Mathematics Across the Curriculum – Vol.1

The Bell that Rings Light

A Primer in Quantum Mechanics and Chemical Bonding

Dorothy Wallace & **Joseph J BelBruno**

The Bell that Rings Light

A Primer in Quantum Mechanics and
Chemical Bonding

Mathematics Across the Curriculum

Series Editor: Dorothy Wallace *(Dartmouth College, USA)*

Vol. 1: The Bell that Rings Light
A Primer in Quantum Mechanics and Chemical Bonding
by Dorothy Wallace and Joseph J. BelBruno

The Bell that Rings Light

A Primer in Quantum Mechanics and Chemical Bonding

Dorothy Wallace & **Joseph J BelBruno**

Dartmouth College, USA

Mathematics Across the Curriculum — Vol. 1
THE BELL THAT RINGS LIGHT
A Primer in Quantum Mechanics and Chemical Bonding

To Kathy, Joe and Lizzy:
Your love and enthusiasm
provide the encouragement
for my many projects.

J.J. BelBruno

To Maria:
Love and sweet reason toss
this rose at your feet.
Read it some day.

D.I. Wallace

This page is intentionally left blank

Acknowledgement

This page is intentionally left blank

Preface

Once upon a time I wanted to be a chemist. I guess almost everybody goes through a lot of different imaginings during childhood, and I suppose society has a right to worry about some of them. But if you are like I was, a fair amount of your energy goes into imagining how you might someday make your living, and whether or not you will ever find something you can truly call your vocation.

Now, vocation is not just some three syllable word for "job". It has connotations of what the clergy name a "calling", as in, "Have you felt called to the service of the Lord?" A lucky few people hear such a calling, although most hear faint siren voices, luring them toward ends that neither compel nor provide a living. You can hear these voices too, just practice your favorite hobby or sport for several days in a row and see if you can't hear a whisper or two telling you to make this your passion and livelihood. Well, anyway, all this is to say that once when I was still in high school I thought maybe chemistry was calling me in this way.

We had just finished studying some fairly difficult stuff, I no longer remember what. I was feeling on top of the material and for no real reason sought out the science section of the town library. In it, I found two books, both entitled "The Hydrogen Atom". If you are reading this story, you are likely to know that the hydrogen atom is lesson number one for high school chemistry students. No atom is simpler, just one little proton and one even littler electron account for everything the little guy does. And here, right in front of me, are two books on just this one atom, the first one truly huge, as big as our whole chemistry textbook, and the second one about half that size. I took the small one, under the very mistaken impression that small equals simple, and sat down for a while to read. The first very noticeable thing about this book was the absence of the following picture:
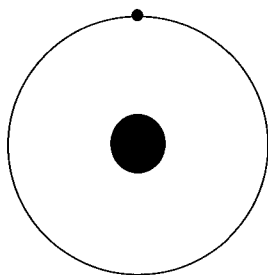
You must know that this picture is required, by law, to precede every discussion of the hydrogen atom. And the discussion always starts, "Now, *this* (pointing) is a proton and *this* is an electron, and the little one goes around the big one, just as Rutherford figured out in 210 B.C. and this is the gospel truth!" Now, may be you can't tell that I am trying to make sport of science textbooks, so here I let you in on my little secret. The minute anybody tries to tell you that some scientific explanation for something is the truth, you have to know you are in the presence of someone who has written, is writing, or is about to write a textbook. At the moment in my life when I opened that book on the hydrogen atom in the San Mateo public library, textbooks were all I had ever seen. And this new book did not resemble any of them. It had no pictures of genteel electrons orbiting politely stationary nuclei, it made no mention of Rutherford or Bohr; it made no reference to anything in my familiar old chemistry textbook. The sole intersection of that book and my understanding lay in the use of the word "hydrogen" and the ubiquitous display of derivatives of various functions, everywhere, standing in bizarre relationships to one another. In fact, the little book on the hydrogen atom seemed to be exactly the same as the big book on the hydrogen atom, except that *all of the words had been removed.*

Some time later that same year I found out that I had been in the presence of quantum mechanics, a way to look at small-scale phenomena in terms of quantities that they possess, such as energy, momentum, location. These functions describing the object stand in for the actual object itself, and all relationships among objects are newly expressed by relationships between the functions that describe them. I will dwell more on this later, I only mention it now to explain the presence of all those derivatives and equations that made up most of the text of the book I was holding in my hands.

Well, physics is not my vocation and neither is chemistry, although the mysterious book on the hydrogen atom did motivate me to enroll in and then drop out of a college quantum mechanics course. I enrolled in it to understand the book I had found and I dropped out of it because it began, more or less, with "this is Schrödinger's equation", providing none of the connection I sought between Mr. Schrödinger and poor old Rutherford and Bohr. Meanwhile, I became a mathematician. And because of that little book, for the last twenty years I have made it my hobby to piece together the story of the hydrogen atom, how it grew from a simple little sun-plus-planet into the set of equations that Schrodinger gave, and how the solution to those equations answers questions posed by Bohr himself.

This little book is my gift to myself. It is the book I wish I had found next to those two others when I went to the library, so that I could have reached, with my still limited knowledge of physics and mathematics, the place where the other books began. This book is for you, too, especially if you are taking a physics or chemistry course now. In it, you will find some glue to help patch up your picture of the universe, especially the very small things in it.

D. I. Wallace

This page is intentionally left blank

Contents

CHAPTER 1

Rutherford, Bohr and Balmer

The notion that the material world is composed of "atoms" is an old one. The first record we have of it is the version held by Democritus, in opposition to Aristotle's world picture. It never dominated the scientific imagination until well after Galileo invented the telescope. Seeing the Milky Way dissolve into a myriad of individual stars did something to the scientific imagination of the Renaissance that has yet to be completely undone. In short, if the universe at large is filled with distinct stars wheeling about, then why shouldn't the universe in miniature behave thus? And suddenly Democritus was no longer about something preposterous. Isaac Newton then gave the world some laws of physics which could conceivably apply to these little objects and, behold, a new science was born. If you think I am oversimplifying all of scientific history, you are right. But just remember how far Euclid got with only three objects (point, line, plane) and five laws to govern them. Well, you can also go pretty far with just atoms and Newton's laws of motion.

What you *cannot* do with these ingredients, however, is explain chemical reactions. When baking soda mixes with vinegar, the outcome supercedes anything that can be described by a bunch of elastic collisions. Newton's laws, in other words, are adequate for describing what happens when you pour water into water, but not what happens when lye, for example, meets vinegar. This is why, while physics was enjoying a flowering of ideas in the late Rennaissance, chemistry was still all about finding the philosopher's stone and had more in common with magic than with what we now distinguish by the name of science. Once the idea of the atom was firmly ensconced in the imagination, however, chemists were able to base a fruitful approach on the simple assumption that *atoms of different substances behaved differently and hence had different structures from one another.*

So the indivisible atom became just divisible enough to share electrons. Protons were big and captured the essential nature of the atom, such as whether it was a hydrogen atom or an oxygen atom. Electrons were small and could be lost or gained during chemical reaction. In fact, a chemical reaction itself came to be defined in terms of electron transfer among atoms. This gain and loss of electrons didn't much affect the weight of the atom, nor did it change it into another substance. Atomists everywhere heaved a sigh of relief over this. Democritus slept more easily in his grave. Of course, to keep an atom in a neutral state, that is a chemically inactive state, it is necessary to balance various forces, so protons and electrons are supposed to be equal in number and to balance each other out exactly. Of course, the atomic weights require something different to happen, so the neutral neutron has to go along for the ride.

With all of this basic equipment in place, chemists were able to figure out rules for a lot of different kinds of chemical reactions. The problem they were tackling looked something like this: Imagine you can see the scorecards for two teams playing some sport you have never seen before. Looking at the scores for a large number of games, you begin to see numerical patterns appear. From these patterns, deduce the rules of the game being played.

It should be obvious that, in a situation like this, there must be multiple "right" answers. For example, if you were staring at a list of final scores for a basketball game, it would be hard to deduce from it how many players were on each team. It would be very hard not to rely on all sorts of longstanding assumptions and peripheral evidence when guessing that the scores came from the familiar game of basketball. And rely on such assumptions was exactly what those chemists did. If the universe at large consists of planets revolving around stars, then in miniature it should do the same. Electrons should revolve around the nucleus of protons and neutrons. The nucleus should never be disturbed. Certain numbers of electrons fit in each orbit. The outside orbits lose or gain electrons first, according to simple mathematical rules with divinely mandated integer answers. Now, it is just a matter of working out which numbers work to predict the observed reactions.

Should it surprise us that the model these fellows concocted worked so remarkably well to explain so many chemical phenomena? In fact, it worked to such an extent that it is still being taught to high school students today, a hundred years later. It had only a few parameters to adjust, namely number and capacity of orbits of electrons and rules for losing, gaining and sharing of outside electrons. Yet it explained, in the end, a virtual infinity of chemical reactions of wide ranging variety. No wonder that the picture Bohr

proposed of an atom remains even today the one that leaps immediately to mind for anybody who survived normal high school chemistry.

But eventually a fellow named Balmer found some interesting numerical properties of an experiment that was hard to explain in terms of this model. The experiment is also described in every elementary chemistry book in the known universe and I'm going to describe it again right now, just in case you forgot about it. You put hydrogen (let us say) atoms in a dark location and then shoot energy (light? radiation of another sort? electric current, the story goes on ...) at the atom to "excite" it. Remember, this business of exciting the electrons means that they gain energy and go up to an orbit farther from the nucleus of the atom. The current repeatedly boosts the electron into an "excited" state, whereupon it decays back into its unexcited, "ground" state. The ongoing process of boost-and-decay results in emission of energy, whose frequency (or wavelength, a simple relation) distribution is shown in Fig. 1.1.

Figure 1.1 represents what happens when the light emitted from the atom is passed through a prism. In graphical form, it is shown in Fig. 1.2.

Only certain frequencies were emitted. For a given type of atom, always the same frequencies were present. Atoms of different substances had a characteristic "spectrum", as it was called. Bohr explained this phenomenon in terms of his own model of the atom by saying that the orbits containing electrons occurred at discrete intervals, pictured as distances from the nucleus, and that electrons had to "jump" from one of these to the next in a more or less discontinuous fashion, so that the difference in energy required to promote the electron resulted in a discrete line appearing in the spectrum of the atom.

Now, you may be sufficiently brainwashed by twentieth century nonchalance to see absolutely no problem with this interpretation, but there are plenty of problems. For starters, the underlying assumption that the microscopic universe should mirror the macroscopic one must be set aside. After all, a planet does not go jumping willy-nilly from one orbit of its star to another that is far further away, no matter how the energy is added. What's it supposed to do, just *disappear* from one location and *reappear* in another? Secondly, this kind of upstart behavior is not something you get from Newton's laws, another of the system's underlying premises. And worst of all, without Newton's laws there is no physical mechanism to explain any behavior of any sort that an electron might have. So here, and not for the first or last time in the history of science, we have a model with great predictive value in some ways, but one whose incapacity to explain one
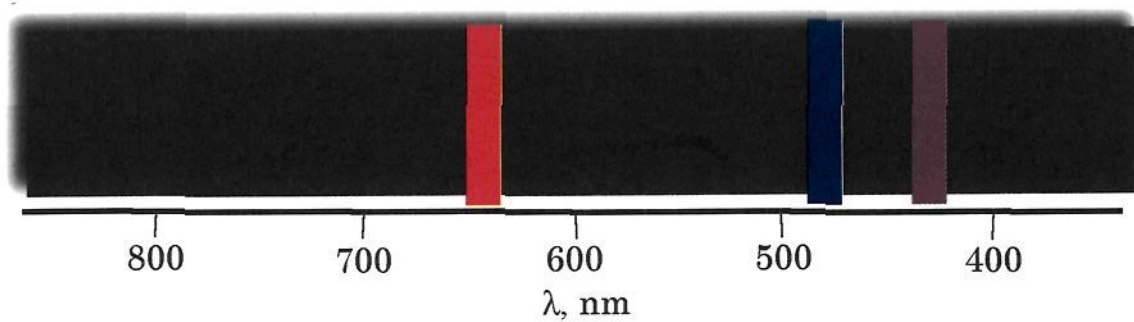
Figure 1.1. The Balmer spectrum of hydrogen. Note that only three frequencies are present.
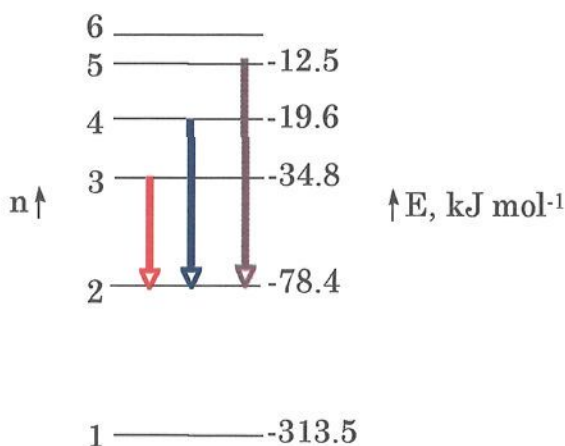
Figure 1.2. The energy level (stationary state) changes within the hydrogen atom resulting in the spectrum shown in Fig. 1.1.

Figure 1.3. Plot of the electron probability density as a function of the radial distance from the nucleus for a hydrogen 1s orbital. The relative density of points at any value of distance reflects the likelihood of localizing the electron near that point.

persistent phenomenon forces the scientific community to rethink the very premises on which the model was initially based.

Later, quantum mechanics would offer a mathematical model of the energy states of the hydrogen atom and it would yield shapes like the one shown in Fig. 1.3, which, of course, blow to bits our beloved image of the hydrogen atom as a little star with a fast little planet circling it.

This page is intentionally left blank

CHAPTER 2

Some Important Experiments

The two fundamental concepts we need before we approach the idea of quantization are the nature of light and the nature of the electron. You might wonder why we would want to ponder over these topics, after all, light is a wave and electron is a particle. That is clear, or is it? In our macroscopic view of the world such assumptions would be correct, but we need to look more closely at the microscopic nature of things. The best way to consider these topics is through a brief review of scientific history. Much of what we are about to do depends on our understanding of Coulomb's Law, therefore, we'll begin with a review of that topic and then look at seminal experiments that defined the nature of light and matter.

Coulomb's Law

Coulomb's Law defines the forces between charged objects

$$F = -C\frac{q_1 q_2}{r^2},\tag{2.1}$$

where q_i is a charge and r is the distance between the charges. The Coulombic potential energy is simply the negative integral of the force

$$V = -\int F dr = C\frac{q_1 q_2}{r}.\tag{2.2}$$

If Eq. 2.2 leaves you uncomfortable, your memory might be jogged by looking at a graphical representation of the Coulombic potential energy as in Fig. 2.1.

1.2 *Electrons*

We "assume" that electrons are particles, but why is that? What experimental results led us to this assumption? We can trace history back to Faraday
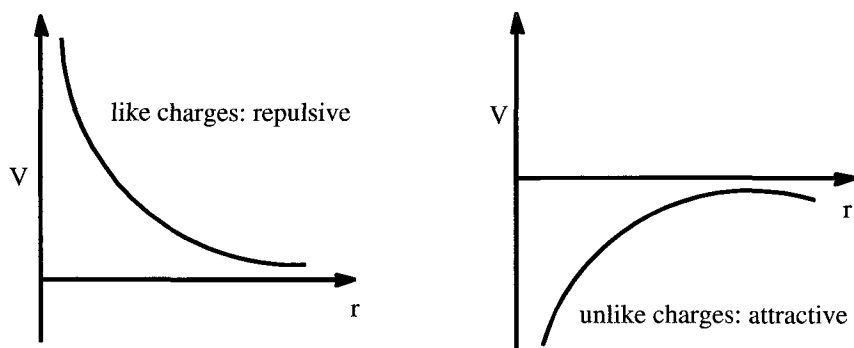
Figure 2.1. Graphical representation of the Coulombic potential as given in Eq. 2.2.

and his electrolysis experiments. In these experiments, an ion "collided with" an electron and deposited metal at an electrode. Faraday's observations included the fact that the quantity of deposited material depended upon the current, which is given in units of Coulombs (units of charge) per unit time. Of course, one may relate the total charge to the number of electrons. Therefore, the amount of material (atomic or molecular) deposited at the electrodes was a function of the number of electrons and the molar weight of the ion.

Does our consideration of the nature of the electron really matter? Well, scientists in the late 19th century were concerned with "cathode rays" and their nature — were they waves? Not according to Faraday's results. The "rays" were actually beams of particles, electrons. Need more evidence? Look to the experiments of J.J. Thomson, as shown in the diagram below.

Thomson observed that one could deflect the "rays" with either an electric or a magnetic field — can you do that to a wave? Of course not, that behavior is characteristic of matter. Thomson, from this experiment, found the ratio of the electron charge to its mass, e/m, by analysis of deflecting electric and restoring magnetic fields. The value of e/m was 1000 times greater than that for any known ion, so the question became: Was e large or was m small?

The definitive experiment by R. A. Millikan proved that all electric charges were multiples of 1.6×10^{-19} C (the elementary charge, e). Therefore, he could calculate the mass of the electron. A schematic of his apparatus is shown in Fig. 2.3 and briefly described below.

Oil droplets were charged by collisions with ions. In the absence of an additional potential, they fell under the force of gravity. In the presence
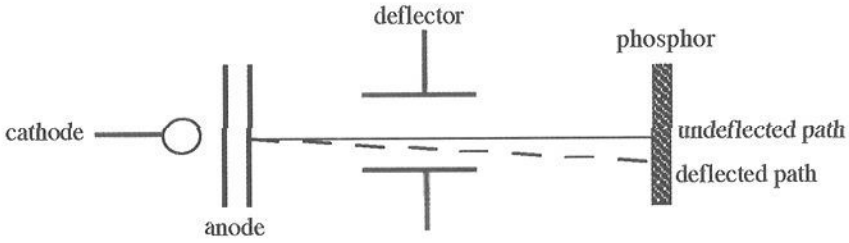
Figure 2.2. The experimental apparatus of J.J. Thomson. Electrons are emitted by the cathode, accelerated by the anode and detected by a phosphor at the end of the tube. A magnetic or electric field may be applied and will deflect the beam of electrons.
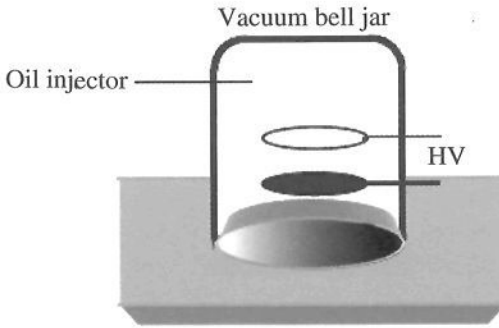
Figure 2.3. Schematic diagram of the Mullikan oil drop experiment. An atomizer injects charged oil droplets into the vacuum chamber where they fall under the influence of gravity. The application of an electric field alters the motion.

of an external potential, the droplet acceleration was changed; from this change, m was calculated to be 9.1×10^{-28} g. The particle nature of electrons was now well established: particles may be deflected and tracked. The electron was clearly a particle.

Light

Waves are characterized by frequency, ν, wavelength, λ, and amplitude. We can relate the frequency and wavelength of light from "wave mechanics",

$$\lambda \nu = c, \tag{2.3}$$

Xrays	vuv	uv	vis	NIR	FIR	μ waves

(ν, cm^{-1}) 10^6 5×10^4 10^4 500 10 10^{-1}

(λ, nm) 10 50 200 320 800 2000 10^6

Figure 2.4. The spectrum of electromagnetic radiation.

where c is the speed of light, $\sim3 \times 10^8$ ms^{-1}. We represent a portion of the spectrum above. Note that "frequency" (expressed in units of the wave-number, cm^{-1}, not Hertz, s^{-1}) and wavelength increase in opposite directions.

The nature of light was also obvious, at least in the late 1800's — it must be a wave, correct? Let's explore that characterization. We begin by looking at blackbody radiation. We consider the topic qualitatively and use the result of the exact mathematical manipulation.
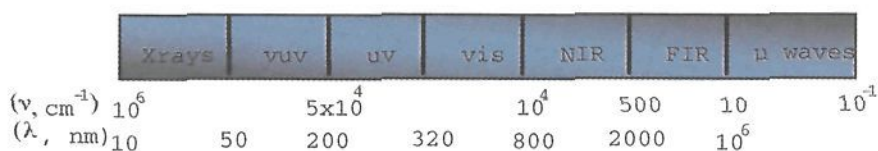
A blackbody is one that absorbs and emits all frequencies. Experimentally, we accomplish this by the following process. As you heat a body (say, a stove burner), you will observe that the perceived color of the object will make a transition from red to yellow-orange. It could turn white, and even blue, as the temperature increases. The color appears to change because the maximum frequency of the observed light moves to higher frequencies (lower wavelength) as the blackbody is heated. We can record the output, the emission spectrum, of the blackbody and the result is shown in Fig. 2.5 for two different temperatures.

The density of radiative energy, $\rho\,(\nu,\text{T})$, for a frequency between ν and $\nu + d\nu$ (in J m^{-3}) is given from classical theory by the following equation, sometimes called the Rayleigh–Jean model

$$\rho(\nu, \text{T})d\nu = \frac{8\pi k\text{T}}{c^3}\nu^2 d\nu, \tag{2.4}$$

where c is the speed of light and k is the Boltzmann constant, which has the value 1.38×10^{-23} J mol^{-1}K^{-1}. The problem is that the theory does not agree with the experiment. Theory indicates that the intensity rises as ν^2 (or λ^{-2}) and asymptotically goes to infinity for $\lambda = 0$. Max Planck found the solution to the dilemma. In his model, just as in classical theory shown in Eq. 2.4, the radiation is due to oscillations of the electrons in the atoms of the blackbody; this is an antenna problem. In the Rayleigh model, the energies of the oscillators had no restrictions. Classical physics is continuous (all values of the variables are allowed), not discrete (variables are allowed
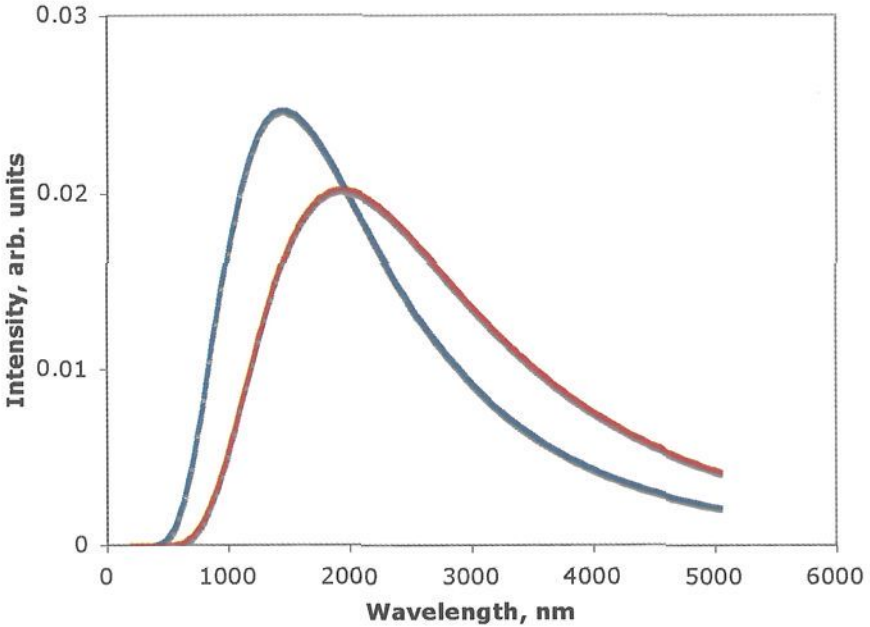
Figure 2.5. Experimental blackbody curves (unnormalized) for two different temperatures.

to take on only certain values). Planck assumed that the oscillator energies were restricted to integral multiples, n, of the frequency, $E = nh\nu$. Using the techniques of what we now call statistical mechanics, Planck derived an equation which agreed with all of the experimental data, where $h = 6.62 \times 10^{-34}$ Js is known as Planck's constant,

$$\rho(\nu, T)d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{d\nu}{e^{\frac{h\nu}{kT}} - 1}. \tag{2.5}$$

Planck's result was not widely accepted in the physics community of the time (early 1900's). The theoreticians were certain that a classical solution to this problem would eventually be discovered. Even Planck was uncomfortable with the quantized results, but this was the beginning of the microscopic view of the world. This was the start of **quantum mechanics**.

The final, convincing evidence for the legitimacy of Planck's explanation of the blackbody radiation results came from Einstein and his Nobel Prize winning theory of the *photoelectric effect*. What is the photoelectric effect? It is schematically described in Fig. 2.6. In short, UV light causes
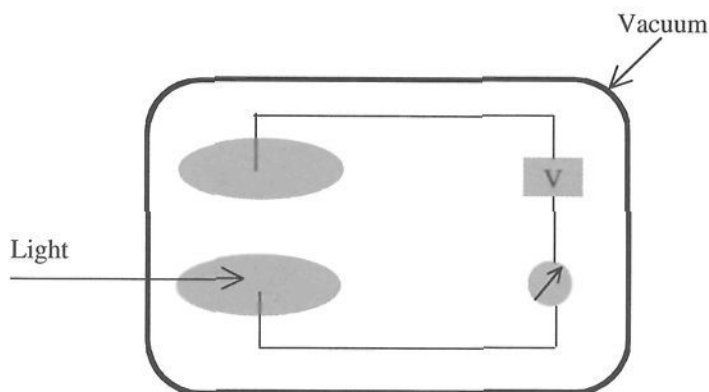
Figure 2.6. The apparatus used to observe the photoelectric effect. Light strikes the photocathode, an electron is emitted, moves toward the anode and is detected.

electrons to be emitted from a metallic surface held in a vacuum. The following *experimental observations* were well known at the time, but were left unexplained by classical physics:

- the kinetic energy of the electrons is independent of the intensity of the incident light;
- there is a threshold frequency and below it, there is no photoelectric effect; and
- the kinetic energy of ejected electrons increases with increasing frequency of the incident light.

It is instructive to examine the predictions from classical physics. It would be expected, *if classical physics were valid*, that

- as the intensity of the light increases, so does the induced oscillation of the electrons and they break away. That is, higher intensity induces more violent oscillation and higher electron kinetic energy at escape and
- the photoelectric effect should be frequency-independent, but intensity dependent.

Looks like trouble for classical physics!

Now, we return to Einstein's work. He knew of and used Planck's results for the oscillators. Einstein proposed that light consisted of packets of energy, $E = h\nu$, called *photons*. Then, using conservation of energy, he wrote

$$\frac{1}{2}mv^2 = h\nu - \phi, \qquad (2.6)$$

where ϕ is the work function or threshold energy of a particular metal. This is the minimum energy required for electron ejection, $\phi = h\nu_o$. When $h\nu \geq \phi$, an electron is ejected and the excess energy, that energy above ϕ becomes kinetic energy. Finally, the number, but not the energy, of the ejected electrons will increase as the number of photons or the intensity of light, increases. There is exact agreement between the experimental results and Einstein's model. One way to check this agreement is to measure the kinetic energy of the ejected electrons. How do we make these measurements? We use a stopping potential, V_s. That is, the electrons are directed toward a negative electrode and the potential is increased until the electrons are stopped. The equation governing this process is

$$\frac{1}{2}mv^2 = -eV_s,$$

where e is a negative number. We can plot V_s versus ν, as in Fig. 2.7.

Now, we have a problem: we have proposed, actually assumed, that light could be described as a wave. Einstein just invoked a particle-like property to explain an experiment. Is light a wave? or a particle? And, if light is a particle as well as wave, what does that say about a particle? Can a particle also be thought of as a wave? In particular, is an electron a wave as well as a particle?

The Dual Nature of Matter

To address this issue, we skip over some important theoretical and experimental advances for the time being and go to 1924. We will also not try to derive the solution to this apparent dilemma, but rather note that de Broglie
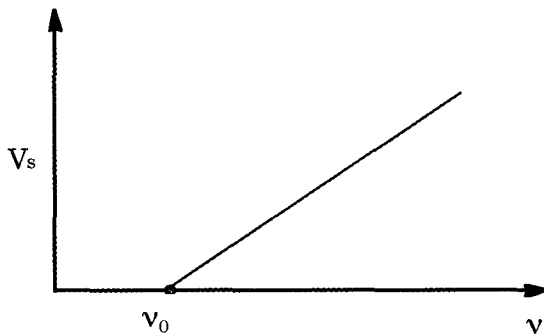

Figure 2.7. Stopping potential for the photoelectron as a function of incident frequency.

realized that, if a light had the properties of a particle, then it must have momentum. He deduced that the relationship between the wave property of wavelength and the particle property of momentum for a photon could be described by

$$\rho = \frac{h}{\lambda}, \tag{2.7}$$

and we can relate the momentum of a photon to its wavelength. More importantly, de Broglie asserted that this was true for matter, where $p = mv$, as well as for light, when $p = mc$. A practical result of this equality is the electron microscope. You have probably seen electron micrographs of insects, cells or atoms on a surface. Electron microscopes are capable of imaging objects as small as tens of nanometers. This high resolution results from the small wavelength of the electron traveling at a substantial fraction of the speed of light (large momentum).

