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Chapter 1

Fundamentals of Quantum Mechanics

If a man will begin with certainties, he shall end in doubts;
But if he will be content to begin with doubts, he shall end in certainties
— Francis Bacon, *Advancement of Learning.*

1.1 Introduction

1.1.1 Why should we study quantum mechanics?

Quantum mechanics used to be the province of atomic, molecular, nuclear, and particle physics. In the last four decades, a wide range of development in basic science in astrophysics, cosmology, quantum optics, condensed matter, chemistry, and materials science and rapid progress in device technology, such as transistors, lasers, magnetic resonance imaging, scanning tunneling microscope, optical tweezers and the Hubble telescope, have made quantum mechanics the fundamental pinning of much of our civilization. Even the remarkable development of the classical nonlinear dynamics in the 20th century was rooted in the appreciation of the conceptual and methodology progress in quantum statistical physics and quantum field theory. The current development of nanoscience in physics, chemistry, biology and materials science elevates the importance of mesoscopic physics, a meeting ground of the microscopic and the macroscopic, where not only one must understanding quantum mechanics but one must also have a clear comprehension of its influence on the macroscopic outcome. Schrödinger's cat is no longer merely part of the gedanken parlor games of the fundamentalists in quantum mechanics. Einstein-Podolsky-Rosen paradox has evolved into "teleporting", quantum computing and cryp-

tography. The availability of lasers and of nanostructures of semiconductors has led to experimental demonstrations of simple quantum mechanical processes which used to be subjects of theoretical arguments and only whose consequences in atoms or molecules are observed. We are no longer content with merely investigating quantum processes in nature. We now strive to trap atoms, to fabricate designer nanostructures and to control the outcome of the quantum processes. These are today the many reasons why an educated person should understand quantum mechanics. It is even more so the case for a physical scientist or an engineer.

1.1.2 What is quantum theory?

Quantum theory consists in states, observables, and time evolution. In this chapter, we set up the framework of the quantum theory starting with the familiar wave mechanics governed by the Schrödinger equation. We shall adopt the axiomatic approach of taking the Schrödinger equation as given and follow Born in giving the wave function a definite meaning. Via the various representations of the state in terms of the position, momentum and energy, we abstract the state as a vector in a space of infinite dimension, independent of any representation.

In classical mechanics, every dynamical property of a system is a function of the positions and momenta of the constituent particles and of time. Hence, a dynamical property is an observable quantity. In quantum theory, we have a prescription to translate a classical property to an operator acting on a wave function. The outcome of a measurement of a property can only be predicted statistically unless the system is in an eigenstate of the operator associated with the property. Some pairs of properties, such as the position and momentum in the same direction, cannot be measured simultaneously with arbitrarily small uncertainties, thus obeying the uncertainty principle. Other pairs are not restricted by the uncertainty principle.

In this chapter, we consider the general theory of the physical observables. We wish to gain a clear picture of what happens after the measurement of a property. It will also be possible to decide which pair of observables is restricted by the uncertainty principle and which pair is not.

The time evolution of the state or the observables will be studied in the next chapter.

The simplicity of the structure of quantum theory belies the rich texture and the depth of the theory, the multitude of microscopic phenomena within its grasp, and the subtlety of the connection to the macroscopic world. The latter are the topics of the rest of the course.

1.2 Pachycephalic Quantum Mechanics

Pachy — from the Greek word pachys, meaning thick.
Cephalic — pertaining to the head.
Thus, pachycephalosaurus is the name given to a dinosaur with a skull bone nine inches thick. The moniker "Pachycephalic Quantum Mechanics" imitates the old course popularly known as "Bonehead English".

You have perhaps seen an attempt to establish wave mechanics in an introductory course. On the way, you might have gone through a lot of arguments purporting to show the reasonableness of the extrapolations from classical mechanics. Such an exercise is valuable in giving physical meaning to the new quantities and equations. For a second course, we can adopt a simpler route to quantum mechanics. Table 1.1 gives a recipe, with one column listing the ingredients in classical mechanics and another column transcribing them to quantum mechanics. One may take the attitude that no amount of arguing about the reasonableness of the procedure is as conclusive as applying the clear recipe to various systems and comparing the results to observation. A loftier treatment than the recipe approach is 'axiomatic' quantum mechanics. It sets down axioms or postulates and derive the Schrödinger equation from them. Such an approach will likely obscure the physical picture of the wave mechanics. Although we shall not have an exposition of axiomatic quantum mechanics, it is comforting to know of its existence. You can get a flavor of it from the book [1] in the bibliography at the end of the chapter.

1.2.1 Schrödinger equation for a particle

For simplicity, consider a point particle with mass m. Extension to a system of many particles will be done later. Associated with the particle is a wave function $\Psi(\vec{r}, t)$ from which we shall deduce the properties of the particle. The time evolution of the wave

Table 1.1: Table of properties in classical mechanics and corresponding ones in quantum mechanics.

Property	classical	quantum
Position	$\vec{r}$	$\vec{r}$
State	path $\vec{r}(t)$ or phase space $(\vec{p}, \vec{r})$	wave function $\Psi(\vec{r}, t)$, probability density at $\vec{r} = \lvert\Psi(\vec{r}, t)\rvert^2$
Momentum	$\vec{p}$	operator on wave function $\vec{P} = \frac{\hbar}{i}\nabla$
Energy	E	operator $i\hbar\frac{\partial}{\partial t}$
Potential energy	$V(\vec{r})$	$V(\vec{r})$
Hamiltonian	$H = \frac{p^2}{2m} + V(\vec{r})$	$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$ as an operator on wave function
Equation of motion	$\frac{d\vec{r}}{dt} = \frac{\partial H}{\partial \vec{p}}$ $\frac{d\vec{p}}{dt} = -\frac{\partial H}{\partial \vec{r}}$	$H\Psi(\vec{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t)$, i.e., $-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$
Property	$A = A(\vec{r}, \vec{p}, t)$	Operator A $A\psi_n = \alpha_n\psi_n, \Psi = \sum_n c_n\psi_n$ Probability of finding A to be α_n $= \lvert c_n\rvert^2$

function is given by the Schrödinger equation in Table 1.1:

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \left\{-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right\}\Psi(\vec{r}, t). \tag{1.2.1}$$

We note some features of the Schrödinger equation:

1. It is a linear and homogeneous partial differential equation. In other words, each term contains exactly one power of the wave function $\Psi(\vec{r}, t)$ or its derivatives. If Ψ_1 and Ψ_2 are two solutions, then any linear combination of them:

$$\Psi = a_1\Psi_1 + a_2\Psi_2 \tag{1.2.2}$$

with constants a_1 and a_2 is also a solution. Thus, the matter wave, just like the electromagnetic wave, obeys the superposition principle. That is, two waves can

be combined to make another wave. The interference and diffraction phenomena follow immediately.

2. It is a first-order differential equation in time. If the wave function is specified at any instant for all positions, then it is completely determined at all times.

3. It should satisfy the correspondence principle. In the classical limit (where $\hbar$ is unimportant), it is possible to find solutions approaching the Newtonian mechanics.

4. The classical wave equation has real coefficients. The complex representation for the solution is just a convenience. The Schrödinger equation has an imaginary coefficient and so the solution is in general complex.

1.2.2 Normalization of the wave function

Consider the integral over all space

$$N = \int d^3r |\Psi(\vec{r}, t)|^2 \tag{1.2.3}$$

where d^3r denotes the volume element $dxdydz$.

If $N = 1$, the wave function is said to be normalized. If N is finite, the wave function is said to be square-integrable. An integrable wave function is trivially normalized by dividing it with the square root of the integral N.

Some wave functions are not square-integrable, e.g., the plane wave. There are at least a couple of ways to deal with them. One way is the so-called box normalization. Take the particle to be in an extremely large box. We are interested in the interior of the box and the boundary condition and the shape of the box are immaterial. For example, consider the plane wave in one dimension. Let the wave function be confined in the interval $(-L/2,\, L/2)$ where L is enormous compared with the wavelength. Then the plane wave can be normalized by choosing the constant C to be $L^{-1/2}$. We shall see a second way later.

1.2.3 Distinction between the classical wave and the matter wave

It might be tempting to conclude that wave mechanics is like the classical theory of waves and that the particle nature can be completely explained in terms of the latter. It is, therefore, important to point to a crucial difference between the classical wave and the quantum wave. The classical wave, say the electromagnetic wave, can be widespread spatially. It is possible to make a measurement of the wave at a small locality hardly disturbing the wave elsewhere. Now consider a matter wave representing an electron. The wave can also be widespread so that there can be diffraction. Is it possible that the wave represents the structure of the electron spatially? One can trap an electron in a small locality whereupon there must be no electron wave outside the locality. This is the crucial difference from the classical wave. It also means that the wave cannot represent the spatial structure of the electron.

1.2.4 Statistical Interpretation of the Wave Function: Born's postulate

The classical electromagnetic wave is a measure of the electric or magnetic field. What property of the material particle does the matter wave represent? We have seen that a classical interpretation of the wave as the actual structure of the material particle runs into difficulties. Born suggested that the wave function should be a measure of the probability of finding the particle at $\vec{r}$ and t. More precisely,

$$\rho(r,t) = |\Psi(\vec{r},t)|^2 \tag{1.2.4}$$

is the probability density, i.e., the probability of finding the particle in a small volume d^3r at time t is $\rho(\vec{r},t)d^3r$. This definition has the following desirable properties:

1. $\rho(\vec{r},t)$ is always a real positive number.

2. ρ is large where Ψ is large and small where Ψ is small.

3. If the wave function is normalized (or box normalized),

$$\int \rho(\vec{r},t)d^3r = 1 \tag{1.2.5}$$

meaning that the probability of finding the particle over all space must be unity. If the wave function is not normalized (or not square-integrable), then $\rho(\vec{r}, t)$ represents the relative probability.

Born's interpretation is statistical. Take the example of a particle in a large box of volume V under no force otherwise. Let the wave function of the particle be the box-normalized plane wave (one of an infinite number of possible solutions of the Schrödinger equation). The probability density is everywhere the same, equal to the constant $1/V$. This gives the chance of locating the particle at one spot. It is as likely to find the particle at one place as at another. Once the particle is located in a small neighborhood by a measurement (how small depends on the sensitivity of the measuring instrument), one will not find it elsewhere immediately afterwards. Thus, the very measuring process changes the plane wave into a wave function concentrating near that particular neighborhood. If a large number of measurements are made at a variety of locations, each on one of a collection of identical boxes, then the position distribution of the particle is given by the probability density of the wave function.

This represents a radical departure from the Descartes objective reality and the classical determinism [2]. In quantum theory, there is still determinism in that the wave function develops according to Schrödinger's equation. However, we do not know for sure the properties of a particle at all times but only the probability of the outcome of a measurement. The very act of observing the particle changes its state. The consequences of the interaction between the microscopic particle and the macroscopic observer (or the apparatus) is unavoidable.

1.2.5 Particle Flux and Probability Conservation

As the wave function changes with time, the probability density distribution over space changes and we can imagine a flow of the probability density has taken place. Since the probability density function represents the density distribution of a large number of particles, the flux can represent the particle current density. Denote the flux or current density by $\vec{J}(\vec{r}, t)$. What is the expression of $\vec{J}(\vec{r}, t)$ in terms of the wave function?

Probability conservation

It follows from the Schrödinger equation that the total probability is time independent. Consider first the probability in a volume Ω enclosed by a fixed surface S:

$$P = \int_\Omega d^3r \rho(\vec{r}, t). \tag{1.2.6}$$

Now,

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi \\ &= \frac{1}{i\hbar} \left\{ \Psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) - \Psi \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right) \right\}. \end{aligned}$$

By using the Schrödinger equation,

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\frac{\hbar}{2mi} \{ \Psi^* \nabla^2 \Psi - (\nabla^2 \Psi^*) \Psi \} \\ &= -\frac{\hbar}{2mi} \nabla \cdot \{ \Psi^* \nabla \Psi - (\nabla \Psi^*) \Psi \}. \end{aligned} \tag{1.2.7}$$

Let the current density be given by

$$\vec{J}(\vec{r}, t) = \frac{\hbar}{2mi} \{ \Psi^* \nabla \Psi - (\nabla \Psi^*) \Psi \}. \tag{1.2.8}$$

The time derivative of the probability in Ω is

$$\begin{aligned} \frac{dP}{dt} &= -\int_\Omega d^3r \nabla \cdot \vec{J}(\vec{r}, t), \qquad \text{using Eq. (1.2.7)} \\ &= -\int_S d\vec{S} \cdot \vec{J}, \end{aligned} \tag{1.2.9}$$

using the divergence theorem.

For the square-integrable wave function, it tends to zero at infinity and $\vec{J}$ from Eq. (1.2.8) does the same. If we let the surface S tend to infinity, then by Eq. (1.2.9)

$$\frac{dP}{dt} = 0 \tag{1.2.10}$$

from which the conservation of the total probability over all space follows.

Expression for the flux or current density

For a finite volume Ω Eq. (1.2.9) still represents conservation of probability with the L.H.S. being the rate of increase of the probability balanced by an influx through the surface S on the R.H.S. Thus, $\vec{J}(\vec{r},t)$ defined by Eq. (1.2.8) is the current density.

Equation (1.2.7) may be rewritten as

$$\frac{\partial \rho}{\partial t} + \text{div}\vec{J} = 0, \tag{1.2.11}$$

the equation of continuity. For electric charges or fluid, the equation of continuity is a consequence of the conservation of charges or matter. Equation (1.2.11) is the quantum mechanical analog.

1.3 The Many Faces of a Quantum State

The wave function $\Psi(\vec{r},t)$ which represents the state of a particle is a function of position and time. It gives us a measure of the probability distribution of the position of the material particle. Why does the property position enjoys such a privileged position? Why can't we replace the position with momentum or energy or any other dynamical property? In this section, it is shown that indeed the quantum state of a particle can be represented as a function of momentum or energy.

1.3.1 Fourier transforms and Dirac's delta function

Definition The Fourier transform $\tilde{\psi}(k)$ of a function $\psi(x)$ is given by

$$\tilde{\psi}(k) = \int_{-\infty}^{+\infty} \frac{dx}{\sqrt{2\pi}} e^{-ikx}\psi(x) \ . \tag{1.3.1}$$

Fourier theorem If $\tilde{\psi}(k)$ is the Fourier transform of the function $\psi(x)$ as given by Eq. (1.3.1), then

$$\psi(x) = \int_{-\infty}^{+\infty} \frac{dk}{\sqrt{2\pi}} e^{ikx}\tilde{\psi}(k) \ . \tag{1.3.2}$$

Lemma The Fourier transform of a Gaussian function is another Gaussian.

Proof of the lemma is given by putting a Gaussian function

$$\psi(x) = \frac{1}{\sqrt{2\sigma^2}} e^{-x^2/4\sigma^2} \tag{1.3.3}$$

with a constant σ into Eq. (1.3.1) and evaluating the integral by completing the square in the exponent and by using the Gaussian integral,

$$\int_{-\infty}^{+\infty} dt\; e^{-t^2} = \sqrt{\pi}, \tag{1.3.4}$$

to obtain the Fourier transform

$$\tilde{\psi}(k) = e^{-\sigma^2 k^2}. \tag{1.3.5}$$

This lemma can now be used to prove the Fourier theorem and also to introduce the concept of the Dirac δ-function. Starting from the right-hand side of the theorem, Eq. (1.3.2), and substituting the definition of the Fourier transform, we obtain

$$\begin{aligned}
&\int_{-\infty}^{+\infty} \frac{dk}{\sqrt{2\pi}} e^{ikx} \tilde{\psi}(k) \\
&= \int_{-\infty}^{+\infty} \frac{dk}{\sqrt{2\pi}} e^{ikx} \int_{-\infty}^{+\infty} \frac{dy}{\sqrt{2\pi}} e^{-iky} \psi(y) \\
&= \lim_{\sigma \to 0} \int_{-\infty}^{+\infty} \frac{dk}{\sqrt{2\pi}} e^{ikx - \sigma^2 k^2} \int_{-\infty}^{+\infty} \frac{dy}{\sqrt{2\pi}} e^{-iky} \psi(y) \\
&\qquad \text{a harmless introduction of a factor of unity,} \\
&= \lim_{\sigma \to 0} \int_{-\infty}^{+\infty} dy\, \psi(y) \int_{-\infty}^{+\infty} \frac{dk}{2\pi}\, e^{ik(x-y) - \sigma^2 k^2} \\
&\qquad \text{reversing order of integration,} \\
&= \int_{-\infty}^{+\infty} dy\, \psi(y) \delta(x-y) \\
&= \psi(x).
\end{aligned}$$

In the last two steps of the proof, we introduced the δ-function

$$\delta(x) = \lim_{\sigma \to 0} \int_{-\infty}^{+\infty} \frac{dk}{2\pi} e^{ikx - \sigma^2 k^2}, \tag{1.3.6}$$

which by the lemma is

$$\delta(x) = \lim_{\sigma\to 0} \frac{1}{2\sigma\sqrt{\pi}} e^{-x^2/4\sigma^2} \tag{1.3.7}$$

$$= \infty, \text{ if } x = 0,$$

$$= 0, \text{ if } x \neq 0. \tag{1.3.8}$$

The limit yields such a strange function that the mathematicians would say that it is not a function but a "distribution". It would be somewhat safer to define the distribution which the physicists call the δ-function as the limit of a series of well defined functions, such as in Eq. (1.3.7). See the delightful little book by M.J. Lighthill [3]. It is easy to verify using the limit definition the two important properties of the δ-function:

$$\int_{-\infty}^{+\infty} dy\, \delta(y) = 1, \tag{1.3.9}$$

$$\int_{-\infty}^{+\infty} dy\, \psi(y)\delta(x-y) = \psi(x). \tag{1.3.10}$$

The limit of Eq. (1.3.6) may be written as

$$\delta(x) = \int_{-\infty}^{+\infty} \frac{dk}{2\pi} e^{ikx}, \tag{1.3.11}$$

which is not well defined unless we take it as a shorthand for Eq. (1.3.6) or, alternatively, as the limit of a finite integral, i.e.

$$\delta(x) = \lim_{K\to\infty} \int_{-K}^{K} \frac{dk}{2\pi}\, e^{ikx} = \lim_{K\to\infty} \frac{\sin(Kx)}{\pi x}. \tag{1.3.12}$$

1.3.2 Transformation from the position space to the momentum space

The Fourier transform of the state wave function $\Psi(\vec{r})$ is

$$\tilde{\Psi}(\vec{k}) = \int \frac{d^3r}{(2\pi)^{3/2}} e^{-i\vec{k}\cdot\vec{r}} \Psi(\vec{r}). \tag{1.3.13}$$

By the Fourier theorem,

$$\Psi(\vec{r}) = \int \frac{d^3k}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{r}} \tilde{\Psi}(\vec{k}). \tag{1.3.14}$$

This relation may be read as exhibiting the fact that the wave function $\Psi(\vec{r})$ is made up of sinusoidal waves of various wave-vectors $\vec{k}$. The Fourier transform $\tilde{\Psi}(\vec{k})$ measures the amount of the sinusoidal wave with wave-vector $\vec{k}$ in the wave function $\Psi(\vec{r})$.

