist James Bjorken has written that

> It is my credo that technological advances drive the progress in experimental physics and that experimental physics in turn drive the theory. Without these ingredients, the most brilliant theoretical constructs languish worthlessly. There is in my opinion no greater calling for a theorist than to help advance the experiments. It is not an easy thing to do.[2]

The growing distinction between theory and experiment, or theorists and experimentalists, which is so strong today, dated only from the last half of the 19th century, and some of the great theorists of that era, for example, Maxwell and Helmholtz, were definitely at home in the laboratory. Even Rutherford has been described as a "crypto-theorist."[3] But in the period covered here, mostly 1925–1940, that kind of

broad perspective was becoming rare. Indeed, after Enrico Fermi, one has to look very hard for examples, though a few, like Fred Reines, are hard to pigeonhole. This is not to deprecate in any way the tributes due many fine experimentalists, who in many cases had almost uncanny instincts for what were the important problems—much less the experimental program itself. It remains the case that no matter how beautiful a theory may be, even how internally consistent it is, in the end it is experiment or observation that will determine its survival.[4] Disagreement with just one experiment, in most cases, means that the theoretical edifice comes crashing down. The imperatives of experimental tests of a theory are inescapable. Finally, it is no secret that although theory may often stimulate an experimental investigation, in many cases experimental discoveries have driven theoretical innovation. We have seen many examples of both of these ways of doing physics in previous chapters.

It is perhaps less remarkable that quantum theory largely arose in the 15-year period that has been emphasized here, leading up to WWII, than that it has survived mostly unchanged for the subsequent three-quarters of a century. The way physics is done, on the other hand, has changed so much that it would be hardly recognizable to those who created quantum mechanics nearly a century ago. Physics, and especially quantum physics, was then a tiny community by today's standards. There was no "big science," no papers with several hundred authors, and only very modest external funding. And yet it was unquestionably a *community* that created quantum mechanics, despite much slower communications and much more difficult travel. And although European centers had dominated fundamental science (but not necessarily technology) for a century, this period, 1925–1940, was one in which American science rapidly gained ascendancy, in part because of the political insanity of post–Weimar Germany and its intellectual self-destruction after 1933.

Today nearly everyone carries a device in his or her pocket that contains direct applications of quantum mechanics. But despite the widespread applications of quantum mechanics in the real world, which include miniaturization of electronic circuity, the ubiquity of digital devices of all kinds, and the birth of quantum computing, one can hardly be appalled at the fact that perhaps the first important real-world application of quantum mechanics was to the nuclear bomb project during WWII. For that mankind has much to answer, but on the other side of the ledger, human lives have benefited enormously from innovations, essentially quantum mechanical or at least based on quantum mechanics. Of course some of these, like superconductivity, could be exploited without being explained by quantum mechanics. But transistors and other solid-state devices are inherently quantum mechanical, as are, of course, lasers. Without lasers there would be no CDs, for example, and without solid-state electronics, there would have been no moon program. Imagine either the on-board computers or those on the ground being powered by vacuum tubes—as they were before the 1960s. Nanotechnology operates very close to the microscopic–macroscopic interface, by which I mean that macroscopic quantum effects might come into play. And in the not-too-distant future is the prospect of practical quantum computing.

To be sure, one message from the chapters that have come before is that, as in any vital field of science, theory and experiment or observation are intertwined, the one feeding the other. Quantum theory is the great scientific discovery of the 20th century, but it is thoroughly built on empirical foundations. But what else have we learned in the course of this narrative? We have, of course, traced the development of quantum mechanics from its beginnings to what became its canonical form in the years leading up to WWII. Further, we have learned that, for now, standard quantum theory as a vehicle for interpreting observations has no challengers. Of course the same was the case with the Ptolemaic theory in the second century and for over a millennium thereafter. We also know that however successful quantum theory may be, its foundations, if not exactly crumbling, at least are under attack. Whether those attacks will fail or simply succeed in deepening our understanding of the theory's foundations, we cannot know. There is, of course, the possibility that this quest will undermine the entire theoretical structure, showing that it is at best an approximation to a more fundamental theory. So be it.

It may not come as a complete surprise that the collection of results that filled a modern quantum-mechanics textbook from the early 1990s, and in particular the theoretical framework that would be found there, almost without exception dates from that fertile period, 1925–1940, to which this work is devoted. Applications are, of course, another matter entirely, and furthermore there are exceptions, but in any case this situation has changed significantly since the 1990s, for several reasons, some theoretical, some experimental. Thus the best of the most modern textbooks, and Weinberg's very recent one stands out above the others, consider many topics that would not have been included, and in some cases were not known, in the 1980s. Examples include path integrals, Berry phase, Landau levels, gauge invariance, the Bohm–Aharanov effect, quantum computing and quantum optics, an emphasis on internal symmetries, and so on. Issues of measurement and interpretation are no longer so easily overlooked and EPR and Bell's inequality will be found in almost all of them.