We continue our chronological digression by considering the work of Walter Heisenberg, also in the mid-1920's. He carefully considered the way in which the measurement of the position of an object using a photon of a given momentum would affect the position of the object being measured. Consider the following: if we wish to locate an electron to within a distance Δx, we must use light of that wavelength or we won't "see" the electron, at least not to that resolution. If we want to increase the resolution or accuracy, then λ must be smaller, but p gets larger as the wavelength is reduced and more momentum will be transferred during the collision causing a larger uncertainty in the position of the observed object. The uncertainty relationship is

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \tag{2.8}$$

where

$$\hbar = \frac{h}{2\pi}.$$

This is a fundamental law for the act of measurement.

Early Quantum Mechanics: The Atom

Now, on to the atom. The atom contains electrons and we may influence the energy of those electrons using electromagnetic radiation. Therefore, our discussion of the nature of electrons and light will be significant in the discussion of the atom. Coulomb's Law will also be invoked in the upcoming discussion.

Prior to the work of Rutherford, the atom was considered an object of constant density. Rutherford (actually Rutherford and his graduate student, Marsden) scattered α-particles (He^{2+}) through metal foils and the data indicated that most of the mass of an atom was localized and the majority of the atom consisted of empty space. These conclusions resulted from an analysis of the scattering of the α-particles. When the α-particle encountered the nucleus, in which most of the mass was localized, the scattering angle was quite large, nearly 180°, that is, directly back at the source. Such observations were relatively rare, since most α-particles simply passed through the foil, undeflected. The conclusion cited above, most of the atom is "empty space", is obvious from these results. This work led to the orbital model of the atom, as shown in Fig. 3.1. However, classical physics tells us that electrons cannot exist in a stable orbit. The electron would nearly instantaneously radiate while dropping into the positively charged nucleus. While the new model was sufficient to explain the distribution of mass, it could not explain the reality of the atom, at least not in terms of classical physics. A new kind of physics was required: **quantum mechanics**.

So finally, our short history leads us to Niels Bohr and early quantum theory. Bohr's analysis of the problem has errors and limited applicability. However, it is the start of a new field, explains the data available at the time and provides an indication of the new direction physical thought had taken. Therefore, we'll treat it in detail here.
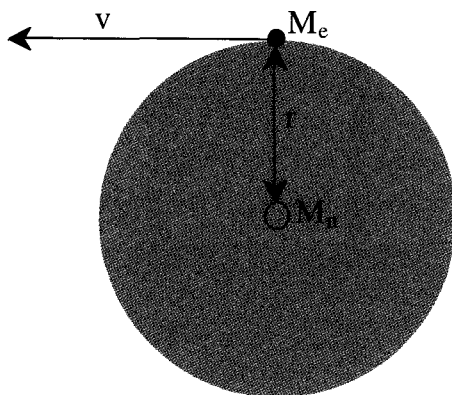
Figure 3.1. The Rutherford representation of the atom.

What was the available data? What information set Bohr off on this new path? If we compare the spectrum of the hydrogen atom, the simplest atom, to that of a blackbody, the difference is striking. The blackbody radiates at all wavelengths, while the only visible light emitted by the hydrogen atom is at three very narrow wavelengths of red, blue and violet light, see Fig. 1.1. These data were well known when Balmer came up with an equation to fit the data (the luck of random curve fitting?)

$$\nu = 8.2202 x 10^{14} \left(\frac{1}{4} - \frac{1}{n^2} \right) \text{Hz}, \quad n = 3, 4, 5, \ldots \tag{3.1a}$$

We can rewrite this, converting ν to $1/\lambda$

$$\bar{\nu} = \frac{1}{\lambda} = 109680 \left(\frac{1}{4} - \frac{1}{n^2} \right) \text{cm}^{-1}, \quad n = 3, 4, 5, \ldots, \tag{3.1b}$$

This is known as the *Balmer Formula* — why is n set equal to integers from 3 to infinity? We'll see shortly! This equation was later generalized by Rydberg to what we now call the Rydberg Equation

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = 109680 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{cm}^{-1}, \quad n = \text{integer.}} \tag{3.2}$$

The constant, $109{,}680\,\text{cm}^{-1}$ in Eq. 3.2, is often given the symbol R_H and is known as the Rydberg constant for hydrogen. This is what Bohr had to work with in his theoretical development, but as you can see, it is an extremely significant empirical result. Now, we go back to the orbital model with which we began this discussion. What do we know from classical physics

about an electron orbiting a positive charge, as in Fig. 3.1? The electron has *angular momentum* given by mvr. There will be a *centripetal force* toward the nucleus, $F = \dfrac{mv^2}{r}$ and the electron should radiate and fall into the nucleus! **Bohr simply assumed that the electron didn't radiate and fall into the nucleus and examined the consequences**. He built a theory based on four postulates:

(1) electrons have allowed energies called stationary states;
(2) electrons in stationary states do not radiate; radiation is due to changes in the stationary state of an electron;
(3) electrons move in circular orbits; and
(4) stationary states have angular momentum in multiples of $\hbar$ or $h/2\pi$; $mvr = n\hbar$.

The centripetal force is Coulombic, after all we are looking at an electron and a collection of protons

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \text{or} \quad \frac{Ze^2}{r} = mv^2, \tag{3.3}$$

where Ze is the nuclear charge and e is the electron charge.

$$\frac{Ze^2}{r} = mv^2, \tag{3.4}$$

but, from Postulate 4, $\qquad v^2 = \dfrac{n^2\hbar^2}{m^2r^2} \tag{3.5}$

so $\qquad\qquad\qquad\qquad r = \dfrac{n^2\hbar^2}{Zme^2}. \tag{3.6}$

and is defined as the radius of the Bohr orbit. The radius is quantized, that is, it depends only on an integer, n.

$$r = 0.530\frac{n^2}{Z} \text{ Å}, \tag{3.7}$$

where $1 \text{ Å} = 10^{-8}$ cm. Now look at the energy of such an atom using equation 3.4 for K, the kinetic energy

$$E = K + V = \frac{1}{2}mv^2 - \frac{Ze^2}{r} = -\frac{1}{2}\frac{Ze^2}{r},$$

$$E = -\frac{1}{2}\frac{Z^2e^4m}{\hbar^2n^2}, \quad n = 1, 2, 3, \dots, \tag{3.8}$$

where n is a *quantum number*. This is the stationary state energy of an electron in a one electron atom. At the limit $n \to \infty$, $E \to 0$ and the atom is *ionized*.
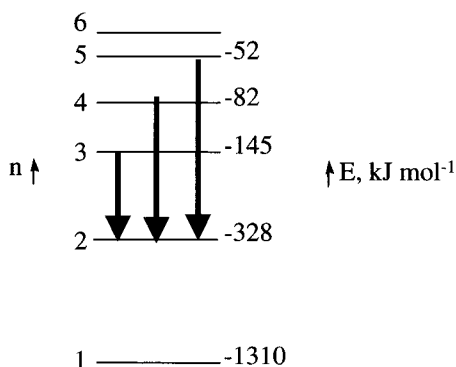
Figure 3.2. Schematic representation of the transitions in the hydrogen atom.

Can we get to Rydberg's Equation? Sure! We even get R_H, the Rydberg constant! We easily recognize the cause of the observed discrete hydrogen atom spectrum using Fig. 3.2.

$$\Delta E = E_{final} - E_{initial} = \frac{1}{2} \frac{Z^2 e^2}{a_0} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad n = 1, 2, 3, \dots$$

What is wrong with this model? There are two significant problems. We know that Bohr took a leap away from classical physics, but we wish to base the answer to the question on some solid physics. If we know r exactly, this model will also provide us with an exact value of p! This is a violation of Heisenberg's Uncertainty Principle.

(1) $r = \dfrac{a_0 n^2}{Z}, \quad p = \dfrac{n\hbar}{r}$ violates $\Delta p \Delta x \geq \dfrac{\hbar}{2}$.

(2) Try to apply this model to the helium atom. Now we have two electrons. What do we do? How do we deal with multielectron systems?

There is no allowance in this model for more than one electron. Some researchers tried to accommodate the extra electrons by using elliptical orbits, but that didn't work. How do we know it failed? We could use the same criterion we used for hydrogen. The question to ask is: Can we reproduce the experimental spectrum? For multi-electron atoms there are far too many lines of nearly the same wavelength. The Bohr model cannot predict the occurrence of these transitions. We need a new model; the "new" quantum mechanics. We shall use a formulation due to Schrödinger.

New Assumptions

Certain old assumptions die hard, particularly those having to do with circularity of motion. The circle is a sacrosanct figure for many cultures and, though it may be refuted as the actual description of a natural phenomenon, it is never completely abandoned as the ideal for which nature somehow strives. Bohr's circular orbits would give way to other models but the role of the circle itself continued to enlarge. Here we are going to explore, not quantum theory itself but the assumptions on which it is based. These include the circle, or more accurately the sphere, in a prominent role.

The prospect of an electron disappearing from one orbit in order to reappear in another was sufficiently disturbing to prompt a review of what an electron might actually be. In fact, the question of what it *is* rapidly gave way to the question of what properties it might *have* that one could observe. Presumably it had location, and some locations were more likely for it to be in than others. Anything that had position could have velocity and acceleration too. And it had mass, which meant it also would have momentum.

Also it possessed energy, and in discrete frequencies, as observed in the Balmer experiment. As we saw in an earlier chapter, this would mean that in some respects it behaved more like a wave than a particle. Specifically, a "particle", imagined perhaps as a billiard ball, can have any speed, any momentum, any acceleration. A continuum of possibilities exists for the billiard ball, or the particle. An old-fashioned wave, although it can have any amplitude, has to decide what its frequency will be. Of course waves can be superimposed to make new waves, but one can describe what frequencies will be present in the sum. And hydrogen, in its emission of beautiful red light during the Balmer experiment, always chooses the exact same frequency to emit. In this choice, hydrogen behaves more like a wave than like a particle.

Now, as soon as you have an object that resists classification as matter or energy or wave or whatever, it is arguably natural to think in terms of observable properties the object might have rather than actual attributes of itself. You might think these are the same, but they most certainly are not. In the case of hydrogen, it is very profitable to think of the electron as having, not a particular position and momentum, but rather a set of probabilities that describe the likelihood of finding it in a particular region of space at any given time.

A *probability distribution* is nothing more than a function, as shown in Fig. 4.1, that describes the likelihood of the electron being in a certain region. This probability is expressed as the area under the graph of the function and above the region in question. By fiat, the total area is one. These distributions take the place of what was formerly envisioned as the *location* of the electron. Such a distribution could equally well describe either the average time spent by the objectified electron in a particular region, or some other function related to the energy of the electron (according to the laws of physics) which could play the mathematical role of position without all the annoying ideological baggage that goes along with the concept.

It is already hard to imagine an electron as something which simply *might turn up* here or there, and whose average behavior is all one can determine and describe as a probability distribution. This bit of imagination is necessary for our story. But one can even go further, although not out of strict necessity. One could suspend disbelief and attempt to think of an electron, formerly an actual object with a home of its own in one's psyche, not just as an object with characteristic probabilities for being found in various proximities to the nucleus, but as being the actual *probability distribution* itself. If you can do this, you might actually be one step ahead of the average physicist. Or one step behind, depending on how you look at it. It is an ancient doctrine that, at the most basic level of existence, the world is formed out of *number*. This is not science, this is mysticism at its finest. Nonetheless, the world is getting to look more and more that way. If you can imagine all of the properties of the electron, and then mentally *throw away* the actual electron as unnecessary to the many calculations that follow, then you can justifiably say that science is no longer merely science. You would have become a Pythagorean.

Figure 4.1 is a picture of a probability distribution, which you might recognize as the usual bell curve describing grades in a class. If an object moved around on the real axis according to this distribution, it would spend most of its time between $X = -1$ and $X = 1$ and the remainder outside. If

you were to reach between two lines drawn at these points and grab it, you would have a chance of catching it there exactly equaling the area under the curve and between the two lines. The total area under the curve is one, which makes the chance of it being somewhere at all also one. This is a very fancy way of asserting the existence of an electron. In Chapter 10, we'll apply this same formalism to the hydrogen atom.

These are the new objects of physics, replacing the objectified electron in the mind of the quantum mechanist. Furthermore, all the laws will be expressed as if the wave-like properties of the electron were all that mattered. Much has been lost contextually in the passing to such a system, especially certain comforting analogies to the macroscopic world. Much, however, is gained in syntax. To have an object that can be considered equally conveniently as wave or particle or probability distribution, depending on the attributes it presents in a given situation, represents an enormous gain in syntax.

To be specific, treating the electron in this manner places it in a class of mathematical objects which can be acted upon by the tools of partial differential equations, functional analysis, abstract algebra and representation theory, all of which topics we will explore later. Mathematically, the electron behaves not at all like a planet but much more like a weight on a spring. The linguistic capabilities of the mathematics become much stronger in this new situation. Generally speaking, this gain in syntax is the very reason abstraction is valued in mathematics and physics. Often
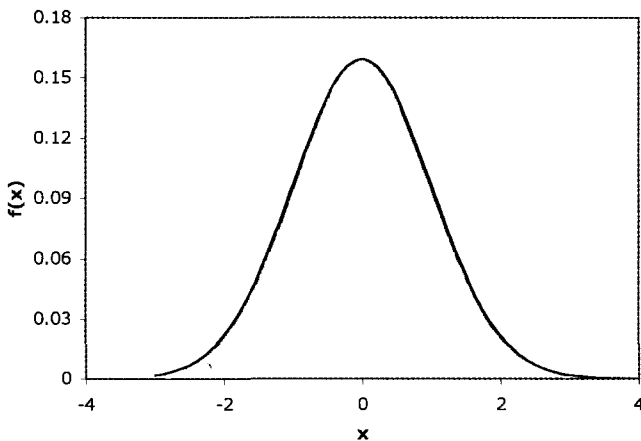

Figure 4.1. The Gaussian distribution function.

abstraction is the first step in the change of viewpoint that increases one's mathematical options in a certain situation. In our situation, the change of viewpoint as to what constitutes an electron resulted in an entire field of study, namely quantum mechanics.

This is half of the story. If the old assumption about the electron made it an object that *moves in a circle*, quantum mechanics replaces the "object" with its observable properties, described in the form of mathematical functions. There is no longer an "object", except as lodged in the conservative mind of the physicist. Whatever we are looking at here doesn't "move", either, in any detectable sense. It remains to ask, what concept arises to take the place of the "circle", and how must it relate to the new notions of what an electron ought to be?

Let us return to the experiment of Balmer that gave us hydrogen's line spectrum. The radiation of light from, say, a light bulb, is such a commonplace occurrence now that it is difficult to find novelty in the observation that the photon emitted by the electron was the same frequency when viewed from all directions. This may seem most unsurprising, as how should the electron be able to know which direction to send its energy? Yet, this simple observation provides the atom with the desired spherical symmetry. That is, whatever laws describe the atom's energy spectrum must also respect the spherical symmetry of the spatial variables. Rotate the three-dimensional space variables through any angle, along any axis, and the laws of physics must remain unchanged. The same color light must be emitted. In fact, this observation yields a whole set of symmetries for the atom, as big as the set of isometries of the sphere. An *isometry* is a rigid motion of an object that sets it down back upon itself. In this case, the isometries of the sphere consist of rotations about any diameter of it.

Here we have circles, and in abundance. The collection of isometries of the sphere is an object with rich mathematical structure. It has a beautiful interaction with the laws of physics as described by Schrödinger's equation. The mathematics brought to bear on the problem is of a depth and flavor attained only in this century. It represents the combined efforts of both mathematicians and physicists, spawning much of the current activity in both fields. The story of the hydrogen atom in this century exemplifies also what has happened to much of the physical sciences, as mathematical "laws", which are theorems, and mathematical "objects", which are sometimes complete abstractions, grew into the conceptual roles formerly filled by familiar physical objects, such as planets, billiard balls, and the like.

CHAPTER 5

Zetetics

It would be tempting, and in some sense enough, to say that because we observe certain behaviors in small particles that are characteristic of waves, we are therefore justified in describing these objects by a classical wave equation. If it walks like a wave and quacks like a wave, we may as well call it a wave. So it would be nice to be able to arrive at the wave equation for a quantum particle by reasoning from a few basic premises that make sense in the context of quantum mechanics. Just as the classical wave equation for a vibrating string can be derived from a discussion of forces acting on the string, so we would equally appreciate a derivation of the same equation based on the first principles of quantum mechanics.

The ancient Greeks had words to describe different parts of the process of doing a geometric construction. They required an argument at the start of the construction that would convince the reader that the set-up of the construction did indeed reflect the requirements of the problem. This phase of the solution they called "zetetics". After the construction was completed, a proof was required to show that the figure constructed was what it was supposed to be (*e.g.* an equilateral triangle). This part of the solution was called "poristics". The middle part of the problem, the actual sequence of compass and ruler moves, was reported but not really explained. In modern mathematics classes, we tend to focus on that middle part. How do you solve the equation? In advanced mathematics classes, we focus on poristics. How can we prove our answer is the only possible solution? But the aesthetics of applied mathematics also requires zetetics. Why do we believe we are considering the right equation in the first place?

The Schrödinger equation is a bit of a mystery the first few times it is encountered. And with good reason. It is more or less "given" as something worth studying without any real justification, except perhaps, some statement such as: "it is valuable because it works." The Schrödinger equation is

not something that can be derived from Newton's laws or Maxwell's equations, or some other accepted "law" of physics. But when you think about it, those "laws" are themselves presented to us and not derived. The justification for them is that they agree with experimental results (in other words "they work") but somehow the Schrödinger equation seems different, probably because the physics that results from it is so uttterly unlike the Newtonian sort to which we have become accustomed.

Having said that one cannot really derive the Schrödinger equation, we now want to make it plausible. There are excellent biographies of Schrödinger and more complete histories of quantum mechanics than that provided here. These may provide insight into exactly how it really came about. The intent here is to show that it is in some sense reasonable, given what we know of classical physics.

The basic premise of quantum mechanics is that a small particle, such as an electron or a photon, is not described by a fixed location and speed at a given time. Rather, it is described by something called a wavefunction, f(x). If we know the wavefunction (as a function of position, x) for a quantum mechanical system, how do we use it to find location and speed? Our rule is that the magnitude of the wavefunction squared gives something called a probability density that we will denote as $\rho = |f(x)|^2$. What does it mean to ask for the location of a particle when all we know is this probability density function? Even for a single variable this is a slightly tricky question. What is the probability of finding the particle at a particular point, x? It is zero! A probability density yields a probability when it is integrated between two points. What we can also find is the average value of location. You may remember how to do this computation from your freshman calculus class. This is just the integral of the expression "$x|f(x)|^2$".

We would also like to know the momentum of the particle. Because momentum is mass times velocity, this is equivalent to knowing the velocity of the particle, as the mass is not changing. So let us imagine that the wavefunction is dependent on time as well as space. Let us further imagine that the particle is moving along the x-axis at a constant rate of speed, which is a reasonable approximation over a (very) short period of time. We can achieve this by writing f(x) = f($y + kt$), where y is the starting place. In other words, we make x a function of time by setting $x = y + kt$. The speed of motion is determined by the constant k. To retreive it, we would compute df/dt which, by the Chain Rule in calculus, is given by: $df/dt = df/dx\, dx/dt = k\,df/dx$. So if you can measure the speed of the distribution, it is equivalent to knowing df/dx.

We have just invented two operators. An operator is a special kind of function that has as its domain a space of functions and which returns a function as output in its range. Our two operators are:

1) $\hat{x}$, which operates on the wavefunction (by simple multiplication) to give us position, and

2) $\hat{p}$, which operates on the wavefunction (by taking first derivative with respect to position) to yield momentum

The main feature of the two operators, x and $\mathrm{d}/\mathrm{d}x$, is that they do not commute. This observation is where our zetetics begin.

Let's try two different approaches to reaching the Schrödinger equation. Our first approach will begin by asking a simple question: what is the result of the following difference where x is position and p is momentum?

$$xp - px =?$$

This is known as a commutation relation and in algebra, of course, the result would be zero. Classical physics would also predict that the result is zero, but in quantum mechanics it isn't. We can think about this in the following manner. Classical physics is a macroscopic approximation to quantum physics; in the limit of large dimensions, quantum physics goes over to classical physics. The commutator, defined as $xp - px$, is small, but
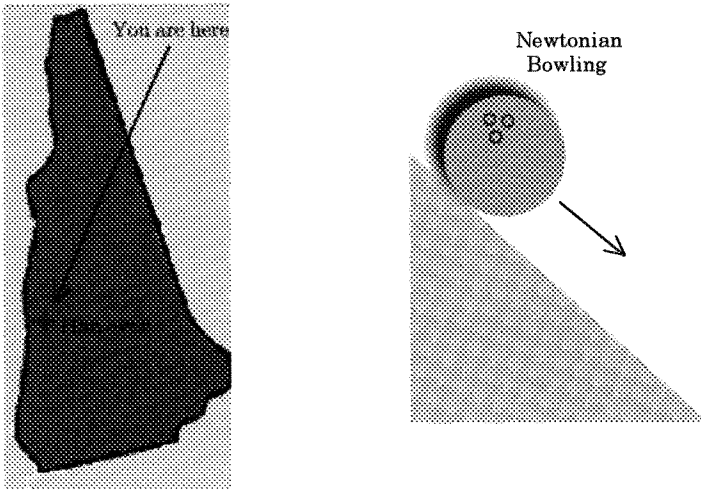

Figure 5.1. Standard perception of position and momentum in the macroscopic world.

not zero. The reason that this is true is that in quantum mechanics we need operators, denoted by the caret, ^. The result, which we assume, rather than derive here is

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar, \tag{5.1}$$

where $\hbar$ is Planck's constant, h, divided by 2π and i is the imaginary number, $-1^{1/2}$. In classical physics, the observables, the quantities we measure, are dealt with directly and are functions of time according to Newton's Laws. In quantum mechanics, we do not deal directly with the observables, but rather with *operators* corresponding to the observables; $\hat{x}$ and $\hat{p}$ are the position and momentum *operators*, respectively. The result of an operator acting on a function is the observable, that is, the result of the momentum operator acting on some appropriate function (to be defined!) is the momentum. If we step back a minute, we'll see that the commutation relation is actually Heisenberg's Uncertainty Principle in another form. If we assume that the commutation relation is valid, then we can define $\hat{x}$ and $\hat{p}$ from that expression. Let's arbitrarily define the operator $\hat{x}$ to be "multiply the subsequent function by the coordinate x". Then, in order to satisfy the commutation relationship, $\hat{p}$ must be given by the following

$$(-i\hbar)\left(\frac{\partial}{\partial x}\right). \tag{5.2}$$

We can test the validity of our assignments using the function Ψ (remember that the operators need a function on which to act)

$$\begin{aligned}
(\hat{x}\hat{p} - \hat{p}\hat{x})\Psi &= \hat{x}\hat{p}\Psi - \hat{p}\hat{x}\Psi \\
&= x(-i\hbar)\frac{\partial}{\partial x}\Psi - (-i\hbar)\frac{\partial}{\partial x}(x\Psi) \\
&= -i\hbar x\frac{\partial}{\partial x}\Psi + (i\hbar)\Psi + i\hbar x\frac{\partial}{\partial x}\Psi \\
&= \boxed{i\hbar\Psi}
\end{aligned} \tag{5.3}$$

This indicates that we have correctly defined our operators. Well, if we know $\hat{x}$ and $\hat{p}$, we are all set. Classically we know that there are two energy components, kinetic energy given as $p^2/2m$, and the potential energy, V. The total energy is the sum of these two. In one-dimension, we may write the total classical energy as

$$\frac{p^2}{2m} + V(x) = E.$$

Now, look at the corresponding quantum mechanical expression using operators

$$\frac{\hat{p}^2}{2m} + V(x) = E.$$

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}\right)\Psi + V(x)\Psi = E\Psi \qquad (5.4)$$

We can define a new operator, the Hamiltonian operator, $\hat{H}$, the result of applying this operator on our "eigenfunction", Ψ, is the total energy of our system

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}\right) + V(x). \qquad (5.5)$$

The one-dimensional, time-independent Schrödinger Equation is now easily formulated

$$\hat{H}\Psi = E\Psi. \qquad (5.6)$$

We can easily generalize to three dimensions:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right) + V(x,y,z) \qquad (5.7a)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \qquad (5.7b)$$

$\hat{H}\Psi = E\Psi$ is an *eigenvalue equation,* something that appears with regularity in physics and engineering. We've already indicated that the functions Ψ are *called eigenfunctions,* in this case we also refer to them as *wavefunctions,* since they will be related to solutions of the wave equation. If we can solve these equations, we are all done! How do we solve it? We don't know what these functions called eigenfunctions are and we still have no idea as to the potential energy function. It seems as if we are a long way off from a solution to anything. However, before we try to examine the solution to the Schrödinger equation, let's discuss a different approach to obtaining the equation itself; an approach based upon knowledge of classical wave mechanics.

The wavelike behavior of particles is the fundamental observation upon which the discussion is based. If a particle has attributes of a wave, describe

it using the classical equation for a traveling wave:

$$\Psi(x,t) = Ce^{i(kx-\omega t)},\qquad(5.8)$$

where the wave number, k, is related to the wavelength by

$$k = \frac{2\pi}{\lambda},\qquad(5.9)$$

and the angular frequency, ω, is related to the frequency by

$$\omega = 2\pi\nu.\qquad(5.10)$$

Of course, all of this begs the question of what it is that $\Psi(x,t)$ represents. If this were a description of water waves, $\Psi(x,t)$ would be the height of the water in the wave above "sea level" or some other such reference height; if this were a description of an electromagnetic wave then $\Psi(x,t)$ would represent the magnitude of the electric or magnetic field in the wave. But this wave is representing a particle. So what is "waving?" The answer, thanks to Max Born, is that $\Psi(x,t)$ is *related to* the probability of finding a particle at a given point in space at a given time. For the present, just say that somehow or other $\Psi(x,t)$ will represent attributes of the particle that can be measured in the laboratory (actually, not a bad statement to make about Ψ when all is said and done).

But we know more than the fact that a particle has attributes of a wave. From the work of Einstein and deBroglie, we know that the energy of the particle is related to the frequency of the corresponding wave by

$$E = h\nu,$$

or

$$E = \omega\hbar,$$

and we can solve this for the angular frequency of the wave:

$$\omega = E/\hbar.$$

But we also know that the momentum of the particle is related to the wavelength of its associated wave,

$$p = \frac{h}{\lambda},$$

or

$$p = \hbar k,$$

and we can also write the wave number

$$k = \frac{p}{\hbar},$$

so that an alternate way of writing the equation for the traveling wave is

$$\Psi(x, t) = Ce^{i(px - Et)/\hbar}. \tag{5.11}$$

It is clear that Ψ has something to do with the energy and momentum of the particle that it is representing. Speaking mathematically, how might we extract a measurable value for these quantities from the equation for Ψ that has been proposed? Consider the partial derivative of Ψ with respect to position x:

$$\frac{\partial \Psi}{\partial x} = iC \left(\frac{p}{\hbar} \right) e^{i(px - Et)/\hbar} = ip\Psi, \tag{5.12}$$

which may be rewritten as

$$\frac{\partial}{\partial x} \Psi = ip\Psi. \tag{5.13}$$

We recognize this to be an eigenvalue equation where the momentum of the particle, p, is the eigenvalue. In short, the mathematical operator

$$-i\hbar \frac{\partial}{\partial x} \tag{5.14}$$

extracts the momentum of the particle from the wave function Ψ. We can write this fact like this:

$$-i\hbar \frac{\partial}{\partial x} \to p. \tag{5.15}$$

In this sense, then, the operator,

$$-i\hbar \frac{\partial}{\partial x},$$

assumes the role of an analogue to momentum for purposes of working with the wave equation. It is sometimes said that this operator "represents" the momentum of the particle. Consider the partial derivative of Ψ with respect

to time.

$$\frac{\partial}{\partial t}\Psi = iC\left(\frac{E}{\hbar}\right)e^{-i(px-Et)/\hbar},$$

$$\frac{\partial}{\partial t}\Psi = -i\left(\frac{E}{\hbar}\right)\Psi.$$

This is another eigenvalue problem, this time with the energy, E, being the eigenvalue. The operator,

$$i\hbar\frac{\partial}{\partial t},$$

acts to "extract" the energy from the wave function, and it may be said to represent energy in quantum theory,

$$i\hbar\frac{\partial}{\partial t} \to E.$$

In classical physics, the energy and momentum of a particle are related quantities. In particular,

$$E = \frac{p^2}{2m} + V.$$

We are now going to use the quantum mechanical operator analogues to energy and momentum in this classical relationship to see how these operators might be related. What justifies doing this? Analogy. Remember that this is not a derivation, it is a discussion to make the Schrödinger equation seem plausible and reasonable. Notice that the classical expression for total energy involves the square of the momentum. In the case of an operator, we will interpret this as the operator acting on itself like this:

$$p^2 \to i\hbar\left(\frac{\partial}{\partial x}\right) \cdot i\hbar\left(\frac{\partial}{\partial x}\right), \tag{5.16}$$

and carrying out the indicated operations

$$p^2 \to -\hbar^2\left(\frac{\partial^2}{\partial x^2}\right).$$

Substituting this result into the equation for the total energy,

$$E = -\left(\frac{\hbar^2}{2m}\right)\left(\frac{\partial^2}{\partial x^2}\right) + V \tag{5.17}$$

or

$$i\hbar\frac{\partial}{\partial t}\Psi = -\left[\left(\frac{\hbar^2}{2m}\right)\left(\frac{\partial^2}{\partial x^2}\right) + V\right]\Psi \tag{5.18}$$

which is the *Schrödinger equation*.