1.3.3 Momentum wave function and probability distribution

By the operator form for the momentum given in the Table 1.1, we see that a plane wave with wave-vector $\vec{k}$ is an eigenstate of the momentum,

$$\frac{\hbar}{i}\nabla\frac{1}{(2\pi\hbar)^{3/2}}e^{i\vec{p}\cdot\vec{r}/\hbar} = \vec{p}\frac{1}{(2\pi\hbar)^{3/2}}e^{i\vec{p}\cdot\vec{r}/\hbar}, \tag{1.3.15}$$

i.e., the plane wave represents a quantum state which carries a definite momentum $\vec{p} = \hbar\vec{k}$. The constant in front of the plane wave is chosen by normalization.

The Fourier expansion of the wave function, Eq. (1.3.14), may be written in terms of the momentum eigenvalue $\vec{p}$,

$$\Psi(\vec{r}) = \int \frac{d^3p}{(2\pi\hbar)^{3/2}}e^{i\vec{p}\cdot\vec{r}/\hbar}\Phi(\vec{p}), \tag{1.3.16}$$

where the coefficient of the expansion,

$$\Phi(\vec{p}) = \tilde{\Psi}(\vec{p}/\hbar) \div \hbar^{3/2}, \tag{1.3.17}$$

is the probability amplitude of the momentum by the rules governing the operator in Table 1.1. The probability density for the momentum value $\vec{p}$ is

$$\Pi(\vec{p}) = |\Phi(\vec{p})|^2. \tag{1.3.18}$$

$\Pi(\vec{p})$ is always real and positive and, because we have taken care of the normalization of the basis states,

$$\begin{aligned}
\int d^3p\Pi(\vec{p}) &= \int d^3p|\Phi(\vec{p})|^2 \\
&= \int d^3k|\tilde{\Psi}(\vec{k})|^2 \\
&= \int d^3k\tilde{\Psi}^*(\vec{k})\int\frac{d^3r}{(2\pi)^{3/2}}e^{-i\vec{k}\cdot\vec{r}}\Psi(\vec{r}) \\
&= \int d^3r\Psi^*(\vec{r})\Psi(\vec{r}), \\
&= 1,
\end{aligned} \tag{1.3.19}$$

using Eq. (1.3.13) and its complex conjugate.

1.3.4 The momentum operator

Sometimes it is too cumbersome to Fourier transform the wave function in order to find the information about the momentum. In quantum theory, the most information about the momentum (or position, or any other property) one can have is in its momentum wave function. A large amount of information is contained in the probability distribution of the momentum. Equivalent to this latter is the knowledge of all the moments of $\vec{p}$. In practice, one commonly needs or measures only the mean and the variance from repeating a large number of experiments. It is possible to calculate the mean value of any function of the momentum directly from the position wave function rather than Fourier transforming first.

The mean value of the momentum is

$$\begin{aligned} \langle \vec{p} \rangle &= \int d^3p \, \vec{p} \, \Pi(\vec{p}) \\ &= \int d^3p \, \Phi^*(\vec{p}) \vec{p} \Phi(\vec{p}). \end{aligned} \tag{1.3.20}$$

Differentiating Eq. (1.3.14) with respect to position,

$$\frac{\hbar}{i} \nabla \Psi = (2\pi)^{-3/2} \int d^3k \hbar \vec{k} e^{i\vec{k}\cdot\vec{r}} \tilde{\Psi}(\vec{k}). \tag{1.3.21}$$

Multiplying the equation by Ψ^* and integrating,

$$\begin{aligned} \int d^3r \Psi^* \frac{\hbar}{i} \nabla \Psi &= (2\pi)^{-3/2} \int d^3k \int d^3r \Psi^*(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \hbar \vec{k} \tilde{\Psi}(\vec{k}) \\ &= \int d^3k \tilde{\Psi}^*(\vec{k}) \hbar \vec{k} \tilde{\Psi}(\vec{k}) \\ &= \int d^3p \Phi^*(\vec{p}) \vec{p} \Phi(\vec{p}) \\ &= \langle \vec{p} \rangle. \end{aligned} \tag{1.3.22}$$

Similarly, it can be shown that

$$\langle F(\vec{p}) \rangle = \int d^3r \Psi^*(\vec{r}) F\left(\frac{\hbar}{i} \nabla\right) \Psi(\vec{r}). \tag{1.3.23}$$

To calculate the mean value of any function of the momentum directly from the position wave function, one simply replaces the momentum by the momentum operator:

$$\vec{p} \to \vec{P} = \frac{\hbar}{i} \nabla. \tag{1.3.24}$$

We have gone full circle from the momentum operator to the momentum value $\vec{p}$ and back.

1.3.5 State representation in terms of the energy eigenstates

Energy eigenstates and eigenvalues

The time development of the wave function of a particle obeys the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = H\Psi(\vec{r},t), \tag{1.3.25}$$

where H is the Hamiltonian of the particle. In classical mechanics, the Hamiltonian is said to be conservative if it does not depend explicitly on time. In that case, the total energy E is a constant of motion. In quantum mechanics, there is a corresponding constant energy state.

The energy eigenstate is given by the time-independent Schrödinger equation

$$H\psi(\vec{r}) = E\psi(\vec{r}). \tag{1.3.26}$$

Or, more explicitly,

$$\left\{-\frac{\hbar^2}{2m}\,\nabla^2 + V(\vec{r})\right\}\psi(\vec{r}) = E\psi(\vec{r}). \tag{1.3.27}$$

The time-dependent wave function is given by

$$\Psi(\vec{r},t) = \psi(\vec{r})e^{-iEt/\hbar}. \tag{1.3.28}$$

Orthogonality of eigenstates

Depending on the nature of the potential, the energy eigenvalue can be continuous or discrete. For the simplicity of exposition, we shall first represent the energy eigenvalues as discrete. Let us order the energy in increasing values by the integer n. Some of the energy values may be equal (degenerate).

$$H\psi_n(\vec{r}) = E_n\psi_n(\vec{r}). \tag{1.3.29}$$

The eigenstates $\{\psi_n(\vec{r})\}$ are orthogonal in the sense that for $m \neq n$,

$$\langle\psi_m|\psi_n\rangle \equiv \int d^3r\ \psi_m^*(\vec{r})\psi_n(\vec{r}) = 0, \tag{1.3.30}$$

where we have introduced the angular brackets as the shorthand notation (due to Dirac) for the integral of the product of the complex conjugate of a wave function with another wave function. Later, we shall prove that eigenstates of any Hermitian operator (H being one,) are orthogonal to one another. The eigenfunctions ψ_n are said to form an orthonormal set if they are normalized ($\langle\psi_n|\psi_n\rangle = 1$) and orthogonal to each other, i.e.,

$$\langle\psi_m|\psi_n\rangle = \delta_{mn}, \tag{1.3.31}$$

δ_{mn} being the Kronecker delta, zero unless $m = n$ whence it is 1.

Energy eigenstate expansion

If the eigenstates form a complete set, any state of the system with the Hamiltonian H (or any confined system for that matter) can be expressed as a series

$$\Psi(\vec{r}) = \sum_n \psi_n(\vec{r})c_n, \tag{1.3.32}$$

with the constants c_n given by

$$c_n = \langle\psi_n|\Psi\rangle. \tag{1.3.33}$$

1.3.6 Meaning of the expansion coefficients

For simplicity, we shall assume here that each energy eigenvalue is nondegenerate. In later chapters, we shall characterize the degenerate states with additional quantum numbers such as the angular momentum quantum numbers and include the symmetry considerations of the Hamiltonian. For a general state represented by the wave function (1.3.32), let us calculate the mean energy,

$$\begin{aligned} E = \langle H\rangle &= \langle\Psi|H|\Psi\rangle \\ &= \int d^3r\ \Psi^*(\vec{r})H\sum_n \psi_n(\vec{r})c_n \\ &= \sum_n E_n \int d^3r\ \Psi^*(\vec{r})\psi_n(\vec{r})c_n \\ &= \sum_n E_n|c_n|^2. \end{aligned} \tag{1.3.34}$$

Similarly, the mean value of any function of H, $f(H)$, is

$$\langle f(H)\rangle = \sum_n f(E_n)|c_n|^2. \tag{1.3.35}$$

This is consistent with the last rule in Table 1.1 that the probability of finding the state $\Psi(x)$ with energy value E_n is

$$P(E_n) = |c_n|^2. \tag{1.3.36}$$

Continuous energy eigenvalues

The case of the continuous energy eigenvalues is important in the scattering problem. The foregoing results are extended by replacing the quantum number n by the continuous variable E and a set of quantum numbers denoted by λ which distinguishes the states with the same energy:

$$H\psi_\lambda(\vec{r}, E) = E\psi_\lambda(\vec{r}, E). \tag{1.3.37}$$

In the case of a spherically symmetric potential, for example, the quantum numbers λ stand for the angular momentum quantum numbers ℓ, m, which will be derived in Chapter 4. The orthonormality is replaced by

$$\langle\psi_\lambda(E)|\psi_{\lambda'}(E')\rangle = \delta(E - E')\delta_{\lambda,\lambda'}. \tag{1.3.38}$$

A state can be expressed as an integral of the energy eigenstates:

$$\Psi(\vec{r}) = \sum_\lambda \int dE\, \psi_\lambda(\vec{r}, E)c_\lambda(E). \tag{1.3.39}$$

As an example, the plane wave is an energy eigenstate (as well as a momentum eigenstate) of a free particle. A state expressed as an integral of the plane waves is related to the Fourier integral.

Clearly, the foregoing expansion in terms of the eigenstates can be applied to any Hermitian operator which shares the property of orthonormality. In particular, the probability meaning of the expansion coefficients holds for any physical property.

1.4 State Vectors

Dirac [4] developed quantum theory in terms of the concept of the state vector and was able to use it to demonstrate the equivalence between Schrödinger's wave mechanics and Heisenberg's matrix mechanics. We follow the path of the wave function for a state and make an abstraction of the state as a vector.

1.4.1 Concept of a state vector

A vector in three dimension, $\vec{v}$, is an abstract object which represents three numbers in a Cartesian frame of reference, or an arrow with magnitude and direction in terms of two angles, etc. By analogy, the state Ψ, which has a representation $\Psi(\vec{r})$ in the position space, $\Phi(\vec{p})$ in the momentum space, and $c_\lambda(E)$ in the energy space, etc., can be regarded as a vector in the infinite dimensional vector space (infinite because the number of eigenstates which serve as a basis set is infinite). To distinguish the state Ψ from its conjugate Ψ^*, Dirac [4] adopted the notation $|\Psi\rangle$ for the former. This is known as the Dirac "ket" vector. Its Hermitian conjugate, Ψ^*, is represented by the "bra" vector $\langle\Psi|$ as part of the bracket, for, say, the normalization integral $\langle\Psi|\Psi\rangle$. If we need to denote the time dependence, we simply use $|\Psi(t)\rangle$.

We introduced in the last section the Dirac notation $\langle\psi_m|\psi_n\rangle$ for the overlap integral in Eq. (1.3.30) as a matter of convenience. The notation now stands for the inner (or scalar) product of a bra vector and a ket vector, independent of representation. The product could equally well have been an integral over wave functions as functions of the position or momentum variables.

1.4.2 Representation of a state vector

To reverse the process of abstraction of a state vector, we can also choose a complete set of basis states $|q\rangle$, where q denotes a set of quantum numbers such as x, y, z, or p_x, p_y, p_z, or E, λ. Then,

$$|\Psi\rangle = \int dq|q\rangle\langle q|\Psi\rangle. \tag{1.4.1}$$

The inner product between the two state vectors, $\langle q|\Psi\rangle$, is the probability amplitude of the state $|\Psi\rangle$ being found in state $|q\rangle$.

To make the vector nature of the state representation more obvious, we introduce a discrete set of orthonormal states $|u_j\rangle$, j being chosen as a set of integers. A state vector is expanded as a series in terms of these basis states:

$$|\psi\rangle = \sum_j |u_j\rangle c_j \ , \tag{1.4.2}$$

where

$$c_j = \langle u_j|\psi\rangle. \tag{1.4.3}$$

The explicit matrix form of Eq. (1.4.2) is

$$|\psi\rangle = [|u_1\rangle \ \ |u_2\rangle \ \ \dots \ ] \begin{bmatrix} c_1 \\ c_2 \\ . \\ . \\ . \end{bmatrix} \tag{1.4.4}$$

Instead of using the wave function $\psi(r)$ to represent the dynamical state of a particle at a particular time, we can use, with respect to the chosen basis set, the column vector with elements c_j, i.e.,

$$\begin{bmatrix} c_1 \\ c_2 \\ . \\ . \\ . \end{bmatrix} \tag{1.4.5}$$

1.4.3 General properties of the state vectors

The infinite dimensional vector space of the states $|\psi\rangle$ is known as the Hilbert space. It possesses all the properties of the finite dimensional vector space with which we are familiar. The overlap integral $\langle\phi|\psi\rangle$ is the inner (or scalar) product of the two vectors $|\phi\rangle$ and $|\psi\rangle$. The length of a vector $|\psi\rangle$ is defined as $\sqrt{\langle\psi|\psi\rangle}$. The triangular inequality, which in the ordinary vector notation is given by

$$|\vec{a} + \vec{b}| \leq |\vec{a}| + |\vec{b}| \tag{1.4.6}$$

becomes

$$\sqrt{\langle\psi + \phi|\psi + \phi\rangle} \leq \sqrt{\langle\psi|\psi\rangle} + \sqrt{\langle\phi|\phi\rangle}. \tag{1.4.7}$$

The Schwartz inequality, which for common vectors is given by

$$|\vec{a}\cdot\vec{b}| \leq |\vec{a}|\ |\vec{b}| \tag{1.4.8}$$

becomes

$$|\langle\psi|\phi\rangle|^2 \leq \langle\psi|\psi\rangle\langle\phi|\phi\rangle \tag{1.4.9}$$

of which we shall have more to say later.

1.5 Observables As Hermitian Operators

Consider a system of one particle only. Extension to many particles will be studied later. By analogy with the action of the physical observable x or p_x on the wave function transforming it to another wave function, each observable property of the system is represented by an operator A, which acts on a state vector $|\Psi\rangle$, transforming it into another state denoted by $|\Psi'\rangle$,

$$|\Psi'\rangle = A|\Psi\rangle. \tag{1.5.1}$$

We shall find occasions when it is convenient to use the shorthand $A\Psi$ for Ψ' such that the transformed state of $|\Psi\rangle$ is denoted by $|A\Psi\rangle$. Examples of observables which we shall study presently are the position coordinates X, Y, Z, momentum components P_x, P_y, P_z, kinetic energy $\vec{P}^2/2m$, potential energy $V(\vec{R}\,)$ and the Hamiltonian H. In the configuration space, the action of the observables x or p_x on the wave function may be written as the wave function of the transformed state given by

$$\langle x|X|\Psi\rangle = x\langle x|\Psi\rangle, \tag{1.5.2}$$

$$\langle x|P_x|\Psi\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\Psi\rangle. \tag{1.5.3}$$

1.5.1 Definition of a Hermitian conjugate

The Hermitian conjugate of an operator A, denoted by $A^\dagger$, is defined as an operator acting on the bra state to the left which yields the Hermitian conjugate of the transformed state resulting from A acting on the ket:

$$\langle\Psi|A^\dagger = \langle A\Psi|. \tag{1.5.4}$$

As a consequence, the matrix element of the Hermitian conjugate operator with respect to any two states is given by

$$\langle \Psi_a | A^\dagger | \Psi_b \rangle = \langle A\Psi_a | \Psi_b \rangle = \langle \Psi_b | A\Psi_a \rangle^* = \langle \Psi_b | A | \Psi_a \rangle^*. \tag{1.5.5}$$

1.5.2 Examples of Hermitian conjugates

1. Position operator: $X^\dagger = X$.

   X denotes the position operator for the coordinate x. Thus,

$$\begin{aligned} \langle \Psi_a | X^\dagger | \Psi_b \rangle &= \langle X\Psi_a | \Psi_b \rangle = [\langle \Psi_b | X | \Psi_a \rangle]^* \\ &= \left[\int d^3r \Psi_b^*(\vec{r}) x \Psi_a(\vec{r}) \right]^* = \int d^3r \Psi_a^*(\vec{r}) x \Psi_b(\vec{r}) \\ &= \langle \Psi_a | X | \Psi_b \rangle. \end{aligned} \tag{1.5.6}$$

   Since this is true for any two states, the equation $X^\dagger = X$ follows. This seems a rather involved way to show that the coordinate x is real but (1) it does show the connection between the Hermitian property of an operator and the measurable number it represents and (2) the logical process involved is a useful exercise in preparation for a less well-known physical observable.

2. If A is defined as the operator with the position representation $\frac{\partial}{\partial x}$, then $A^\dagger$ has the position representation $-\frac{\partial}{\partial x}$.

   To prove this, we start with the right-hand side of the defining equation (1.5.5),

$$\begin{aligned} \langle A\Psi_a | \Psi_b \rangle &= \int d^3r \left(\frac{\partial}{\partial x} \Psi_a \right)^* \Psi_b = \int d^3r \left(\frac{\partial}{\partial x} \Psi_a^* \right) \Psi_b \\ &= \int_S dS_x \Psi_a^* \Psi_b - \int d^3r \Psi_a^* \frac{\partial}{\partial x} \Psi_b, \end{aligned} \tag{1.5.7}$$

   having used a variant of the divergence theorem, with S being a large sphere ultimately taken to be infinitely large. If the wave functions vanish at infinity, then the surface integral tends to zero. Otherwise, the volume integrals are $O(V)$, where V is the volume enclosed by S and the surface integral is $O(V^{2/3})$, smaller than the

volume terms. In either case, we have

$$\begin{aligned} \int d^3r \left(\frac{\partial}{\partial x}\Psi^a\right)^* \Psi_b &= \int d^3r \Psi_a^* \left(-\frac{\partial}{\partial x}\right) \Psi_b, \\ \text{or, } \langle A\Psi_a|\Psi_b\rangle &= \langle \Psi_a| - A|\Psi_b\rangle \end{aligned} \tag{1.5.8}$$

Hence, by definition, the Hermitian conjugate of a first-order differential operator is minus the operator.