That said, and despite the fact that the formalism has been in a mature state for three-quarters of a century, the issues of interpretation, explored at length in the Chapter 14, remain largely unsolved. At the very least, anything like a consensus is lacking. Despite our confidence in applying quantum mechanics on the atomic and subatomic scale, the discomfiture felt by many physicists in considering how the transition to the macroscopic, classical world takes place is such that they turn away, almost in despair. But quantum theory would be much less interesting, indeed, less exciting, if all of its subtleties were suddenly explained or explained away.

At the very beginning of this narrative, we took notice of the recent anniversary of the first quantum-mechanical calculation by Bohr in 1913, and so we have come full circle. For we have also just put behind us the centenary year of Rutherford's discovery of the nucleus in 1911, without which the Bohr theory and what followed would not have been possible. We are now duly celebrating, if that is the proper word, the 4 years of the "Great War," which to a considerable degree determined when the quantum revolution could take place. Not until 1918 or 1919 could real progress toward the

theory described in this work resume in earnest. Thus it is, that in just under a decade we will fully honor the beginning of what we have called "the heroic age," as the first century of quantum mechanics comes to a close.

CONCLUSION

Thousands of words have been devoted to what happened between 1925 and 1940 in explanation of how quantum theory came to be. But with the exception of some mild speculation earlier, we have not tried to show "why?," which is one of the mandates of a historical account. In any scientific discipline, of course, there are well-known internal or intrinsic imperatives, the fact that the theory has, as it were, a life of its own that carries it forward. In some cases new experiments force investigators to find a theoretical explanation or description; in others it is the state of the theory itself, its incompleteness, its inelegance, the knowledge that the theoretical step that has been taken is only a start. Here we have again the old internalist versus externalist debate.

Context is all, some would say, and in the case of writing about culture and politics, that may very well be true. The upheavals that characterize literary and artistic expression between, say, 1870 and 1920 were undoubtedly driven by developments in politics, technology (including the automobile, the airplane, military weaponry . . .) social mores, and eventually the conflict of WWI, whose conclusion we are on the verge of celebrating. That science, and physics in particular, should not be immune to such influences must be obvious to anyone. It is no accident that the data described in earlier chapters as leading to the quantum revolution really were not available until just before the turn of the century, and indeed *could not* have accumulated earlier. Electrification, we should remember, began to be widespread only after the first power stations appeared in 1881–1882. So, in one sense, at least, quantum theory evolved out of the raw material made available by the technological developments of the last quarter of the old century. The effects of the war itself have already been examined.

But what of the *character* of quantum theory itself? Earlier the controversial "Forman thesis" was mentioned, which argues that the willingness of the founders of quantum theory to accept indeterminism and to challenge causality was in some sense a reflection of an irrationalist, intuitionist streak prevalent in the Weimar years, which had its origin in the thought of Schopenhauer, Schelling, and even Spengler.[5] That is, it was due to external rather than internal influences. Apart from the difficulty of showing how this philosophical milieu might have influenced Bohr, Heisenberg, or Pauli, there are good reasons to believe that these men and others actively rejected the "Weimar zeitgeist." Dirac, who as much as anyone constructed the edifice of quantum indeterminism, was notably unphilosophical, thoroughly unaffected by external events, and the German irrationalist thought got little traction in England. On the other hand, Marxism was growing in popularity, and its influence even found its way into the Cavendish laboratory despite Rutherford's strong hand. So we are left without answers, but perhaps with a healthy dose of skepticism about this thesis.

Finally, of course, there are the personal factors, the ambition and creativity that characterized the handfuls of individuals who created quantum theory. It is fair to say that no one achieves greatness without a hefty dose of ambition, intellectual or otherwise. Why do physicists with comparable skills diverge completely in their accomplishments? This is clearly a matter for psychologists, and there is much writing about genius, but when one looks at the diverse careers of Bohr, Pauli, Dirac, and others, few patterns emerge, except that they were all driven. They had their differences, of course. Bohr was prolix and overbearing, Pauli intellectually aggressive, Dirac laconic and almost pathologically retiring. And so on. If there is a pattern there, it has escaped this observer.

NOTES

1. I can appreciate the objection that the early data on which nuclear physics was built date from the first decade of the 20th century as well, but I still think the point is basically true.
2. Bjorken (1997). Quoted in Schweber (2015).
3. Or "theoretician." See Goldhaber's comment in Chapter 15.
4. We saw in Chapter 14 that there are assaults on this fundamental tenet of scientific discovery. It is hard to see how this viewpoint can survive, and although it may be true that the universe has properties that are not accessible to observation or experiment, that also means that we cannot know whether our theories about them are true or false. Our ability to test does evolve in time, however, and as we pointed out earlier, theories that are untestable today may yield to observation or experiment in the future.
5. Forman (1971). Much has been written in response, including Hendry (1980) or Kraft and Kroes (1984).