CHAPTER 6

Classical Waves

Because so much of what happens next rides on the assumption that an electron behaves like a wave, we thought it best to digress momentarily to show you some of the mathematical tools typically employed in discussions of ordinary waves, such as those one would see in a vibrating guitar string, for example. Several positions over time of a string plucked at its midpoint are shown in Fig. 6.1, and if you were to plot the displacement at the point $x = 0.5$ throughout time, you would see an oscillating pattern, like Fig. 6.2, which is why the equation describing the plucked string is one of those generically called the "*wave equation*".

Now, the equation which governs the displacement at point x and time t is given by:

$$F_{xx}(x,t) = kF_{tt}(x,t). \tag{6.1}$$

This equation is derived from a discussion of forces acting on the guitar string in the form of tension, elasticity and other properties of actual or imagined guitar strings. These forces are usually described in terms of vectors acting on some point on the string. Since the equation involves an unknown function and a relationship between its various partial derivatives, it is an example of a *partial differential equation*. We are going to ignore the model that gives us this equation because our intent here is not to examine how such a model is constructed, but rather to see where it leads in the solution of the problem. But I will say three things about it. First of all, the mysterious constant, k, is one of those numbers that is going to depend on the particulars of the string in question. Is it nylon or steel? Is it tight or loose? And so forth. Second, k is always positive. Third, this equation doesn't take damping into account, so when we finally get to a solution of it, the string will seem to continue to oscillate forever. Don't worry, real strings won't do that.
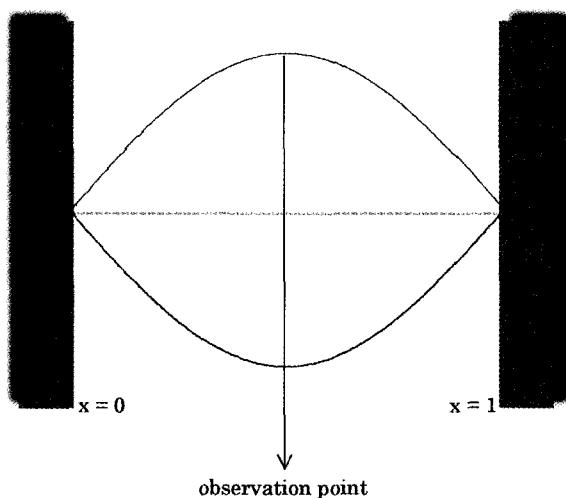
Figure 6.1. Three positions of a string vibrating (undamped) after it is plucked at its mid-point.
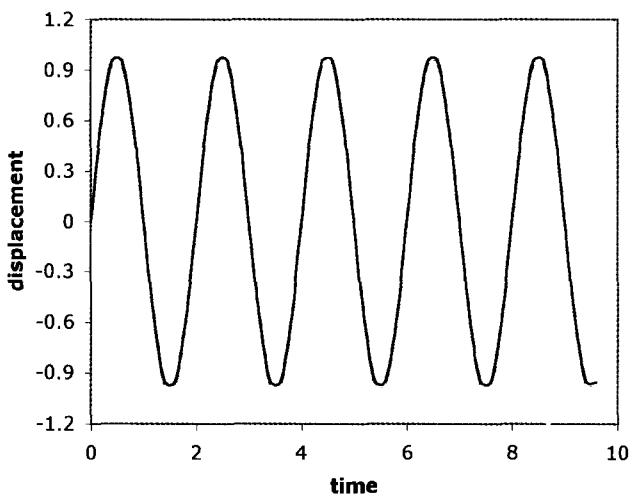

Figure 6.2. The temporal oscillations observed at $x = 0.5$ for the vibrating string shown in Fig. 6.1.

It is worth asking, under these circumstances, what exactly constitutes a "problem" and what does it mean to find "the solution"? To those who live to see math problems everywhere, this is a non-question. To anyone else, it may be the only real question. Well, in this case, the *problem* is to describe the range of possible behaviors of a vibrating string, including the most observable of its behaviors, namely the pitch you hear. Mathematically, this amounts to figuring out which functions could possibly describe the evolution of the position of the string over time, and what frequencies occur in the wave pictured above. Since any such function presumably satisfies the equation we wrote down, in terms of its second derivative in the x variable and its second derivative in the t variable, a *solution* means a function of x and t that satisfies that equation. To find *the solution* means to describe all such functions.

Before tackling the equation above, there is one more ingredient that is absolutely necessary to making a definitive statement about the nature of the vibrations. That is the *length of the string*. A guitar string is firmly secured in two places, let us say at $x = 0$ and at $x = 1$, just as is indicated in the drawing above. Mathematically, this means that the function $F(x, t)$ has to be equal to zero in certain places, namely:

$$F(0, t) = F(1, t) = 0. \tag{6.2}$$

This is what is called a "boundary condition" for a partial differential equation. Such conditions are often as important in determining the nature of the solution as the actual equation itself. (In fact, perpetrating changes of variables in these sorts of equations in order to swap a certain kind of boundary condition for some other one is an art form unto itself, and if you don't believe this, check out the phenomenon known as the soliton.) Now, what happens next is going to look like sleight-of-hand to the uninitiated (that would be you). It is one of those old and venerable tricks of the trade, first used by Fourier himself, the granddaddy of the wave equation. Fourier was an engineer and the trick he used was based on an act of faith that is often well rewarded in the area of differential equations. Here is the assumption behind what happens next: *If I can find one kind of solution to that equation, I can figure out how to get all of them.* So the general strategy is to find one solution, or one family of solutions, then use them to get a very large set of solutions. Then, after the fact, go back and prove that you did, indeed, find all of the possible solutions.

So, this particular trick is called "separation of variables". All we do is assume the function $F(x, t)$ is really the product of two functions:

$f(x)$ and $g(t)$. Not only that, but we will suppose that f obeys the boundary conditions above. Now Eq. 6.1 above becomes:

$$f_{xx}g = kfg_{tt}$$
$$f(0) = f(1) = 0,$$

(6.3)

where the derivative in x only affects the function f and the derivative in t only affects the function g. Fooling around with the algebra gives you:

$$\frac{f_{xx}}{f} = k\frac{g_{tt}}{g}.$$

(6.4)

The alert reader will notice that although the left-hand-side of this equation depends only on x, the right-hand-side depends only on t. So both sides must be equal to the same constant. Now you have two easy ordinary differential equations in one unknown each. Also you have an unidentified flying parameter, namely the constant that both sides of the equation must equal. In the grand tradition of calculus textbooks, let us call this constant C. So now we have two separate equations to deal with, each in only one variable. The first one is:

$$\frac{f_{xx}}{f} = C$$
$$f(0) = f(1) = 0.$$

(6.5)

And the second is:

$$k\frac{g_{tt}}{g} = C.$$

(6.6)

Of course, we could rewrite these equations by multiplying both sides by either f or g, as appropriate. Then the first would look like:

$$f_{xx} = Cf.$$

(6.7)

An equation of this sort, which has some expression in f on the left similar to this one (mathematicians call taking the second derivative a linear operator, and that is what we mean by "similar to this one"), and a constant times f on the right, is called an *eigenvalue* problem. C is the "eigenvalue" in this problem. The function f is the "eigenfunction". Some people spend their lives studying eigenvalue problems like this one, which crop up all through mathematics and physics.

Let us look at that first equation. If C is negative then it looks just like the equation for a spring that comes from Hooke's Law. That is, there are

two functions, which are familiar to everyone, that solve this equation,

$$f_1(x) = \sin\left(\sqrt{|C|}x\right)$$

and   (6.8)

$$f_2(x) = \cos\left(\sqrt{|C|}x\right).$$

Furthermore, all combinations of the form $af_1 + bf_2$ will also solve the equation in x. However, to get the boundary conditions we have to make sure $f_1(x)$ and $f_2(x)$ assume a value of zero at $x = 0$ and $x = 1$. This puts restrictions on what C could be. If you think about it, C must now be a negative integer multiple of π. Furthermore, the cosine solutions don't work at all.

But what if C is positive? Well, then the solution looks very different. It is easy to check that the two functions

$$f_1(x) = e^{(\sqrt{C}x)}$$

and   (6.9)

$$f_2(x) = e^{(-\sqrt{C}x)}$$

do the job quite nicely, except that neither of them satisfies the boundary conditions. So, with supreme aplomb, we reject these solutions as possibilities.

A brief reading here is about the use of the pronoun "we" in scientific writing. Of course, you had no part in the above calculation whatsoever except to read it. But such was my training as a mathematician that I believe in some core of my being that I will be struck with a pox if I write scientific stuff in the first person. Therefore I am forced to pretend that you and I are writing this and doing all the calculations together. This pretense some college professors actually seem to believe, for example when they say "I taught it to them but they didn't learn it". I, however, am not deceived, and that is why you will find a pile of similar problems on our website, www.math.dartmouth.edu/~matceBookshelf/physicalsci/index.html, all for you to work out by yourself. Of course, if you hand them in to anyone you will write in the first person plural, so that when your grader reads them she can pretend she did them too.

Now, let me, talk about this business of rejecting solutions that aren't as nice as we might like. If you are starting to get the idea that solving a problem of this sort requires making a bunch of somewhat arbitrary and not wholly justified decisions, proceeding somewhat blindly to see what happens, and finally checking later to see if your guesses were good, then you are more or less correct. Historically, this is what seems to have happened. In very applied contexts, such as engineering, it is still the way to proceed. Because this problem has been very well studied, however, it is possible to use a lot of fancy mathematics to justify some of these decisions up front. For example, the entire mathematical field called *harmonic analysis* stems from the proof of the observation that the sines and cosines we got for our solution when C was negative, taken together are big enough to build all the other solutions by taking infinite linear combinations of them. You could spend your life studying this phenomenon as it occurs in various contexts. You could get your Ph.D. doing this. I know. I did. In the short run, you could learn a lot by taking one of those advanced math classes called *analysis*, whose job it is to put a foundation under the kind of calculation we are doing now. But for the present, I shall proceed as Fourier did, following my nose to see where it might take me. You come along, too.

Let me summarize where we are now. By a series of assumptions and calculations we have narrowed down our acceptable solutions to those of the form:

$$f_1(x) = \sin\left(\sqrt{|C|}x\right), \tag{6.10}$$

where C must be a negative integer multiple of π. Now we must turn our attention to the equation in the variable t:

$$k\frac{g_{tt}}{g} = C \tag{6.11}$$

which we can rewrite as

$$g_{tt} = \frac{C}{k}g \tag{6.12}$$

and, as before we get solutions of the form:

$$g_1(t) = \sin\left(\sqrt{\frac{|C|}{k}}t\right)$$

and

$$g_2(t) = \cos\left(\sqrt{\frac{|C|}{k}}t\right). \tag{6.13}$$

Now, the boundary conditions are in the x variable and do not affect g, so we do not need to eliminate the cosine solutions this time. So now we have a large family of solutions to this equation, given by:

$$F_{n,1}(x,t) = \sin(n\pi x) \sin\left(\frac{n\pi}{\sqrt{k}}t\right)$$

and   (6.14)

$$F_{n,2}(x,t) = \sin(n\pi x) \cos\left(\frac{n\pi}{\sqrt{k}}t\right).$$

Out of these infinitely many solutions we can construct a sort of generic one that looks like:

$$F(x,t) = \sum_n a_n F_{n,1}(x,t) + b_n F_{n,2}(x,t) \tag{6.15}$$

which can be expanded as:

$$F(x,t) = \sum_n a_n \sin(n\pi x) \sin\left(\frac{n\pi}{\sqrt{k}}t\right) + b_n \sin(n\pi x) \cos\left(\frac{n\pi}{\sqrt{k}}t\right). \tag{6.16}$$

Tah Dah! Now if you are not totally convinced that anything of this form is in fact a solution to the original wave equation, you should plug it in and see for yourself. Once you convince yourself of that, the only remaining question is whether such a scheme gives every possible solution. There are two ways to think about this question. I will, in the interests of convincing you that I have just done something sensible, offer both. Briefly, one way uses physics, and the other uses math.

First I'll talk about the physics. If you believe that the wave equation above is a good model for a vibrating string, and if you believe in physics, then you should also believe that, given an initial state for the string there will be only one possible behavior stemming from it. By "initial state" I mean a description of how the string is deformed at $t = 0$. If you pluck a guitar string in a certain way and let it go, it should obey whatever physical laws control it and *always do exactly the same thing*. So, if you can match any initial condition, then you have described all possible solutions of the problem. Setting $t = 0$ gives:

$$F(x,0) = \sum_{n>0}^{n} b_n \sin(n\pi x). \tag{6.17}$$

The theory of Fourier series tells us that we can find all of the different b_n needed to match any initial condition $F(x,0)$. At this point alarms

should be going off in your head because this approach doesn't tell us anything about any a_n. The physical explanation for that is that we could also have given our string an initial velocity distribution, $F_t(x, 0)$. This can be achieved with a real guitar by musical techniques such as "hammering on" or "pulling off", and must be taken into account. To do this, we have to compute:

$$F_t(x, 0) = \sum_{n \geq 0} a_n \frac{n\pi}{\sqrt{k}} \sin(n\pi x). \qquad (6.18)$$

Hooray! Now we can match two sets of initial conditions at once and get a unique answer using Fourier series. This is a physical approach.

A more mathematical approach would invoke a theorem of differential equations, which says that a second order partial differential equation that is as nice as the one we have here, with two initial conditions of the form we just used, must have a unique solution. The branch of mathematics you would have to study to learn this theorem is called *partial differential equations* sometimes, or if the professor plans to give you the most general version, the area of study might be called *differential operators on manifolds*. Mathematically, this type of theorem makes the claim for our *model of nature* that the physical explanation is attempting to make for *nature herself*. Then we would again invoke the theory of Fourier series to tell us that the sines and cosines are good enough to do the job.

As an interdisciplinary aside, we could also consider the computer science approach, which would be to spend a few days programming our hypothetical solution up and using our program to try to match a bunch of initial conditions to see if we can get a good approximation to them, and then using this as *experimental evidence* that we have found all of the possible solutions. As a mathematician, I feel obliged to point out that such an approach would take a lot longer than either of the ones above. This is because computers are such marvelous time saving inventions, although not as time saving as either a good theorem or genuine physical insight.

Particle-in-a-Box

Before going on to something as complex as an atom, let's look at a model problem in some detail. The first one is the one-dimensional particle-in-a-box problem. This turns out to be an excellent conceptual model for conjugated dye molecules (see Chapter 21) and also a model for trapped charged particles. The problem and its solutions are similar to the vibrating string just discussed. The potential term is shown graphically and mathematically in Fig. 7.1.

The formulation of the problem begins with the one-dimensional Schrödinger equation. Note that the Schrödinger equation is always valid, the nature of the problem will change the potential energy function, $V(x)$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \rightarrow -\left(\frac{\hbar^2}{2m}\right)\left(\frac{\partial^2}{\partial x^2}\right)\Psi = E\Psi.$$

The potential energy is zero within the box and the walls are infinitely high since the potential energy is infinite outside of the box. We expect that the particle will only be found within the box and that the probability (and wavefunction) outside of the box is zero. What happens at the walls? This is a boundary value problem and we solve the equation by using the boundary conditions. In this case, we assume that the wavefunction also vanishes at the walls,

$$\Psi(0) = 0 \quad \text{and} \quad \Psi(L) = 0.$$

The general solution to this one-dimensional Schrödinger equation is well known. You could easily solve it with your knowledge of differential equations (Chapter 6) or locate it in tables of solutions to differential equations. The general solution is

$$\Psi(x) = C\cos kx + D\sin kx, \tag{7.1}$$

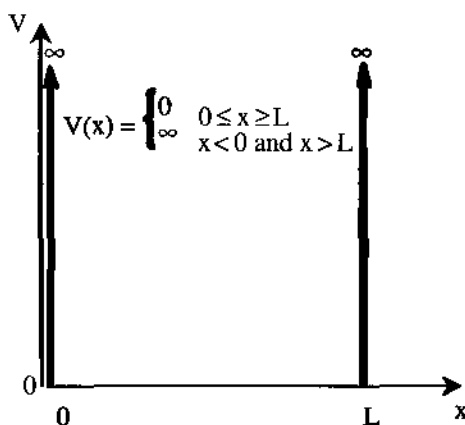$$\text{where } k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}.$$

Figure 7.1. The potential energy for the one-dimensional particle-in-a-box.

Now, use the boundary conditions in order to obtain the specific solution from the general one. At $x = 0$, $\sin x = 0$ and then C must also equal zero and we do not learn anything about our system. At $x = L$, we must satisfy the equation

$$\psi(L) = D \sin kL = 0,$$

where

$$\sin kL = 0, \quad \text{if } kL = n\pi, \quad \text{and} \quad n = 1, 2, 3, \ldots$$

So, the solution is

$$k = \left(\frac{n\pi}{L}\right) \quad \text{so, } E = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad n = 1, 2, 3, \ldots$$

and the energy is *quantized*, where n is the quantum number! Note that nowhere did we assume that the energy was quantized, àla Bohr. We formulated the problem, solved it and the quantization fell out of the solution.

One last problem remains to be solved, what is D? We need to define a new quantity to answer that question. The quantity $|\psi|^2$ is known as the probability density, that is, the probability per unit distance for a one-dimensional problem (see Chapter 4). If we integrate the probability density over all space, the result must be unity, since the particle must be somewhere! Let's do the integral using the wavefunction with the as yet

undefined value of D

$$1 = \int \Psi * \Psi dx = D^2 \int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx = \frac{1}{2} L D^2 \tag{7.2}$$

So,

$$D = \left(\frac{2}{L} \right)^{1/2}$$

and we are done! The results for the wavefunction and the energy are summarized below. These are specific to the problem at hand. Other quantum mechanical problems will have different solutions, but the technique of reaching that solution will be analogous to that we have just completed:

$$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n = 1, 2, 3, \ldots$$
$$\Psi_n(x) = \left(\frac{2}{L} \right)^{1/2} \sin \left(\frac{n\pi x}{L} \right).$$

We may graphically examine the wavefunctions and the probability densities as we vary the quantum number, n. There is no reason to expect that the wavefunctions will be the same. In fact, the solutions look as shown in Fig. 7.2. A **node** is defined as a point at which ψ and $|\psi|^2$ are zero. We will not find the particle at this position. The wavefunctions, ψ are identical to the standing waves generated by the vibrating string, an example with which we are all much more familiar and has been treated in the previous chapter. Note especially, that the $n = 1$ wavefunction for the particle-in-a-box is identical to the string plucked at its midpoint in Fig. 6.1.

The energy of the particle in a box depends upon the quantum number, increasing as n increases. However, it also depends upon the length of the box. As L gets very large, the energy decreases, as does the separation between two adjacent energy levels. In fact, in the limit of very large L, the particle-in-a-box asymptotically approaches a free particle. In this limit, we make a transition from quantum mechanics with discrete energy levels to classical physics with continuous energy levels.

What is ΔE for the particle-in-a-box? That is, what is the separation between energy levels? We need to ask this question, because experimentally, the energy differences are what we observe. Recall Bohr's postulate stating that electrons in atoms do not radiate, the radiation is due to changes in stationary states. So, if we observe radiation from an atom,
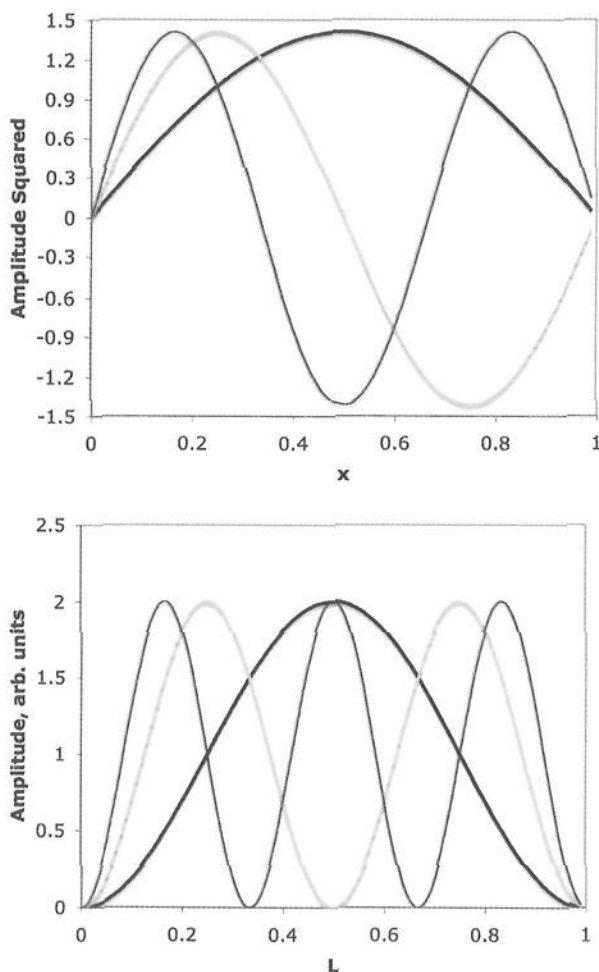
Figure 7.2. The wavefunctions (top) and probability densities (bottom) for the first three states of the particle-in-a-box: $n = 1$ (heavy black), $n = 2$ (gray) and $n = 3$ (black).

we are observing the energy difference between two levels. The energy difference is readily obtained by use of n and $n + 1$ as quantum numbers in the expression we derived for the one-dimensional case

$$\Delta E = E_{n+1} - E_n = \frac{(2n + 1)\pi^2 \hbar^2}{2mL^2}. \tag{7.3}$$

Notice in Fig. 7.3, that unlike the Bohr atom (and all real atoms and molecules), the energy levels get farther apart with increasing n.
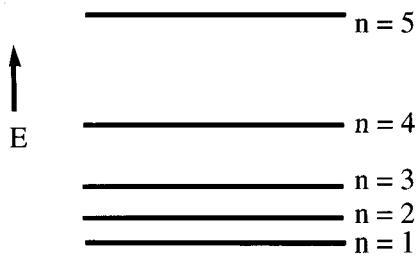
Figure 7.3. Schematic representation of the energy levels for the one-dimensional particle-in-a-box.

This page is intentionally left blank

CHAPTER 8

Exploring the Analogy

It is worth spending a little time looking at how the wave equation will directly inform our approach to the hydrogen atom. We have seen the formalism applied to the particle-in-a-box problem, but hydrogen is much more complex. It is better to use the analogy with the vibrating string for our initial foray. All of the phenomena mentioned in the discussion of the vibrating string have a direct analogy to some aspect of the wave equation. If we can see how the analogy works, perhaps we will gain an insight into how to approach the puzzle of hydrogen.

When you pluck the string of a guitar, you always have the sensation of hearing a particular tone or pitch. The same is true of most instruments. The lowest tone the string can produce is called the *fundamental frequency* of the string (or instrument or equation). This lowest tone has the same mathematical expression as the smallest eigenvalue of the wave equation describing the string (remember? that was $\frac{\pi}{k}$). That is, what you hear when you pluck a guitar string is basically what is predicted by the wave equation. This is because the lowest eigenvalue tells you the rate of oscillation (in time) of the string. This oscillation sets up an oscillation of air molecules of the same frequency, which carries the "sound" to your ear. The vibrating air hits your eardrum, which transfers the vibration to lots of little hairs inside your ear. These hairs are of various sizes and stiffnesses and each one has a fundamental frequency of its own. Each hair behaves like a little spring, and the vibrating air behaves like a forcing function for the spring equation. When the frequency of the air vibration is just right and matches up with the oscillating frequency of the hair, the hair starts to vibrate a lot, triggering a nerve ending that identifies the pitch.

Of course, you can also pluck the string very cleverly so that the first coefficient in the Fourier expansion (b_n) is zero, or nearly so.

If you do this, you can arrange for the lowest eigenvalue to be absent (or nearly absent) from the Fourier expansion of the solution. Then you will hear the next eigenvalue. $\left(\text{Remember? that was } \dfrac{2\pi}{k}\right)$. This tone is called the *first harmonic* or *first overtone*. It has exactly twice the frequency of the first one, and sounds a note exactly one octave higher than the original. This is the same as the $n = 2$ wavefunction in Fig. 7.2. The tone is quite eery because the string is not held in the middle, but allowed to vibrate throughout its full length. Your ear registers the higher tone because its Fourier coefficient is the largest, so that frequency of oscillation dominates. If several Fourier coefficients are of roughly the same magnitude, then none of the frequencies dominate and many hairs may vibrate simultaneously in your ear, causing you to hear a *chord*. Your ear is basically a mechanism for computing the largest Fourier coefficients present in a sound wave. A mathematician would say that your ear *computes the Fourier transform* of a sound wave. In effect, it solves an eigenvalue problem by building machinery (the hair) that mimics the physics of the thing that generates the sound (the guitar string).

The frequencies of vibration corresponding to the Fourier coefficients in this example are the *normal modes* of oscillation of the string. They tell all there is to tell about the pitch or pitches you hear when you pluck it. They depend on the length of the string and its tension. They occur at discrete intervals, ($\pi, 2\pi$, etc.), giving an infinite sequence of possible tones, going higher and higher. In this way, they resemble the spectrum of lines of color associated with the hydrogen atom, which also occur as an infinite sequence of discrete frequencies with a characteristic distribution. For the hydrogen atom there is also a lowest frequency present, and all the rest are greater in frequency. In fact, the eigenvalues of the wave equation are referred to as the *spectrum* of the differential operator $\dfrac{d^2}{dx^2}$. The analogy is a good one because for the string you hear its normal modes, (frequencies, eigenvalues, spectrum) directly. That is, you *hear* which frequencies are present in the sound, while for the glowing hydrogen atom you *see* which frequencies are present.

Your eye is not built to separate the frequencies in the same way your ear is. You can test this first hand by mixing paint. If you mix two pure hues together (such as red and green), what you perceive is not *red plus green*, what you perceive is brown or gray. This is quite different from your perception of sound. If you play two different notes simultaneously, your ear separates them and you hear a chord, the musical equivalent of *red plus green*. Your eye, on the other hand, will not identify separately all the

frequencies present in a ray of light. That is why the light must be passed through a prism in order to see the various frequencies present. The prism is computing the Fourier transform of the light wave for us in this case.

There is another aspect of the wave equation to which we had best pay close attention as well, and that is symmetry. There is a symmetry to the set of equations:

$$F_{xx}(x, t) = kF_{tt}(x, t)$$
$$F(0, t) = F(1, t) = 0. \tag{8.1}$$

The partial differential operators are linear operators. That means they are invariant with respect to changes of variables of the form $y = x + c$. So you could replace x by $1 - x$. This does not change the first of the two equations at all, and it flips the role of 0 and 1 in the second, leaving it invariant also. That is, a symmetric flip of the x-axis around $x = 1/2$ leaves the equations invariant. Now, notice that all of the solutions to the eigenvalue problem in x are also related by the same symmetry. For example:

$$f_1(x) = \sin(2\pi x) \tag{8.2}$$

is an example of a solution. What happens if we replace x by $1 - x$ in this function? Trigonometry gives:

$$f_1(1 - x) = \sin(2\pi(1 - x)) = -\sin(2\pi x). \tag{8.3}$$

In other words, the symmetry in the original equation acts on the solutions of the eigenvalue problem derived from that equation. The symmetry itself yields an eigenvalue of -1 when applied to these functions. Listen to this again: the symmetry, (x goes to $1 - x$), behaves just like the differential operator $\left(\dfrac{d^2}{dx^2}\right)$. It has the same eigenfunctions, each of which has eigenvalue plus or minus one. This observation is a very special, easy case of a truly useful piece of mathematical machinery known as *Schur's lemma*.