3. If a is a complex number and $B = aA$, then

$$B^\dagger = a^* A^\dagger. \tag{1.5.9}$$

4. If $p_x = -i\hbar\frac{\partial}{\partial x}$, then

$$\begin{aligned} p_x^\dagger &= (-i\hbar)^* \left(-\frac{\partial}{\partial x}\right) \text{ , using Ex. 3 and Ex. 2 above,} \\ &= -i\hbar\frac{\partial}{\partial x} \\ &= p_x. \end{aligned} \tag{1.5.10}$$

5. The Hermitian conjugate of the Hermitian conjugate of A is A:

$$(A^\dagger)^\dagger = A, \tag{1.5.11}$$

by taking the complex conjugate of the defining equation (1.5.5).

1.5.3 Hermitian operator

The operator A is Hermitian if

$$A^\dagger = A, \tag{1.5.12}$$

or equivalently, for any two states Ψ_a and Ψ_b,

$$\{\langle \Psi_a|A|\Psi_b\rangle\}^* = \langle \Psi_b|A|\Psi_a\rangle. \tag{1.5.13}$$

Examples of the Hermitian operators are the position operator X, the momentum P_x, and the Hamiltonian H.

1.5.4 Corollary

It follows immediately from Eq. (1.5.13) that the mean value of a Hermitian operator for any state of a system is real.

1.5.5 Implication of the corollary

In classical physics, a physical property usually can take on real values. Although sometimes we use complex properties, they always denote two physical properties. For example, the complex electric or magnetic field really represents two properties: the amplitude and the phase. Or, the complex impedance really represents the resistance and the reactance. So let us take a physical property to mean one quantity which, in classical physics, takes on real values only. We have seen that a physically meaningful quantity is the mean value of the operator associated with the property with respect to a dynamical state. By the correspondence principle, it is reasonable to postulate that the mean value is always real. It follows that an operator which represents a physical observable must be an Hermitian operator. It is comforting to note that all the operators representing measurables which we have come across are indeed Hermitian: such as the position, the momentum, the potential energy, the kinetic energy, the angular momentum and the Hamiltonian.

1.6 Matrix Representation of a Physical Observable

Consider an operator A. It transforms a state $|u_k\rangle$ to another state $A|u_k\rangle$, which can be expanded in terms of the basis set:

$$A|u_k\rangle = \sum_j |u_j\rangle A_{jk}. \tag{1.6.1}$$

Or in explicit matrix form,

$$[A|u_1\rangle \quad A|u_2\rangle \quad \ldots] = [u_1\rangle \quad |u_2\rangle \quad \ldots] \begin{bmatrix} A_{11} & A_{12} & \ldots \\ A_{21} & A_{22} & \ldots \\ \ldots & \ldots & \ldots \end{bmatrix}. \tag{1.6.2}$$

Using the orthonormality of the states $|u_j\rangle$, we have

$$A_{jk} = \langle u_j|A|u_k\rangle. \tag{1.6.3}$$

With respect to the basis set, the operator A can be regarded as a matrix with elements A_{jk}. Without fear of confusion, we can use the same symbol A to represent the operator as well as the matrix.

An operator A acting on a state $|\psi\rangle$ changes it into a state $|\psi'\rangle$ where

$$|\psi'\rangle = A|\psi\rangle. \tag{1.6.4}$$

Let $|\psi\rangle$ be represented by a vector $\vec{c}$ with elements c_j given by Eq. (1.4.3) and $|\psi'\rangle$ be represented by the vector $\vec{c}'$ with respect to the same basis set. Then

$$c'_j = \sum_k A_{jk} c_k, \tag{1.6.5}$$

or, in matrix notation,

$$\vec{c}' = A \cdot \vec{c}. \tag{1.6.6}$$

Proof: From Eq. (1.6.1), we have

$$|\psi'\rangle = A|\psi\rangle = \sum_k A|u_k\rangle c_k = \sum_{kj} |u_j\rangle A_{jk} c_k. \tag{1.6.7}$$

Multiplying both sides by the bra vector $\langle u_j|$, we obtain Eq. (1.6.5).

The result of an operator A acting on the state $|\psi\rangle$ is just a linear transformation of the state vector $\vec{c}$ to the state vector $A\vec{c}$.

The inner product of a bra and a ket vector, $\langle\phi|\psi\rangle$ is a scalar. The outer product of a ket and a bra is an operator $|\phi\rangle\langle\psi|$ transforms any state to the state $|\phi\rangle$. It is also called the projection operator. From Eq. (1.6.1), we can express a general operator in terms of the basis set as

$$A = \sum_{j,k} |u_j\rangle A_{jk} \langle u_k|. \tag{1.6.8}$$

1.6.1 Hermitian matrix

From the definition of the Hermitian conjugate, Eq. (1.4.2) the matrix elements of the conjugate $A^\dagger$ are related to those of A by

$$A^\dagger_{jk} = (A_{kj})^*, \tag{1.6.9}$$

i.e., to get the matrix A, one not only transposes the matrix A but also takes the complex conjugate of each element.

For a Hermitian operator A,

$$A_{jk} = (A_{kj})^*, \tag{1.6.10}$$

or in matrix notation,

$$A = A^\dagger, \tag{1.6.11}$$

which is of the same form as the operator equation (1.4.9).

1.6.2 Product of operators

The matrix representation of the product AB of two operators A and B is just the matrix product of the matrices of A and B:

$$(AB)_{ij} = \sum_k A_{ik} B_{kj}. \tag{1.6.12}$$

Proof: Let $C = AB$.

$$\begin{aligned} C|u_j\rangle &= A(B|u_j\rangle) = A \sum_k |u_k\rangle B_{kj} \\ &= \sum_k (A|u_k\rangle) B_{kj} \\ &= \sum_{ik} |u_i\rangle A_{ik} B_{kj}. \end{aligned} \tag{1.6.13}$$

By definition,

$$C|u_j\rangle = \sum_i |u_i\rangle C_{ij}. \tag{1.6.14}$$

By comparing the two sums, we obtain Eq. (1.6.12).

Thus, the operator equation (1.6.13) can also be read as the matrix equation. To find out whether two operators commute, we simply have to see if the corresponding matrices commute.

1.6.3 Expectation value

$$\begin{aligned} \langle A \rangle &= \langle \psi | A | \psi \rangle = \sum_{ij} c_i^* A_{ij} c_j \\ &= \vec{c}^{\,\dagger} \cdot A \cdot \vec{c}, \end{aligned} \tag{1.6.15}$$

the last expression being in matrix notation, with $\vec{c}$ as a column vector and $\vec{c}^{\,\dagger}$ its Hermitian conjugate (a row vector), i.e.

$$[c_1^* \;\; c_2^* \;\; \dots \;] \begin{bmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \dots \end{bmatrix}. \tag{1.6.16}$$

1.6.4 Examples of a continuous basis set

While it is straightforward to extend the previous results written out in a discrete basis set to a continuous set, here are some examples where care has to be exercised. For the position states $|x\rangle$,

$$\langle x | X | x' \rangle = x \langle x | x' \rangle = x \delta(x - x'), \tag{1.6.17}$$

$$\langle x | P_x | x' \rangle = \frac{\hbar}{i} \frac{\partial}{\partial x} \langle x | x' \rangle = \frac{\hbar}{i} \frac{\partial}{\partial x} \delta(x - x'), \tag{1.6.18}$$

using Eqs. (1.5.2) and (1.5.3).

1.7 Eigenvalues and Eigenstates of a Physical Observable

1.7.1 Definition

A state, $|\psi\rangle$, which satisfies the equation

$$A|\psi\rangle = \alpha|\psi\rangle, \tag{1.7.1}$$

A being an operator and α being a number, is called an eigenstate of the operator A with the eigenvalue α.

1.7.2 Properties of an eigenstate of an operator A

1. Function of an operator

$$f(A)|\psi\rangle = f(\alpha)|\psi\rangle. \tag{1.7.2}$$

Starting with Eq. (1.7.1), we can show

$$A^2\psi = A(A\psi) = A(\alpha\psi) = \alpha(A\psi) = \alpha^2\psi, \tag{1.7.3}$$

and, by induction, that Eq. (1.7.2) holds for any powers of A. Eq. (1.7.2) is then valid for any function $f(A)$ which can be expressed as a Taylor series in powers of A.

2. The mean value of the observable A for the system in an eigenstate is given by the eigenvalue:

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \alpha, \tag{1.7.4}$$

and the uncertainty [defined as the variance, see Eq. (1.7.24)] is zero:

$$(\Delta A)^2 = \langle A^2\rangle - \langle A\rangle^2 = \alpha^2 - \alpha^2 = 0. \tag{1.7.5}$$

1.7.3 Theorem

Eigenvalues of a Hermitian operator are real.

Proof: Suppose an operator A has an eigenstate $|\psi\rangle$ with eigenvalue α.

$$A|\psi\rangle = \alpha|\psi\rangle. \tag{1.7.6}$$

Hence,

$$\langle\psi|A|\psi\rangle = \alpha\langle\psi|\psi\rangle. \tag{1.7.7}$$

Since A is Hermitian, taking the complex conjugate of the last equation, we obtain

$$\langle\psi|A|\psi\rangle^* = \langle\psi|A^\dagger|\psi\rangle = \langle\psi|A|\psi\rangle. \tag{1.7.8}$$

Therefore,

$$\alpha^* = \alpha. \tag{1.7.9}$$

Q.E.D.

1.7.4 Orthogonality theorem

Two eigenstates of a Hermitian operator with unequal eigenvalues are orthogonal.

Proof: Let A be the Hermitian operator and

$$A|\psi_i\rangle = \alpha_i|\psi_i\rangle, \tag{1.7.10}$$

$$A|\psi_j\rangle = \alpha_j|\psi_j\rangle, \tag{1.7.11}$$

where the eigenvalues α_i and α_j are not equal. Hence,

$$\langle\psi_j|A|\psi_i\rangle = \alpha_i\langle\psi_j|\psi_i\rangle, \tag{1.7.12}$$

and

$$\langle\psi_i|A|\psi_j\rangle = \alpha_j\langle\psi_i|\psi_j\rangle. \tag{1.7.13}$$

Take the complex conjugate of the second equation:

$$\langle\psi_j|A|\psi_i\rangle = \alpha_j\langle\psi_j|\psi_i\rangle, \tag{1.7.14}$$

where on the left we have used the Hermitian property of the operator A and on the right we have made use of the fact that α_j is real and

$$\langle\psi_i|\psi_j\rangle^* = \langle\psi_j|\psi_i\rangle. \tag{1.7.15}$$

Subtracting (1.7.14) from (1.7.12),

$$(\alpha_i - \alpha_j)\langle\psi_j|\psi_i\rangle = 0. \tag{1.7.16}$$

Since the two eigenvalues are not equal,

$$\langle\psi_i|\psi_j\rangle = 0. \tag{1.7.17}$$

1.7.5 Gram-Schmidt orthogonalization procedure

If the two eigenvalues α_i and α_j are equal, it is always possible to construct two orthogonal eigenstates even if $|\psi_i\rangle$ and $|\psi_\rangle$ are not orthogonal.

$$|\psi_j'\rangle = |\psi_j\rangle - |\psi_i\rangle\frac{\langle\psi_i|\psi_j\rangle}{\langle\psi_i|\psi_i\rangle}, \tag{1.7.18}$$

is orthogonal to $|\psi_i\rangle$, and is also an eigenstate with the same eigenvalue.

1.7.6 Physical meaning of eigenvalues and eigenstates

In quantum mechanics, we represent an observable property by a Hermitian operator. Because the systems in which we are now interested are microscopic, a measurement of the property of a system presents a non-negligible interaction of the measuring instrument with the system under investigation. We postulate that (1) the only possible outcome of one measurement of the property A is one of the eigenvalues of A, and (2) whatever the initial state of the system, after the measurement, the system will be in the eigenstate (or one of the eigenstates, if they are degenerate) whose eigenvalue is the outcome.

If the system is in one of the eigenstates of A before the measurement, a measurement of the property A will definitely yield the eigenvalue associated with the state, and will leave the system in the same eigenstate. It follows that the mean value of A is the eigenvalue and that the uncertainty is zero.

If the system is not in an eigenstate of A, then a measurement of the property A will put the system in an eigenstate. If the measurement is repeated immediately, the outcome will be the same eigenvalue and the system stays in the same eigenstate. In this sense, a measurement is repeatable. The repeated measurement is required to be performed immediately after the first one because, if the system stays in an eigenstate of A which is not an eigenstate of the Hamiltonian, given time it will evolve into a state which is not an eigenstate of A.

1.7.7 Eigenstate expansion and probability distribution

When the system is not in an eigenstate of the Hermitian operator A, it is not possible to predict exactly which eigenvalue of A will be the outcome of a measurement of A. What can be done within the framework of quantum mechanics is to examine the mix of the eigenstates which make up the state of the system and then to give odds on each possible result, i.e., to associate each eigenvalue of A with a probability of being the outcome of a measurement.

The orthogonality and completeness theorems enable one to expand any state of the system in terms of a set of eigenstates of any observable property. Let $\{|\psi_i\rangle\}$, i being a set of integers, be a complete set of orthonormal eigenstates of a Hermitian operator

A. (Extension to continuous eigenvalues is straightforward and will be done below by example. We choose not to burden the notation system to cover the most general case.) Then

$$A|\psi_i\rangle = \alpha_i|\psi_i\rangle, \tag{1.7.19}$$

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}. \tag{1.7.20}$$

Completeness means that any state of the system, represented by the wave function $|\Psi\rangle$ can be expanded as a series in the eigenfunctions:

$$|\Psi\rangle = \sum_j |\psi_j\rangle a_j. \tag{1.7.21}$$

To find the coefficients a_j, multiply both sides of the equation by $\langle\psi_i|$:

$$\begin{aligned}\langle\psi_i|\Psi\rangle &= \sum_j \langle\psi_i|\psi_j\rangle a_j = \sum_j \delta_{ij} a_j \\ &= a_i \end{aligned} \tag{1.7.22}$$

The state $|\Psi\rangle$ has a probability distribution $|a_j|^2$ among the eigenstates $\{|\psi_i\rangle\}$ of A. The reasonableness of the statement is seen as follows. The expectation value of A in the state $|\Psi\rangle$ is, by means of the eigenstate expansion, given by

$$\langle\Psi|A|\Psi\rangle = \sum_i \alpha_i |a_i|^2. \tag{1.7.23}$$

If at a time t, the state of the system is represented by the wave function $|\Psi\rangle$, then $|a_j|^2$ is the probability of finding the system to be in the eigenstate ψ_j immediately after a measurement of the property A. This probability interpretation is consistent with the expression for the average value of A given by Eq. (1.7.23) or with the corresponding expression for any powers of A. The coefficient a_j itself is called the probability amplitude.

Besides the expectation value, another important quantity which characterizes the probability distribution is the uncertainty ΔA, defined by

$$(\Delta A)^2 = \langle\Psi|A^2|\Psi\rangle - \langle\Psi|A|\Psi\rangle^2. \tag{1.7.24}$$

1.7.8 Important examples of eigenstates

1. Energy

   We have come across this property many times. We take the Hermitian operator for energy to be the Hamiltonian operator. The eigenfunctions were treated in Section 1.3.5.

2. Position of a particle

   Although we have considered only eigenfunction expansion in the case of discrete eigenvalues, continuous eigenvalues can be treated in a similar way, for example, by taking the index to be continuous. The position operator X, when measured, can yield a continuous spectrum of values x. We express this fact as the eigen-equation:

   $$X|a\rangle = a|a\rangle, \tag{1.7.25}$$

   where $|a\rangle$ is the state where the particle is definitely at the coordinate $x = a$. By exploiting the property of the δ-function

   $$x\delta(x-a) = a\delta(x-a), \tag{1.7.26}$$

   we can identify the position eigen-wavefunction for the specific position a as

   $$\langle x|a\rangle = \delta(x-a), \tag{1.7.27}$$

   where x is the position coordinate variable. The equation can also be read as the orthonormal condition for the position states with continuous eigenvalues. The position eigenfunction expansion for any state $|\Psi\rangle$ is, by extension to continuous eigenvalues of Eqs. (1.7.21) and (1.7.22),

   $$|\Psi\rangle = \int dx|x\rangle\langle x|\Psi\rangle, \tag{1.7.28}$$

   where we have used the completeness relation

   $$\int dx\ |x\rangle\langle x| = 1. \tag{1.7.29}$$

   The probability $\langle x|\Psi\rangle$ is the wave function $\Psi(x)$.

3. Momentum of a particle

The momentum operator P in a particular direction (say, along the x axis) is another example of a property which has continuous eigenvalues p:

$$P|p\rangle = p|p\rangle. \tag{1.7.30}$$

Capping both sides of Eq. (1.7.30) leads by means of Eq. (1.5.3) to

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|p\rangle = p\langle x|p\rangle. \tag{1.7.31}$$

Integration of the above leads to the momentum eigen-wavefunction

$$\langle x|p\rangle = Ce^{ipx/\hbar}, \tag{1.7.32}$$

with the normalization constant C to be determined.

The orthonormality condition of the momentum eigenstates

$$\langle p|p'\rangle = \int dx|C|^2 e^{-ipx/\hbar}e^{ip'x/\hbar} = \delta(p-p') \tag{1.7.33}$$

leads to

$$|C|^2 2\pi\hbar = 1, \tag{1.7.34}$$

or

$$C = \frac{1}{\sqrt{2\pi\hbar}}, \tag{1.7.35}$$

with the arbitrary choice of zero phase for C.

A general state of the particle has the momentum eigenfunction expansion

$$|\Psi\rangle = \int dp|p\rangle\langle p|\Psi\rangle, \tag{1.7.36}$$

which in the position representation is the Fourier relation:

$$\langle x|\Psi\rangle = \int dp\langle x|p\rangle\langle p|\Psi\rangle \tag{1.7.37}$$

where the momentum probability amplitude $\Phi(p,t) = \langle p|\Psi(t)\rangle$ is just the Fourier transform of the wave function.

1.8 Commutative Observables and Simultaneous Measurements

According to Heisenberg's uncertainty principle, a conjugate pair of dynamic variables in the classical mechanics sense, such as x and p_x, cannot be measured simultaneously to arbitrary accuracy in the quantum regime. A more convenient criterion to determine if a pair of physical observables can be measured simultaneously is the commutability of their corresponding operators.