APPENDIX

Heisenberg's Argument

Here we present the central part of Heisenberg's argument for the interested reader. The essential ingredients are Bohr's "frequency condition" $[E(n+n')-E(n)]/h = \nu$ and the quantum condition

$$J = \int p\,dq = nh.$$

We begin with a Fourier representation of $x(t)$:

$$X(t) = \sum_{\alpha=-\infty}^{\infty} a_\alpha(n) e^{i\omega(n)t} \tag{A1}$$

Then,

$$J = \int p\,dx = m\int (dx/dt)(dx/dt)dt = m\int (dx/dt)^2\,dt$$

$= m\int \sum_{\alpha=-\infty}^{\infty} \sum_{\alpha'=-\infty}^{\infty} a_\alpha(n) a_{\alpha'}(n)\,\alpha\alpha'\omega_{n^2}\left[(2\pi/\omega_n)\delta(\alpha+\alpha')\right]$, after integrating, where the δ-function is a Kroenecker delta,

$$= 4\pi m \sum_{\alpha=0}^{\infty} |a_\alpha(n)|^2 \alpha^2 \omega_{n,} \text{ since } a_{-\alpha} = a_\alpha^*$$

Therefore,

$$dJ/dn = h = 4\pi m \sum_{\alpha=0}^{\infty} = \alpha\, d/dn\left[\alpha |a_\alpha(n)|^2 \omega_n\right]$$

Now the crucial step. By analogy with Bohr's frequency condition, the derivative is replaced by a difference:

$$h = 4\pi m \sum_{\alpha=0}^{\infty} = \alpha\left[\omega(n, n+\alpha)\left|a(n, n+\alpha)\right|^2 - \omega(n, n-\alpha)|a(n, n-\alpha)|^2\right] \tag{A2}$$

Now suppose we want to compute $x^2(t)$. Using Eq. (A1), we obtain

$$x^2(n,t) = \sum_{\alpha=-\infty}^{\infty} \sum_{\alpha'=-\infty}^{\infty} a_\alpha(n) a_{\alpha'}(n) e^{i\omega n(\alpha+\alpha')t}$$

If we write this as $\Sigma_\beta b_\beta(n)e^{i\omega n\beta t}$, it follows that

$$b_\beta(n)e^{i\omega n\beta t} = \sum_\alpha a_\alpha(n)a_{\beta-\alpha}(n)e^{i\omega n(\alpha+\beta-\alpha)t},$$

Or, $b_\beta(n)=\sum_\alpha a_\beta(n)\, a_{\beta-\alpha}(n)$

The quantum analogy would be, in Heisenberg's words "almost a necessary consequence of the frequency rule",

$$b(n,n-\beta)=\Sigma_\alpha[a(n,n-\alpha)\, a(n-\alpha, n-\beta)] \tag{A3}$$

Soon, Born and Jordan would see this as $b_{ij} = \Sigma_k a_{ik}a_{kj}$

Next we compute x(t) y(t). By the same argument,

$$x(t)y(t)=\sum_{\alpha=-\infty}^{\infty}\sum_{\alpha'=-\infty}^{\infty} a_\alpha(n)b_{\alpha'}(n)e^{i\omega n(\alpha+\alpha')t}$$

$$=\sum_\gamma c_\gamma a e^{i\omega n\gamma t}$$

So that, quantum mechanically,

$$c(n, n-\gamma)=\sum_\alpha a(n, n-\alpha)b(n-\alpha,n-\gamma), \quad \text{or} \quad c_{ij}=\sum_k a_{ik}b_{kj}. \tag{A4}$$

Similarly, computing y(t)x(t), we get:

$$d(n, n-\gamma)=\sum_\alpha b(n, n-\alpha)a(n-\alpha,n-\gamma), \quad \text{or} \quad d_{ij}=\sum_k b_{ik}a_{kj} \tag{A5}$$

And Eqns. (A4) and (A5) are not necessarily the same, a central discovery in the paper. Born and Jordan would recognize that (A4) and (A5) could be seen as matrix multiplication, which in general is non-commutative.

The reader who would like to see some further elaboration could consult van der Waerden's summary, Hund's *The History of Quantum Theory*, Aitchison, et al or even Weinberg's modern text.[1]

NOTE

1. Van der Waerden (1967), Hund (1974), Aitchison, et al (2004), Weinberg (2013).

BIBLIOGRAPHY

Abbreviations

AHQP Archive for the History of Quantum Physics
AIP American Institute of Physics
Ann. Chim. Phys. Annales de chimie et de physique
Ann. d. Physik. Annalen der Physik (including *Annalen der Physik und Chemie*)
BHJ Born, Heisenberg, and Jordan (1926)
CHP AIP Center for the History of Physics
DSB *Dictionary of Scientific Biography*
IAEA. International Atomic Energy Agency.
Leiden Com (*Communications from the Physical Laboratory of the University of Leiden*).
Naturwiss. Naturwissenschaften
Phys. Zeit. Physikalische Zeitschrift
SI, SII, SIII, SIV Schrödinger (1926a, 1926b, 1926d, 1926e)
Verh. Phys. Ges. Berlin. Verhandlungen der Deutschen Physikalischen Gesellschaft zu Berlin
Z. f. Physik. Zeitschrift für Physik
Z. f. Phys.Chemie. Zeitschrift für Physikalische Chemie

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