Now, remember from chapter two that, although we might not look at hydrogen as a teeny sun with little planets moving around it in circles, still the Balmer lines respected a spherical symmetry. That is, they gave the same frequencies no matter in what direction you measured. Later we will use Schur's lemma to capitalize on the presence of these symmetries so that we can solve Schrödinger's equation for the hydrogen atom. We didn't need to notice the symmetry of the wave equation to be able to solve it, but we will definitely need it for the hydrogen atom.

I want to impress upon you the full set of implications of this analogy between sound and light, between the plucked string and the hydrogen

atom. First of all, the analogy doesn't make much sense if your model of the atom is Bohr's model. Kepler, studying the distribution of planets in the solar system, made a lot out of the fact that the various distances of planets to sun seemed to have a nice arithmetic relationship to each other, and he even used the term "music of the spheres" to describe the orderliness of these relationships. This analogy did not withstand the test of time, however, because Newtonian mechanics allow planets to be at any distance you like from the sun. This is handy because, as a corollary, satellites can be any distance you like from the earth, an observation we have utilized quite effectively this century. No, the analogy only starts to make sense from the point of view of quantum mechanics.

If you are willing to think of hydrogen's lone electron as being characterized by the probability of its being in a certain region of space, then the function which describes the probability distribution tells us what kind of behavior is possible for that electron, in a statistical or average sense. So we are now discussing a certain set of functions associated with hydrogen, namely all those which describe physically possible probability distributions for electron position. We know lots of different functions are possible, because hydrogen is observed to have different "excited states" or "levels of energy". These are exactly the phenomena we are hoping to explain with our model, so we expect lots of different solutions.

These probability distributions are exactly of the form $F(x, t)$, providing you allow x to be a vector in space which describes a position of the electron. For a given solution, F, the integral

$$\int_R F(x, t)\, dx$$

describes the probability that the electron will be in the region R at time t.

Now, we have abandoned Newton in our search for an explanation of the Balmer lines. What new laws will govern the function F and what form will they take? There is only one possibility for the second part of that question: a partial differential equation. When we find that equation we will treat it as we treated the wave equation. We will make some assumptions about the form of the final solution so that we can separate variables in x and t and we will attempt to turn the equation into a pair of eigenvalue problems. We will solve each of them separately and hope that the solutions, as well as boundary values that come from physical considerations, tell us which eigenvalues are possible and how the solutions themselves might look. We will imagine that hydrogen is some sort of musical chime, and we will calculate the sound of its ringing. It just happens that hydrogen *rings light*.

CHAPTER 9

Dr. Schrödinger, I Presume?

The historical development of the Schrödinger equation is available for your edification in some quantum mechanics texts, and good luck to you, too. Seriously, the way people figured these things out was as an axiomatic system whose laws lead you to the results observed in nature. By *axiomatic*, I simply mean that the basic underlying assumption that an electron might obey a wave equation strikes me as an *axiom* upon which quantum mechanics rests. The alternative assumption of an electron behaving like a body orbiting another body according to Newton's laws leads to radically different conclusions. In this approach you see the shadows of Euclid and Newton, standing off in the dim distance and cheering the brave physicists on. But, unlike Euclidean geometry or Newtonian physics, the answer to be explained was far from believable. While Euclid took the profound step of placing logical foundations under everyday geometric phenomena, and where Newton was able to use his assumptions to predict everyday physical phenomena, the physicists of the early part of the twentieth century were attempting to put a foundation under atomic phenomena, which foundation itself undermined Newton. In fact, the axioms themselves were very close to certain of the phenomena. So, while one might use them to predict what would happen, they were very unsatisfying answers to the question *why?*

Certain clues and pointers did lie in the wavelike nature of light, however. After a long and somewhat convoluted development, it was Schrödinger who finally suggested that a particle with no forces acting on it should naturally obey the wave equation. For this he got the Nobel prize. In fact, in the context of particles, the wave equation is actually called the Schrödinger equation, even though Fourier, for heavens sakes! had solved it a hundred years before. The mathematician in me is showing through again, isn't it?

Of course, an electron that is part of an atom does indeed have forces acting on it, otherwise it couldn't remain attached to its proton. This is where Schrödinger's equation really starts to do something interesting. There are various candidates for the potential field that would keep an electron in "orbit", but by now we know that it would have to have spherical symmetry. That is, any force acting on the electron should be expressed as a function of r only, where r is the radius from the electron to the center of the atom. In addition, that force should die away at great distance from the proton, because if an electron gets far enough from its proton, it is lost. The simplest candidate for a function of r that does this job is $1/r$, and indeed, this function (up to a constant multiple) does the trick. In keeping with the spirit of forces acting on springs, we just add it on to the list of operators affecting our position function for the electron. For reasons of tradition, that function is always called Ψ. In this case, it would be $\Psi(x, y, z, t)$.

Now, the wave equation in one spatial variable has the operator $\dfrac{d^2}{dx^2}$. What operator does this job in three variables? It is possible to write down a Schrödinger equation for a particle in less than three dimensions, but for this you don't get the Nobel prize. Whatever operator we use must be unable to distinguish directions from the origin. The only second order operator with this property is (up to multiplication by a constant)

$$\Delta = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}. \tag{9.1}$$

You will notice that I am using a mathematician's favorite notation for this operator, which is not the same as the standard physics text; the symbol Δ. This is the Laplace operator, or the *Laplacian*. With this notation in place, Schrödinger's equation is:

$$\left(\Delta + \frac{c}{r}\right)\Psi = k\frac{d^2}{dt^2}\Psi, \tag{9.2}$$

where

$$r = \sqrt{x^2 + y^2 + z^2}$$

is the distance to the origin of the spatial variable.

Compared with the vibrating string we seem to have an awful lot of variables here. We will want to *separate variables* in the same way we did for the wave equation in Chapter 6, but which variables shall we use? The key here lies in the spherical symmetry that can be read off the equation itself. Initially there are four variables, x, y, z, t, but obviously, t and r play

distinguished roles in this equation. Perhaps you remember from spherical geometry how to write the Cartesian coordinates x, y, z in spherical coordinates so that r becomes one of the variables. In case you do not, here are the formulas:

$$x = r \sin \theta \cos \phi$$
$$y = r \sin \theta \sin \phi$$
$$z = r \cos \theta. \tag{9.3}$$

Here the variables θ and ϕ are given these labels because they are actually the Euler angles for spherical coordinates, as shown in Fig. 9.1. If you set $r = 1$ and let θ and ϕ change, you will get points that lie on the sphere of radius one. So these are the natural coordinates for points on the sphere.

It is an interesting exercise in multivariable calculus to rewrite the Laplacian in terms of these new variables. If you do this you will get:

$$\Delta = (r^2 \sin \theta)^{-1} \left[\frac{\partial}{\partial r} \left(r^2 \sin \theta \frac{\partial \Psi}{\partial r} \right) \right.$$
$$+ \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right)$$
$$+ \left. \frac{\partial}{\partial \phi} \left((\sin \theta)^{-1} \frac{\partial \Psi}{\partial \phi} \right) \right] \tag{9.4}$$

And now, if you write

$$\Psi(x, y, z, t) = g(t)\, \omega(r) Y(\theta, \phi)$$
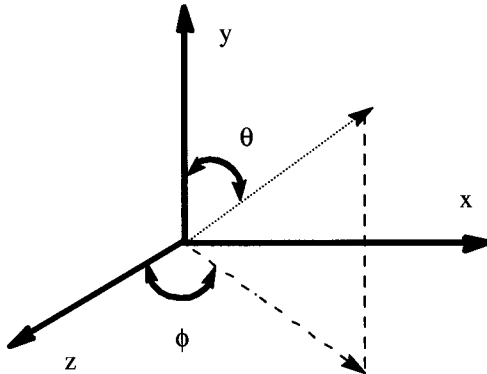
Figure 9.1. The Euler variables in terms of the Cartesian coordinates.

you can separate variables to get three equations, one for each of these new functions. You will have ordinary differential equations in t and r, because these variables occur alone. You will have a partial differential equation in θ and ϕ which you should not separate further, for very good reasons having to do with a lot of abstract algebra which we will talk about later. Fooling around with the Laplacian in spherical coordinates yields this equation:

$$\frac{(2r\omega' + r^2\omega'' + cr\omega)}{\omega} - r^2 E = \frac{-\Delta_S Y}{Y} = K, \tag{9.5}$$

where

$$\Delta_S = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \sin\theta^{-2}\frac{\partial^2 Y}{\partial\phi^2} \tag{9.6}$$

which, as you can see, separates variables. The exact values of K, E and c will tell us the position of the spectral lines. The equation in ω simplifies further to give

$$(r^2\omega')' - r^2\left(E - \frac{c}{r} - \frac{K}{r^2}\right)\omega = 0. \tag{9.7}$$

Now, let us remind ourselves of the roles of these three numbers, E, c, K. The constant c is a parameter of the original equation and cannot have more than one value. The possible values for K we will determine by studying the equation in Y, rather than the one in r. For a given choice of K, we will then determine which possibilities for E are allowed, and part of this determination will rest on physical assumptions about the system, as well as some general theory about this particular kind of equation that we will use to eliminate undesirable solutions. In particular, one of our assumptions will be about the total energy allowed in the system, which will result in a boundary condition that requires ω to approach zero as r approaches infinity. When all is said and done, there will be one constant left undetermined. By choosing it (which will amount to a choice of c), we will specify the lowest value possible for E, and that will determine all the other eigenvalues.

The Quantum Numbers

We can now write the Schrödinger equation for any system. The problem is: how can we solve it for any system, or for even one system? It turns out that we can solve the equation exactly for a one-electron system. All other cases will require some form of approximation. We'll not try to reproduce that solution here. For now we shall concentrate only the solutions and interpret them. A word of warning; we revert back to the physicist's notation. In a subsequent chapter, we will explicitly connect the language of the physicist to that of the mathematician. We begin, for completeness, with the Schrödinger equation once more

$$\hat{H}\Psi = E\Psi, \tag{10.1}$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z) \tag{10.2}$$

Recall that while Bohr assumed quantum numbers they result from the solution of the Schrödinger Equation. Let's look at the quantum numbers resulting from the solution and assign physical significance to them.

Recall that in our one-dimensional particle in a box, we have one quantum number. In a three-dimensional box, we have three. In short, we have one quantum number per coordinate (actually, per squared coordinate or degree of freedom, but we'll leave that distinction for another time). Below, we look at the quantum numbers and assess their significance.

(1) The quantum number, n, is the "principal quantum number", and is related to the energy of an electron in an atom

$$E = -\frac{me^4 Z^2}{n^2 \hbar^2}, \quad n = 1, 2, 3, \ldots \tag{10.3}$$

where Z is the atomic number, m and e are the mass and charge of the electron and $\hbar$ is Planck's constant divided by 2π. The energy level spacing grows smaller as n increases. As $n \rightarrow \infty$, $E = 0$ and the atom is ionized. You can easily see that Schrödinger and Bohr were in agreement for the hydrogen atom, as they should be.

(2) The angular momentum quantum number, ℓ is required to accurately express the average electron distance from the nucleus

$$\bar{r} = \frac{a_0 n^2}{Z} \left(\frac{3}{2} - \frac{\ell(\ell+1)}{2n^2} \right), \quad 0 \le \ell \le n - 1 \qquad (10.4)$$

$\ell = 0 \Rightarrow s$ orbital

$\ell = 1 \Rightarrow p$ orbital, etc.

where s, p, etc. are the customary chemist's names for the stationary states.

(3) The magnetic quantum number, m_l, determines orientation in, and is only important for, atoms in a magnetic field. The values are restricted to

$$-\ell \le m_\ell \le \ell \qquad (10.5)$$

(4) There is a fourth quantum number that is necessary but does not result from the solution to the Schrödinger equation as we have written it. Rather, it results from a relativistic form of the equation. This is the spin quantum number, m_s, which is needed for many-electron atoms and has values

$$m_S = \pm 1/2. \qquad (10.6)$$

How do we use these quantum numbers? We can specify the state of an atom (and later, a molecule) using quantum numbers. Let's see how by finding the answer to the following question: "What are the quantum numbers for the ground (lowest energy) state of the hydrogen atom?" We come to the solution by writing the lowest possible values for each of the quantum numbers. That would be the following set:

$$n = 1$$
$$\ell = 0$$
$$m_\ell = 0$$
$$m_s = \pm \frac{1}{2}.$$

There are two possible sets of quantum numbers. Now take this concept one step further: what about the first excited state of the hydrogen atom?

$$
\left.
\begin{array}{c}
n = 1 \\
\ell = 0 \quad \text{or} \quad 1 \\
\swarrow \qquad \searrow \\
m_\ell = 0 \quad m_\ell = 0, 1 \\
m_s = \pm\frac{1}{2}
\end{array}
\right\}
$$

Eight possible sets of quantum numbers

$$2, 0, 0, \pm 1/2$$
$$2, 1, (-1, 0, 1), \pm 1/2$$

We could use a table to see this more clearly:

n	ℓ	m_ℓ	m_s	E, kcal/mol	Number states
1	0 ($1s$)	0	$\pm 1/2$	-1310	2
2	0 ($2s$)	0	$\pm 1/2$	-328	8
	1 ($2p$)	$-1, 0, 1$	$\pm 1/2$		
3	0 ($3s$)	0	$\pm 1/2$	-145	16
	1 ($3p$)	$-1, 0, 1$	$\pm 1/2$		
	2 ($3d$)	$-2, 1, 0, 1, 2$	$\pm 1/2$		

There are always $2n^2$ possible combinations of quantum numbers. We divide these into orbitals. Orbitals are maps of the probability of the electron being located at a certain region in space. They are designated by their angular momentum quantum numbers. The values of magnetic and spin quantum numbers define the electrons within an orbital.

As you have seen, the Schrödinger equation may be written in spherical polar coordinates using the usual transformation. As a result, we can write a radial part and an angular part for the wavefunction Ψ. As an example, let's look at the wavefunction for the $1s$ and $2p_z$ orbitals in the hydrogen atom. These orbitals have the quantum numbers $n = 1$, $\ell = 0$, $m_\ell = 0$ and $n = 2$, $\ell = 1$, $m_\ell = 0$, respectively.

$$
\psi_{1s} = \left(\frac{1}{4\pi} \right)^{1/2} \cdot 2 \left(\frac{1}{a} \right)^{1/2} e^{-\frac{r}{a}} \tag{10.7}
$$

$$
\psi_{2p_z} = \underbrace{\left(\frac{3}{4\pi} \right)^{1/2} \cos\theta}_{\Phi(\theta,\phi)} \cdot \underbrace{\frac{1}{\sqrt{3}} \left(\frac{1}{2a} \right)^{3/2} \left(\frac{r}{a} \right) e^{-\frac{r}{a}}}_{R(r)} \tag{10.8}
$$

where $a = \dfrac{a_0}{Z}$ (for H, $a = a_0$, the Bohr radius $= 0.529 \times 10^{-10}\,\text{m}$).
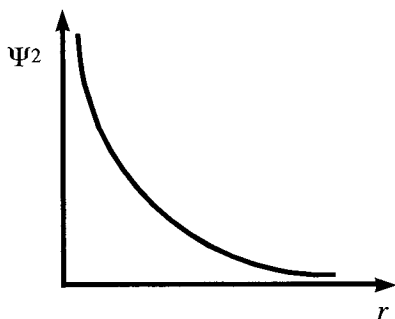
Figure 10.1. The probability density for the $1s$ orbital of hydrogen.

Finally, let us return to the issue of probability, one that we ducked a while back. Consider $\Psi_{1s}^2(r)$, the probability per unit volume within the $1s$ orbital. This is shown for the $1s$ orbital of hydrogen in Fig. 10.1.

There is a maximum at the nucleus. This is correct, but is contrary to our pre-conceived notion that the electron is not in the nucleus. Well, our common sense is correct. We are looking at the probability density and we need to multiply the probability density by a volume element to get a probability. The volume element of the nucleus is very small and so the probability of locating the electron at the nucleus is negligible (but not zero!). This can all be clarified by looking at a different function. It is easier to consider the probability of finding the electron at r, regardless of angular part of wavefunction. So, we construct the radial probability distribution function, obtained by integrating over all angles. We treated distribution functions in Chapter 4. The result in the present case is $r^2 R^2$. This is shown in Fig. 10.2 for several different orbitals.

In general, all s orbitals have some probability near the nucleus. Why do p and s orbitals look different? This seems to have no relationship to the radial function we just discussed. That correct! The difference in shape is due to angular terms. Let's ignore the radial part of the wavefunction and explore the angular term, $\Phi(\theta, \phi)$. In that case, we can write

$$|\Phi_{2p_z}|^2 \propto \cos^2 \theta \quad \text{and} \quad |\Phi_{1s}|^2 \propto 1 \tag{10.9}$$

Clearly, $|\Phi_{1s}|^2$ will not have any angular dependence. That is, it will generate a sphere in three-dimensions. $|\Phi_{2p_z}|^2$, on the other hand, is a periodic function and the probability density is shown in Fig. 10.3. Values of θ
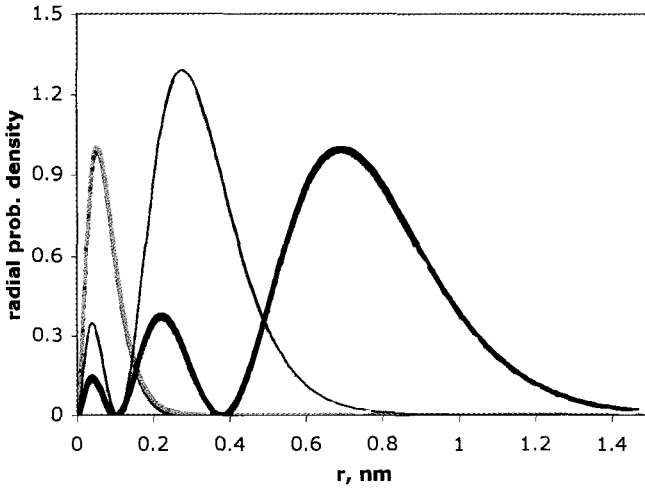
Figure 10.2. The radial probability distribution functions for hydrogen orbitals: 1s (gray); 2s (black) and 3s (heavy black).
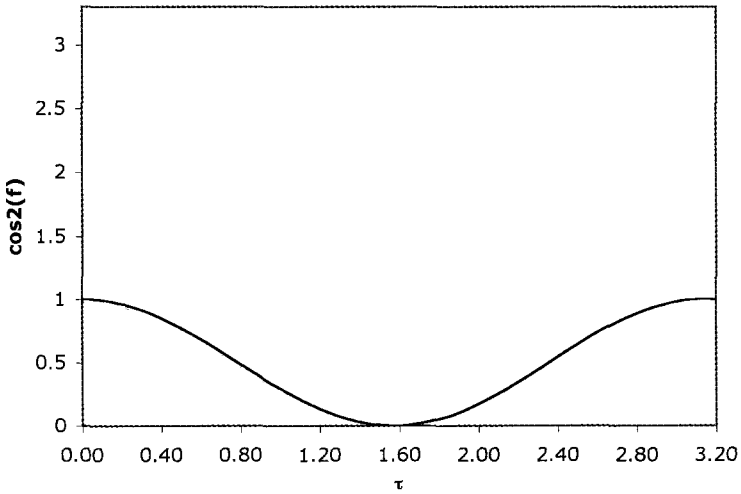
Figure 10.3. The angular dependence (in radians) of the unnormalized hydrogen $2p_z$ wavefunction.
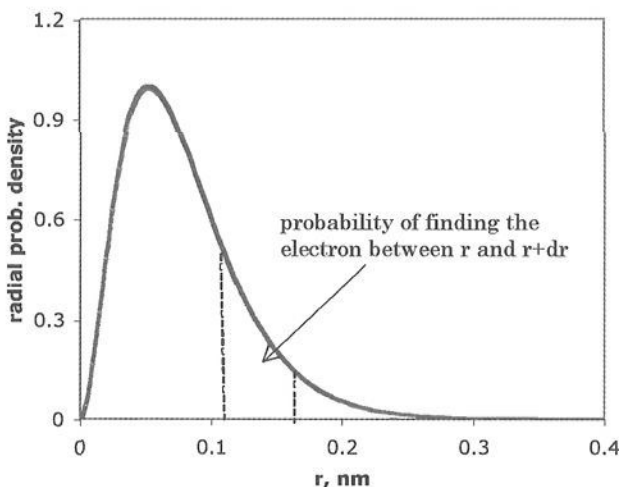
Figure 10.4. Use of the radial probability distribution function to calculate probability.

range from 0 to π and the angular dependence of the full wavefunction (think about rotating the curves in Fig. 10.3) will have the well-known "dumbbell" shape.

Finally, a note on interpretation. What are the differences between ψ, ψ^2, R^2, etc.?

- Evaluating $\psi^2(r, \theta, \phi) \Rightarrow$ the probability density at r, θ, ϕ (the probability per unit volume of finding the electron in a volume element near (r, θ, ϕ).
- R^2 is the radial probability density. This is the probability of finding an electron between r and $r + dr$, regardless of θ and ϕ.
- The radial probability is $R^2(r) \times$ volume. This is the volume of a spherical shell between r and $r + dr$ and is $\sim r^2 dr$. So, the radial probability equals $r^2 R(r^2) dr$, as shown in Fig. 10.4.

Pleased to Meet you, Dr. Schur

By now you should be suspecting that the symmetries of the sphere that we investigated in Chapter 4 are going to play a major role in solving the equation we set up in Chapter 6. Chemistry and physics texts skirt the issue in truly paranoid fashion. Mark my words, however — you can have all the toy models you want of energy levels arranged in concentric circles around a gumball proton with little ball bearings pretending to be electrons zooming about, so many to each orbit, but none of this stuff will tell you where the spectral lines of hydrogen lie. Only the solution to Schrodinger's equation will tell you that, and the key to unlocking that equation is the group of its symmetries.

A *group* is defined to be a set of objects (such as the real numbers or the rotation matrices) together with an *operation*, (such as addition in the first case and matrix multiplication in the second case), which takes a pair of these objects to a third one. Certain axioms must be satisfied. First of all, there has to be an object (called the *identity*) that preserves all the rest under the operation (such as addition of zero in the first example or multiplication by the identity matrix in the second). Secondly, every object has to have an inverse under the operation. An inverse of an object composed with the original object ought to give the identity. For the real numbers with addition, the identity is zero and the inverse of any number is its negative. What do you suppose the inverse of a rotation matrix will be? Finally, the operation specified for the group must be associative. Every kid learns that addition is associative, so there is no problem with the first example. Proving that matrix multiplication is associative is an amusing exercise.

It's worth knowing the definition of a group because some of the principles we will be using to solve Schrodinger's equation are applicable to lots of situations involving groups, even though we will only be thinking about the group of rotations of the sphere, which has the special name SO(3, R). The

nomenclature is part of a group classification program for matrix groups, whose work spans a century. The "*S*" stands for "*simple*", which is code for having determinant one. The "*O*" stands for "*orthogonal*", because the matrices for rotations all share the common property that their rows are perpendicular vectors, as are their columns. Orthogonal is a fancy word for perpendicular. The "3" stands for 3 by 3 matrices and the "*R*" indicates that the entries are real numbers, rather than complex numbers or some other sort of object. These classifications are useful for describing properties of matrix groups in grand generality, a work begun in the 1800's by Sophus Lie. His hope was to use general principles to solve large classes of very difficult types of differential equations, whose symmetry groups these were. As a result, SO(3, R) is called a *Lie group*. As you will soon see, Lie's hunch about how to approach differential equations is very much borne out in the case of the Schrödinger equation.

It's easier to think of the group of rotations as acting on all of three-dimensional space, instead of just the sphere. Any point in space can be rotated about the origin; the sphere is just an invariant of those rotations. Now here is the amazing mathematical revelation: any group that acts on some space (such as three-dimensional space or the sphere), also acts on functions of that spatial variable. Here is an example of how it works. We are cowards, you and I, so we'll start with an "easy" example.

Suppose the group we are thinking about is just the *real numbers with addition*. A member of this group (say, 3, for example) acts on the real number line by taking every number on the line and adding that group element to it (5 becomes 8, π becomes $\pi + 3$). This has the effect of sliding the line to the right or left so many spaces, where it obligingly lies down right back on top of itself. How do we make this action into one on functions? By translating the variable, of course, so that for a group element y (or 3) and a function $f(x)$, we get a new function:

$$f_y = f(x - y)$$

or   (11.1)

$$f_3 = f(x - 3).$$

You can check that this new action is *linear*. In other words, a group element acting on the sum of two functions will have the same result as it would were it to act on each function separately and then one were to sum them. In other words, if the space of functions is a *vector space*, which it is, then every single element of this group acts like a *matrix* on this space of functions.

Ponder this. Hold this example in your head. Hold on tight to it because it is the inspiration for all that follows.

For the case we care more about, the group SO(3, R) acts on functions in three space by *rotating the spatial variable.* So a function $f(x, y, z)$ becomes $f(Ax + By + Cz, Dx + Ey + Fz, Gx + Hy + Iz)$ where the matrix

$$\begin{pmatrix} A & B & C \\ D & E & F \\ G & H & I \end{pmatrix} \tag{11.2}$$

lies in SO(3, R). In other words, its rows form an orthogonal basis of R and so do its columns. In spherical coordinates, (r, θ, φ), this action would send $f(r, \theta, \phi)$ to $f(r, \theta + \alpha, \phi + \beta)$ and it would look *remarkably* like the last example! (Of course, the transformation $\theta \to \theta + \alpha$ is <u>not</u> a true rotation. In fact, α and β would both be complicated functions of θ and φ as well as the entries of the matrix above. That is why α and β are a bad choice of coordinate system for rotations of the sphere.)

In both of these examples we are looking at a phenomenon known as a *group representation.* This just means that we have expressed (or represented) our group as linear operators (in both cases translation of the functional variable) on a vector space (of functions of a particular sort). In this way, we can think of the group as a large matrix. As we have seen from Fourier analysis when we looked at the wave equation, the dimension of one of these spaces of functions is infinitely large, so although we started out with matrix groups (1 by 1 matrices in the first case and 3 by 3 matrices in the second), we ended up with infinitely large matrices that act on spaces of functions. Entries of the matrix for the representation, called *matrix coefficients* for obvious reasons, will depend on the choice of basis for the vector space of functions.

Let's introduce some simple notation for what is going on in these two examples. In both cases we have a group, say G, with group elements, one of which might be g. Each of these group elements acts on a function by changing the functional variables in some way. Let us denote that action as

$$f(g^{-1}x) = \rho(g)f. \tag{11.3}$$

The reason for this notation is largely convention. This is the way a *representation theorist* would write it. It's convenient because composition of matrices works out well this way, that is if g and h are two group elements,

$$f((gh)^{-1}x) = f(h^{-1}g^{-1}x) = \rho(g)\rho(h) = \rho(gh)f. \tag{11.4}$$

Check it out. This consistency of order makes certain kinds of algebraic manipulations a little easier, so this is how the action is written.

Now we are equipped to ask the important question of this chapter. How do the spatial symmetries evident in the spectrum of hydrogen translate into a statement about the solutions of Schrödinger's equation? Remember that the spectral lines are invariant with respect to the observer's position. That means that if hydrogen is behaving as the solution to a differential equation, then when that solution is rotated according to any element of the symmetry group, we must obtain another solution. In other words, instead of moving the observer, think of rotating the atom. By doing this rotation, you must get another solution to Schrödinger's equation that gives the same spectral line. With our notation from Chapter 9 and this one, it must be that

$$\Delta_S \rho(g) f = \rho(g) \Delta_S f. \qquad (11.5)$$

In fact, it is possible to verify this directly by doing the change of variables and then applying Δ_S, and vice-versa. But this notation makes it very clear that the operator Δ_S commutes with the entire family of operators $\rho(g)$, for all g. And this makes our eigenvalue problem a perfect candidate for *Schur's Lemma*.

Schur's Lemma

Suppose (T, V) is an irreducible representation of a group G on a finite-dimensional complex vector space V. If A is a linear map such that $A T(g) = T(g) A$ for all g in G, then there is a complex number c such that $A = cI$, where I is the identity operator (identity matrix in this case).

Schur's lemma is telling us that if we can break our vector space of functions into finite size pieces on which our representation is irreducible, then Δ_S will behave like a diagonal matrix on each piece, with the same number along the diagonal. To complete the picture, an *irreducible representation* is a representation of a group on a vector space that has no invariant subspaces. In other words, the group completely mixes up the various objects it acts on, so that you can't break the representation into two smaller actions. To apply Schur's lemma to our eigenvalue problem above, we need to break up the space of functions on the sphere into subspaces, each of which is the group action given by a rotational change of variables preserves. To return to our easy example of translation of functions of one real variable, we can

see that the action given by

$$f_y(x) = f(x - y) \tag{11.6}$$

preserves certain subspaces of functions. You can see that if

$$f = e^{cx} \text{ then}$$

$$f_y(x) = e^{c(x-y)} = e^{-cy}e^{cx} = Ke^{cx}. \tag{11.7}$$

How does this example relate to Schur's lemma? Well, it is easy to check that translation of the functional variable which gives us our representation in this case, actually commutes with the operator $\dfrac{\mathrm{d}}{\mathrm{d}x}$.