1.8.1 Commutation bracket

Let A and B be two operators representing two observables. Their commutation bracket is defined by:

$$[A, B] = AB - BA. \tag{1.8.1}$$

1.8.2 Commutative operators

Two operators A and B are said to be commutative if

$$AB = BA, \qquad \text{or} \quad [A, B] = 0. \tag{1.8.2}$$

1.8.3 Theorem 1

If A and B are two commutative operators and either A or B has non-degenerate eigenvalues, then its eigenfunctions are also eigenfunctions of the other operator.

Proof: Say,

$$A|\psi_j\rangle = \alpha_j|\psi_j\rangle, \tag{1.8.3}$$

with $|\psi_j\rangle$ being non-degenerate, i.e., all the eigenvalues α_j are distinct.

Operating on both sides of (1.8.3) with B:

$$BA|\psi_j\rangle = B(\alpha_j|\psi_j\rangle) = \alpha_j B|\psi_j\rangle. \tag{1.8.4}$$

Since it is given that

$$AB = BA, \tag{1.8.5}$$

Eq. (1.8.4) becomes

$$A(B|\psi_j\rangle) = \alpha_j(B|\psi_j\rangle), \tag{1.8.6}$$

which means that $B|\psi_j\rangle$ is also an eigenfunction of A with the eigenvalue α_j. Since we assume that the eigenvalue α_j only has one eigenfunction, $B|\psi_j\rangle$ and $|\psi_j\rangle$ must be essentially the same function, i.e.

$$B|\psi_j\rangle = \beta_j|\psi_j\rangle, \tag{1.8.7}$$

for some constant β_j. But, that means $|\psi_j\rangle$ is an eigenfunction of B with the eigenvalue β_j. QED.

1.8.4 Example

Consider a free particle in one dimension. The momentum operator p and the Hamiltonian H, where

$$H = \frac{p^2}{2m}, \tag{1.8.8}$$

are clearly two operators which commute, i.e.,

$$[p, H] = 0. \tag{1.8.9}$$

The plane wave e^{ikx} which has a constant wave vector k is an eigenfunction of the momentum operator p with the eigenvalue $\hbar k$. It is non-degenerate. Therefore, by the foregoing theorem, the plane wave e^{ikx} must be an eigenstate of the Hamiltonian H, which can be checked explicitly:

$$He^{ikx} = \left(\frac{\hbar^2 k^2}{2m}\right) e^{ikx}. \tag{1.8.10}$$

We note the non-degeneracy requirement of the theorem. The eigenstates of the Hamiltonian are doubly degenerate and they are not necessarily the eigenstates of the momentum even though the two properties commute. From Eq. (1.8.10), it can be seen that e^{ikx} and e^{-ikx} are two degenerate eigenstates of the Hamiltonian with the same energy value $\hbar^2 k^2/2m$. These states happen to be also eigenstates of the momentum.

However, we could have chosen two different linear combinations as the two degenerate eigenstates for the same energy eigenvalue, such as the even and odd parity solutions

$$\psi_s = \frac{1}{2}(e^{ikx} + e^{-ikx}) = \cos kx, \tag{1.8.11}$$

$$\psi_a = \frac{1}{2i}(e^{ikx} - e^{-ikx}) = \sin kx, \tag{1.8.12}$$

which clearly are energy eigenstates with the same eigenvalue $\hbar^2 k^2/2m$. Indeed, they are not eigenstates of the momentum, since

$$p\psi_s = -i\hbar\frac{\partial}{\partial x}\cos kx = i\hbar k \sin kx = i\hbar k\psi_a, \tag{1.8.13}$$

and

$$p\psi_a = -i\hbar k\psi_s. \tag{1.8.14}$$

From these two linear equations, it is easy to construct the eigenstates of p. By inspection, they are $\psi_s \pm i\psi_a$.

1.8.5 Theorem 2

If A and B are two commutative operators, then there exists a complete set of eigenstates which are simultaneously eigenstates of A and B.

Proof: Let us forget the proof of the completeness and concentrate on the existence of a set of common eigenstates.

Case I. If the eigenstates of one of the operators are all non-degenerate, then Theorem 1 gives the result.

Case II. Some of the eigenstates, say of A, are degenerate. Let us illustrate the proof with just two-fold degeneracy:

$$A|\psi_j\rangle = \alpha|\psi_j\rangle, \quad \text{for } j = 1, 2. \tag{1.8.15}$$

The proof can be extended straightforwardly to any multiple fold of degeneracy.

By using the comutativity of A and B, we can show that $B|\psi_j\rangle$ is also an eigenstate of A with the same eigenvalue α:

$$A(B|\psi_j\rangle) = BA|\psi_j\rangle = \alpha B|\psi_j\rangle. \tag{1.8.16}$$

Since we assume that there are only two eigenstates with the eigenvalue α, the two states $B|\psi_1\rangle$ and $B|\psi_2\rangle$ must be linear combinations of the eigenstates $|\psi_1\rangle$ and $|\psi_2\rangle$:

$$\left[\begin{array}{cc} B|\psi_1\rangle & B|\psi_2\rangle \end{array}\right] = \left[\begin{array}{cc} |\psi_1\rangle & |\psi_2\rangle \end{array}\right] \left[\begin{array}{cc} b_{11} & b_{12} \\ b_{21} & b_{22} \end{array}\right], \tag{1.8.17}$$

where the b_{ij}'s are constants. If the off-diagonal elements b_{12} and b_{21} are not both zero, then $|\psi_1\rangle$ and $|\psi_2\rangle$ are not eigenstates of B.

However, it is possible to choose two linear combinations of the eigenstates of A, $|\psi_1\rangle$ and $|\psi_2\rangle$, which, of course, are still eigenstates of A with the same eigenvalue α, and which are now eigenstates of B as well, i.e.,

$$B(|\psi_1\rangle c_1 + |\psi_2\rangle c_2) = \beta(|\psi_1\rangle c_1 + |\psi_2\rangle c_2), \tag{1.8.18}$$

where B is an operator acting the state wave functions $|\psi_1\rangle$, and $|\psi_2\rangle$, β is an eigenvalue of B, and c_1 and c_2 are scalar coefficients. Substituting Eq. (1.8.17) into the above equation and identifying the coefficients of $|\psi_1\rangle$ and $|\psi_2\rangle$, we arrive at the secular equation:

$$\left[\begin{array}{cc} b_{11} & b_{12} \\ b_{21} & b_{22} \end{array}\right] \left[\begin{array}{c} c_1 \\ c_2 \end{array}\right] = \beta \left[\begin{array}{c} c_1 \\ c_2 \end{array}\right]. \tag{1.8.19}$$

By diagonalizing the 2×2 matrix with coefficients b_{ij}, we find two eigenvalues β_i, with $i = 1, 2$, and their corresponding eigenvectors $\left[\begin{array}{c} c_{1i} \\ c_{2i} \end{array}\right]$.

1.8.6 Implications of the theorems

These theorems enable us to decide whether it is possible to measure two observables simultaneously to any desired accuracy or whether the observables obey the uncertainty principle.

If the two observables A and B commute, then it is possible to find or prepare the system to be in a state which is the common eigenstate of both operators, in which the measured values for A and B can both be accurate to any arbitrary degree. Examples of such pairs of properties are components of position in two different directions, components of momentum in two different directions, and energy and momentum for a free particle.

Generalization of the position eigenstate $|x\rangle$ to three dimensions is now trivial. Since the three components X, Y, Z of the position vector operator $\vec{R}$ commute with each other, we can have a simultaneous eigenstates of all three position coordinates $|\vec{r}\rangle$ with

eigenvalues $\vec{r} = (x, y, z)$. Similarly for the momentum eigenstate $|\vec{p}\rangle$ in three dimension. The transformation matrix between the two spaces is

$$\langle \vec{r}|\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\vec{p}\cdot\vec{r}/\hbar} \tag{1.8.20}$$

For a pair of observables which do not commute, we give the following generalized statement of the uncertainty principle.

1.9 The Uncertainty Principle

Denote the commutation bracket of a pair of physical observables, represented by the Hermitian operators A and B by

$$[A, B] = iC, \tag{1.9.1}$$

then C must be either a real constant or a Hermitian operator. A and B are said to be conjugate observables. For any state of the system,

$$\Delta A \cdot \Delta B \geq \frac{1}{2}|\langle C\rangle|. \tag{1.9.2}$$

1.9.1 The Schwartz inequality

We need this lemma to prove the general uncertainty principle. For any two states Φ and Ξ,

$$|\langle \Xi|\Phi\rangle|^2 \leq \langle \Xi|\Xi\rangle \cdot \langle \Phi|\Phi\rangle \tag{1.9.3}$$

This inequality is the functional analog of the vector inequality

$$|\vec{a} \cdot \vec{b}|^2 \leq |\vec{a}|^2 |\vec{b}|^2. \tag{1.9.4}$$

We give a proof which relies on the geometrical meaning of the vector inequality. The projection $\vec{b} \cdot \vec{a}/|\vec{b}|$ is the magnitude of the component of vector $\vec{a}$ along the direction of $\vec{b}$. The magnitude of the component of $\vec{a}$ perpendicular to $\vec{b}$ is $|\vec{a} - \vec{b}(\vec{b} \cdot \vec{a}/)|\vec{b}|^2|$ which cannot be less than zero. Squaring and expanding this expression will lead to the vector inequality. So we follow the same method for the two states:

$$\left[\langle \Xi| - \frac{\langle \Xi|\Phi\rangle}{\langle \Phi|\Phi\rangle}\langle \Phi|\right]\left[|\Xi\rangle - |\Phi\rangle\frac{\langle \Phi|\Xi\rangle}{\langle \Phi|\Phi\rangle}\right] \geq 0. \tag{1.9.5}$$

Expansion of this inequality leads to the Schwartz inequality.

1.9.2 Proof of the uncertainty principle

Suppose the system is in the state $|\Psi\rangle$. It is convenient to change the operator to one with zero expectation value in that state, e.g.,

$$\delta A = A - \langle A \rangle, \tag{1.9.6}$$

$\langle A \rangle$ being the shorthand for the mean value $\langle \Psi | A | \Psi \rangle$.

To facilitate the use of the Schwartz inequality, we let

$$\begin{aligned} |\Xi\rangle &= \delta A |\Psi\rangle, \\ |\Phi\rangle &= \delta B |\Psi\rangle. \end{aligned} \tag{1.9.7}$$

Since δA and δB are Hermitian operators, it is easy to show that the uncertainties are given by

$$\begin{aligned} (\Delta A)^2 &= \langle \Xi | \Xi \rangle \\ (\Delta B)^2 &= \langle \Phi | \Phi \rangle. \end{aligned} \tag{1.9.8}$$

The Schwartz inequality (1.9.3) then takes us a step towards the uncertainty relation:

$$(\Delta A)^2 (\Delta B)^2 \geq |\langle \Xi | \Phi \rangle|^2, \tag{1.9.9}$$

where,

$$\langle \Xi | \Phi \rangle = \langle \Psi | \delta A \, \delta B | \Psi \rangle, \tag{1.9.10}$$

having used the Hermitian property of A. The product operator may be written in terms of the symmetrized and antisymmetrized products:

$$\delta A \, \delta B = S + iT, \tag{1.9.11}$$

$$\text{where} \quad S = \frac{1}{2} (\delta A \, \delta B + \delta B \, \delta A) \equiv \frac{1}{2} \{ \delta A, \delta B \}, \tag{1.9.12}$$

$$T = \frac{1}{2i} (\delta A \, \delta B - \delta B \, \delta A) \equiv \frac{1}{2i} [\delta A, \delta B], \tag{1.9.13}$$

so that both the expectation values $\langle S\rangle$ and $\langle T\rangle$ are real. We have introduced the anticommutation brackets $\{A, B\} = AB + BA$ in addition to the commutation brackets. The expectation value of T is

$$\langle T\rangle = \frac{1}{2i}\langle [A, B]\rangle = \frac{1}{2}\langle C\rangle. \tag{1.9.14}$$

Hence,

$$\begin{aligned} |\langle \Xi|\Phi\rangle|^2 &= |\langle S + iT\rangle|^2 \\ &= |\langle S\rangle|^2 + |\langle T\rangle|^2 \\ &\geq |\langle T\rangle|^2 = \frac{1}{4}|\langle C\rangle|^2. \end{aligned} \tag{1.9.15}$$

The symmetrized part $\langle S\rangle$ is a measure of the correlation between the two operators δA and δB, which is an important quantity in quantum dynamics. It also contributes to the product of the uncertainties. Since the correlation may exist also in the classical regime, this portion of the uncertainty is not necessarily quantum in nature. The anti-symmetrized part which provides the minimum uncertainty product is quintessentially quantum mechanical since all classical observables commute.

From the general statement of the uncertainty principle here we can derive the special case for the pair of operators x and p_x. Since $[x, p_x] = i\hbar$, then

$$\Delta x \Delta p_x \geq \frac{1}{2}\hbar. \tag{1.9.16}$$

1.9.3 Applications of the uncertainty principle

We have seen that the uncertainty principle is a consequence of the quantum mechanics. It is a succinct statement of an essentially quantum phenomenon. It is also useful in two aspects: it provides a physical understanding of some microscopic phenomena completely outside the realm of classical physics and it can be used to yield some semi-quantitative estimates.

A particle under gravity

Consider a familiar problem in mechanics. A particle falls under gravity towards an impenetrable floor. According to classical mechanics, the ground state (the state of least

energy) is one in which the particle is at rest on the floor. Let us measure the distance vertically from the floor and call it x. Thus, we know the position of the particle in its ground state ($x = 0$) and also its momentum ($p = 0$). This contradicts the uncertainty principle.

We can solve the problem by quantum mechanics. The potential energy of the particle is

$$\begin{aligned} V(x) &= mgx \quad \text{if } x > 0, \\ &= +\infty \quad \text{if } x < 0. \end{aligned} \tag{1.9.17}$$

Just plug this into the Schrödinger equation and solve it. Let us try a simple estimate here. The ground state will differ from the classical solution by having an uncertainty in position of Δx and momentum Δp where

$$\Delta p \sim \hbar/\Delta x. \tag{1.9.18}$$

Then the energy is approximately,

$$E \sim \frac{(\Delta p)^2}{2m} + mg\Delta x \sim \frac{\hbar^2}{2m(\Delta x)^2} + mg\Delta x. \tag{1.9.19}$$

Minimizing the energy with respect to Δx, we obtain

$$\Delta x \sim \left(\frac{\hbar^2}{m^2 g}\right)^{1/3} \sim \left(\frac{m_e}{m}\right)^{2/3} \times 1.11 \times 10^{-3}\text{meter}. \tag{1.9.20}$$

where m_e is the mass of the electron.

From the uncertainty principle, we have deduced that a particle cannot rest on a floor even under the pull of gravity. Even in the lowest energy state, the particle bounces up and down with a range given by (1.9.20).

Stability of the electron orbit in an atom

Bohr had postulated that the orbits are 'stationary.' Once we accept the uncertainty principle, we can understand the stability of the smallest Bohr orbit. Consider the hydrogen atom. We shall come back to the detailed solution of the Schrödinger equation later. The electron is prevented from radiating electromagnetic energy and falling into the nucleus by the following considerations. The closer the electron gets to the nucleus, the larger the uncertainty of its momentum is. Then there is the possibility that its

kinetic energy becomes larger than its potential energy, thus escaping from the nucleus. Therefore, in the ground state, the electron compromises by staying at a distance from the nucleus.

We can obtain a more quantitative estimate. Let the root-mean-square distance of the electron from the proton be Δr. The uncertainty in momentum is

$$\Delta p \sim \hbar/\Delta r. \tag{1.9.21}$$

The energy of the ground state is roughly,

$$\begin{aligned} E &\sim \frac{(\Delta p)^2}{2m} - \frac{e'^2}{\Delta r} \\ &\sim \frac{\hbar^2}{2m(\Delta r)^2} - \frac{e^2}{\Delta r}. \end{aligned} \tag{1.9.22}$$

where, in SI units, $e'^2 = e^2/4\pi\epsilon_0$, e being the proton charge. The minimum energy is given by

$$\Delta r \sim \hbar^2/me^2 = a_0 \sim 0.5 \text{ Å, (the Bohr radius).} \tag{1.9.23}$$

It is a fluke that we obtain exactly the right energy because in (1.9.18) we can only be certain to an order of magnitude of the coefficient multiplying $\hbar$.

From Eq. (1.9.20), the range of bounce of a ground state electron on the floor under gravity is about 1 mm, surprisingly large compared with the uncertainty in position in the atom. The reason is that the force of attraction on the electron by the proton is much stronger than the gravity pull. Another inference is that the stronger the attraction, the larger the range of possible speed. For the hydrogen atom, the speed is about 10^6 m/s which is small enough compared with the speed of light that non-relativistic mechanics is valid. For inner electrons in very heavy atoms or nucleons (neutrons and protons) in the nucleus, the force of attraction is much stronger and the speed of the particle is close enough to c that relativistic quantum mechanics must be used.

Time for the spread of a wave-packet

In section 1.10.1, an explicit calculation yields the time taken to double the width of a Gaussian wave-packet. Here is a more general derivation for the order of magnitude of the time T.

Suppose a wave-packet initially has uncertainty Δx in position and Δp in momentum. Initially, the wave-packet has components of plane waves with wave-vectors in a range $\Delta p/\hbar$. Consider the motion of two components of plane waves, one with the wave-vector of the mean and one with wave-vector differing by one standard deviation. The two plane waves have wave-vectors different by $\Delta p/\hbar$ and, therefore, speeds differing by $\Delta p/m$. If initially the two plane waves both have crests at the average position of the wave-packet, after time T, they will be at a distance $T\Delta p/m$ apart. Since T is the time taken for the wave-packet to double its width, this distance $T\Delta p/m$ must be of the same order as the initial width Δx:

$$\Delta x \sim T\Delta p/m. \tag{1.9.24}$$

Hence,

$$T \sim m\Delta x/\Delta p \sim m(\Delta x)^2/\hbar. \tag{1.9.25}$$

in agreement with Eq. (1.10.9).

1.10 Examples

Example is the school of mankind, and they will learn at no other. – Edmund Burke

1.10.1 The Gaussian wave packet

Given that at $t = 0$ the particle is at $x = 0 \pm \sigma$ (with uncertainty σ in position) and with mean momentum $\hbar K$, what happens to the particle at a later time t?