Check this out. Since the space of functions spanned by the *single function* e^{cx} is a finite-dimensional vector space of dimension one, translation becomes an example of an irreducible representation on this space. The hypotheses of Schur's lemma are satisfied and we can conclude without computation that

$$\frac{\mathrm{d}}{\mathrm{d}x}e^{cx} = Ce^{cx} \tag{11.8}$$

for some value of c. Schur's lemma doesn't tell us what that constant will be. Of course, anyone reading this will certainly be able to work the problem directly to see that $c = C$.

For such an easy, familiar example, Schur's lemma doesn't gain us any new or particularly enlightening information. But for the case of rotations in three-dimensional space, it certainly will. In this situation, the invariant subspaces that are fixed by the group action will not be one-dimensional. Yet the lemma tells us that every element of such a subspace will be an eigenfunction of our spherical Laplace operator, Δ, and will always have the same eigenvalue. So we need to only compute the action of Δ on one function in each space to determine the eigenvalue. Furthermore, the dimensions of these invariant subspaces (which we can calculate) will have an actual physical interpretation, as we will see later.

This page is intentionally left blank

The Spherical Harmonics

It is the general consensus among mathematicians I know that "The Spherical Harmonics" would be a great name for a rock group, or possibly a barbershop quartet with somewhat portly members. Language conjures an image, no matter how technical the language may be. All of the discussion we have been having about groups and symmetries is part of the corner of mathematics called *algebra*, or sometimes out of honesty, *abstract algebra*. It is indeed a direct descendent of that Arabic and late medieval activity whose name is derived from the word *al-jabr*, meaning *to restore*. In its abstract form, it bears little resemblance to either the medieval subject or its renaissance counterpart as taught in high school, which we all have studied and whose exposition can be found in books entitled "College Algebra". That title is a tip-off that the contents of the book restore (*al-jabr*) what was supposed to have been learned in high school. In contrast, the most abstract renderings of modern algebra can be found in texts ingenuously titled "Basic Algebra 1". It is some matter of debate whether language is doing its job in these cases.

The spherical harmonics are really the families of functions of the Euler angle variables, (ϕ, θ) which are invariant under rotation. The orthogonal group is not commutative, so its action on these variables doesn't amount to simply adding angles independently to the Euler angle variables. Rather, there is some complex interaction between rotations in ϕ and θ which you could work out if you had to do it. A simpler approach is to view every function on the sphere as the restriction of a function in three-dimensional space, where the action of the orthogonal group is given by a matrix by which one multiplies the vector (x, y, z).

Just as before, a function $f(x, y, z)$ becomes $f(Ax + By + Cz, Dx + Ey + Fz, Gx + Hy + Iz)$, where the matrix $\rho(g)$ is given by:

$$\begin{pmatrix} A & B & C \\ D & E & F \\ G & H & I \end{pmatrix} \tag{12.1}$$

lies in SO(3, R). This function, when restricted to values of (x, y, z) where $x^2 + y^2 + z^2 = 1$, gives a function of the points on the sphere. Of course, we will have to be careful because more than one function might be the same when restricted to just the sphere. So we will have to worry about that when we make our count of how many there are in each invariant subspace.

Suppose we look at a particular function,

$$f(x, y, z) = x^3. \tag{12.2}$$

Then, if we transform the function according to the matrix above,

$$\rho(g)f = (Ax + By + Cz)^3. \tag{12.3}$$

What aspects of f are preserved by such a transformation? Multiplying the terms out gives us a major hint. Every term of the transformed polynomial has the same degree as the original, namely 3. So, if we took as a subspace of our huge vector space of functions those polynomials which are *homogeneous of degree n*, which means that every term has exponents which add up to n, then we would have a subspace that is invariant under our group action. Now, we have to be careful because some of them are really the same function when confined to the sphere. For example,

$$f(x, y, z) = x^2 + y^2 + z^2 \tag{12.4}$$

is really a constant function on the sphere, so its degree goes down by 2. Because we believe in the mathematical phenomenon known as Taylor Series, we know that these polynomials are enough to generate all functions on the sphere.

It's worth noting the weirdness of this example. Normally if you take a second derivative of a polynomial of a certain degree, that degree goes down by 2. In other words, this trick of using polynomials won't work for the regular Laplace operator, so why should it work for the spherical one? The key lies in the finite dimensional hypothesis in Schur's lemma. For the lemma to work, the group G and the operator Δ must commute on this

finite dimensional space. The operator

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (12.5)$$

does not preserve the space of polynomials of any particular degree, so we can't use Schur's lemma on it. In other words, although the group breaks the space of polynomials of degree *less than or equal to x* into invariant subspaces, the Laplacian doesn't cooperate by respecting those subspaces, at least not superficially. In fact, if it is going to be true that the Laplace operator has an eigenfunction that is a polynomial, then the eigenvalue must be *zero*. Do such functions exist? Yes they do, and they are called the *harmonic polynomials*. Here are some examples:

$$x, y, z$$
$$x - y^2, y - z^2, xy, yz$$
$$3x^2y - y^3$$
$$x^3y - xy^3 \qquad (12.6)$$

and so on. Since each of these is an eigenfunction of Δ, if we use any one of them to make more by changing variables under the rotation group, we will construct many new eigenfunctions in this way. *Now* we have made spaces which satisfy the hypotheses of Schur's lemma, although the eigenvalue corresponding to the operator Δ is always zero. Of course, what we really care about is the eigenvalue corresponding to Δ_S, which will not be zero.

As a matter of fact, if we look at what happens to those polynomials when we substitute Euler angles and set the radius to 1, we find something quite different. The polynomial z, for example, becomes

$$f(\phi, \theta) = \cos(\theta). \qquad (12.7)$$

If we apply the spherical Laplacian, we get

$$\Delta_S f = -2\cos(\theta). \qquad (12.8)$$

If we pass to polynomials of degree 2, we have to be careful. They do not always look homogeneous when we finish setting $x^2 + y^2 + z^2 = 1$. Let us look at z^2, for example, which is not harmonic and so should not be an eigenfunction of Δ. Passing to spherical coordinates, and setting $r = 1$, this gives the function

$$g(\phi, \theta) = \cos^2(\theta). \qquad (12.9)$$

You can check that

$$\Delta_S g = 2 - 6\cos^2(\theta). \tag{12.10}$$

Clearly, if we try a new function

$$G(\phi, \theta) = \cos^2(\phi) - \frac{1}{3}. \tag{12.11}$$

Then, G is an eigenfunction of Δ_S with eigenvalue -6. Now, if we were to create a bunch of new functions by applying our rotation group to this one, we would indeed create the irreducible representation described by Schur's lemma. Does this correspond to a harmonic function in x, y, z? Well, you can check that

$$z^2 - \frac{1}{3}(x^2 + y^2 + z^2) \tag{12.12}$$

is in fact harmonic, and restricts to

$$z^2 - \frac{1}{3} \tag{12.13}$$

on the unit sphere. It is pretty easy to construct a harmonic polynomial for any given degree if you mess around long enough, but kind of hard to write down a general recipe for getting one of an arbitrary degree.

In fact, eigenfunctions for the spherical Laplacian can be written down explicitly in terms of *Legendre polynomials*. The Legendre polynomials are defined in terms of two indices as follows:

$$P_n^m(\omega) = (1 - x^2)\frac{d^m P_n(x)}{dx^m} \tag{12.14}$$

where

$$P_n(x) = \frac{1}{2^n n!}\frac{d^n}{dx^n}((x^2 - 1)^n). \tag{12.15}$$

Armed with all of this notation, the function

$$e^{im\phi}P_n^m(\cos\theta) \tag{12.16}$$

is an eigenfunction of Δ_S with eigenvalue $-n(n+1)$.

So, like a lot of math problems, this is one you can "solve" once you know what the answer is. And, like a lot of math problems, the modern approach (which in this case uses group theory and the fancy algebra of Schur's lemma) harkens back to famous families of "special functions", like the Legendre polynomials. For our purposes, the main fact we have gleaned is that the K of Chapter 9 is equal to $n(n+1)$ for some positive integer, n.

Figure 12.1. Graphical representation of Eq. 12.17. This is also a stylized representation of a 2*p* orbital.

You can also do a fancy counting argument to figure out the *dimension* of each space of eigenfunctions, and you will find that the dimension of the space of functions whose eigenvalue is $-n(n+1)$ is, in fact, $2n+1$. This fact will figure in much later, when we know more about the final solution to Schrödinger's equation.

Without even solving the equation in the radial variable, just knowing the spherical harmonics gives us a lot of information about the structure of the atom. The probability distribution of the electron is usually pictured as a cloud, where the density of the cloud denotes greater probability. Nodes of the spherical functions are choices of θ and ϕ where the solution is zero. For example,

$$f(\phi, \theta) = \cos \theta \tag{12.17}$$

has a node at $\theta = \pi/2$, which is the entire x–y plane. The electron cloud for this solution looks like the drawing in Fig. 12.1. This figure represents one of the orbitals portrayed in any chemistry or modern physics book.

This page is intentionally left blank

CHAPTER 13

More French Mathematicians

To finish the computation of the energy level E we set out to find in Chapter 9, we must look again at the equation:

$$(r^2\omega')' - r^2\left(E - \frac{c}{r} + \frac{n(n+1)}{r^2}\right)\omega = 0, \qquad (13.1)$$

where we have acknowledged that $K = -n(n+1)$. Earlier, we hinted at the need for certain physical considerations to eliminate some kinds of solutions to this equation. As you are aware if you have studied differential equations, sometimes what matters most is the long term behavior of the solution rather than a nice formula for it. This is one of those cases, because physicists like to assume that an electron can only have finite energy. That means, when translated, that the function of r that solves the above equation had better die out as r approaches infinity. The energy of the electron is somehow related to the integral of the absolute value of the function ω from zero to infinity. If the function doesn't go to zero as r gets large, that integral cannot be finite. This is an absolutely minimal criterion for the integral to be finite, and as you know if you remember your calculus, it is not nearly enough. But, if the function does go to zero, we can then do some extra work to check that the integral will also converge.

The easiest way to get at the nature of the solution to our equation is to invoke *power series* to help us solve it. You might remember that a power series is a way to express a nice function (called *analytic*) as an overblown polynomial. Let

$$\omega(r) = a_0 + a_1 r + a_2 r^2 + \cdots \qquad (13.2)$$

where the three dots mean that this series is actually infinitely long. By investigating this series, we can learn a lot about the long term behavior of the solution, depending on different choices of E and c. Unfortunately, if you plug it right in to the equation as it currently stands, you will get a

71

major mess. Try it if you want to, but don't blame me for what happens. Instead, we will break it down into pieces, none of which are that bad.

Working through this problem, I realized that reading an exposition of it would actually be worse than working through it myself. So, in what follows, I have parsed the problem into small pieces, most of which do not use anything unfamiliar to a calculus student. There is a place toward the end of the exercises where you will have to do some messy estimates of how fast terms in the power series are growing. This sort of analysis is very akin to the kind of questions that come up in studying when power series converge. In the end, allowable choices of E will rest entirely on these estimates. This is because it is the *boundary values* in this problem that are controlling much of what goes on. The requirement that the solutions to Schrödinger's equation die out fast enough as r gets large so that the total energy is finite represents a physical requirement. Basically, this is the requirement that the electron be actually associated with the atom. Therefore, the allowable E that come out represent the *bound states* of hydrogen.

In the end you will see that the answer to this chapter's equation is given by a family of classical functions, called the *Laguerre polynomials*. The Laguerre polynomials were studied long before this particular problem. It certainly seems to be the case that the same sorts of functions tend to reappear in physics with great frequency, along with the somewhat startling roles played by the integers and the circle. Why should physical phenomena so often be represented by the very sorts of number patterns and functions that humans find so easy to comprehend? This question has led to a phrase coined by Stanislaw Ulam, *"the unreasonable effectiveness of mathematics"*. It's enough to make a Pythagorean out of any of us.

A Guided Tour of the Radial Part of Schrödinger's Equation

1. Do a change of variables on the equation in r. Let $K = n(n+1)$ and let

$$\omega = r^m y$$

and compute what sort of equation it must then solve. You should get

$$(m(m-1) + 2m - K - r^2 E + cr)y + (2m+2)ry' + r^2 y'' = 0. \quad (13.3)$$

Notice the expression,

$$m(m-1) + 2m - K = m^2 + m - K. \quad (13.4)$$

Since $K = n(n+1)$, if you set $m = n$, this expression will be zero. Do this and the equation becomes:

$$(-r^2E + cr)y + 2(n+1)ry' + r^2y'' = 0. \qquad (13.5)$$

Notice that an r cancels out to give:

$$(-rE + c)y + 2(n+1)y' + ry'' = 0. \qquad (13.6)$$

2. Do another change of variables. Set $s = cr$ and compute the new differential equation resulting. Then set

$$E = c^2M.$$

Setting $u(s) = y(r)$, you should get

$$(1 - sM)u + 2(n+1)u' + su'' = 0. \qquad (13.7)$$

Now, this equation looks perfectly amenable to plugging in a power series for u and chugging away. We have eliminated one degree of the variable and one of the constants. However, you will find, if you attempt a power series solution at this point, that you can write down a dependence among

$$a_{n-1}, a_n, \text{ and } a_{n+1}.$$

This is ok as far as it goes, but a *two-step recursion* like this makes it hard to deduce the long term properties of the a_n. A *one-step recursion* would be much better. So we will do one more change of variables.

3. This time, set $u = e^{-F_s}\nu$, where F is some constant. Compute the new differential equation and see that if you set $F = \sqrt{M}$ you will obtain:

$$(1 - 2(n+1)F)\nu + (2(n+1) - 2sF)\nu' + s\nu'' = 0. \qquad (13.8)$$

This has the effect of moving the s from the coefficient of v to that of v', making the next computation easier.

4. Are you ready to boogie? Set

$$\nu = a_0 + a_1s + \cdots + a_js^j + \cdots. \qquad (13.9)$$

Compute v' and v''. Use the differential equation to figure out what the general coefficient, a_{j+1}, ought to be in terms of the previous

coefficient a_j. I find it easier in this case to look at an equation of the form:

$$A\nu + (B - Cs)\nu' + s\nu'' = 0, \tag{13.10}$$

where all of the constants are positive, because then I get the general relationship:

$$a_{j+1} = \frac{Cj - A}{(B + j)(J + 1)} a_j. \tag{13.11}$$

This *recursion formula* is of the general form

$$a_{j+1} = Q a_j, \tag{13.12}$$

where Q has some sort of dependence on j. The remaining exercises allow us to analyze the recursion formula we have obtained.

5. First notice that if there is some j for which $Cj - A = 0$, then the series terminates and the solution will be a polynomial. In our example, $C = 2F$ and $A = 1 - 2(n + 1)F$. What relationship of j to F gives a polynomial solution? Show that, for a_{j+1} to be zero, it must be that

$$F = \frac{1}{2(j + n + 1)}. \tag{13.13}$$

Then work backwards through your substitutions to show that this implies that

$$E = \frac{c^2}{4(j + n + 1)^2} \tag{13.14}$$

and show that the solution corresponding to this choice dies out exponentially fast as r goes to infinity. This involves working backwards through all of the various substitutions to get a general form for the solution. It so happens that these solutions can also be written as *Laguerre polynomials* times an exponential. It is the exponential introduced in Step 3 that gives the rate at which the function dies out at infinity. These are solutions to Schrödinger's equation that obey all of the constraints we originally put upon them.

6. Now we will look at the case where the power series does not terminate. This series, of course, will only represent the actual solution of your equation if the power series actually converges everywhere. Use an argument that compares the coefficients to those of an exponential function to show that the coefficients die out fast enough to guarantee convergence everywhere.

Next, we will compute a lower bound for the same coefficients. Show that, for a large enough J, all the a_j for $j > J$ are of the same sign. And now show that the absolute value of the expression

$$\frac{Cj - A}{(B + j)(j + 1)} \tag{13.15}$$

is bounded below by

$$\frac{P}{j + 1} \tag{13.16}$$

and that, therefore, the coefficient a_{j+1} is bounded below by

$$N \frac{P^{j+1}}{(j + 1)!}, \tag{13.17}$$

where $(j + 1) = (j + 1)(j)(j - 1) \cdots 1$, which is called $(j + 1)$ *factorial*.

Comparing these coefficients with those of an exponential functions allows you to say that the solution to your differential equation grows (in s) at least as fast as an exponential function divided by some power of s.

Finally show that when you work backwards through the substitutions, this large rate of growth is maintained. Actually, the only thing likely to cause trouble for you is the presence of the exponential in Step 3. You will have to show that the rate of growth of the function represented by your power series is greater than that of some exponential. You can conclude from this annoying foray into power series that *none of these solutions is allowed by the assumptions on Schrödinger's equation.* Therefore, the only solutions are those you found in Step 5.

This page is intentionally left blank

CHAPTER 14

Reprise: The Quantum Numbers

Gentle reader, you have tolerated much to get to this point. Together we have made forays into almost every corner of mathematics in search of an explanation of the marvelous light of hydrogen. Will it pay? I assure you it will pay, and handsomely. But do not hope for perfection, because that is not what science gives. Only mathematics can ever be perfect. In this chapter, we will explore the quantum number. The language will be that of the mathematician. You might want a translator, if you are more comfortable with the chemical or physical dialect. Later chapters will do this for you.

What have we found thus far? A magical integer, n, which tells about the space of spherical polynomials of degree n. Another magical integer, $k = j + n + 1$ tells us the eigenvalue

$$E = \frac{c^2}{4k^2}, \tag{14.1}$$

which ought to yield the spectral lines. Of course, there is still the constant c which must be determined to give the full information contained in the model. This can be done, either experimentally or from first principles (and good luck to you, too!). Either way, it turns out that

$$E = \frac{m^2 e^4}{h^4 k^2}, \tag{14.2}$$

where m is the mass of the electron, e is the charge on the electron, and h is Planck's constant. Of course, everything is in units that would make a physicist happy. What do we observe when we run Balmer's experiment? Well, we ought to see the difference in energies as the electron changes its natural frequency of oscillation to a lower energy one, while ringing light. Or we can evoke the prosaic language of chemistry texts, and claim that the "electron jumps from one energy level to the next". In any case, we

77

expect to see a difference that looks like

$$\nu = Rk_2^{-2} - Rk_1^{-2}, \tag{14.3}$$

where k_1 and k_2 are two choices of the k which determine E. This k is called the *principal quantum number* as it completely determines the observed spectral lines. (Of course, chemists and some physicists use a different set of variable descriptors, see Chapters 3 and 10!) R is the Rydberg constant, which you get by taking one of the values of E that we chose and plugging it in to the time-dependent part of the wave equation that gave us Schrödinger's equation. We discussed this constant back in Chapter 3, but with a primitive mathematical model. In other words, you are looking for the frequency associated with the equation:

$$-K\frac{d^2 f}{dt^2} = Ef, \tag{14.4}$$

where $\Psi(x, y, z, t) = \psi(x, y, z)f(t)$.

The difference,

$$E_2 - E_1, \tag{14.5}$$

is given off as $h\nu$ where ν is the frequency of light emitted. In the end,

$$R = 2\pi^2 m e^4 h^{-3} \tag{14.6}$$

and so our model provides a very good explanation of the spectral lines, observable in the visible range when $k_2 = 2$. If $k_2 = 1$, we get spectra in the ultraviolet range, found by Lyman in 1909.

But this is by no means the whole story. It is also possible to use what we know about the dimensions of the spaces of solutions to these equations to see other possibilities for interpretation. For example, you can attempt to count up a set of linearly independent solutions to Schrödinger's equation for a fixed E. Remember from our discussion that

$$E = \frac{m^2 e^4}{h^4 k^2}, \tag{14.7}$$

where $k = j + n + 1$. So the largest eigenvalue occurs when $k = 0$, which can only happen when both j and n are zero (what chemists and physicists call the $1s$ orbital!). When $n = 0$ the corresponding spherical harmonic is the constant function, and there is one possibility for the Laguerre polynomial corresponding to each j. Since we are looking at products of these, we have a solution space of dimension 1. Of course, the time-dependent part will have two linearly-independent solutions, just like in an ordinary wave equation.
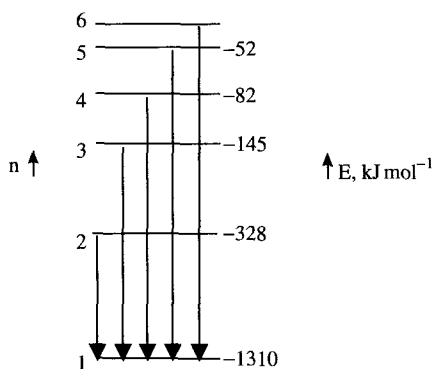
Figure 14.1. The energy level diagram that leads to the Lyman spectrum in the ultraviolet region.

So there will always be twice as many solutions to the full wave equation as there are to the corresponding Schrödinger equation. (Or two electrons per orbital, says the chemist!)

It is an interesting exercise to rewrite the quantum numbers in Eq. 14.7 in the form physicists and chemists like to use, as in Chapter 10. We leave this to the reader.

What happens as we go to higher energy solutions? If $k = 2$, there are two possibilities. One is that $n = 0$ and $j = 1$, in which case, again there is one solution (the 2s orbital). But one can also have $n = 1$ and $j = 0$. For $n = 1$, the spherical polynomials have dimension $2n + 1 = 3$ (the 2p orbtials) and so the total number of solutions for this value of E is 4. It is easy to see in general that for a given k there are

$$\sum_{n=0}^{k-1} (2n + 1) = k^2 \tag{14.8}$$

different solutions to the equation. Physicists call this the k^2-*fold degeneracy*. The number n has a special name, too. It's called the *azimuthal quantum number*. There is even a way to index the spherical functions corresponding to a given n to get a distinguished basis indexed by some variable p, which is then called the magnetic quantum number. This number shows up experimentally. For a given k and n, there are $2n + 1$ indistinguishable states corresponding to the dimension of the space of spherical polynomials of degree n. But the states are only indistinguishable if the *symmetry* we observed is maintained. One way to see these states is to break the

rotational symmetry of SO(3) and see what happens. In practice, this is done by placing hydrogen in a magnetic field, so that one of the directions of the sphere is distorted. There only remains a circular symmetry, namely that of SO(2). Because every irreducible representation of SO(2) is one-dimensional, the spaces of spherical polynomials are broken up. Each space contains $2n + 1$ linearly independent functions, so each of the Balmer lines breaks up into an odd number of lines, in what is called the *Zeeman effect.*

There is more good news. Anyone who has stared at the periodic table and has taken basic chemistry knows that the orbital structure postulated for atoms is the same for all kinds of atoms. And all atoms exhibit a line spectrum that is independent of the viewer's position. So there is no reason, in principle, why you couldn't solve this problem for other sorts of atoms too. The basic ideas are indeed the same. Of course, problems arise in interpretation. For example, if we are interpreting our little electron as a wave, then what are we supposed to do with *two* electrons? After all, a wave plus a wave is still just a wave. As near as I can tell, quantum mechanics still has a way to go before it replaces the old fashioned pictures of helium, lithium and other, more complex, atoms. And any physicist can tell you that molecules, stripped of their pretty spherical symmetry, are trouble indeed.

And now for the bad news. Although most of the things predicted by our model can be observed, some things can be found that the model will not predict. For example, there is a way to observe a degeneracy of one spectral line into $(n + 1)^2$ different lines, rather than just $2n + 1$. This was explained by Fock, who reinterpreted Schrödinger's equation in a way that was invariant under SO(4, R). A larger symmetry group means bigger sub-spaces corresponding to a given eigenvalue, hence more degeneracy under asymmetrical conditions. The story of hydrogen is far from over.

CHAPTER 15

Chemistry and Bonding

1. Introduction

The number of known chemical compounds, molecules, is staggering. Clearly, there is a propensity for atoms to combine into larger units. Can we apply the quantum ideas we previously developed to this problem? As you already know, an instructor never asks this type of rhetorical question unless the answer is yes! So, one of the basic questions we must address, regardless of our bonding theory, must be: "why does bonding occur?" We might expect to find the answer in thermodynamics, but let's put off explicitly answering that question until we make a few observations:

(1) The X–O–H bond angle is approximately the same ($\sim 109°$) regardless of the molecule in which it occurs, be it water (H–O–H) or methanol (C–O–H).
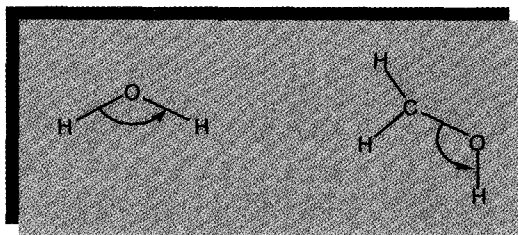
(2) Bond energy, for a given type of bond, does not appear to differ greatly from molecule to molecule. The energy of the C–H bond in CH_4 is $\sim 103\,\mathrm{kcal\ mole^{-1}}$, while in C_2H_6 it is $96\,\mathrm{kcal\ mole^{-1}}$.

(3) Elements in a given column of the periodic table have similar bonding characteristics. C, Si and Ge all form four bonds with H and all have H–X–H bond angles of ∼109°.

It seems as if these brief observations have provided us with additional criteria for any bonding theory that we might consider. That is, a successful theory of bonding must account for the molecular formula and the molecular geometry, as well as the driving force for bonding.

To complicate matters even more, we note that while we all have some familiarity with the terms *covalent bond* and *ionic bond*, this is not the exclusive set of bonding types. In fact, few molecules are purely covalent or purely ionic. In addition to these chemical bonds, there are non-bonding interactions among atoms to provide what are generically known as weakly bound species. Included among this group are molecules with hydrogen bonding. This and the next few chapters will describe three "bonding theories". A later chapter will address hydrogen bonding and, finally, other weak interactions.

Lewis Dot Structures

Lewis dot structures are the simplest approach to rationalizing chemical bonds. There are three different versions of this elementary idea. We start with the original by Lewis himself (1916):

"... atoms strive to achieve inert gas electron distributions by sharing electrons".

Note that no distinctions are made between *s* and *p* electrons, because no one knew about such things in 1916. We represent atoms by dot structures; one dot per outer shell electron:
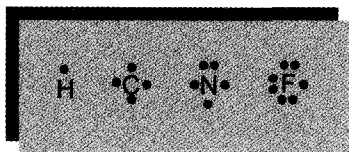
I left as many unpaired electrons as I could.

We represent molecules by bringing such atoms together to make bonds, where a dash may be used to represent two electrons in a bond:
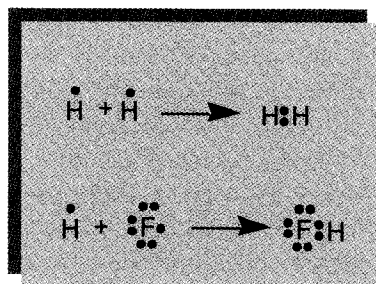
In these molecules, each atom has an inert gas configuration; for H, it is that of He, and for F, it is that of Ne.

The second form of Lewis' model is known as the "octet rule":

"... except for H (and Li, Be and B), atoms form bonds until surrounded by eight electrons".

This "rule" is valid for atoms with $Z \leq 10$ and shows why ammonia has three N–H bonds:
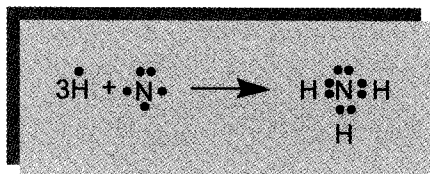
However, look at the reaction between P and Cl:
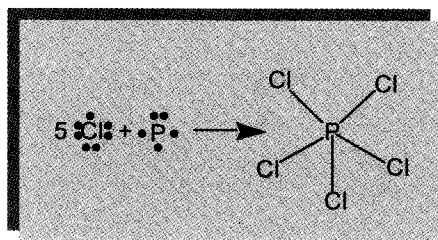
The phosphorous atom has ten electrons associated with it, in clear violation of the octet rule. However, we must remember that P has $Z = 15$, so there is no reason to believe that the octet rule will be obeyed.

This leads to the last (and best) version of the Lewis dot structure rules:

"... form as many bonds, at least there is the potential to form
as many bonds, as there are available electrons".