The information which we possess is not sufficient to determine the wave function at $t = 0$ completely. A reasonable approximation for the initial wave function which agrees with the given data is

$$\Psi(x, 0) = f(x) = (2\pi\sigma^2)^{-1/4} \exp\left(-\frac{x^2}{4\sigma^2} + iKx\right), \tag{1.10.1}$$

with the mean position at $x = 0$ and the uncertainty $\Delta x = \sigma$. The initial wave function is modulated with a Gaussian envelope (Fig. 1.1) and the probability density is Gaussian (Fig. 1.2).

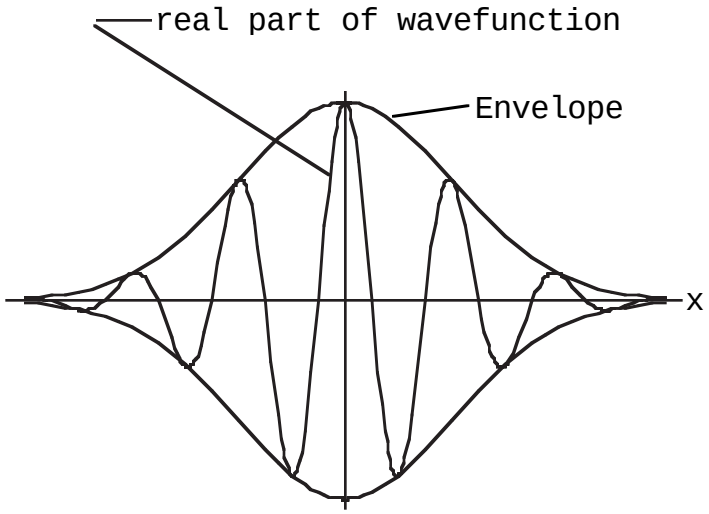

Figure 1.1: The real part of a Gaussian wave function and its envelope.

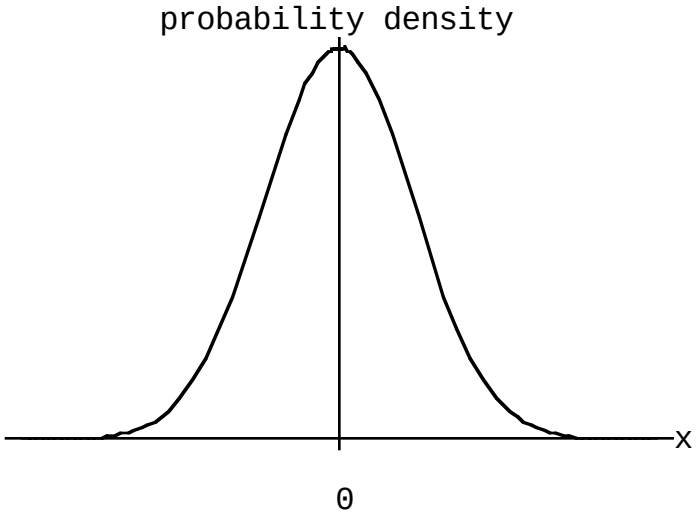

Figure 1.2: Probability density from a Gaussian wave function.

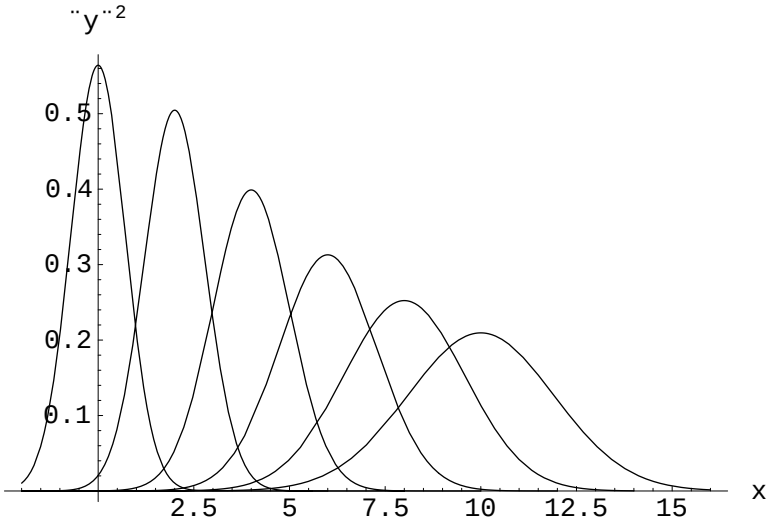

Figure 1.3: Propagation of a Gaussian wave packet from left to right.

The Fourier transform of a Gaussian is another Gaussian, Eq. (1.3.5):

$$\phi(k) = (2\sigma^2/\pi)^{1/4} e^{-\sigma^2(k-K)^2}, \tag{1.10.2}$$

and the momentum probability density

$$\Pi(k) = |\phi(k)|^2 = (2\sigma^2/\pi)^{1/2} e^{-2\sigma^2(k-K)^2}. \tag{1.10.3}$$

By comparing it with the standard Gaussian, we see that the mean momentum is

$$\langle p \rangle = \hbar \langle k \rangle = \hbar K, \tag{1.10.4}$$

as given, and the uncertainty in momentum is

$$\Delta p = \hbar \Delta k = \hbar / 2\sigma. \tag{1.10.5}$$

Substituting the Fourier transform (1.10.2) into the general solution of the Schrödinger equation, we obtain the wave function at time t:

$$\begin{aligned} \psi(x,t) &= \int \frac{dk}{\sqrt{2\pi}} (2\sigma^2/\pi)^{1/4} e^{-\sigma^2(k-K)^2 + ikx - i\hbar k^2 t/2m} \qquad (1.10.6) \\ &= (2\pi\sigma^2)^{-1/4} \left(1 + \frac{i\hbar t}{2m\sigma^2}\right)^{-1/2} \exp\left\{ iKx - it\hbar K^2/2m - \frac{(x - t\hbar K/m)^2}{4\sigma^2 \left(1 + \frac{i\hbar t}{2m\sigma^2}\right)} \right\}. \end{aligned}$$

The wave function is a plane wave with a Gaussian envelope. At time t, the mean position is

$$\langle x \rangle = \hbar K t/m, \tag{1.10.7}$$

with uncertainty

$$\Delta x = \sigma \left\{ 1 + \left(\frac{\hbar t}{2m\sigma^2} \right)^2 \right\}^{1/4}. \tag{1.10.8}$$

An example of the probability density of this wave function is plotted as a function of position for a sequence of time values in Fig. 1.3.

To simulate a classical particle, we 'prepare' a wave-packet centered at $x = 0$ with mean momentum $\hbar K$. By wave mechanics, we deduce that the wave-packet travels with its peak moving with speed $\hbar K/m$, identical with the classical particle speed. However, the width of the wave-packet (i.e. the uncertainty in position of the particle) grows with time such that for $t \gg T$ where

$$T = m\sigma^2/\hbar, \tag{1.10.9}$$

the wave-packet spreads out so much that it no longer has any resemblance to the classical particle.

We have studied the motion of a wave-packet using a Gaussian envelope. The speed of the peak of the wave-packet (called the group velocity) is the same for the wave-packet of any other shape. The order of magnitude of the time T for the spreading of the wave-packet is also the same.

Order of magnitude of time of spread of wave packet

Dust particle

Say, $m \simeq 10^{-6}$ Kg and $\sigma \simeq 10^{-6}$ meter $= 1\mu$

$$T \simeq 10^{-6} \times (10^{-6})^2/10^{-34} = 10^{16} \text{ sec.}$$

(1 year $= 3 \times 10^7$ sec). This example shows that a particle of macroscopic dimension will stay like a classical particle for a long time.

Electron

$$\begin{aligned} m &\simeq 10^{-30} \text{ kg} \\ T &\simeq 10^4 \times \sigma^2 \text{ sec.} \end{aligned}$$

(i) Electron in an atom

$$\begin{aligned} \sigma &\simeq \text{ size of atom} \simeq a_0 = 0.5 \times 10^{-10} \text{ meter.} \\ T &\simeq 10^{-16} \text{ sec.} \end{aligned}$$

From the Bohr theory of the hydrogen, in particular Eqs. (1.6.5) and (1.6.6), for the electron in its ground state the period of revolution around the proton is about 10^{-16} sec. Hence, it is impossible to make a wave-packet for the electron in an atom and to try to follow its progress.

(ii) Electron in a thermionic tube

$$\begin{aligned} \text{Energy} \quad E &\simeq 5 \text{ ev} \simeq 10^{-18} J. \\ \text{Speed} \quad v &\simeq (2E/m)^{1/2} \simeq 10^6 \text{ m/s.} \end{aligned}$$

The time taken by the electron to travel 1 cm is about 10^{-8} sec, 1 centimeter being taken as the order of magnitude dimension of the thermionic tube. If the electrons can be treated as classical particles, then $T \gtrsim 10^{-8}$ sec and $\sigma = (10^{-4}T)^{1/2} \gtrsim 10^{-6}$ meters. The uncertainty in position is a lot larger than the atomic dimension.

1.10.2 Fourier transform of the Yukawa potential

Here is an example of Fourier transform in three dimensions. Find the Fourier transform of the potential

$$V(r) = \frac{e^{-\alpha r}}{r}\,, \tag{1.10.10}$$

where r is the radial distance from the origin.

Solution — The Fourier transform of the potential is given by

$$U(\vec{k}) = \int d^3r\, \frac{1}{r} e^{-\alpha r - i\vec{k}\cdot\vec{r}}, \tag{1.10.11}$$

where we find it convenient to drop the factor $(2\pi)^{-3/2}$ in the Fourier integral here and put it in the inverse Fourier integral. In the spherical polar coordinates (r, θ, ϕ) with the z-axis chosen along the wave vector $\vec{k}$, the integral is

$$\begin{aligned} U(k) &= \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \, \frac{1}{r} e^{-\alpha r - ikr\cos\theta} \\ &= 2\pi \int_0^\infty r dr \int_{-1}^1 d\mu \, e^{-\alpha r - ikr\mu} \\ &= 4\pi \int_0^\infty dr \, \Im\left[\frac{1}{k} e^{-\alpha r + ikr}\right] \\ &= \frac{4\pi}{\alpha^2 + k^2}, \end{aligned} \tag{1.10.12}$$

where $\Im[\ ]$ denotes the imaginary part of the expression in the square brackets and we have changed the variable $\mu = \cos\theta$ for the θ integration.

As a bonus, by taking the limit of α to zero, we find the Fourier transform of the Coulomb potential $1/r$ to be $4\pi/k^2$.

1.10.3 Interference and beat

1. The wave function of a free particle in one dimension at time $t = 0$ is made up of two plane waves of the same amplitude with wave-vectors k_1 and k_2:

$$\psi(x, t = 0) = C(e^{ik_1 x} + e^{ik_2 x}) \, . \tag{1.10.13}$$

Find the wave function at time t. What is the probability of finding the particle at time t with momentum $\hbar k_1$?

Solution — The most general way to find the solution at time t is by Fourier transforming the solution at $t = 0$. Since Fourier transform is just a way to decompose a function of x into plane-wave components and since we are already given a discrete sum of two plane waves which is a special case of the Fourier integral, we can simply proceed to find the time dependence of each plane wave which satisfies the Schrödinger equation and place them back into the sum which will then be a solution of the Schrödinger equation, i.e.

$$\psi(x, t) = C(e^{ik_1 x - i\omega_1 t} + e^{ik_2 x - i\omega_2 t}) \, , \tag{1.10.14}$$

where

$$\omega_n = \frac{\hbar k_n^2}{2m}. \tag{1.10.15}$$

The moduli squared of the coefficients in front of the plane waves give the relative probabilities of finding the particle in the respective plane-wave states. Thus, the probability of finding it in k_1 state is one-half.

2. Suppose $k_1 = k$ and $k_2 = -k$. Find the wave function at time t and discuss the interference effect by contrasting the probability density of the wave function with that of each plane-wave component alone.

Solution — The wave function is

$$\psi(x,t) = 2C\cos(kx)e^{-i\omega t}, \tag{1.10.16}$$

with

$$\omega = \frac{\hbar k^2}{2m}. \tag{1.10.17}$$

The probability density distribution is

$$\rho(x,t) = |\psi(x,t)|^2 = 4|C|^2(\cos kx)^2, \tag{1.10.18}$$

which varies sinusoidally between 0 and $4|C|^2$, in contrast with the constant density associated with a single plane wave.

3. Suppose $k_1 = k - \Delta k$ and $k_2 = k + \Delta k$, $\Delta k \ll k$. Describe the resultant wave function. Find the speed of the "beat" pattern. Show that the current density satisfies the equation of continuity.

Solution — Let $\omega_1 = \omega - \Delta\omega$ and $\omega_2 = \omega + \Delta\omega$. Then,

$$\Delta\omega = \frac{\hbar k}{m}\,\Delta k + 0(\Delta k)^2\,, \tag{1.10.19}$$

neglecting terms of second order in the small quantity Δk. The wave function,

$$\psi(x,t) = 2Ce^{ikx-i\omega t}\cos(\Delta kx - \Delta\omega t), \tag{1.10.20}$$

is a plane wave $e^{ikx-i\omega t}$ with its amplitude modulated by a cosine wave form $\cos(\Delta kx - \Delta\omega t)$. The crest of the modulation wave moves with speed

$$v_g = \frac{\Delta\omega}{\Delta k} = \frac{\hbar k}{m}. \tag{1.10.21}$$

The current density is given by

$$\begin{aligned} J(x,t) &= \Im\left(\frac{\hbar}{m}\psi\frac{\partial\psi^*}{\partial x}\right) \\ &= \frac{\hbar k}{m}4|C|^2\cos^2(\Delta kx - \Delta\omega t)\,. \end{aligned} \tag{1.10.22}$$

With the density

$$\rho(x,t) = 4|C|^2\cos^2(\Delta kx - \Delta\omega t) \tag{1.10.23}$$

it is easy to see that they satisfy the continuity equation

$$\frac{\partial\rho}{\partial t} + \frac{\partial J}{\partial x} = 0. \tag{1.10.24}$$

1.10.4 Constant of motion

If the Hamiltonian of a particle does not depend explicitly on time, show that the mean energy of any state is a constant of motion.

Solution — The expectation value of the Hamiltonian is

$$E = \langle\Psi(t)|H|\Psi(t)\rangle. \tag{1.10.25}$$

To see if it is a constant in time, we just differentiate it with respect to time:

$$\frac{dE}{dt} = \frac{\partial\langle\Psi(t)|}{\partial t}H|\Psi(t)\rangle + \langle\Psi(t)|H\frac{\partial|\Psi(t)\rangle}{\partial t}\,, \tag{1.10.26}$$

where we have used the fact that H is independent of t. The time rate of change of the state is given by the Schrödinger equation,

$$H|\Psi(t)\rangle = i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t}, \tag{1.10.27}$$

and its complex conjugate,

$$\langle\Psi(t)|H = -i\hbar\frac{\partial\langle\Psi(t)|}{\partial t}, \tag{1.10.28}$$

where we have used the Hermitian property of H. Thus,

$$\frac{dE}{dt} = \langle\Psi(t)|H^2|\Psi(t)\rangle - \langle\Psi(t)|H^2|\Psi(t)\rangle = 0. \tag{1.10.29}$$

1.10.5 The inversion symmetry

Consider a particle in three dimensional space. Let P be the inversion operator, i.e., if $\psi(\vec{r})$ is any wave function, then

$$P\psi(\vec{r}) = \psi(-\vec{r}). \tag{1.10.30}$$

1. Show that $P^2 = 1$.

   Solution — From the definition of P^2, acting on any wave function,

   $$P^2\psi(\vec{r}) = P\{P\psi(\vec{r})\} = P\psi(-\vec{r}) = \psi(\vec{r}). \tag{1.10.31}$$

   Thus, $P^2 = 1$, the identity operator.

2. Show that P is Hermitian.

   Solution — The Hermitian conjugate $P^\dagger$ of P is defined by

   $$\langle\Psi|P^\dagger|\Phi\rangle = \langle P\Psi|\Phi\rangle, \tag{1.10.32}$$

   valid for any pair of states. The right-hand side is by the action of P

   $$\int d^3r\ \Psi^*(-\vec{r})\Phi(\vec{r}) = \int d^3r\ \Psi^*(\vec{r})\Phi(-\vec{r}) = \int d^3r\ \Psi^* P\Phi, \tag{1.10.33}$$

   where in the intermediate step we change the sign of the variable of integration and in the last step we restore the appearance of P by its definition. Since we have shown that

   $$\langle\Psi|P^\dagger|\Phi\rangle = \langle\Psi|P|\Phi\rangle, \tag{1.10.34}$$

   for any pair of states, $P^\dagger$ must be the same as P, i.e. P is Hermitian.

3. Show that the eigenvalues of P are $+1$ and -1. The eigenfunctions are said to be of even and of odd parity, respectively.

   Solution — Consider the eigenequation:

   $$P\psi = \alpha\psi, \tag{1.10.35}$$

where α is a number. Operating P on both side of the equation leads to

$$P^2\psi = \alpha^2\psi. \tag{1.10.36}$$

Since from part (a), $P^2 = 1$, α^2 must be equal to unity. So, $\alpha = \pm 1$.

When $\alpha = 1$, the eigenfunction is given

$$P\psi_e(\vec{r}) = \psi_e(\vec{r}), \tag{1.10.37}$$

i.e. it is of even parity:

$$\psi_e(-\vec{r}) = \psi_e(\vec{r}). \tag{1.10.38}$$

When $\alpha = -1$, the eigenfunction is given

$$P\psi_o(\vec{r}) = -\psi_o(\vec{r}), \tag{1.10.39}$$

i.e. it is of odd parity:

$$\psi_o(-\vec{r}) = -\psi_o(\vec{r}). \tag{1.10.40}$$

4. Show that any wave function can be expressed as a linear sum of the eigenfunctions of P, i.e., of functions of even and odd parity.

Solution — Any wave function may be written as

$$\begin{aligned} \psi(\vec{r}) &= \frac{1}{2}\{\psi(\vec{r}) + \psi(-\vec{r})\} + \frac{1}{2}\{\psi(\vec{r}) - \psi(-\vec{r})\} \\ &= \frac{1}{\sqrt{2}}\{\psi_e(\vec{r}) + \psi_o(\vec{r})\}, \end{aligned} \tag{1.10.41}$$

where we have put

$$\begin{aligned} \psi_e(\vec{r}) &= \frac{1}{\sqrt{2}}\{\psi(\vec{r}) + \psi(-\vec{r})\}, \\ \psi_o(\vec{r}) &= \frac{1}{\sqrt{2}}\{\psi(\vec{r}) - \psi(-\vec{r})\}, \end{aligned} \tag{1.10.42}$$

whose respective even and odd parity are easy to establish.