We define available electrons as the maximum number of unpaired electrons.
This is not the standard definition! Going back to the PCl_5 example, the
phosphorous atom may have five unpaired electrons because d orbitals are
available. For the related N atom, no d orbitals are available $(n = 2)$, so
the maximum number of unpaired electrons is three. We can also return to
the carbon example cited at the beginning of this section. The four outer
shell electrons can be distributed among the four total s and p orbitals, so
carbon can form four bonds.

The best way to see what all of the above text implies is to try it out.
We'll do that by looking at some real molecules.

Our first example is tetrafluoromethane, CF_4. The total number of available (outershell) electrons (32) is given by the carbon contribution of four
electrons and the contribution of seven electrons from each fluorine atom.
The structure we draw follows the octet rule (recall that the line represents
two electrons in a bond):
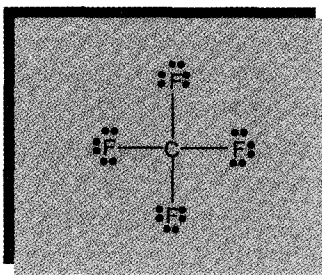
Molecular nitrogen, N_2, is a slightly more complicated example. Each
nitrogen atom contributes five electrons, so that the total number of available electrons is ten. Begin by drawing a structure that obeys the octet rule
while ignoring the total number of electrons:
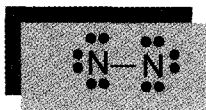
This requires 14 electrons, which is four electrons too many! Therefore, we replace the single bond with a double bond. This reduces total number of electrons in our dot structure by two, and still satisfies the octet rule:

$$\ddot{N}=\ddot{N}$$
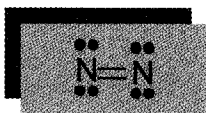
We still have too many, 12, electrons in the structure, so we add another bond:

$$:N\equiv N:$$
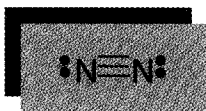
This works! The lesson to take from this example: *adding a double bond reduces the total number of electrons by two and a triple bond reduces that number by four.* These steps, shown in the N_2 example, exemplify the general procedure to follow in writing Lewis dot structures.

The final example will require us to pursue a new concept. The molecule is the nitroamide anion, $N_2HO_2^-$. The number of available electrons, 24, is given by the sum of those from N (10), H (1), O (12) and the charge (1). Our trial structure would be:
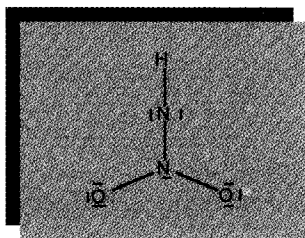
which requires 26 electrons. We need to add one double bond to our trial structure, but there are three possible positions for the double bond, as shown in the structures below:
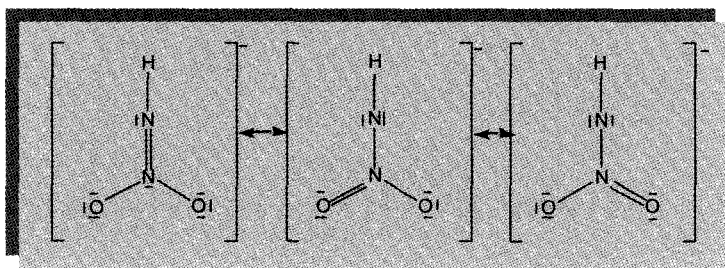
These structures are known as **resonance structures**. The true structure is some weighted average of these three. That is, each N–O bond is between a single and double bond in length, as is the N–N bond. In order to rank the relative importance of each structure, we need to use **formal charges**. Formal charge, FC, is an arbitrary property. We define the formal charge on a specific atom by

FC = *number of outer shell electrons on the free atom*

$-$*number of non-bonded electrons on the atom in the molecule*

$-1/2$ *of the number of bonding electrons around the atom.*

For structures (I) and (II), respectively, we find the formal charges:

$$FC_H = 1 - 0 - \frac{1}{2}(2) = 0 \qquad FC_H = 1 - 0 - \frac{1}{2}(2) = 0$$

$$FC_N = 5 - 4 - \frac{1}{2}(4) = -1 \qquad FC_O = 6 - 6 - \frac{1}{2}(2) = -1$$

$$FC_N = 5 - 0 - \frac{1}{2}(8) = 1 \qquad FC_N = 5 - 2 - \frac{1}{2}(6) = 0$$

$$FC_O = 6 - 6 - \frac{1}{2}(2) = -1 \qquad FC_N = 5 - 0 - \frac{1}{2}(8) = 1$$

$$FC_O = 6 - 4 - \frac{1}{2}(4) = 0$$

(I) (II)
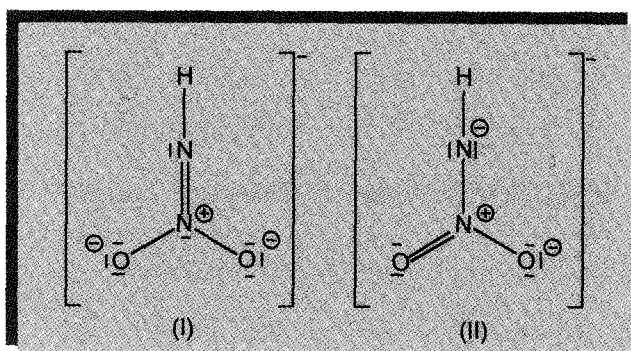
A calculation identical to that for (II) may be made for (III).

We have three "rules" to assist in the assignment of the contributions of each structure to the observed structure:

(i) Electroneutrality is preferred, so that the "best" structure has no formal charge at all.

(ii) We wish to minimize the formal charges, so that charges of ±1 are preferable to ±2, etc. Negative charges are preferably positioned on more electronegative elements.

(iii) Opposite charges should be as close as possible, while like charges should be as far apart as possible.

Based on these criteria, we conclude that structure (I) is more important or contributes a larger fraction to the observed structure. We base this on assigning negative formal charges to oxygen rather than nitrogen atoms. The final assignment of the order of weight given to the structures is (I) > (II) = (III).

We conclude by asking "how well does the Lewis dot structure formalism satisfy our criteria for a satisfactory bonding theory?" The obvious answer is "not very well". It will predict the correct molecular formula, but does not address geometry or the rationale for bonding. We'll improve our bonding theories in the next chapter.

This page is intentionally left blank

Valence Shell Electron Pair Repulsion

One way to deal with the specific geometry of a molecule is to return to Coulomb's law, that is, to look at electron–electron repulsion. VSEPR is such an electrostatic theory of bonding. As with Lewis dot structures, it ignores specific orbitals. The observed geometry reflects the attempt to minimize electron–electron repulsion by maximizing the distance between electrons. Bond angles are determined solely by the number of valence electrons around a central atom. It is instructive to use examples:

(1) BeH_2: Be has two valence electrons, so that the maximum separation between two electrons is $180°$, leading to a linear geometry when the molecule is formed:
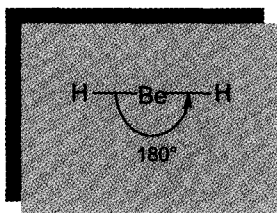
(2) BH_3: B has three valence electrons with a maximum separation of $120°$, leading to a trigonal molecular geometry:
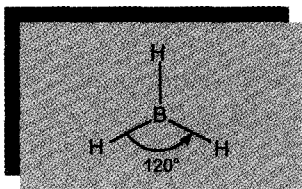
(3) SF_6: S has an "expanded" octet, that is, it can "use" d-orbitals since $Z > 10$. Therefore, using the broadest version of the Lewis dot structure rules, S has six available electrons and can form molecules using six equivalent bonds, 90° apart with octahedral geometry:
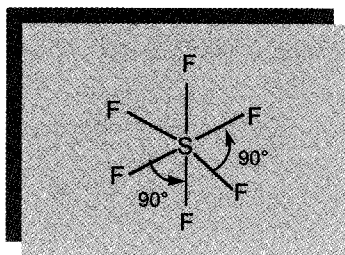
(4) We saw PCl_5 earlier. The bond angles are not equivalent. The geometry is called trigonal bipyramidal, where the equatorial bonds are 120° apart and the axial bonds are 90° from the equatorial:
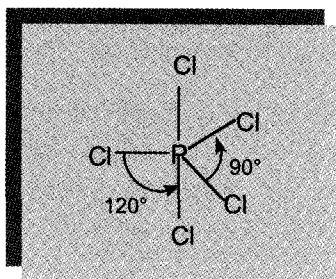
Recall an earlier discussion of the bonding in ammonia. The nitrogen atom has a non-bonding pair of electrons. How does this change the geometry according to the VSEPR model? We treat the pair of electrons as a "bond" for purposes of assigning an *ideal* or *hypothetical geometry*. We consider NH_3 to have four "bonds". The maximum separation would arrange the bonds in a regular tetrahedron with bond angles of 109.5°. However, electrons not involved in bonding are not as localized in space and distort the ideal geometry. The ammonia H–N–H bond angle is less than 109.5°; approximately 107°. The observed ammonia geometry is pyramidal. Similar geometric distortions are observed in the experimental geometries of H_2O and SF_4.

    We have also seen multiply-bonded atoms. What effect do multiple bonds have on the VSEPR geometry? For purposes of geometry, we simply
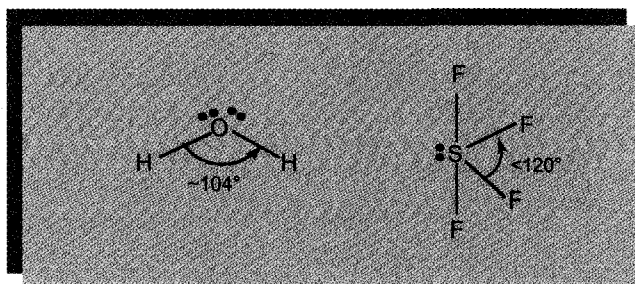
treat multiple bonds as single bonds. Consider ethylene, C_2H_4:
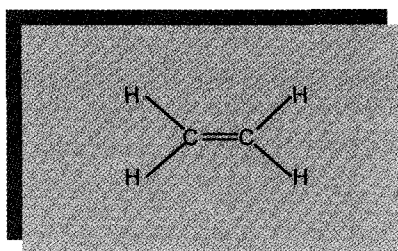
The geometry around each carbon is trigonal planar, as though only three bonds were present.

VSEPR Summary

- electron pairs around a central atom will adopt a spatial arrangement to minimize electron–electron repulsion;
- maximum repulsion occurs between two pairs of non-bonding electrons, followed by non-bonding electron interactions with bonding electrons, etc.;
- if a structure involves a 90° interaction, the most favored orientation is one with the fewest 90° nonbonding electron interactions;
- geometry is determined by the number of bonds;

molecule	number bonds	geometry	example
AX_2	2	linear	CO_2
AX_3	3	trigonal	BF_3
AX_4	4	tetrahedral	CF_4
AX_5	5	trigonal bipyramidal	PF_5
AX_6	6	octahedral	SF_6

- multiple bonds are counted as one bond; and
- non-bonding electrons are counted as a "bond" and will distort the "ideal" geometry. Compare AX_3 and AX_2:
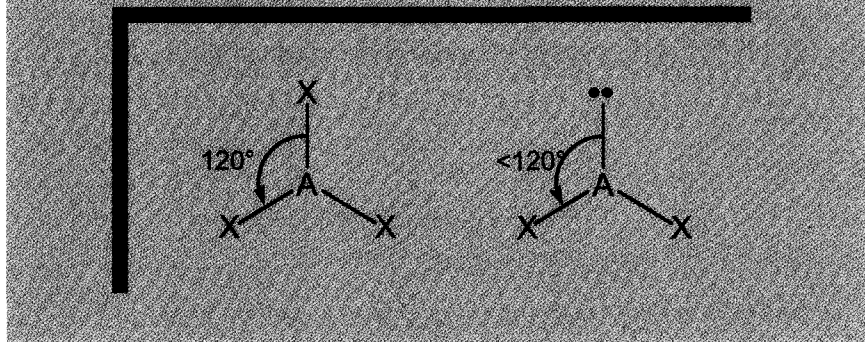
It is time to reflect on how well VSEPR satisfies the criteria for a "successful" bonding theory. Since it combines the features of Lewis dot structures (molecular formula) with a geometric prediction, we fulfill two of the three requirements, but we still have not answered the major question, that is, "What is the rationale for bonding?" Our search must continue.

The Shape of an Orbital

I have personally met students who are majoring in chemistry or physics or math and believe that those pictures of orbitals you see in every chemistry or physics book are shapes that have actually been measured or observed in some way. They are not. There is no scientific instrument that can *directly* measure the shape of an electron orbital. The reason is not merely that scientists just don't try hard enough. The reason is Heisenberg's Uncertainty Principle.

We discussed this topic earlier, but loosely stated this says that something smaller than the wavelength of light can't be "seen" by light. What does "size" mean anyway? It makes more sense to look at the experiments. If you put energy into the solitary electron of a hydrogen atom, one of two things happens:

1. nothing; or
2. a change of energy level.

In the first case, you can't "see" anything as no change has been observed. In the second case you changed the state of the electron by attempting to observe it. If you try to "see" the new state, you will just change it again. So you can never see what is actually there. To draw the analogy with the particle-in-a-box, you are trying to find out where the particle is by shaking the box. It is a method doomed to failure.

So where do all these pictures of s, p and d orbitals come from? Well, they are nothing more or less than three-dimensional graphs of the solutions to Schrödinger's equation corresponding to different choices of eigenvalues and different solutions corresponding to each choice of eigenvalue.

Let us be clear. A solution to Schrödinger's equation is a function of three spatial variables that describes the probability distribution of the position of an electron (if it is a particle and if it has a position in any meaningful

sense) as a wave form. We picture it as a cloud in three-dimensional space. The darker the cloud, the higher the distribution function is in that region and the more likely the electron is "found" there. That is why the orbitals are always portrayed as clouds.

Now, what did we learn from grinding through the complete solution to Schrödinger's equation? We learned that we can construct solutions of the form:

$$\Psi(x, y, z, t) = g(t)\,\omega(r)\,Y(\theta, \phi). \tag{17.1}$$

In such cases, Y is a spherical harmonic and ω is a product of a power of r, an exponential function, and a Legendre polynomial in r. We want to take a snapshot so time is fixed and we only care about the spatial coordinates. If we want to visualize these solutions, it is useful to think about where the functions are zero and what sorts of symmetry they have.

We begin with the simplest case, the energy level corresponding to $k = 1$. You should recall that $k = j + n + 1$ where n is the degree of Y as a polynomial and where j is the degree of the polynomial part of ω. So, in this situation, j and n are both zero. In other words, the polynomials in question are constants. This leaves only the non-polynomial part of ω free to vary, and that part is just a decreasing exponential in r. So the entire solution depends only on r and decreases exponentially away from the origin (where we placed the nucleus of the atom). This how we get our standard picture of the $1s$ orbital shown in Fig. 17.1:
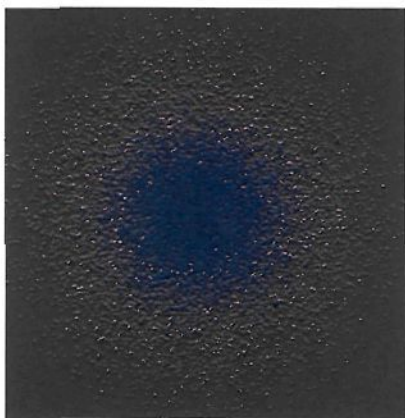
Figure 17.1. The $1s$ orbital; the nucleus is at the center of the plot.

It is necessary to return to the slight annoyance of notation here. Physicists like to call the principal quantum number "n" but mathematicians like to use "n" for the degree of the polynomial Y. So in this chapter, we are using k for the principal quantum number to be consistent with our mathematical derivation of the solutions in earlier chapters. It is k that tells you the energy level.

You can also see from this analysis that this is the only solution corresponding to $k = 1$. That is, there is only one possible orbital shape for the lowest energy level for hydrogen.

All of the s orbitals correspond to solutions where Y is constant. So the next one we want to look at is the $2s$ orbital. The principal quantum number, $k = 2$ but $n = 0$ and $j = 1$ (physics notation: $n = 2$, $l = 0$, $n_l = 0$). Our solution is still given only in terms of r, but now the associated Legendre polynomial has degree 1 and there is one value of r for which it is zero. This gives a picture with concentric shells of positive density, the $2s$ orbital shown in Fig. 17.2:

A similar discussion leads to pictures of the $3s$, $4s$, $5s$, orbitals, see Fig. 17.3, all with more and more shells of positive density as the degree of the Legendre polynomial goes up.

Of course, if the principal quantum number is 2 then it is also possible to get this by setting $n = 1$ and $j = 0$ (in physics a $2p$ orbital: $n = 2$, $l = 1$, $n_l = -1, 0, 1$). When $j = 0$, the function ω is decreasing exponentially. But if the degree of the polynomial that gives us Y is 1, then Y might
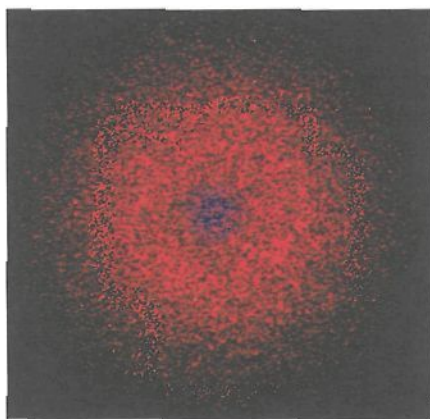
Figure 17.2. The $2s$ orbital. Note the presence of a node at the transition from blue to red.
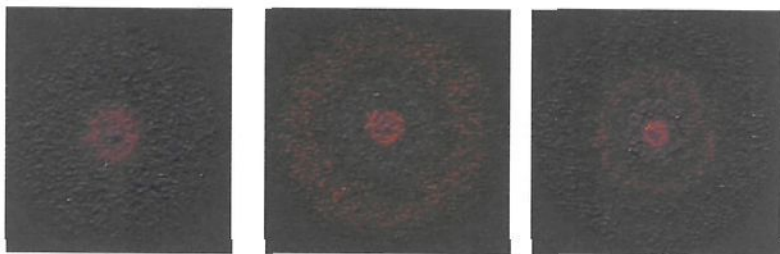
Figure 17.3. The $3s$, $4s$ and $5s$ orbitals. Note that the number of nodes increases with the increase in principal quantum number.

come from any combination of three possibilities: x, y or z. The solutions corresponding to these three are given by the relations:

$$x = r \sin \theta \cos \phi$$
$$y = r \sin \theta \sin \phi \qquad (17.2)$$
$$z = r \cos \theta,$$

so setting $r = 1$ yields three distinct candidates for Y:

$$Y = \sin \theta \cos \phi$$
$$Y = \sin \theta \sin \phi \qquad (17.3)$$
$$Y = \cos \theta.$$

If we look at the last of these, $Y = \cos \theta$ we can ask where this expression is zero and where it is largest. We know that $\cos \theta = 0$ when $\theta = \pi/2$ or $90°$ down from the positive z axis. That is, Y is zero exactly when z is zero, or on the x–y plane. If you take this piece of information and put it with the exponentially decreasing $\omega(r)$, you get a two-lobed orbital lined up with the z axis as in Fig. 17.4:

Figure 17.4. The $2p_z$ orbital: the nucleus is located at the node.
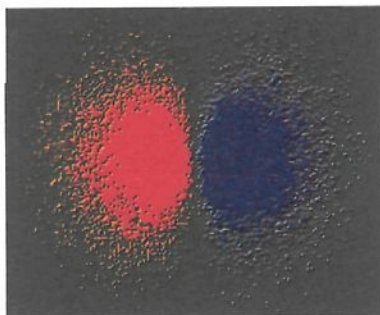
Figure 17.5. The $2p_x$ orbital. It is identical in shape to that shown in Fig. 17.4, but lies on the x-axis.

This is the $2p$ orbital. There are usually three $2p$ orbitals considered possible, and they are given by the three distinguishable solutions above. The solution that comes from the polynomial x, $Y = \sin\theta\cos\phi$ is zero when x is zero. You can use the properties of the polynomial to get this or you can actually work it out from the angular variables. It just looks like a rotated version of the last solution, see Fig. 17.5:

Because of Schur's lemma, we should not be surprised by this phenomenon. Any rotated version of a solution to Schrödinger's equation will yield another solution with the same eigenvalue (or energy level, or principal quantum number). So of course there is a third $2p$ orbital as indicated in Fig. 17.6:
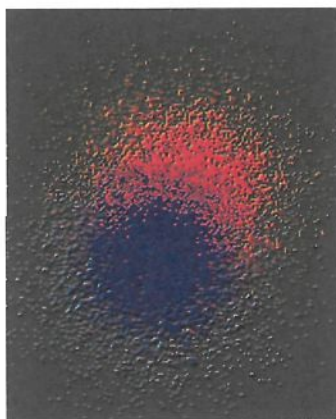
Figure 17.6. The $2p_y$ orbital.

This one is aligned with the y axis. But any orientation of a $2p$ orbital gives some kind of $2p$ orbital, so the choice of these three as standard candidates is somewhat arbitrary. On the other hand, the number 3 is the dimension of the vector space of solutions corresponding to $n = 1$, $j = 0$, so it is a very important number. Chemists use this number to determine the number of orbitals that can fit in a given atomic "shell". The number of orbitals in the shell corresponding to the principal quantum number 2 is four — one $2s$ orbital and three $2p$ orbitals.

What happens if the principal quantum number is 3? There are three ways to achieve this, with $n = 2$, 1, or 0. If $n = 0$ and $j = 2$, you get the $3s$ orbital as in Fig. 17.3. If $n = 1$ you get the same solutions for Y as you would in the case of the $2p$ orbital. Now, however, these are multiplied by Legendre polynomials of degree 1. These introduce a node at a fixed value of r. This cuts the p orbital in two by creating a sphere of zero density at this particular value of r. The result is the $3p$ orbitals, of which there are three linearly independent choices (the rest being made up by linear combinations of these three). A typical one looks like that in Fig. 17.7:

The rest are all rotated versions of this one.

Finally we should consider the case where $n = 2$ and $j = 0$ (in physics a $3d$ orbital: $n = 3$, $l = 2$, $n_l = -2, -1, 0, 1, 2$). Now there will be no radial nodes because the Legendre polynomial is constant. All the action will be in the angular variables. When $n = 2$ there are several harmonic polynomials that are easy to check: xy, yz, xz. It is easy to see where these are zero.
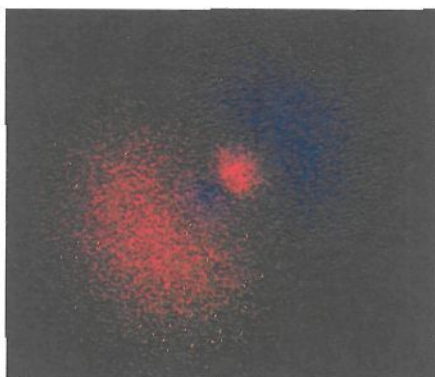
Figure 17.7. The $3p_y$ orbital. Note the presence of nodes that are not seen in the $2p_y$ orbital.
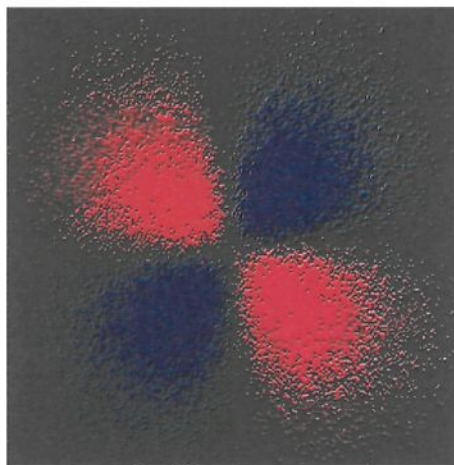
Figure 17.8. The $3d_{xy}$ orbital. This lowest energy d-orbital has two nodes. Recall that the lowest s-orbital had no nodes and the lowest p-orbital had a single node.

The first one, for example, is zero if $x = 0$ or if $y = 0$. These are the y–z and x–z planes, respectively. So the solution corresponding to xy has four lobes in each of the four quadrants of the x–y plane, The function $\omega(r)$ ensures that the distribution dies off exponentially away from the origin. The result gives a $3d$ orbital shown in Fig. 17.8:

One can rotate this picture to give the other two easy harmonic polynomials of degree 2, yz and xz. But this is not the whole story because the dimension of the space of homogeneous polynomials of degree two is 6 (given by combinations of xy, xz, yz, xx, yy, zz) and we only lose one dimension by setting

$$x^2 + y^2 + z^2 = 1. \tag{17.4}$$

We would expect five distinguishable solutions altogether. But recall that there are some subtle ones such as:

$$z^2 - \frac{1}{3}(x^2 + y^2 + z^2) \tag{17.5}$$

which reduces to

$$z^2 - \frac{1}{3} \tag{17.6}$$

Figure 17.9. The $3d_{z_2}$ orbital, which has a unique shape.

on the unit sphere. When this is put in spherical coordinates it is given by

$$G(\phi, \theta) = \cos^2(\theta) - \frac{1}{3}. \tag{17.7}$$

This solution is zero exactly when θ is at some fixed angle. So the node is a cone perpendicular to the z axis at that fixed angle. The solution corresponding to this polynomial has lobes along the z axis and also a donut shaped cloud around the z axis below the node and is shown in Fig. 17.9.

You can see from the formula that the solution doesn't depend on ϕ, therefore you see a circular symmetry around the z axis. This is one of the d orbitals frequently pictured in texts. There are two linearly independent forms of this, for a total of five possible d orbitals, no matter what energy level. So for principal quantum number three, there are five d-orbitals, three p-orbitals and one s-orbital forming a total of nine possible states. Of course you can continue this analysis for as long as you want, generating pictures and formulas for orbitals of arbitrary quantum number and complexity. Although in what follows we will not use more than the s and p orbitals, it is good to know that the mathematical machine that produced them is capable of producing many, many more.

Before we proceed with our discussion, it might be useful to point out how typical this development is in science. We have replaced our axiomatic model of electrons in shells with a much more sophisticated model derived

from Schrödinger's equation and its specific solutions. This allows us to use the shapes of orbitals, which are really the shapes of waveforms solving a particular equation, to predict bonding angles and other properties. But, we can't see the orbitals directly by any scientific experiment. They are a mathematical construction, not an observable fact. Yet, they are close enough to being correct to allow us to improve our model of how atoms bond. In fact, they represent a huge breakthrough in how we look at these very small things. What the mathematics has done is to allow our main assumption (the electron is a wave) its full predictive power. Next, we'll apply all of this information to our bonding problem.

This page is intentionally left blank

CHAPTER 18

Molecular Orbital Theory

Our quest for a bonding theory leads now to molecular orbital theory (MO theory). This is an extension of the atomic orbital theory we have just learned. If it is "correct" for atoms, we must also be able to apply it to molecules, right? We'll start with an "easy" case. Consider the simplest molecule, H_2^+, a one-electron system; the molecular analogy to the hydrogen atom. Begin with a thought experiment. Imagine that we could measure the probability density, Ψ^2, that is, the probability per unit volume of finding the electron in H_2^+. If we construct a plot of Ψ^2 as a function of the distance from the hydrogen atoms, we would see the plot shown in Fig. 18.1.

The probability of locating the electron on a line between the two nuclei is substantial. Ψ^2 is symmetric about both atoms. It is the molecular analog of the hydrogen atom orbital, a molecular orbital (MO) that we call a "sigma" orbital, σ. Now compare $\Psi^2_{H_2^+}$ with $\Psi^2_H + \Psi^2_H$ (the unbonded case) in Fig. 18.2. Formation of the bond increases the probability density between the nuclei at the expense of regions outside of that area. $\Psi^2_{H_2^+}$ decreases much faster outside of the "bond". H_2^+ has only one electron, a rather strange bond given our Lewis dot structure discussion, but Coulomb's law still applies:

$$V = -\left(\frac{e^2}{r_A} + \frac{e^2}{r_B}\right) + \frac{e^2}{r_{AB}}. \qquad (18.1)$$

The first term is electron–nucleus attraction, while the second is nuclear–nuclear repulsion. The potential energy is lowest when the electron is near one of the nuclei or close to both of them. We conclude that bond formation permits the electron to be located in a large region of space for which the energy is low. The total energy is lowered by forming the bond. We have found the rationale for bonding! Occupation of an orbital such as
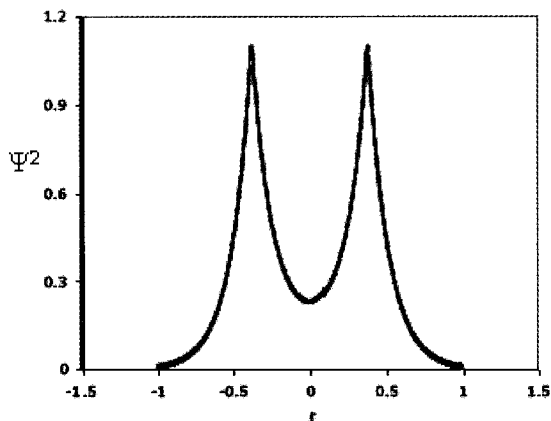
Figure 18.1. The σ_{1s} orbital for H_2^+. The hydrogen nuclei are located at the peaks in the distribution.
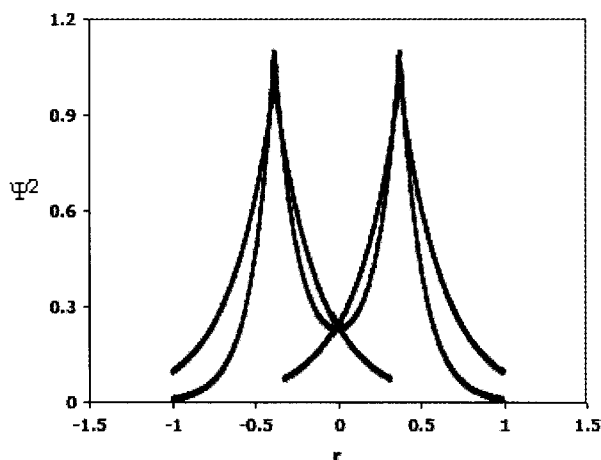
Figure 18.2. Comparison of σ_{1s} orbital (red) for H_2^+ with two H_{1s} orbitals, located at the peaks in the distribution.

that shown above leads to a stable bond. It is called a *bonding orbital*. The ground electronic state of H_2^+ has the single electron in this orbital.

Let's go back to our thought experiment. We can create the first excited state of H_2^+. Look at this probability density plot in Fig. 18.3.
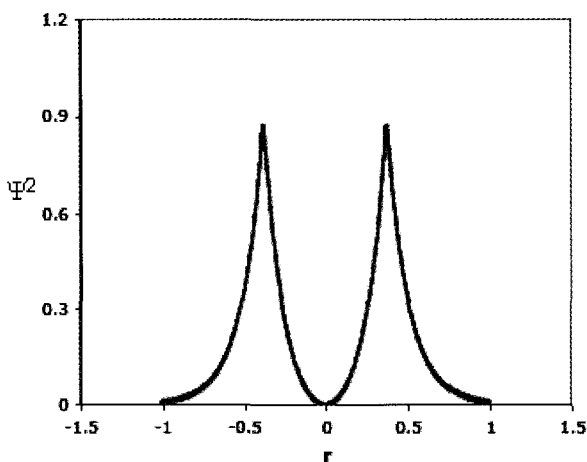
Figure 18.3. The σ_{1s}^* orbital for H_2^+.

Now, the probability density between the two hydrogen atoms is very small, almost zero. So, the electron is most likely to be found somewhere other than between the nuclei. This orbital does not lead to a stable bond and we expect dissociation to $H + H^+$. This is an *antibonding orbital*. We label the antibonding orbital σ_{1s}^* and the bonding orbital σ_{1s}.

The question you should now be asking is whether or not atomic orbitals have any relationship to molecular orbitals. In fact, we can form MOs from a **L**inear **C**ombination of **A**tomic **O**rbitals, MO-LCAO. Mathematically, the MO would be expressed as

$$\Psi_{\sigma_{1s}} \propto \Psi_a(1s) + \Psi_b(1s)$$

$$\Psi_{\sigma_{1s}^*} \propto \Psi_a(1s) - \Psi_b(1s),$$

$$(18.2)$$

where only normalization constants are missing. Figures 18.1–18.3 demonstrate this mathematical process. However, sometimes pictures are better than equations (only sometimes!). We could combine orbital shapes instead of wavefunctions for a symbolic representation of the formation of MOs from AOs, as we have done in Fig. 18.4.

The *Pauli Exclusion Principle* (two electrons per orbital), *Hund's Rule* (put one electron into each orbital with the same energy before pairing electrons) and the *Aufbau Principle* (fill orbitals with electrons in order from lowest energy to highest) all apply to MOs. We can draw an MO energy
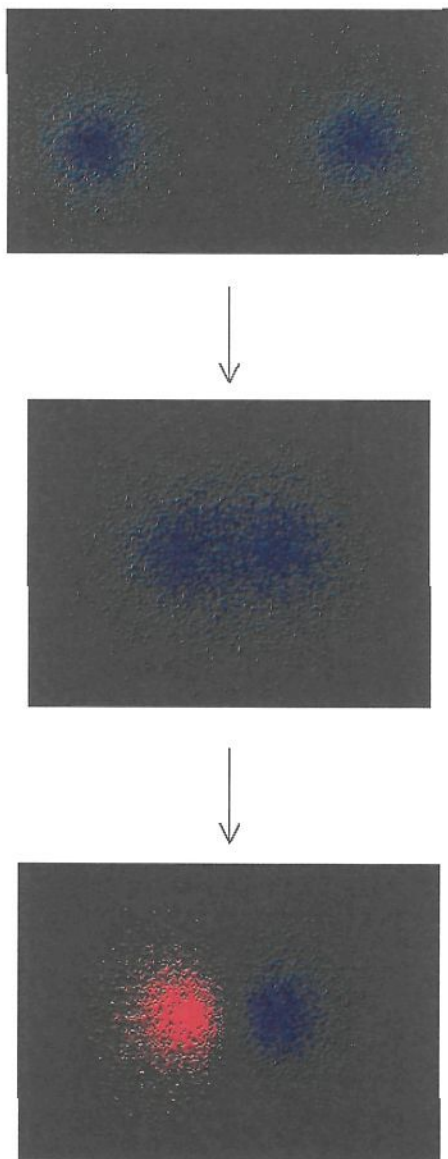
Figure 18.4. Schematic view of the formation of σ_{1s} and σ_{1s}^{*} orbitals from H_{1s} orbitals. Two separated $1s$ orbitals are shown in the top panel. If the two orbitals combine in phase (add), the bonding orbital in the middle panel is obtained. If they combine out of phase (subtract), the antibonding orbital shown in the bottom panel results.

level diagram to correlate the atomic and molecular energy levels for H_2^+ as we do in Fig. 18.5:
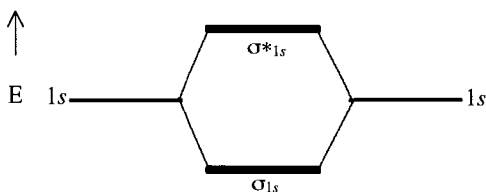
Figure 18.5. Lowest energy MOs for molecules with four or fewer electrons.

We write the H_2^+ electron configuration as σ_{1s}. Note the analogy to the hydrogen atom ground state electron configuration, denoted as $1s$ (we're simply changing the alphabet). Let's look at the electron configurations of the four simplest molecules. That is, look at those formed from atoms having only $1s$ electrons.

$$H_2^+ : \sigma_{1s} \qquad He_2^+ : \sigma_{1s}^2 \sigma_{1s}^*$$
$$H_2 : \sigma_{1s}^2 \qquad He_2 : \sigma_{1s}^2 \sigma_{1s}^{*2}$$
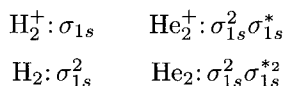
The MO electron configurations allow the following definition of bond order. Bond order (BO) is defined as

$$BO = \frac{1}{2}(number\ of\ bonding\ electrons)$$
$$-\frac{1}{2}(number\ of\ antibonding\ electrons)$$

If BO $= 1$, we have a single bond, etc. Now we can write bond orders for these molecules and correlate the bond orders with experimental bond energies (BE).

$$H_2^+ \text{ has BO} = \frac{1}{2} \text{ and } BE \sim 270\,\text{kJ mole}^{-1}$$
$$H_2 \text{ has BO} = 1 \text{ and } BE \sim 450\,\text{kJ mole}^{-1}$$

For He_2^+ and He_2, the results are BO $= \frac{1}{2}$; BE $\sim 310\,\text{kJ mole}^{-1}$ and BO $= 0$; BE $= 0$, respectively.

Bond energy is the energy required to break the bond. A larger bond energy indicates a more stable molecule. Therefore, we can make the following statements. H_2 is the most stable of these molecules because it has the highest bond energy/bond order. He_2 has a bond order of zero, so it
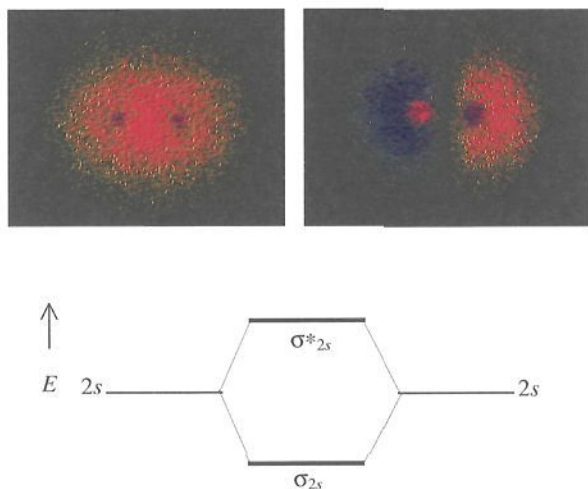
Figure 18.6. The LCAO σ_{2s} and σ_{2s}^* orbitals (top); corresponding energy level diagram (bottom).

will not exist. (Note that recent experimental results indicate that He_2 is very weakly bound, with a "bond energy" of less than $1\,kJ\,mole^{-1}$ and an effective "bond length" of 15 Å!)

The next molecules to explore are Li_2, Be_2, B_2, etc. Clearly, we need additional AOs for the construction of new MOs. The next AO is the $2s$ orbital. We might guess that we can form MOs as we did with $1s$ orbitals and that would be correct as shown in Fig. 18.6.

Since the $2s$ orbital is higher in energy than the $1s$, we expect that the σ_{2s} and σ_{2s}^* will be higher in energy than the σ_{1s} and σ_{1s}^*. Again, our expectations are valid.

Let's keep adding AOs to our scheme. The next AO is $2p$. This orbital is not spherically symmetric, so the MOs must have a different shape. We need to define an axis for the nuclei. Let's follow convention and assume that the nuclei lie on the z axis. Begin with the p_z orbital, since in this orbital lies on the internuclear axis.

$$\Psi_{\sigma_{2p_z}^*} \propto \Psi_{2p_z}(A) + \Psi_{2p_z}(B). \tag{18.3}$$

The combination, as shown in Fig. 18.7, has a decrease in probability density between the nuclei. We do not get a bonding orbital! The sum of two p_z orbitals is $\sigma_{2p_x}^*$!
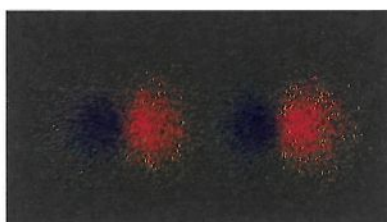
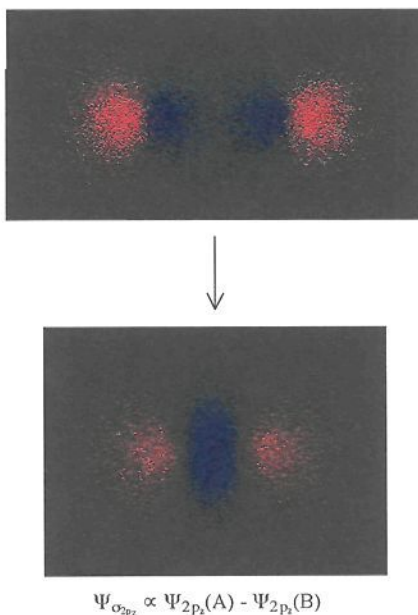$$\Psi_{\sigma_{2p_z}^*} \propto \Psi_{2p_z}(A) + \Psi_{2p_z}(B)$$

Figure 18.7. LCAO formation of σ_{2p}^* orbital. The two p-orbitals are combined in phase, but this combination corresponds to an antibonding orbital.

Now, try subtracting two p_z orbitals. If you are assuming that this will create a bonding orbital, Fig. 18.8 indicates that you are correct. This is the opposite of s-based σ orbitals!

$$\Psi_{\sigma_{2p_z}} \propto \Psi_{2p_z}(A) - \Psi_{2p_z}(B). \tag{18.4}$$

We still must combine the remaining p-orbitals into MOs. Since p orbitals have directionality, we must combine p_x with p_x and p_y with p_y. (This is because p_x has a nodal plane in the y-plane and vice versa). Let's look at the combinations of p_x orbitals and then we can generalize.

Note that in this MO, shown in Figs. 18.9 and 18.10, we have increased the probability density between the nuclei, but off the internuclear axis. This is a π-bonding orbital. We can surely suggest what will happen if we subtract two p_x orbitals. We will get a decrease in probability density between the nuclei and off the axis, a π^* or antibonding, orbital.

Now, we can combine all of this into an energy level diagram for p-orbital based MOs, as shown in Fig. 18.11.

$$\Psi_{\sigma_{2p_z}} \propto \Psi_{2p_z}(A) - \Psi_{2p_z}(B)$$

Figure 18.8. LCAO formation of σ_{2p} orbital. The two p-orbitals are combined out of phase, and this combination corresponds to a bonding orbital.
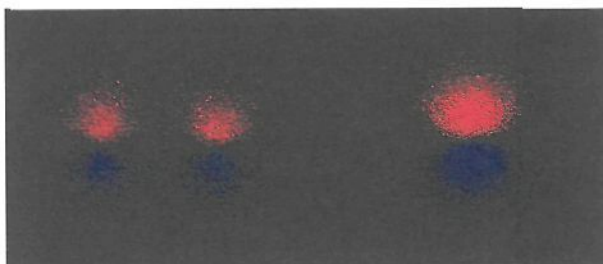
Figure 18.9. LCAO formation of π_{2p} orbital from two p_x or two p_y orbitals combined in phase.

This is a good time to review what we know so far about the LCAO-MO method. The energy of a particular MO is dependent upon:

- The type of AO — MOs from $1s$ orbitals have lower energies than those from $2s$ orbitals since $E_{1s} < E_{2s}$.
- Whether the MO is bonding or antibonding — clearly, antibonding orbitals are higher in energy than the corresponding bonding orbitals.
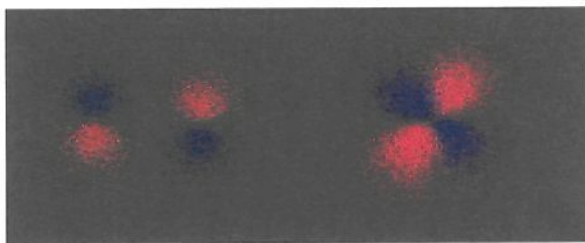
Figure 18.10. LCAO formation of $\pi*_{2p}$ orbital from two p_x or two p_y orbitals combined out of phase.
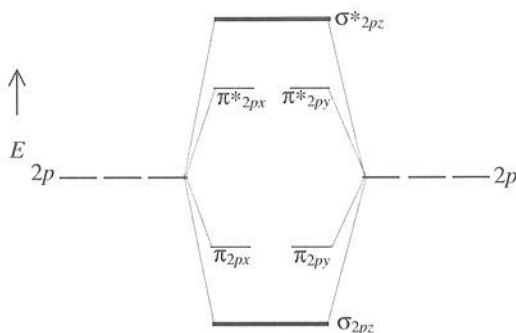
Figure 18.11. Energy level diagram for MOs formed from $2p$ orbitals.

- How well the AOs overlap — looking at the different shapes of s and p orbitals, we see that, for bonding orbitals, s orbitals will overlap to a greater extent than p orbitals. Will p_z orbitals overlap more or less than p_x and p_y? Unfortunately, there are other less obvious factors to be considered and the relative ordering of σ_{2p_z} and π_{2p_z}/π_{2p_y} orbitals is molecule-dependent.

For heavy atoms, O and F, the $2s$ and $2p$ orbitals are very different in energy and the σ_{2p_z} orbital is filled before the π_{2p} orbital. The opposite is true for the atoms Li through N. The energy levels are shown in Fig. 18.12.

The change in ordering for the light atoms is due to a repulsive interaction between σ_{2s} and σ_{2p}, which occurs because the atomic s and p orbitals are close in energy. It's time to do a few examples to make all of this concrete.

$$\sigma^*_{2pz} \text{ ——}$$

$$\pi^*_{2px} \text{ ——} \qquad \text{——} \pi^*_{2py}$$

$$\pi_{2px} \text{ ——} \qquad \text{——} \pi_{2py}$$

$$\sigma_{2pz} \text{ ——}$$

$$\sigma^*_{2s} \text{ ——}$$

$$\sigma_{2s} \text{ ——}$$

$$\sigma^*_{1s} \text{ ——}$$

$$\sigma_{1s} \text{ ——}$$

$$\sigma^*_{2pz} \text{ ——}$$

$$\pi^*_{2px} \text{ ——} \qquad \text{——} \pi^*_{2py}$$

$$\sigma_{2pz} \text{ ——}$$

$$\pi_{2px} \text{ ——} \qquad \text{——} \pi_{2py}$$

$$\sigma^*_{2s} \text{ ——}$$

$$\sigma_{2s} \text{ ——}$$

$$\sigma^*_{1s} \text{ ——}$$

$$\sigma_{1s} \text{ ——}$$
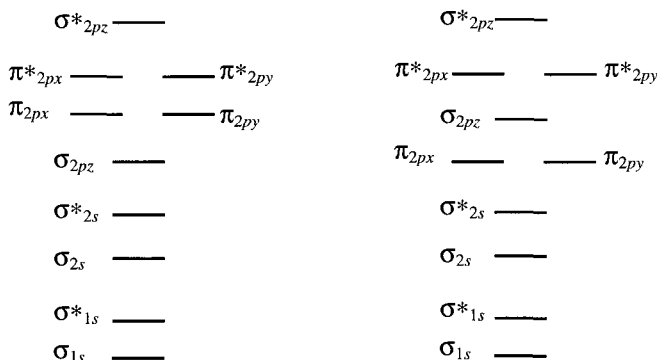
Figure 18.12. Energy level diagrams for MOs from atomic orbitals through $2p$. The ordering of the levels for both light (right) and heavy (left) atoms is shown.

Examples

O_2 has a total of 16 electrons. The electron configuration must be

$$\sigma^2_{1s}\sigma^{*2}_{1s}\sigma^2_{2s}\sigma^{*2}_{2s}\sigma^2_{2p}\pi^2_{2p_x}\pi^2_{2p_y}\pi^*_{2p_x}\pi^*_{2p_y}$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

$$\left.\begin{array}{l} \pi \text{ Bond order} = \dfrac{4-2}{2} = 1 \\[2mm] \sigma \text{ Bond order} = \dfrac{6-4}{2} = 1 \end{array}\right\} \text{ one } \sigma \text{ and one } \pi \text{ bond}$$

There are two unpaired electrons in O_2, so it will be **paramagnetic** (a molecule with all electrons paired is **diamagnetic**, that is, not magnetic).

N_2 has fourteen total electrons. The configuration is:

$$\sigma^2_{1s}\sigma^{*2}_{1s}\sigma^2_{2s}\sigma^{*2}_{2s}\pi^2_{2p_x}\pi^2_{2p_y}\sigma^2_{2p}$$

$$\text{Bond order} = \frac{10-4}{2} = 3 \text{ with one } \sigma \text{ and two } \pi \text{ bonds.}$$

All of the electrons are paired, so nitrogen will be a diamagnetic molecule.

An aside: We can check the magnetic predictions by pouring liquid O_2 and liquid N_2 through a magnet. The O_2 should be attracted to the poles, but not the N_2.

This analysis is valid for ions as well as molecules. Let's compare the bonding in N_2 with that in N_2^+ and N_2^-.

$$N_2^+ \text{ (13 electrons) } \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^2 \pi_{2p_y}^2 \sigma_{2p}$$

Ionization removes a bonding electron, so the bond order = 2.5.

$$N_2^- \text{ (15 electrons)} \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^2 \pi_{2p_y}^2 \sigma_{2p}^2 \pi_{2p}^*$$

The additional electron is placed in an antibonding orbital, so that the bond order = 2.5. N_2^+ and N_2^- have approximately the same bond energy.

We have restricted all of this to homonuclear diatomic molecules. These are obviously a very small subset of the possible diatomic molecules. It is time to move on to heteronuclear molecules. We already know what needs to be considered. Let's write some configurations first, then look at the MOs in detail.

Molecule	Configuration	Bond Order
CN (13 electrons)	$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_x}^4 \sigma_{2p}$	2.5
CO (14 electrons)	$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4$	3
NO (15 electrons)	$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^*$	2.5

We need to compare heteronuclear and homonuclear results. Are N_2 and CO really the same, since they are isoelectronic? Isoelectronic molecules have the same number of electrons and the same electron configuration. We can make this comparison graphically, in Fig. 18.13.

$$\Psi_{\sigma_{1s}} = c_A \psi_{1s}(A) + c_B \psi_{1s}(B); \quad c_A = c_B = 0.5, \tag{18.5}$$

$$\Psi_{\sigma_{1s}} = c_A \psi_{1s}(C) + c_B \psi_{1s}(O); \quad c_B > c_A. \tag{18.6}$$

The asymmetry in the CO probability density is due to the difference in AO energies and correlates with electronegativity; probability density is greater near the more electronegative atom. The MO energy diagram for CO, shown below, reflects this difference. The bonding MO energy is closer
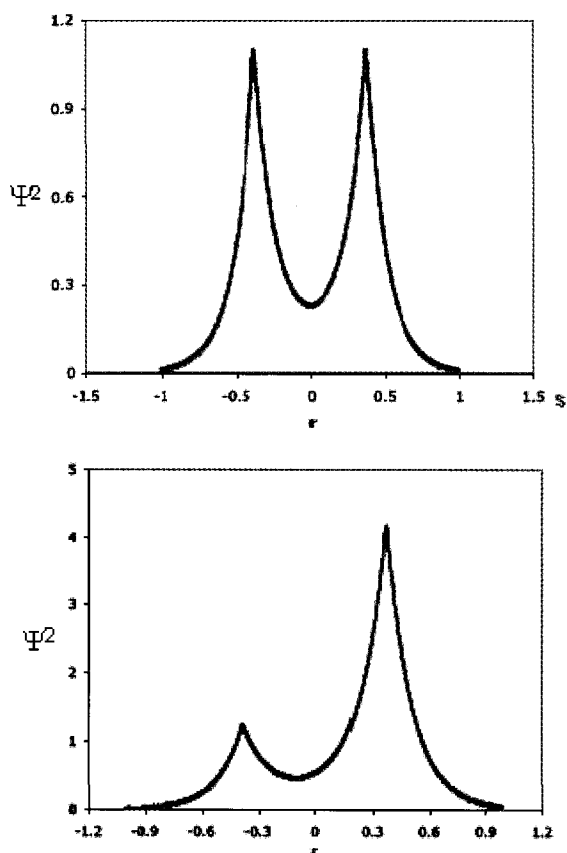
Figure 18.13. LCAO formation of σ_{1s} orbitals for N_2 (top) and CO (bottom).

to the oxygen AO energy, while antibonding MO energy is closer to the carbon AO energy, see Fig. 18.14.

Let's look at an extreme example of this asymmetry, the nearly ionic molecule HF. The first step is to determine the orbital energies so that we can decide which AOs will combine.

$$H_{1s}: -1310\,\text{kJ mole}^{-1} \quad F_{1s}: -42000\,\text{kJ mole}^{-1}$$
$$F_{2s}: -3400\,\text{kJ mole}^{-1}$$
$$F_{2p}: -1400\,\text{kJ mole}^{-1}$$

F_{1s} will not combine with H_{1s} because the energy of the fluorine orbital is so low. An energy mismatch also occurs between the F_{2s} and H_{1s} orbitals. The bond must form by combining the H_{1s} and F_{2p} orbitals. To produce
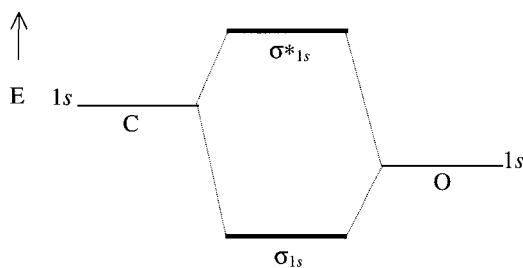
Figure 18.14. CO molecular orbital energies for σ_{1s} and σ_{1s} orbitals.
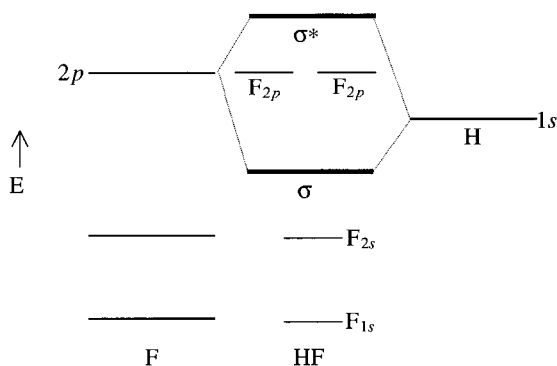
Figure 18.15. HF molecular orbital energies.

a σ orbital, we can only combine F_{2p_z} with H_{1s}, with the resulting energy diagram shown in Fig. 18.15.

HF has a total of ten electrons. Using the Pauli exclusion principle and the Aufbau principle, we fill the orbitals with electrons starting from the lowest orbital. The resulting electron configuration is

$$F_{1s}^2 F_{2s}^2 \sigma^2 F_{2p_x}^2 F_{2p_y}^2.$$

The bond order is one and the F_{1s}, F_{2s} and F_{2p} orbitals are all nonbonding orbitals (that is, neither bonding nor antibonding).

To review, we have found a successful bonding model! MO theory provides us with the important rationale for bonding. It directly provides a numerical result for the lowering of the energy that occurs when bonds form from atoms. It also provides structural details for the molecule. MO theory has proven quite successful and is the most widely used model for the formation of molecules.

This page is intentionally left blank

CHAPTER 19

Valence Bond Theory

We have listed this as a separate bonding model, but in reality this is not a different theory. We can make VB theory take the same mathematical form as MO theory, if we wish. However, this defeats its major benefit: a physical picture of bonding in large (especially organic) molecules. As always, we begin with something simple. In this case, we start with BeH_2. We already know that the H–Be–H bond angle is 180°. Be has two valence electrons; a $1s^2 2s^2$ configuration. Since all of the electrons are paired, we can only imagine forming two bonds (actually, we can't imagine forming any bonds without changing the electron configuration) by unpairing the $2s$ electrons, so that the electron configuration becomes $1s^2 2s 2p$. But how can this help? There are two problems:

(i) $2p$ electrons are higher in energy than $2s$, so how can we justify unpairing the electrons?

(ii) How can we get two equivalent bonds from a $1s^2 2s 2p$ electron configuration?

The solution to both of these difficulties is to use hybrid *atomic* orbitals. It is best to view these pictorially as in Fig. 19.1.

The two sp orbitals then combine with two H ($1s$) orbitals to form two bonds, 180° apart. The two σ bonds will be equivalent since each consists of an overlap between a Be (sp) orbital and a H ($1s$) orbital.

Hybrid atomic orbitals are mathematical combinations of the "normal" atomic orbitals. They are as "real" as hydrogen-like AOs! Hybrid orbitals are an effective way to describe multielectron/multiatom systems, i.e. molecules. They are extremely useful in organic chemistry since the molecules are too large to treat with MO theory *and* extract a physical picture.
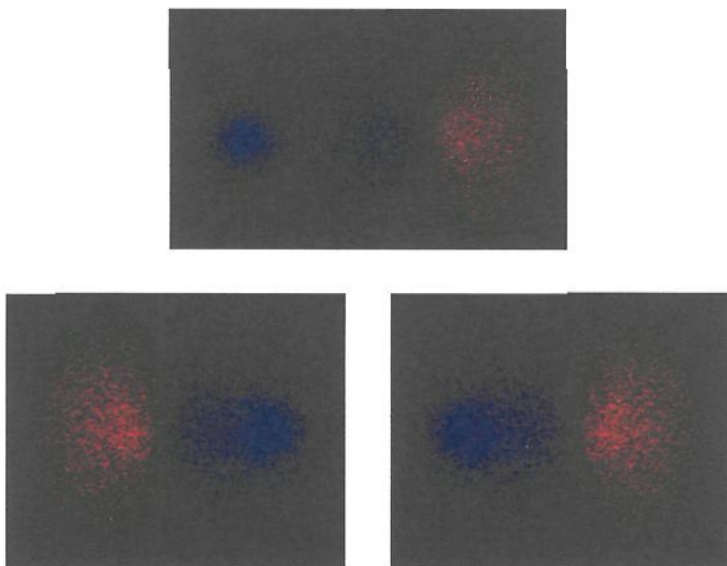
Figure 19.1. Schematic for formation of sp hybrid orbitals in Be. The top panel shows the s and p orbitals at a large distance and the bottom panel shows the two hybrid orbitals formed by the sum and difference of the two atomic orbitals. They point $180°$ apart.