5. Show that the eigenfunctions of the Hamiltonian H are of definite parity if and only if $[H, P] = 0$.

   Solution — The statement follows from the theorem on the existence of simultaneous eigenfunctions of commuting operators.

6. Show that $[H, P] = 0$ if and only if the potential $V(\vec{r})$ is invariant under inversion, i.e., $V(\vec{r}) = V(-\vec{r})$.

   Solution — The Hamiltonian is composed of the kinetic energy and the potential energy:

$$H = K + V. \tag{1.10.43}$$

   The kinetic energy

$$K = -\frac{\hbar^2}{2m}\nabla^2 \tag{1.10.44}$$

   is unchanged under the inversion operation P. Thus, K commutes with P, i.e.

$$PK\psi(\vec{r}) = K\psi(-\vec{r}) = KP\psi(\vec{r}). \tag{1.10.45}$$

   The equation

$$[H, P] = [K, P] + [V, P] \tag{1.10.46}$$

   vanishes if and only if $[V, P] = 0$, which is the same statement as

$$PV\psi(\vec{r}) = VP\psi(\vec{r}) \tag{1.10.47}$$

   or

$$V(-\vec{r})\psi(\vec{r}) = V(\vec{r})\psi(-\vec{r}). \tag{1.10.48}$$

1.10.6 The Virial Theorem

Consider a particle moving in a potential $V(\vec{r})$. Classically, the kinetic energy is given by

$$\langle T\rangle = -\frac{1}{2}\langle \vec{r}\cdot\vec{F}\rangle, \tag{1.10.49}$$

where $\vec{F}$ is the force on the particle and $\langle \ldots \rangle$ denotes the time average.

Prove the quantum equivalent that when the particle is in an energy eigenstate,

$$\langle T \rangle = \frac{1}{2} \langle \vec{r} \cdot \nabla V(\vec{r}) \rangle, \tag{1.10.50}$$

where $\langle \ldots \rangle$ now denotes the expectation value. Hint: use the results of Prob. 10 (c) and (d) to evaluate the equation

$$\langle x[H, p_x] \rangle = \langle [x, H] p_x + [H, x p_x] \rangle. \tag{1.10.51}$$

Hence, show that for the Coulomb potential

$$\langle T \rangle = -1/2 \langle V \rangle \tag{1.10.52}$$

and that for the harmonic oscillator,

$$\langle T \rangle = \langle V \rangle. \tag{1.10.53}$$

Solution — We start with a term on the right-hand side of Eq. (1.10.50):

$$x \frac{\partial V}{\partial x} = x \frac{i}{\hbar} \, [p_x, H]. \tag{1.10.54}$$

Taking the expectation value on both sides,

$$\begin{aligned} \langle x \frac{\partial V}{\partial x} \rangle &= \frac{i}{\hbar} \, \langle \psi | x [p_x, H] | \psi \rangle \\ &= \frac{i}{\hbar} \, \langle \psi | (x p_x H - H x p_x + H x p_x - x H p_x) | \psi \rangle, \end{aligned} \tag{1.10.55}$$

where we have introduce the middle two terms which cancel each other. The first two terms cancel each other because of the energy eigenstate

$$\begin{aligned} H|\psi\rangle &= E|\psi\rangle, \\ \langle \psi | H &= \langle \psi | E. \end{aligned} \tag{1.10.56}$$

Thus,

$$\begin{aligned} \frac{1}{2} \langle x \frac{\partial V}{\partial x} \rangle &= \frac{i}{2\hbar} \, \langle \psi | [H, x] p_x | \psi \rangle \\ &= \frac{i}{2\hbar} \, \langle \psi | \frac{\hbar}{im} p_x p_x | \psi \rangle \\ &= \langle \psi | \frac{p_x^2}{2m} | \psi \rangle. \end{aligned} \tag{1.10.57}$$

There are two similar equations for the y and z components. Adding up all three components, we obtain the virial theorem,

$$\frac{1}{2}\langle \vec{r} \cdot \nabla V \rangle = \langle \psi | T | \psi \rangle. \tag{1.10.58}$$

For the Coulomb potential,

$$V(\vec{r}) = -\frac{e^2}{r}, \tag{1.10.59}$$

and

$$\vec{r} \cdot \nabla V = -V. \tag{1.10.60}$$

Hence,

$$\langle T \rangle = -\frac{1}{2}\langle V \rangle. \tag{1.10.61}$$

For the harmonic potential,

$$V(\vec{r}) = \frac{1}{2}\, kr^2, \tag{1.10.62}$$

and

$$\vec{r} \cdot \nabla V = 2V. \tag{1.10.63}$$

Hence,

$$\langle T \rangle = \langle V \rangle. \tag{1.10.64}$$

1.10.7 Translational Symmetry Group

Consider a particle moving in one dimension.

1. T_a denotes the translation operator:

$$T_a |b\rangle = |b + a\rangle. \tag{1.10.65}$$

The equation simply means that we change the state with a well-defined position at x to a state at a new position $x + a$. Show that for any wave function $\psi(x)$, the effect of the translation operator is

$$T_a \psi(x) = \psi(x - a). \tag{1.10.66}$$

Proof —

$$\begin{aligned} T_a\psi(x) &= \langle x|T_a|\psi\rangle \\ &= \int dx'\langle x|T_a|x'\rangle\langle x'|\psi\rangle \\ &= \int dx'\langle x|x'+a\rangle\langle x'|\psi\rangle \\ &= \int dx'\langle x|x'\rangle\langle x'-a|\psi\rangle \\ &= \int dx'\delta(x-x')\langle x'-a|\psi\rangle \\ &= \psi(x-a). \end{aligned} \tag{1.10.67}$$

Incidentally, we have also proved that the Hermitian conjugate does

$$\begin{aligned} T_a^\dagger|x\rangle &= |x-a\rangle \\ T_a^\dagger = T_{-a} &= T_a^{-1}, \end{aligned} \tag{1.10.68}$$

where the last term denotes the inverse translation operator.

2. Show that

$$T_a = e^{-\frac{ia}{\hbar}P_x}, \tag{1.10.69}$$

where P_x is the momentum operator along the x axis.

Solution — By using the series of expansion for the exponential function and the Taylor theorem,

$$\begin{aligned} \psi(x-a) &= \psi(x) - a\,\frac{d}{dx}\,\psi(x) + \frac{1}{2}a^2\,\frac{d^2}{dx^2}\,\psi(x) + \ldots \\ &= \sum_{n=0}^{\infty}\,\frac{1}{n!}\,\left(-a\,\frac{d}{dx}\right)^n\,\psi(x) \\ &= e^{-a\,\frac{d}{dx}}\,\psi(x) \\ &= e^{-\frac{i}{\hbar}ap_x}\,\psi(x). \end{aligned} \tag{1.10.70}$$

3. Is T_a an observable?

Solution — No, because it is non-Hermitian unless $a = 0$, which can be seen from part (a). The Hermitian conjugate is

$$T_a^\dagger = T_{-a} \neq T_a. \tag{1.10.71}$$

4. Show that the translation operators T_a with a belonging to the field of real numbers form an Abelian (i.e., commutative) group.

   Solution — A group $\mathcal{G}$ is a set of elements $\{A\}$ which possess the following properties:

   (a) There is a binary operation called multiplication between two elements such that if $A \in \mathcal{G}$ and $B \in \mathcal{G}$, then $A \times B \in \mathcal{G}$.

   (b) Associativity:

   $$A \times (B \times C) = (A \times B) \times C. \tag{1.10.72}$$

   (c) There exists a unit element I such that

   $$A \times I = I \times A = A. \tag{1.10.73}$$

   (d) For every element A, there exists an inverse A^{-1} such that

   $$A^{-1} \times A = I. \tag{1.10.74}$$

   For the translation operator

   $$T_a = e^{-iap/\hbar}, \tag{1.10.75}$$

   the binary operation is just successive translation operation:

   $$T_a T_b = e^{-i(a+b)p/\hbar} = T_{a+b}, \tag{1.10.76}$$

   which is certainly another translation operator. Associativity is easily shown. In addition, there is commutativity:

   $$T_a T_b = T_b T_a. \tag{1.10.77}$$

   The unit element is zero translation, T_0. The inverse of T_a is T_{-a}.

5. **Symmetry operator.** Show that T_a is a symmetry operator of the free particle Hamiltonian H in the sense that:

   $$T_a H T_a^{-1} = H. \tag{1.10.78}$$

Solution — $H = p^2/2m$ is a function of p and therefore commutes with any other function of p, including T_a.

6. **Symmetry operator and its generator.** Consider an infinitesimal translation dx. The generator G for the symmetry operator T_{dx} is defined by

$$T_{dx} = 1 - \frac{idx}{\hbar} G. \tag{1.10.79}$$

Show that $G = P$ and that G commutes with H.

Solution — Just expand the expression $T_{dx} = e^{-i(dx/\hbar)P_x}$ to first order in dx. $[H, P] = 0$ for the same reason that $[H, T_{dx}] = 0$.

7. Show that the eigenfunctions of the generator of the translation operators are also the energy eigenfunctions. Does the theorem on the common eigenstates of commutative operators guarantee that they are also eigenstates of the free particle Hamiltonian?

Solution — Consider the plane wave

$$\psi_k = e^{ikx}. \tag{1.10.80}$$

It is an eigenstate of the generator P with eigenvalue $\hbar k$. Since

$$T_a \psi_k = e^{ik(x-a)} = e^{-ika} \psi_k, \tag{1.10.81}$$

it is also an eigenstate of T_a with the eigenvalue e^{-ika}. Yes, since the eigenstates of P are nondegenerate, they are also eigenstates of H which commutes with P.

8. Show that the sine and cosine wave solutions of the energy eigenfunctions are not eigenfunctions of the translation operators in general. Does this fact contradict any of the theorems about the common eigenstates of commutative operators?

Solution — Consider the sine wave

$$\phi_k = \sin(kx). \tag{1.10.82}$$

It is an eigenstate of H:

$$H\phi_k = \frac{\hbar^2 k^2}{2m}\phi_k. \tag{1.10.83}$$

However,

$$\begin{aligned} T_a\phi_k &= \sin k(x-a) \\ &= \sin kx \cos ka - \cos kx \sin ka \\ &\neq \quad \text{constant} \quad \phi_k, \end{aligned} \tag{1.10.84}$$

unless $ka = 0$. This fact does not contradict the theorem which states that only non-degenerate eigenstates of one operator are necessarily the eigenstates of another which commutes with the operator nor the theorem that there *exist* common eigenstates of two commutative operators.

1.11 Problems

1. Consider a relativistic particle of rest mass m moving in a straight line under no force. The energy-momentum relation in classical mechanics is

$$E^2 = p^2c^2 + m^2c^4. \tag{1.11.1}$$

   (a) By starting with a plane wave for the wave function $\Psi(x,t)$ and using de Broglie's relations, show that a reasonable partial differential equation for the relativistic particle is the Klein-Gordon equation:

$$\frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = \frac{\partial^2\Psi}{\partial x^2} - \left(\frac{mc}{\hbar}\right)^2\Psi. \tag{1.11.2}$$

   (b) Compare and contrast the Klein-Gordon equation with the Schrödinger equation, pointing out the important physical consequences.

2. For the state $|\Psi\rangle$, with wave function as a function of position, $\langle\vec{r}|\Psi\rangle = \Psi(\vec{r})$, momentum is represented by the differential operator $-i\hbar\nabla$ acting on the wave function. Suppose we wish to represent the dynamical state by a wave function in momentum, $\langle\vec{p}|\Psi\rangle = \Phi(\vec{p},t)$.

   (a) Deduce a representation for the position operators $\vec{R} = (X,Y,Z)$ acting on $\Phi(\vec{p},t)$.

   (b) Deduce the form of the Schrödinger equation in the momentum representation.

   (c) Is the momentum representation in general as convenient as the position representation? Comment on the harmonic oscillator problem in this context.

   (d) Prove that for the momentum operator P_x,

$$P_x|x\rangle = i\hbar\frac{\partial}{\partial x}|x\rangle. \tag{1.11.3}$$

3. A reasonable requirement for the quantum mechanical representation of a dynamical property is that its mean value be real if the corresponding classical property is real.

   (a) Verify this property for position, momentum, and the Hamiltonian of a particle. (Hint: A number is real if its complex conjugate is equal to the number.)

(b) Show that, if p_x stands for $-i\hbar\frac{\partial}{\partial x}$, the quantum mechanical representation for xp_x is the symmetrized form $\frac{1}{2}(xp_x + p_x x)$ in order to satisfy the above requirement.

4. The wave function of a free particle in one dimension at $t = 0$ is a Gaussian modulated plane wave:

$$\Psi(x, t = 0) = (2\pi\sigma^2)^{-1/4} e^{iKx - x^2/4\sigma^2}. \tag{1.11.4}$$

(a) Find the probability of finding the particle at $t = 0$ within one uncertainty of its mean position (i.e. in the range between $-\sigma$ and σ).

(b) Find the uncertainty in momentum at a subsequent time t. (You may use the results in the notes.)

5. **Applications of the uncertainty principle.**

(a) By using the uncertainty principle in the form $\Delta x \Delta p = \frac{\hbar}{2}$, estimate the ground-state energy for a harmonic oscillator in one dimension. The harmonic oscillator is a particle of mass m and subject to a restoring force proportional to its displacement with the force constant $m\omega^2$.

(b) It has become possible to confine an electron in a semiconductor system to a region almost like a one-dimensional wire, called a quantum wire. If the electron so confined is attracted by a fixed Coulomb charge in the wire giving it a potential energy

$$V(x) = -\frac{e^2}{|x|}, \tag{1.11.5}$$

where x is the position of the electron measured from the fixed charge, use the same method as part (a) to estimate the ground-state energy.

(c) A nucleus is composed of a number of hadrons each with the mass of the order of the proton mass. The radius of the nucleus is of the order of 10 fermi ($1fm = 10^{-15}$ m). Estimate the magnitude of the interaction energy which binds the hadrons. Can the interaction be of electrical origin?

6. **Non-conservation of particles.**

In terms of the wave function $\Psi(\vec{r},t)$, one may define

$$N(t) = \int d^3r \Psi^*(\vec{r},t)\Psi(\vec{r},t) \tag{1.11.6}$$

as the total number of particles in the system. Suppose $N(0) = 1$.

(a) If the Hamiltonian H is complex, with the potential energy given by

$$V_c = V - i\Gamma/2, \tag{1.11.7}$$

where V and Γ are real functions of $\vec{r}$, show that

$$dN/dt = -\frac{1}{\hbar}\langle\Gamma\rangle. \tag{1.11.8}$$

(b) Now suppose that $\Gamma = \hbar/\tau$ where τ is a constant. Show that τ has the dimension of time and that τ is a measure of the lifetime of the particle, or more precisely,

$$N(t) = \exp(-t/\tau). \tag{1.11.9}$$

[Thus, the wave function can only be normalized at all times if the potential energy is real.]

7. (a) The position and momentum of the particle in one dimension are expressed in terms of two new operators, c and $c^\dagger$ by

$$X = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(c + c^\dagger), \tag{1.11.10}$$

$$P = \frac{1}{i}\left(\frac{m\hbar\omega}{2}\right)^{1/2}(c - c^\dagger). \tag{1.11.11}$$

Show that c and $c^\dagger$ are Hermitian conjugates of each other.

(b) If A, B, C are three operators such that

$$C = AB,$$

show that

$$C^\dagger = B^\dagger A^\dagger,$$

where $\dagger$ denotes the Hermitian conjugate.

(c) Hence show that $c + c^\dagger$, $i(c - c^\dagger)$ and $c^\dagger c$ are Hermitian operators.

(d) Are c, $c^\dagger$ and $c^\dagger c$ observables? If any one of them is, what does it represent?

8. Deduce whether each of the following operators is Hermitian:

(a) the gradient, $\partial/\partial x$ in the position representation;

(b) the potential energy operator, $V(\vec{R})$, V being a real function;

(c) a momentum component, P_x;

(d) an angular momentum component, $L_z = XP_y - YP_x$;

(e) a component of the torque, $-x\frac{\partial V(\vec{r})}{\partial y} + y\frac{\partial V(\vec{r})}{\partial x}$, in the position representation.

9. Show that the Hamiltonian of a particle is Hermitian and hence, that the energy eigenvalues are all real.

10. **Exercises in commutation.**

(a) Prove that $[A, BC] = [A, B]C + B[A, C]$.

(b) Prove the Jacobi identity, $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$.

(c) Show that

$$\begin{aligned} [P_x, f(\vec{R})] &= \frac{\hbar}{i}\frac{\partial f}{\partial X} \\ \left[X, f(\vec{P})\right] &= i\hbar\frac{\partial f}{\partial P_x}. \end{aligned} \tag{1.11.12}$$

(d) $[P_x, X^2] =?$

(e) $[H, X] =?$, where $H = \frac{\vec{P}^2}{2m} + V(\vec{R})$.

(f) $[H, P_x] =?$

(g) $[L_z, X] =?$

(h) Find $[c, (c^\dagger c)^n]$, where c and $c^\dagger$ are defined in Problem 7.

11. You are given only these facts:

- A and B are two physical observables satisfying the commutation relation,

$$[A, B] = i. \tag{1.11.13}$$

- B has an "orthonormal" set of eigenstates $|\beta\rangle$ with associated eigenvalues β which are all possible real numbers.
- A transformation with any real number γ maps an eigenstate of B to another:

$$T_\gamma|\beta\rangle = |\beta + \gamma\rangle. \tag{1.11.14}$$

(a) Prove that $T_\gamma = e^{i\gamma A}$.

(b) Find the representations of A and B which act on the wave function $\langle\beta|\Psi\rangle$ for any state $|\Psi\rangle$.

12. The rotational operator through an angle π about the z-axis is given by

$$R(\pi)\psi(x, y, z) = \psi(-x, -y, z). \tag{1.11.15}$$

Is $R(\pi)$ Hermitian? Find the eigenvalues and eigenfunctions of $R(\pi)$.

13. **The quantum rotor.** It has applications in the rotational motion of a molecule. A rotor is a rigid body rotating freely about a fixed axis with moment of inertia I. By analogy with the free particle, choose the angular coordinate ϕ and the angular momentum L about the axis as the conjugate dynamical variables.

(a) Show that the $\phi-$representation for the angular momentum operator is $L = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$. Find the Hamiltonian of the free rotor H.

(b) The rotation operator $R(\alpha)$ is defined by

$$R(\alpha)|\phi\rangle = |\phi + \alpha\rangle, \tag{1.11.16}$$

acting on the angular position eigenstate $|\phi\rangle$. Prove the operator relation

$$R(\alpha) = e^{-\frac{i}{\hbar}\alpha L}. \tag{1.11.17}$$

(c) Show that $R(\alpha)$ is not Hermitian but unitary, i.e., its Hermitian conjugate is its inverse.

(d) Show that for a general operator $R(\alpha)$ which is a function of the scalar α, its generator, defined in Eq. (1.10.79), is Hermitian if $R(\alpha)$ is unitary.

(e) Find the generator for the rotational symmetry operator and show that it commutes with the free rotor Hamiltonian H.

(f) Find the common eigenstates of L and H and their respective eigenvalues.

(g) Give an example of an eigenstate of H which is not an eigenstate of L. In the last part, the eigenstates of L are shown to be the eigenstates of H, why is the converse not true?

14. **The Bloch Theorem.** Consider a particle in a one-dimension periodic potential $V(x)$ with period a, i.e., $V(x+a) = V(x)$.

(a) Show that the translation operators (defined in Sec. 1.10.7), T_{na} for all integers n, form an Abelian (commutative) group.

(b) Show that there are wave functions which obey the translation symmetry rule,

$$T_{na}\psi_k(x) = e^{ikna}\psi_k(x). \tag{1.11.18}$$

The discrete translation operator is said to have the (one-dimensional) irreducible representation e^{ikna} for a real number k.

(c) Show that the Hamiltonian of the periodic potential commutes with any translation operator.

(d) Show that the energy eigenstate is of the form $\psi_k(x)$, known as the Bloch wave.

15. **Quantum mechanics of two particles.** A system consists of two particles of mass m_1 and m_2 with an attractive potential $V(\vec{r}_1 - \vec{r}_2)$ depending only on their positions.

(a) Construct the total Hamiltonian H for the system.

(b) Define the total momentum $\vec{P}$ of the system. Find a possible conjugate position to $\vec{P}$. Is it the only solution?

(c) Find the eigenstates of $\vec{P}$.

(d) Does $\vec{P}$ commute with the Hamiltonian? Is it related to the fact that the system Hamiltonian is invariant through the rigid translation of both particles through the same distance. Find the translation operation of the two particles through the same distance $\vec{a}$.

(e) Separate H into the center of mass motion and the relative motion and find the eigenvalues and eigenstates of the total Hamiltonian in terms of the eigenstates of the separated terms.

(f) The two-particle state vector may be considered as a linear combination of the direct products, $|u_\alpha^{(1)}\rangle|u_\beta^{(2)}\rangle$, of the single-particle basis sets of the two particles. Show that an eigenstate of the total Hamiltonian is an entangled state, i.e., not a single direct product of single-particle states of the given particles.

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Chapter 2

Quantum Dynamics and Quantum Statistical Dynamics

Around the ancient track marched, rank on rank,
The army of unalterable law.
— *George Meredith,* Lucifer in Starlight.

2.1 Introduction

Quantum dynamics deals with the time evolution of a conservative system with a Hamiltonian. In Schrödinger's wave mechanics, a dynamical state of a system is represented by a time-dependent wave function and the properties are represented by differential operators acting on this evolving wave function. Heisenberg's approach is to leave the state fixed in time and to allow the physical observables evolve in time. Although the relations between these two approaches can be presented in the abstract Hilbert space, it may be easier to gain physical insight if one is allowed to think in terms of a representation of the state vector or the observable. A particularly important concept is the change of the basis of representation leading to the unitary transformation because then time evolution in quantum mechanics may be viewed as a unitary transformation. Historically, the matrix representation formed the basis of the matrix mechanics of Heisenberg. The wave mechanics and the matrix mechanics were developed independently. We follow Dirac [1] in deriving the latter from the former, thus showing them to be fully equivalent. Yet a third approach to quantum dynamics is the Feynman path integral method [2]. An introduction is given here for two reasons: it presents a very physical way of looking the time propagation and the use of the Lagrangian instead of the Hamiltonian makes it a

powerful method for field theory and many-particle physics.

Quantum statistical dynamics deals with the time evolution of a statistical distribution of the quantum states of a system. This statistics arises out of a certain lack of detailed knowledge of the dynamics of a quantum system as a result of contact with the outside world, in the form of either a measurement apparatus or a reservoir. It is in addition to the probability interpretation of the quantum state itself. The concept of the density matrix is a powerful one to treat the dynamics of an incoherent ensemble of systems. This forms an important link between the dynamics of an ideal quantum system and the measurements of an ensemble of microscopic systems whose initial states are not under control. It leads to a description of irreversible dissipative processes in the system as a result of contact with a reservoir.

2.2 Unitary Transformations

2.2.1 Change of basis

The matrix representations of the states and the observables may be made with respect to any orthonormal set of states. It is therefore necessary to establish the procedure to change the basis set, say, from $\{u_i\}$ to $\{v_m\}$. Let the old basis set be related to the new set by

$$|u_i\rangle = \sum_m |v_m\rangle S_{mi}, \tag{2.2.1}$$

where

$$S_{mi} = \langle v_m|u_i\rangle. \tag{2.2.2}$$

The matrix S is called the transformation matrix. It may be regarded as an operator which transforms the new basis state $\{v_i\}$ back to the old, $\{u_i\}$,

$$|u_i\rangle = S|v_i\rangle. \tag{2.2.3}$$

Because of the orthonormality of both basis sets, S is a unitary matrix, i.e.,

$$S^\dagger = S^{-1}, \tag{2.2.4}$$

where the left-hand side is the Hermitian conjugate of S, i.e., the transpose and complex conjugate of S, and the right-hand side is the inverse of the matrix S.

Proof:

$$\begin{aligned} \delta_{ij} &= \langle u_i|u_j\rangle = \sum_{mn} S^*_{mi}\langle v_m|v_n\rangle S_{nj} \\ &= \sum_{mn} S^*_{mi}\delta_{mn}S_{nj} = \sum_m S^\dagger_{im}S_{mj}. \end{aligned} \tag{2.2.5}$$

In matrix notation,

$$S^\dagger \cdot S = I, \tag{2.2.6}$$

where I denotes the unit matrix. Hence, Eq. (2.2.4) follows.

As a simple example of the transformation of basis, consider the two dimensional vector space. A state vector $\vec{r}$ in the basis $(\vec{u}_1, \vec{u}_2)$ is represented by the column vector

$$\begin{bmatrix} x \\ y \end{bmatrix}. \tag{2.2.7}$$

A new basis set $(\vec{v}_1, \vec{v}_2)$ is rotated by an angle θ from the old basis. The new representation for the same state vector $\vec{r}$ is

$$\begin{aligned} \begin{bmatrix} \xi \\ \eta \end{bmatrix} &= \begin{bmatrix} < v_1|u_1 > & < v_1|u_2 > \\ < v_2|u_1 > & < v_2|u_2 > \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}, \\ &= \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}. \end{aligned} \tag{2.2.8}$$

The inner products of the basis vectors, $< v_i|u_j >$, are worked out by reference to Fig. 2.1.

2.2.2 Transformation of the state representation

The two representations of the state $|\psi\rangle$ is

$$|\psi\rangle = \sum_i |u_i\rangle c_i = \sum_m |v_m\rangle \tilde{c}_m. \tag{2.2.9}$$

By the relation of the old basis set to the new, Eq. (2.2.1),

$$|\psi\rangle = \sum_{im} |v_m\rangle S_{mi} c_i. \tag{2.2.10}$$

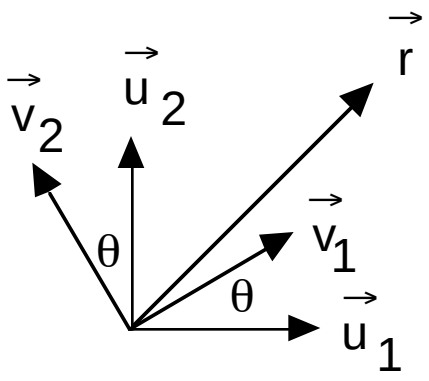

Figure 2.1: Rotation of basis in two dimension vector space.

Comparing it with Eq. (2.2.9), we have

$$\tilde{c}_m = \sum_i S_{mi} c_i. \tag{2.2.11}$$

In matrix notation, the new representation of the state, the state vector $\tilde{c}$ is related to the old representation, c by

$$\tilde{c} = S \cdot c, \tag{2.2.12}$$

where we have omitted the arrows over the vectors for fear of over-dressing $\tilde{c}$.

2.2.3 Transformation of the matrix representation of an operator

Let the new matrix representation of an operator A be

$$\tilde{A}_{mn} = \langle v_m | A | v_n \rangle. \tag{2.2.13}$$

Now,

$$\begin{aligned} A_{ij} &= \langle u_i | A | u_j \rangle = \sum_{mn} S^*_{mi} \langle v_m | A | v_n \rangle S_{nj} \\ &= \sum_{mn} S^\dagger_{im} \tilde{A}_{mn} S_{nj} \end{aligned} \tag{2.2.14}$$

or,

$$\tilde{A} = S \cdot A \cdot S^\dagger. \tag{2.2.15}$$

In matrix algebra, such a relation is called a unitary transformation.

2.2.4 Invariance under a unitary transformation

The following properties are invariant after a unitary transformation:

1. Inner product between two states $|\psi\rangle$ and $|\phi\rangle$

$$\langle\psi|\phi\rangle = \vec{c}^{\,\dagger} \cdot \vec{d}, \tag{2.2.16}$$

   where $\vec{c}$ and $\vec{d}$ are the vector representations of $|\psi\rangle$ and $|\phi\rangle$.

2. Eigenvalues of an operator.

3. Operator relations.

2.2.5 Diagonalization of a Hermitian operator

Suppose a Hermitian operator A has a complete set of orthonormal eigenstates $\{|\psi_i\rangle\}$ with eigenvalues α_i. We may choose to use the eigenstates of A as the basis set. Then the matrix of A is a diagonal matrix Λ with elements $\alpha_i\delta_{ij}$.

If we start off with representation in a basis set which are not eigenstates of A, the unitary transformation is found by solving for the eigenvectors and the eigenvalues of the matrix A:

$$A \cdot \vec{c}^{\,i} = \alpha_i \vec{c}^{\,i}. \tag{2.2.17}$$

The transformation matrix which diagonalizes A is formed by the column vectors $\vec{c}^{\,i}$:

$$S^\dagger = [\vec{c}^{\,1} \;\; \vec{c}^{\,2} \;\; \vec{c}^{\,3} \;\; \ldots], \tag{2.2.18}$$

i.e.,

$$SAS^\dagger = \Lambda = \begin{bmatrix} \alpha_1 & 0 & \ldots \\ 0 & \alpha_2 & \ldots \\ \ldots & \ldots & \ldots \end{bmatrix}. \tag{2.2.19}$$

In particular, the matrix method to solve the time-independent Schrödinger equation is to find the matrix representation of the Hamiltonian H in some basis set and then to diagonalize the matrix H, i.e. find the eigenvectors and eigenvalues of the matrix H. With modern high speed computers, this method is much used for atomic and molecular calculations.

In exactly the same way as the operators, the matrices can only be simultaneously diagonalized by the same set of functions if and only if the matrices commute with one another.

2.3 The Schrödinger and Heisenberg Representations

2.3.1 The Schrödinger representation

In Schrödinger's theory, to find the time dependence of a property of a system, one solves the time-dependent Schrödinger equation for the wave function as a function of time, from which the (statistical) knowledge of any property is obtained. In the abstract form, The Schrödinger equation for the state vector is given by

$$H|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle. \tag{2.3.1}$$

It is easy to verified that, if H is independent of time, the formal solution is

$$|\Psi(t)\rangle = e^{-iHt/\hbar}\,|\Psi(0)\rangle. \tag{2.3.2}$$

The time evolution of a state from time t_0 to time t may be regarded as a unitary transformation (called the evolution operator):

$$\begin{aligned} |\Psi(t)\rangle &= U(t-t_0)\,|\Psi(t_0)\rangle, \\ U(t-t_0) &= e^{-\frac{i}{\hbar}H(t-t_0)}. \end{aligned} \tag{2.3.3}$$

In the chapters on collision theory and on the time-dependent perturbation, the time evolution of a state governed by a time-dependent Hamiltonian will be studied. The unitary transformation preserves the length of the state vector $\langle\Psi(t)|\Psi(t)\rangle$ and, hence, the total probability is constant in time.

The eigenstates $\{|\psi_n\rangle\}$ of the time-independent Hamiltonian H with eigenvalues E_n form a special basis set. Under it, the matrix representation of the evolution operator is diagonal,

$$U_{mn}(t) = \delta_{m,n}e^{-iE_nt/\hbar}. \tag{2.3.4}$$

At time t, the state $|\Psi(t)\rangle$ is represented by

$$|\Psi(t)\rangle = \sum_n |\psi_n\rangle c_n(t), \tag{2.3.5}$$

where

$$c_n(t) = e^{-iE_n t/\hbar}\, c_n(0). \tag{2.3.6}$$

The time dependence of the expectation value of an operator A is given by:

$$\langle A\rangle_t = \langle\Psi(t)|A|\Psi(t)\rangle = \sum_{m,n} c*_m\,(0) A_{m,n} c_n(0) e^{i(E_m - E_n)t/\hbar}. \tag{2.3.7}$$

Aside from any explicit time dependence of the operator A itself, the time development of the mean value of A is expressed through the oscillatory factors $e^{i(E_m-E_n)t/\hbar}$.

2.3.2 The Heisenberg representation

Consider the unitary transformation from any time-independent basis:

$$S = e^{iHt/\hbar}. \tag{2.3.8}$$

The representation with respect to the new set of basis is called the Heisenberg representation. The transformed state for the state vector at time t,

$$|\tilde{\Psi}\rangle = S|\Psi(t)\rangle = |\Psi(0)\rangle, \tag{2.3.9}$$

is independent of time. On the other hand, the matrix representation of an operator is

$$\tilde{A} = S\cdot A\cdot S^\dagger = e^{iHt/\hbar} A e^{-iHt/\hbar}, \tag{2.3.10}$$

which changes with time in addition to any possible explicit time dependence of the operator A.

2.3.3 Equation of motion for an observable in the Heisenberg representation

$$\begin{aligned}\frac{d}{dt}\tilde{A} &= \frac{i}{\hbar}\left[He^{iHt/\hbar}Ae^{-iHt/\hbar} - e^{iHt/\hbar}Ae^{-iHt/\hbar}H\right] + e^{iHt/\hbar}\left\{\frac{\partial A}{\partial t}\right\}e^{-iHt/\hbar} \\ &= \frac{i}{\hbar}[H,\tilde{A}] + \frac{\partial\tilde{A}}{\partial t}.\end{aligned} \tag{2.3.11}$$

In the last term, it is understood that the time derivative is with respect to the explicit time dependence of the operator A.

The matrix form of the equation of motion is

$$\frac{dA}{dt} = \frac{i}{\hbar}[H, A] + \frac{\partial A}{\partial t}. \tag{2.3.12}$$

In the Hamiltonian formulation of classical mechanics, the Hamiltonian $H(q, p)$ and any property $A(q, p, t)$ are functions of the generalized coordinates q and their canonical conjugates p and time t. The equation of motion for A is

$$\begin{aligned} \frac{dA}{dt} &= \frac{\partial A}{\partial p} \cdot \frac{dp}{dt} + \frac{\partial A}{\partial q} \frac{dq}{dt} + \frac{\partial A}{\partial t} \\ &= \frac{\partial A}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial H}{\partial q} + \frac{\partial A}{\partial t} \\ &\equiv -\{H, A\} + \frac{\partial A}{\partial t}. \end{aligned} \tag{2.3.13}$$

The bracket in the last line is known as the Poisson bracket. Notice the parallel forms of the quantum mechanical equation (2.3.12) and of the classical counterpart, Eq. (2.3.13). Indeed, in Heisenberg's version of quantum mechanics, known also as the matrix mechanics, he constructed the quantum equation of motion by replacing the Poisson bracket in the classical equation of motion by $-i/\hbar$ times the commutation bracket and regarding the dynamical variables as matrices. The equivalence of the Schrödinger version and the Heisenberg version of quantum mechanics is thus demonstrated by deriving the latter from the former.

2.3.4 Matrix mechanics of a particle

Consider a particle of mass m in a potential V.

$$H = \vec{P}^{\,2}/2m + V(\vec{R}\,). \tag{2.3.14}$$

The operator X now stands for the position observable in the Heisenberg representation. Since X has no explicit time dependence, its equation of motion is

$$\frac{dX}{dt} = \frac{i}{\hbar}[H, X] = \frac{P_x}{m}, \tag{2.3.15}$$

where P_x is the x-component of the momentum operator. We have used the commutation rule

$$[P_x, X] = -i\hbar. \tag{2.3.16}$$

Similarly,

$$\frac{dP_x}{dt} = \frac{i}{\hbar}[H, P_x] = -\frac{\partial V}{\partial X}. \tag{2.3.17}$$

Here, the force is again an operator or a matrix in the Heisenberg representation.

2.4 Feynman Path Integral Method

The evolution operator in Eq. (2.3.3) is more than a formal solution of the Schrödinger equation. In this section, we examine its physical meaning more closely by the concept of propagator and the path integral method, both due to Feynman.

2.4.1 The Propagator

Consider the single particle case. Multiplying Eq. (2.3.2) from the left by the position eigenstate $\langle\vec{r}\,|$, we obtain the time evolution of the state wave function in the form:

$$\Psi(\vec{r}, t) = \int d^3r'\, U(\vec{r}, \vec{r'}, t - t')\Psi(\vec{r'}, t'), \tag{2.4.1}$$

where the evolution operator U in spatial representation becomes the propagator,

$$U(\vec{r}, \vec{r'}, t - t') = \theta(t - t')\langle\vec{r}|e^{-iH(t-t')/\hbar}|\vec{r'}\rangle. \tag{2.4.2}$$

Note that the propagator is just the time evolution in the particle going from position $\vec{r'}$ at time t' to $\vec{r}$ at time t. We have inserted the step-function $\theta(t - t')$ to denote causality. In the terms of the theory of differential equations, the propagator is just the Green's function which satisfies the equation:

$$\left[i\hbar\frac{\partial}{\partial t} - H\right] U(\vec{r}, \vec{r'}, t - t') = i\hbar\delta(t - t')\delta^3(\vec{r} - \vec{r'}), \tag{2.4.3}$$

with the condition that $U(\vec{r}, \vec{r'}, t - t')$ vanishes for $t < t'$.