Let's look at a more complex molecule and explore the energetics of the bonding process. We'll do a thought experiment and construct a mechanism for the formation of CH_4. Remember, it does not actually form this way. This is only an attempt to rationalize observations. Our mechanism:

(i) start with ground state carbon ($1s^2 2s^2 2p^2$) and four ground state hydrogens ($1s$);

(ii) promote a carbon $2s$ electron to the $2p$ orbital, the configuration becomes $1s^2 2s 2p^3$ and we have four half-filled orbitals;

(iii) use the $2s 2p^3$ electrons to form 4 sp^3 hybrid orbitals; and

(iv) form CH_4 from this configuration.

The process is shown on the energy level diagram, Fig. 19.2.

In our "mechanism", we must have an energy input of $406 \, \text{kJ} \, \text{mol}^{-1}$, but the hybridization process is cost-free in terms of energy. The endoergic process of forming sp^3 orbitals leads to formation of four C–H bonds and an energy lowering of $2068 \, \text{kJ} \, \text{mol}^{-1}$. The net energy change for the overall "mechanism" is more exoergic than it would be if we simply formed CH_2
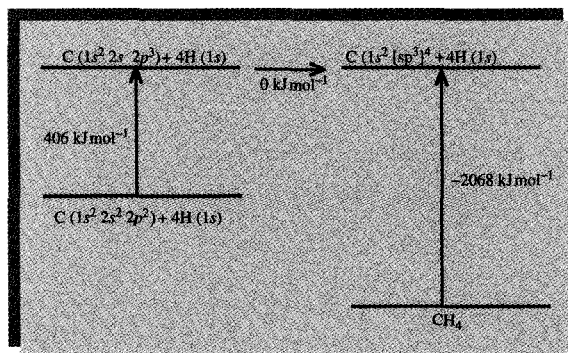
Figure 19.2. Schematic mechanism for formation of CH_4.
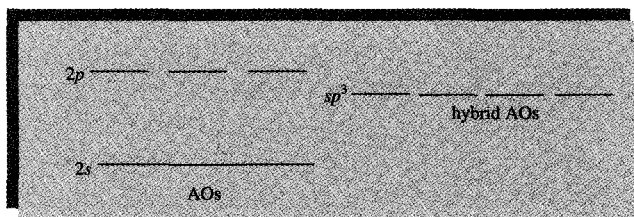
Figure 19.3. Relative ordering of $2s/2p$ atomic and sp^3 hybrid orbitals.

from the ground state carbon atom. In the carbon molecule, the hybrid orbital is $1/4s$ and $3/4p$. The energy of the sp^3 orbital is $3/4$ of the energy of the $2p$, as can be seen in Fig. 19.3.

In the end, for simple molecules, much like VSEPR we have an orbital hybridization based solely on the number of bonds. (We treat non-bonding pairs of electrons as "bonds" and multiple bonds as one; just as in VSEPR). The fundamental difference in comparison to VSEPR is that we now have a theoretical basis for the assignment.

σ bonding electron pairs	hybrid orbitals	ideal geometry
2	sp	linear
3	sp^2	trigonal
4	sp^3	tetrahedral
5	dsp^3	trigonal bipyramidal
6	d^2sp^3	octahedral

Examples of VB Model Application

(1) Nitrogen, N_2

- Begin with Lewis dot structure

$$:N{\equiv}N:$$
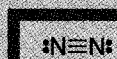
- Each atom has one sigma bond plus one non-bonding pair of electrons, so the hybrid orbitals will be sp.
- The original electron configuration is $1s^2 2s^2 2p^3$
- The hybrid orbital configuration is $1s^2(sp)^3 2p_x 2p_y$ for each N atom.
- One of the sp hybrid orbitals is filled with a non-bonding pair of electrons and the second overlaps the sp orbital from the other N to form a σ bond.
- The two π bonds are formed by overlap of p_x orbitals from the two N atoms with a pair of p_y orbitals.

(2) Acetylene, C_2H_2

- Each C has two "bonds" by our definition. Therefore, we expect sp hybrid orbitals in the molecule for each C.
- The orbital configuration becomes $C(1s^2 \ (sp)^2 p_x p_y)$.
- σ bonds form by overlap of a $H(1s)$ with an sp orbital on each C and between the two C atoms using overlap of an sp orbital from each C.

$$\left.\begin{array}{l} C_{sp}^{(A)}-C_{sp}^{(B)} \\[4pt] C_{sp}^{(A)}-H \\[4pt] C_{sp}^{(B)}-H \end{array}\right\} \sigma \text{ bonds}$$

$$\left.\begin{array}{l} p_{2p_x}^{(A)}-p_{2p_x}^{(B)} \\[4pt] p_{2p_y}^{(A)}-p_{2p_y}^{(B)} \end{array}\right\} s \text{ bonds}$$
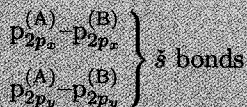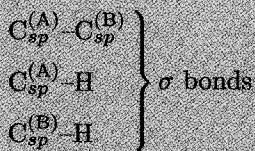
- The π orbitals lock in the geometry. It is not possible to rotate the carbon atoms and maintain the orientation of the p orbitals needed for π bonds. The π bonds are oriented $90°$ apart.

(3) Ethylene, C_2H_4

- There are three pairs of electrons around each C atom. These are used in the σ bonding framework.
- The carbon hybrid electron configuration is $1s^2\,(sp^2)^3 p_x$

$$
\left.
\begin{array}{ll}
C^{(A)}_{sp^2}\text{–}H(1s) & C^{(B)}_{sp^2}\text{–}H(1s) \\[4pt]
C^{(A)}_{sp^2}\ H(1s) & C^{(B)}_{sp^2}\text{–}H(1s) \\[4pt]
C^{(A)}_{sp^2}\text{–}C^{(B)}_{sp^2} &
\end{array}
\right\} \sigma \text{ bonds}
$$

$$
\left.
C^{(A)}_{Px}\text{–}C^{(B)}_{Px}
\right\} \check{s} \text{ bond}
$$
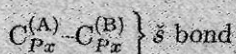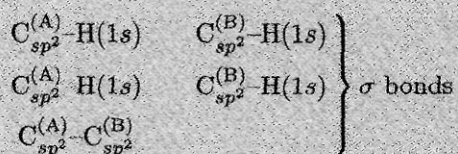
- Again, the π orbital "locks" in the geometry. Since p_x must overlap with p_x, we get a planar geometry. Ethane (C_2H_6) has no π bonds and may freely rotate. Ethane involves C with sp^3 hybrid orbitals.

This page is intentionally left blank

Other Kinds of Bonding

Hydrogen bonds occur in the most polar molecules. That is, those molecules containing the elements with the largest electronegativity: N, O and F. These are not truly bonds in the sense that we have been using that term. Hydrogen has only a single electron involved in bonding. It can closely approach an electronegative atom without any electron–electron repulsion. This interaction is what we call a hydrogen bond. The bonds are a result of the skewed electron distribution in these molecules. One end is essentially positive and the other is essentially negative. For example, look at HF, where dimers are dominant.
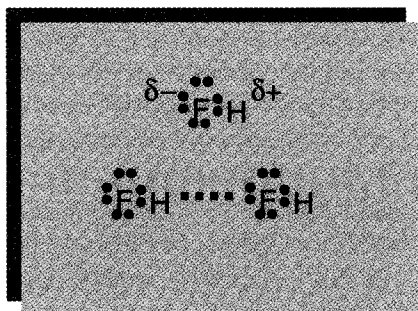
Hydrogen bonds occur in all phases: solid, liquids and gases. Typical hydrogen bond energies are less than $60\,\text{kJ}\,\text{mol}^{-1}$ and bond lengths are approximately $2\,\text{Å}$. Compare those values with a typical covalent bond, where the bond energy is 400–$500\,\text{kJ}\,\text{mol}^{-1}$ and bond lengths are 1.0–$1.3\,\text{Å}$.

Hydrogen bonding is most evident in the determination of boiling points of hydrogen containing molecules. Specifically, compare the boiling points of the hydrides of Groups IV, VI and VII

CH_4	$-170°C$	H_2O	$100°C$	HF	$20°C$
SiH_4	$-110°C$	H_2S	$-60°C$	HCl	$-90°C$
GeH_4	$-95°C$	H_2Se	$-40°C$	HBr	$-70°C$
SnH_4	$-50°C$	H_2Te	$0°C$	HI	$-40°C$

Group IV on the left is our control. As one goes down the Periodic Table, T_{bp} increases. Groups VI and VII exhibit the same trend, except for H_2O and HF. These are the hydrogen-bonded molecules. Without hydrogen bonding, we predict H_2O would boil at $\sim -80°C$! The need to "break" hydrogen bonds contributes to $\Delta H°_{vap}$ and causes an increase in T_{bp}. Hydrogen bonding leads to order in liquids and solids. For example, we have the "Mickey Mouse" model of hydrogen bonding in H_2O, as shown in Fig. 20.1.

Similar, but weaker, interactions occur between other atoms and molecules. What are the forces that cause molecules to be attracted to each other? How are liquids "held" together? The answer is that these processes occur via intermolecular forces — they are much weaker than covalent or ionic bonds, or even hydrogen bonds. We'll look at a series of interactions of varying strength and apply the results to experimental observations.

The first type is a general class called *van der Waals forces*. There are actually several specific types of interactions. They are responsible for deviations from ideal gas behavior at high temperatures and low pressures and also for condensation of gases at sufficiently low temperatures.
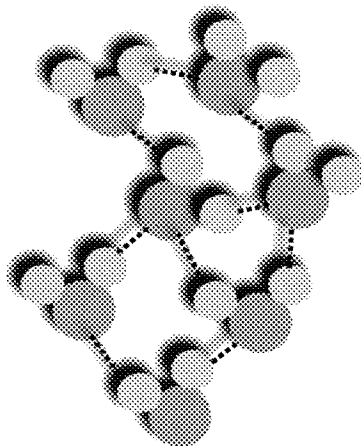
Figure 20.1. Schematic representation of the hydrogen-bonded structure of liquid water.

charge polarization
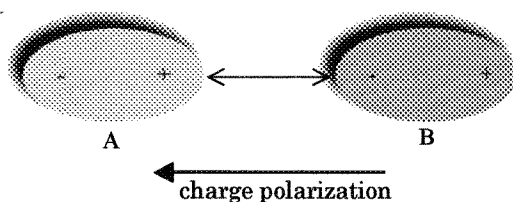
Figure 20.2. Schematic representation of induced polarization.

(1) The *London dispersion force* is depicted in Fig. 20.2.
A momentary fluctuation in the charge distribution of A induces charge polarization on B and this results in an electrostatic attraction. The strength of the interaction is given by

$$V_L = -\frac{A}{r^6}. \tag{20.1}$$

Compare this result with Coulombic forces in ionic bonds, which scale as $1/r$. London forces are operative over a very small range of r. The constant A includes the polarizability of the molecule. It is a measure of the extent of distortion of the electron cloud of an atom by the electric field of nearby atoms. Large atoms generally have the highest polarizability. This occurs because electrons far from the nucleus are more loosely held. Shapes of molecules also effect polarizability; spherical molecules are less polarizable than elongated molecules.

(2) *Dipole–dipole interactions* are stronger than dispersion forces. The drawing in Fig. 20.3 will provide a visual clue to the nature of these interactions. If two molecules are polar and come together, there is an attractive interaction (provided that the alignment is correct). The potential energy has the same form as in (1), but the constant A now depends on the dipole moment rather than the polarizability.

(3) *Repulsive interactions* are operative only at very small intermolecular separations. When molecules approach too closely, electrons in filled atomic orbitals begin to overlap and repel one another. The potential energy is given by

$$V = \frac{B}{r^{12}}. \tag{20.2}$$

We can combine the London attractive term with this repulsive term to construct a realistic potential energy function known as the *Lennard–Jones*
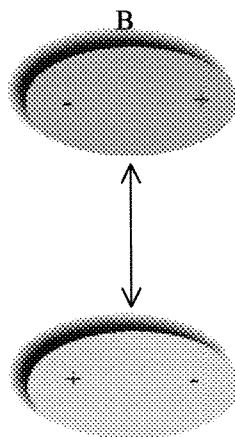
Figure 20.3. Schematic representation of dipole–dipole interactions.

potential shown in Fig. 20.4:

$$V = -\frac{A}{r^6} + \frac{B}{r^{12}} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]. \tag{20.3}$$

The constant ε is the minimum potential energy and σ is the separation at which the potential energy becomes positive. The values of ε are the formal equivalent of bond energies. However, a bond energy is typically $430\,\mathrm{kJ\,mol^{-1}}$ (say for H_2) while ε is $0.3\,\mathrm{kJ\,mol^{-1}}$ (for H_2–H_2). The values
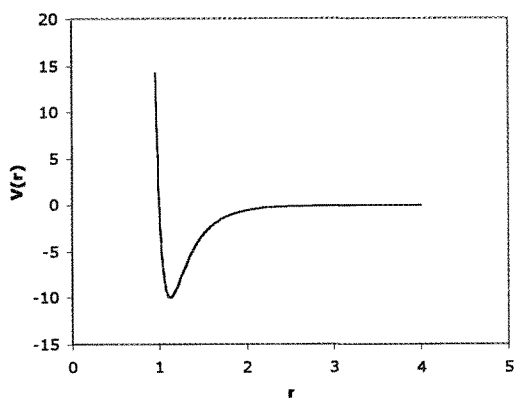
Figure 20.4. The generic Lennard–Jones potential function.
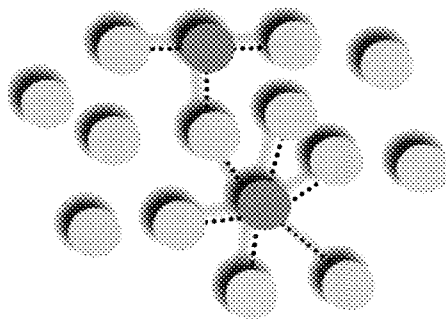
Figure 20.5. IMF and the macroscopic effect of surface tension.

of σ orrespond to the sum of the van der Waals radii of the atoms. We "measure" these effects by determining T_{mp} and T_{bp}.

Intermolecular forces (IMF) also have macroscopic manifestations. Now, we can take a more macroscopic look at these forces. What do we see when we look at liquids or solids rather than individual pairs of atoms or molecules as in the gas phase?

Why do liquids appear as droplets? Let's look at Fig. 20.5.

Focus on the dark molecules. A molecule in the interior experiences a number of attractive interactions from all sides, while a molecule at the surface has fewer possible interactions. The net effect is to pull molecules toward the center, leaving the droplet with a minimum of surface area, that is, a spherical shape. To increase surface area, molecules must move from the interior to the surface. This requires energy since an IMF must be overcome. The resistance to the increase in surface area is *surface tension*. The larger the IMF, the higher the surface tension. These are *cohesive* forces.

Liquids exhibit capillary action. This is the spontaneous rising of a liquid in a small diameter tube. If the molecules of liquid are polar and the tube has a surface with polar bonds (like glass), we observe *adhesive forces* (glass has dangling oxygen atoms with a partial negative charges, which attract the positive end of the H_2O dipole). Water "climbs up" the tube at the walls, but cohesive forces try to pull H_2O away from the walls. There is a balancing effect and we see a *meniscus*. Note that there are two possible shapes, shown in Fig. 20.6.
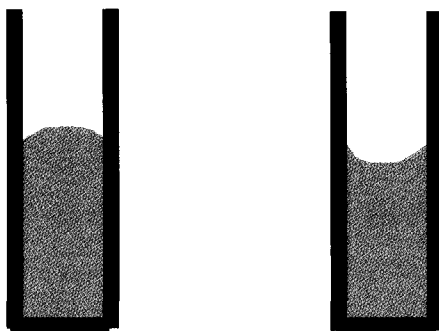
Figure 20.6. The meniscus: convex (left) and concave (right).

A *concave meniscus* occurs in a liquid in which the adhesive forces are greater than the cohesive forces. The liquid climbs to a height where the weight of liquid column balances the attraction to the walls.

A *convex meniscus* occurs in a liquid in which the cohesive forces are greater than the adhesive forces (an example is mercury in a glass tube).

CHAPTER 21

Case Study: Dye Molecules

So, we have completed our journey through basic quantum theory and the application to chemical structure. Is there some way that all of this material can be tied together in an application? Of course, and we'll use extremes: a simple quantum model (the one-dimensional particle-in-a-box) and a very large, complex dye molecule. I'm sure that the particle-in-a-box, especially in one-dimension, seemed useless at the time we developed it. It turns out that it is an excellent model for conjugated (we'll see what that means in a moment) molecules. In short, the dye molecules constitute a *case study* in quantum mechanics and case studies are an excellent way to explore what we have learned in science or any other area of knowledge.

The color of most dyes is due to the interaction between visible light and the atoms (or more correctly, the electrons in the atoms) that make up the molecules. It is a dynamic interaction. Light is continuously absorbed promoting electrons to higher stationary states. The electrons subsequently drop back into the ground state configuration and repeat the cycle. The color we see is that of the incident white light *minus* the absorbed wavelengths. Recall that light will be absorbed only when its energy corresponds to the energy difference between the ground state and some excited state of the molecule,

$$E_{\text{absorbed}} = E_{\text{excited state}} - E_{\text{ground state}} \qquad (21.1)$$

If we wish to predict the absorption spectrum of a molecule, we must know the energy levels of the molecule. Sadly, the hydrogen atom is the only "real" atomic/molecular system for which an analytic solution is known. Luckily for us, for the proper choice of molecule, some of the simpler quantum mechanical models are valid. I guess that means we must select the molecule to fit the theory! But our purpose here is to develop a case study, so we'll accept that and apply the one-dimensional particle-in-a-box model to a

specific type of dye known as a polyene. The model was discussed in detail in Chapter 7 and the analogous vibrating string in Chapter 8. There is no need to repeat those details here. But what is a polyene and how (and why) does it fit the ideal of the square well?

A stylized polyene is shown in the drawing below. In this picture, the molecule is terminated by substituted six-membered rings. The long chain
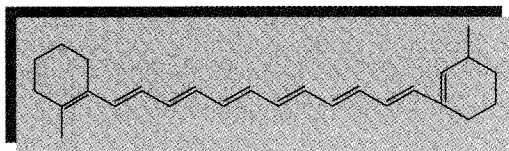
of double bonds represents a *conjugated system* and we'll see that this is our one-dimensional "box". To understand conjugation and the meaning of the chemist's shorthand drawing shown above, we'll look at a smaller molecule that is a fragment of the polyene shown above. This molecule is known as 1,4-butadiene.
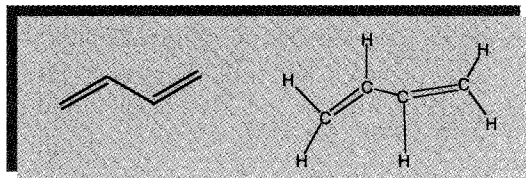
On the left is a shorthand representation as we saw for the polyene. On the right is the equivalent drawing in all of its glory. Using this conversion, you may see what symbols are assumed in the polyene drawing. The important feature in the butadiene molecule is the alternating single and double bonds. This is *conjugation.* For a better understanding of what this means, we can refer to the *p*-orbitals on the carbon atoms. Linear combinations of these orbitals make up the molecular π-orbitals (see Chapter 19), as shown.
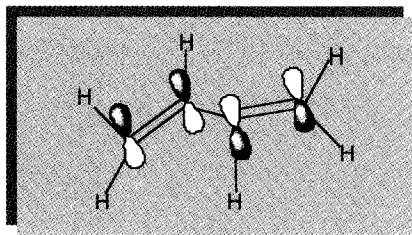
Each carbon atom contributes one electron to the π-orbitals; four carbon atoms means four π-electrons. Since electrons are indistinguishable, we may assume that these four electrons as distributed over the entire four carbon chain. Or, if we are attempting to apply a simple model, these four electrons are in a one-dimensional box with a length equal to the length of the carbon chain. And you probably thought that this simple model was one of these cases of use only in a lecture, not in the real world!

So, a polyene is simply a long chain of alternating single and double bonds; a conjugated system. In our example, there are 16 π-electrons, but the box length is rather undefined. Why? Resonance structures exist and the π system is not really a linear chain.
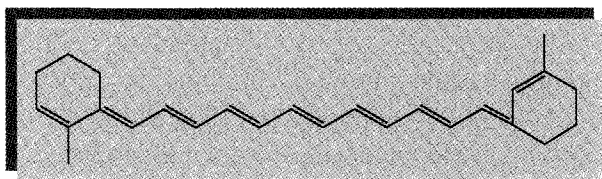
Let's begin the case study and work with something "real". This is an easy experiment to try out. We'll use data that we can take in the lab. The molecules are called cyanine dyes. We'll use three different ones with the following structures, imaginatively labeled A, B and C.

The only difference among these three dye molecules is the length of the carbon chain connecting the two rings. The π-electron system "box" extends from nitrogen to nitrogen across the molecules. The dyes have six, eight and ten π-electrons, respectively, in the box. How big are the boxes? Time for simplifying assumptions: each bond in the chain has an average length of 0.140 nm and we will extend the box one bond beyond each nitrogen atom as did Hans Kuhn (*Journal of Chemical Physics* **17**, 1198 (1949) who first did this type of calculation. So the boxes are 0.84 nm, 1.12 nm and 1.40 nm, respectively.

Recall the expression for the energy of an electron in a one-dimensional box and the resulting energy levels (Chapter 7)

$$E = \frac{n^2 h^2}{8mL^2}, \quad n = 1, 2, 3, \ldots \tag{21.2}$$

There are two electrons per energy level, so levels up to $n = 3, 4$ and 5 are filled for dyes A, B and C, respectively. If the lowest energy transitions
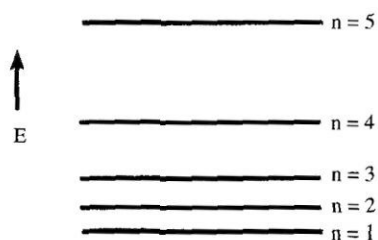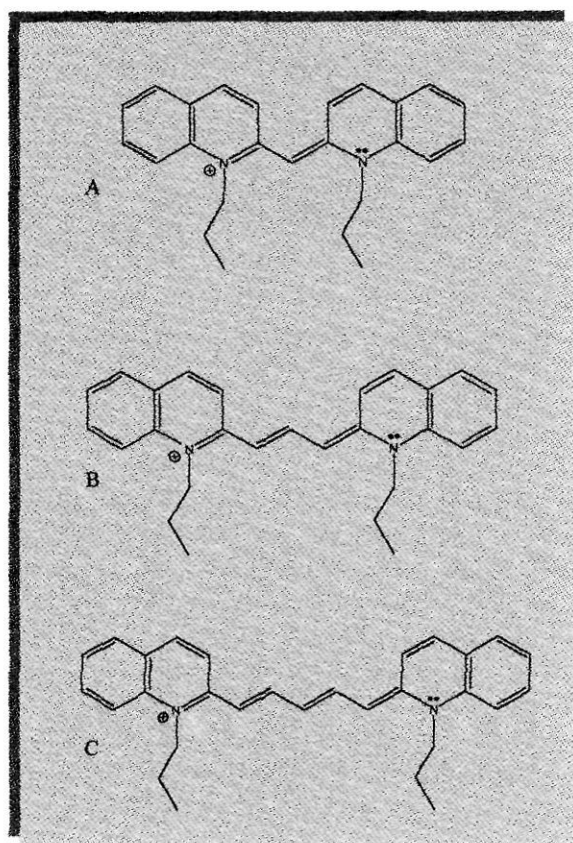
Figure 7.3. Schematic representation of the energy levels for the one-dimensional particle-in-a-box.

are considered, $n > n + 1$, the energy (and wavelength) absorbed will be given by Eq. 21.3,

$$\Delta E = E_{n+1} - E_n = \frac{(2n + 1)h^2}{8mL^2}$$
$$\lambda = \frac{hc}{\Delta E}.$$

(21.3)

Let's do the calculation of the absorbed energy for the lowest transition for each dye. We predict absorption maxima of 333 nm, 461 nm and 589 nm for dyes A, B and C, respectively. How did we do? Well these are easy measurements to make in the lab. In fact, a number of general chemistry programs use this as a lab exercise. So, we have the data with which to compare. The observed maxima (each absorption is really a broad "band" extending over more than 30 nm for reasons beyond the scope of this treatment, but we'll use the wavelength of maximum absorption) are 525 nm, 610 nm and 720 nm. Our calculated values are at lower wavelength, higher energy, than the experimental ones indicating that the one-dimensional box is effectively longer than we estimated. However, this agreement looks worse than it really is. Let's use the experimental results to calculate the corresponding box length. The results are 1.05 nm, 1.29 nm and 1.55 nm, respectively; the discrepancy is less startling using this metric. As we thought, the "box" is longer than we assumed; approximately 1.5 average bond lengths longer. Why?

Faculty are always ready with explanations for the failure of simple theories, but in this case there are legitimate reasons for the discrepancies and a look at those reasons is very instructive. The model assumes that the walls of the box are perpendicular; they rise with an infinite slope. That may approach reality for a charge particle trapped in an electric field, but not for something as complex as a dye molecule. The walls are undoubtedly curved. Curved walls will increase the length of the box. In fact, Kuhn added a term to his box length expression to account for this behavior and it resulted in very good agreement with the experimental data. We could do the same, and effectively scale the results. However, it is not our intention to exactly match the experimental result. We are exploring a case study and we can see that the *relative* dye absorption wavelengths are correct. A smaller error, one that we can usually ignore, is electron–electron repulsion. We have at least six electrons in this box. Way back, we started with Coulomb's law; like charges repel. There will be a small correction due to this effect. Finally, there are "localization" effects. The electrons "remember" the carbon atom

from which they were donated. However, this is an even smaller correction, that is readily ignored.

So, we have applied a simple model, one that we can easily solve, to a complicated problem. We have a reasonable result. A better one may only be obtained with detailed calculations and serious computing. This case study attempted to show you that you have explored a topic with wide applicability. We hope (expect?) that it will whet your appetite to learn about quantum mechanics in more detail. It will be well worth the effort!

CHAPTER 22

Afterword

In the preface, the purpose of this text was described from the perspective of my co-author, a mathematician who, prior to making that career choice, considered chemistry as a career. Here, I will sum up our goals and hopes for you, from the perspective of a chemist, who prior to making that choice considered mathematics (and, subsequently, engineering) as a possible major. If all of this sounds like two (at one time) very confused people, well, it should! The main purpose in writing this book was to combine a very rigorous mathematical approach with a more practical chemical approach and to bring you to a point where you will feel comfortable exploring quantum mechanics in more depth in your advanced courses. Our somewhat confused backgrounds were just what the National Science Foundation ordered, when we began teaching an interdisciplinary course (Integrated Mathematics and Physical Sciences) for incoming first year students. Along with a colleague from the Department of Physics, we covered introductory Calculus, Physics and Chemistry for science and engineering majors in a cohesive, interwoven course that extended over the entire first year. Confused as undergraduates, we were *interdisciplinary* as faculty!

The path we have taken you through began with the early experiments that produced "strange" results — results that piqued the interest of some of the greatest scientific minds. We followed the development of the theory, from a mathematical *and* a practical point of view. That is, using the practical analogy of a "well-plucked" string, we derived the exact solution to the hydrogen atom problem. Of course, from a chemist's viewpoint, the variables were described with unfamiliar names, but the connection to the lab scientist's convention was easily made because of the clarity of the physical model. Finally, we made a gigantic practical leap and examined the results of not just looking at multielectron atoms, but looking at *molecules,*

with many electrons *and* many atoms. In that study of chemical bonding, we took an approach analogous to that we used to study atoms. We began with an oversimplified bonding model and added complexity until we arrived at the molecular equivalent of quantum mechanics: quantum chemistry. We concluded with the application of a simple quantum mechanical model — the particle-in-a-box — to a complex chemical problem, the color of dye molecules. We didn't get the most accurate result we could, BUT even in failure there is much to be learned and we can explain away our absolute error, while enjoying the relative accuracy of the prediction for three different molecules. So, we hope that the novelty of our approach has proven instructive and we expect that you no longer wish to see that "required" illustration (in the preface) of a small sphere orbiting a large sphere. Rather, we expect that the $1s$ probability density shown below is more to your liking!

J.J. BelBruno

Index

The Bell that Rings Light

A Primer in
Quantum Mechanics and
Chemical Bonding

This book is an introduction to quantum mechanics and mathematics that leads to the solution of the Schrodinger equation. It can be read and understood by undergraduates without sacrificing the mathematical details necessary for a complete solution giving the shapes of molecular orbitals seen in every chemistry text. Readers are introduced to many mathematical topics new to the undergraduate curriculum, such as basic representation theory, Schur's lemma, and the Legendre polynomials.