By using the plane-wave eigenstates, it is possible to evaluate the propagator for the free particle (with the potential energy $V = 0$) in one dimension (Problem 7):

$$U(x - x', t - t') = \sqrt{\frac{m}{2\pi i\hbar(t - t')}}\exp\left[\frac{im(x - x')^2}{2\hbar(t - t')}\right]. \tag{2.4.4}$$

You may recognize this from the heat diffusion except for the factor of i in the time.

2.4.2 The Path Integral

We shall consider the one-dimension system. Generalization of the formulation is straightforward. The path integral method gives an expression for the propagator in the following way:

1. Consider all possible paths from the point (x_0, t_0) to (x_f, t_f).
2. Find the action S[x(t)] along each path $C: \quad x = x(t)$.
3. The propagator is proportional to the sum over all possible paths of the exponential, $\exp\{iS[x(t)]/\hbar\}$.

The action is the classical quantity of the integral along the path of the Lagrangian $\mathcal{L}$:

$$S = \int_C dt\ \mathcal{L} = \int_C dt\ \left[\frac{m}{2}\left(\frac{dx}{dt}\right)^2 - V(x)\right]. \tag{2.4.5}$$

We break each path $C: \quad x = x(t)$ from (x_0, t_0) to (x_f, t_f) into N segments with intermediate points $(x_j, t_j), j = 1, 2, \ldots N$ and $j = N$ coinciding with the final point. (See Fig. 2.2). Take the time segments to be equal, $t_j - t_{j-1} = \Delta t$. Then the sum over all paths is given by

$$\left(\prod_{j=1}^{N}\int dx_j\right)\prod_{n=1}^{N} e^{iS(t_n, t_{n-1})/\hbar}, \tag{2.4.6}$$

which, in the limit of infinite N, is called a functional integral:

$$U(x_f, x_0, t_f - t_0) = \int_{x_0}^{x_f} \mathcal{D}[x(t)] e^{i\int_C dt\,\mathcal{L}/\hbar}, \tag{2.4.7}$$

where the constant of proportionality is incorporated into the metric of the integration (see below).

The functional integral expression for the propagator may be derived by considering the propagator as the overlap integral:

$$U(x, x', t - t') = \langle x, t | x', t' \rangle. \tag{2.4.8}$$

Along all the possible paths broken up into N segments,

$$U(x_f, x_0, t_f - t_0) = \left(\prod_{j=1}^{N}\int dx_j\right)\langle x_N, t_N | x_{N-1}, t_{N-1}\rangle\langle x_{N-1}, t_{N-1} | x_{N-2}, t_{N-2}\rangle$$

$$\ldots \langle x_1, t_1 | x_0, t_0\rangle. \tag{2.4.9}$$

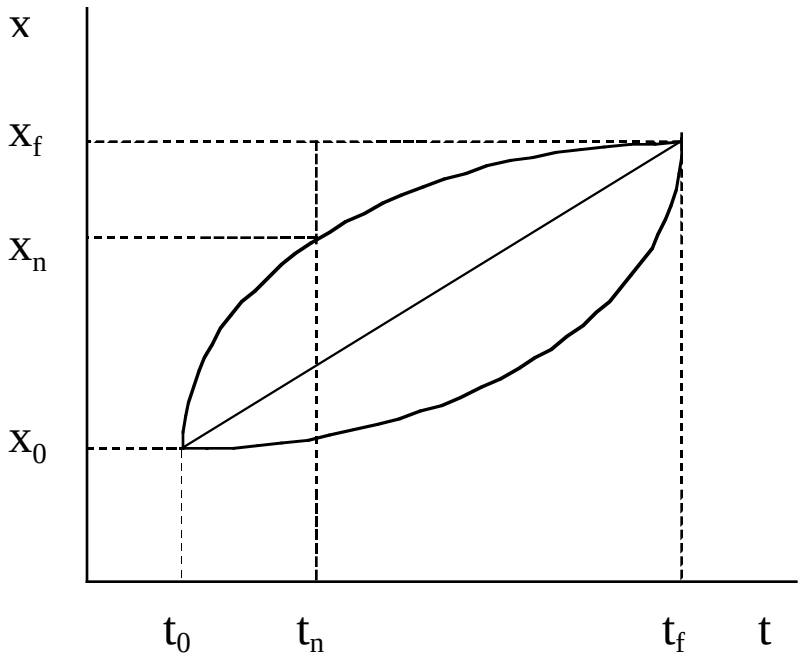

Figure 2.2: Division of coordinates for the path integral.

In each infinitesimal segment, the particle is approximately travelling in a constant potential. By Eq. (2.4.4) extended to include a constant energy term, the propagator in a small segment is given by

$$\begin{aligned}\langle x_j, t_j | x_{j-1}, t_{j-1}\rangle &= \sqrt{\frac{m}{2\pi i\hbar\Delta t}}\exp\left[\frac{im(x_j - x_{j-1})^2}{2\hbar\Delta t} - \frac{i}{\hbar}V\left(\frac{x_j + x_{j-1}}{2}\right)\Delta t\right], \\ &= \sqrt{\frac{m}{2\pi i\hbar\Delta t}}e^{iS(x_j,t_j;x_{j-1},t_{j-1})/\hbar}. \end{aligned} \tag{2.4.10}$$

In the functional integral, each integral $\int dx_j$ carries a factor $\sqrt{m/2\pi i\hbar\Delta t}$.

There are not too many explicit expressions of the functional integrals given: the free electron case (obviously) and the harmonic oscillator. For the latter case, the exponent in Eq. (2.4.10) is quadratic and the Gaussian integral for the ends of the segments can be performed, leading to the propagator:

$$\begin{aligned} U(x, x', t - t') &= \left[\frac{m\omega}{2\pi i\hbar\sin\{\omega(t - t')\}}\right]^{1/2} \\ &\times \exp\left[\frac{im\omega}{2\hbar\sin\{\omega(t - t')\}}\left\{(x^2 + x'^2)\cos\{\omega(t - t')\} - 2xx'\right\}\right]. \end{aligned} \tag{2.4.11}$$

The significance of the path integral formulation is that it is an alternative to the Schrödinger equation and that it is closer to the Hamilton-Jacobi formulation of Newtonian mechanics. Thus, studying the classical limit of the quantum theory is easier. It is readily generalized to many-body systems and fields and is, thus, a powerful tool in statistical mechanics and field theory. The path nature is also useful in studying the interference phenomena along different paths, such as the Bohm-Aharonov effect in a mesoscopic metallic ring which has been observed recently. (See Chapter 9.)

2.5 Mixed Ensembles and Density Matrix

In determining the time evolution of a quantum system, we have so far assumed that the initial state of the system is known. For an ensemble of identical quantum systems, such as a beam of atoms, the initial states may not be known precisely but may be known statistically. How do we describe the state of such an ensemble and its time evolution? In examining the quantum mechanics of such an ensemble, we start with a probability distribution among possible states for the systems in the ensemble. By dissecting the possible differences between two ensembles in which each system has the same probability of distribution among a set of basis states, we shall find situations where the quantum state of one system is inadequate in representing a state of the whole ensemble. This inadequacy illustrates the difference between the classical statistical distribution over states for systems of an ensemble and the quantum nature of a linear combination of states. It will be used to motivate the density matrix as a tool which utilizes the states of a single system to represent all possible states of the ensemble. In the literature, density matrix is also called density operator. We shall not use the latter nomenclature to avoid confusion with the density operator used in the many-body theory in later chapters.

2.5.1 Pure and mixed ensembles

Consider a one-dimension system of a particle bound in a square well with only two bound states (Fig. 2.3). Denote the ground state with even parity by $|+\rangle$ and the excited state with odd parity by $|-\rangle$. There is an ensemble of a large number N of identical copies of this system (which are isolated from one another). Half of them are in the even

state $|+\rangle$ and half in the odd state $|-\rangle$. This example of a mixed ensemble is not the same as the pure ensemble where all the systems are in the same quantum state

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle), \tag{2.5.1}$$

even though on examining a system from either ensemble, the probability of finding the system in either the even or odd state is 1/2 and even though the expectation value of the momentum is zero in either case. If the position of the particle from the center of the square well is measured in the pure ensemble, we expect

$$\langle\psi|X|\psi\rangle = \frac{1}{2}(\langle+| + \langle-|)X(|+\rangle + |-\rangle) = \frac{1}{2}(\langle+|X|-\rangle + \langle-|X|+\rangle) = \xi, \tag{2.5.2}$$

where ξ is the non-zero matrix element of X between the two states if their wave functions are chosen to be real. On the other hand, the expectation value of the position in the mixed ensemble is the average

$$\langle\langle X\rangle\rangle = \frac{1}{2}(\langle+|X|+\rangle + \langle-|X|-\rangle) = 0. \tag{2.5.3}$$

The difference between the two ensembles lies in the fact that the state of a system in the pure ensemble, Eq. (2.5.1) is a *coherent* linear combination of the two basis states whereas the mixed ensemble has an *incoherent* mixture of systems in two separate basis states. Furthermore, Problem 14 illustrates that the coherent linear combination depends on the phase difference between the two terms.

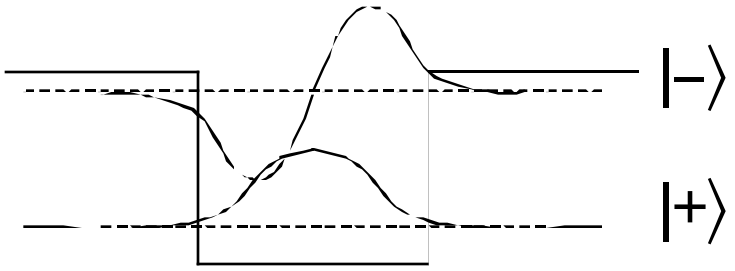

Figure 2.3: Two bound states in a square well.

The ensemble average of the position in the mixed ensemble may be written in the matrix and operator forms,

$$\langle\langle X\rangle\rangle \;=\; \mathrm{Tr}\left(\begin{bmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{bmatrix}\begin{bmatrix} 0 & \xi \\ \xi & 0 \end{bmatrix}\right)$$

$$= \text{Tr}\left(|+\rangle\frac{1}{2}\langle+| + |-\rangle\frac{1}{2}\langle-|\right)X$$

$$= \text{Tr}(\rho X), \tag{2.5.4}$$

where the operator

$$\rho = \left(|+\rangle\frac{1}{2}\langle+| + |-\rangle\frac{1}{2}\langle-|\right), \tag{2.5.5}$$

is a description of the state of the mixed ensemble and is called the density matrix (or density operator, though the latter can be confused with the same term used for density in a many-particle system). The density matrix for the pure-state ensemble above is given by

$$\rho = \frac{1}{2}(|+\rangle + |-\rangle)(\langle+| + \langle-|), \tag{2.5.6}$$

with the matrix representation

$$\begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix}, \tag{2.5.7}$$

in contrast with the diagonal matrix for the mixed ensemble. The off-diagonal term in the density matrix is sometimes described as the coherence (between the two basis states) in the ensemble. A special case of a mixed ensemble whose density matrix is a constant times the identity operator would, of course, have no off-diagonal matrix elements in any basis set and is known as an incoherent mixture. For more discussions of the off-diagonal matrix elements, see Problem 8.

2.5.2 Density Matrix

In general, if the distribution of the systems in a ensemble can be expressed as a fraction w_j in each state $|j\rangle$ of a complete set of orthogonal states, the expectation value (called the ensemble average) of a system property A is then

$$\langle\langle A\rangle\rangle = \sum_j w_j\langle j|A|j\rangle, \tag{2.5.8}$$

$$\sum_j w_j = 1, \tag{2.5.9}$$

where the double angular brackets connote first the quantum mechanical average over the state of the system and then the average over the systems of the ensemble with the

weighting factor w_j. An important example is an ensemble in thermal equilibrium, where $w_j \propto e^{-E_j/k_BT}$ is the thermal distribution of the energy states at temperature T, k_B being the Boltzmann constant.

Now let us separate the average into two components: the physical observable A and the state of the ensemble as characterized by the density matrix,

$$\rho = \sum_j |j\rangle w_j \langle j|. \tag{2.5.10}$$

The ensemble average may be rewritten concisely as

$$\langle\langle A\rangle\rangle = \mathrm{Tr}(\rho A), \tag{2.5.11}$$

where Tr denotes trace of a matrix of the operator in any basis. A few simple properties are easily proved:

1. ρ is hermitian.
2. $Tr(\rho) = 1$.
3. $Tr(\rho^2) \leq 1$.

The pure ensemble is a special case in which every system is in the same state, say $|k\rangle$, i.e., $w_k = 1$. Then,

$$\rho^2 = \rho. \tag{2.5.12}$$

2.5.3 Time evolution of an ensemble

In the Schrödinger representation, from the time evolution of the states

$$|j(t)\rangle = e^{-iHt/\hbar}|j\rangle, \tag{2.5.13}$$

the time dependence of the density matrix is

$$\rho(t) = e^{-iHt/\hbar}\rho e^{iHt/\hbar}. \tag{2.5.14}$$

This leads to the time evolution equation for the density matrix, known as the Liouville equation,

$$i\hbar\frac{\partial\rho(t)}{\partial t} = [H, \rho(t)]. \tag{2.5.15}$$

As a pure ensemble evolves with time, it remains a pure ensemble.

The time dependence of the ensemble average of a property A is

$$\langle\langle A(t)\rangle\rangle = \mathrm{Tr}[\rho(t)A]. \tag{2.5.16}$$

In the Heisenberg representation, the state vectors and hence the density matrix have no explicit time dependence but the physical observable is given the time dependence,

$$A(t) = e^{iHt/\hbar}Ae^{-iHt/\hbar}. \tag{2.5.17}$$

Note the difference with the expression for $\rho(t)$ in the Schrödinger representation and, hence, also the difference in the Heisenberg equation of motion for A with that of ρ. The time dependence of the average

$$\langle\langle A(t)\rangle\rangle = \mathrm{Tr}[\rho A(t)] = \mathrm{Tr}[\rho(t)A], \tag{2.5.18}$$

$$\text{since} \qquad \mathrm{Tr}(ABC) = \mathrm{Tr}(BCA). \tag{2.5.19}$$

2.6 Dissipative Processes in Quantum Dynamics

We have so far considered a system with a Hamiltonian which is a Hermitian operator. Consequently, the evolution operator on any state is unitary. The quantum dynamics conserves the norm of the state and the energy. In particular, if the system is in an energy eigenstate, it will always be in that state albeit with a phase change. There are observed processes which either do not conserve energy or particle number and which are irreversible. We give a number of important examples below. These fall outside the unitary evolution. We begin the study of such quantum processes by first making the distinction between the closed system which obeys the quantum Hamiltonian dynamics and the open system which can exhibit the dissipative processes. We set up the framework for the study of an open system by making a larger closed system which contains the open system. We leave to later chapters the study of the quantum dynamics of the larger system and how the dissipative processes of the smaller open system arise. Instead, we introduce here a phenomenological theory which can be used to describe a number of common relaxation processes, frequently restricted to weak coupling to the outside of the open system.

The subject of the dissipative processes, also known under the rubric of "decoherence", is active and controversial. It is becoming of ever greater importance as the single microscopic systems assume a more prominent role in scientific research and device development. Further reading is highly recommended. Weiss's [3] book gives a comprehensive and up-to-date treatise of the subject. In this book, the central tool is the functional integral (see Sec. 2.4). A good alternative is the book by Gardiner and Zoller [4]. The dissipative phenomena have been treated for a long time, especially in spin resonances [5] and in quantum optics [6, 7, 8, 9].

2.6.1 Examples of dissipative processes

There are many examples of systems which do not apparently behave like the conservative Hamiltonian system.

1. In Chapter 11, we shall study the energy levels of the electron in a hydrogen atom. The electron in an appropriate excited state of the hydrogen atom may decay to the ground state with the spontaneous emission of a photon (a quantum of light) with a mean time of the order $\tau \sim$10 ns. This gives an energy uncertainty $\Gamma = \hbar/\tau$ known as the radiation linewidth of the energy level of the order 10^{-7} eV. Since the ratio of the transition energy (of the order 10 eV) to Γ is 10^8, there is a period of time much shorter than the radiative lifetime τ within which the state obeys the unitary evolution quite accurately. For dynamics in time of the order of the radiative time or longer, the decay of the energy eigenstate must be accounted for.

2. Under an electric field, while the electron in the ground state of the hydrogen atom may have a negligible probability of tunneling out of the confining Coulomb potential, the electron in a highly excited state could tunnel out in a finite time. The escape represents another type of decay of the excited state.

3. In Gamow's model of alpha decay of a nucleus, alpha particles (each being a composite particle with two neutrons and two protons) are trapped in a nuclear potential of the form in Fig. 2.4. The wave function of the bound state at energy E_n can tunnel out of the potential barrier.

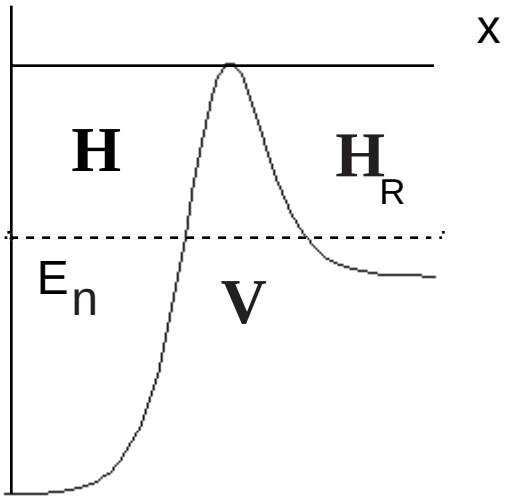

Figure 2.4: A potential which contains a bound state at energy E_n indicated by the dashed line. The particle trapped in the bound state can escape by tunneling through the potential barrier.

4. A muon atom of a muon μ^- and a proton p^+ behaves rather like a hydrogen atom in its energy levels since the muon has the same charge as the electron (but has 200 times the electron mass). Now μ^- decays into an electron e^-, a neutrino ν_μ and an antineutrino $\bar{\nu}_e$, with a mean time of the order of 10^{-6} s [10].

5. A rare-earth atom in a crystal may have f levels almost identical to its isolated cousin but the impurity is coupled to the vibrations of the crystal lattice. Electronic transitions in the impurity atom may involve the emission of a photon in combination with zero, one or more phonons (energy quanta of vibration modes).

6. In Chapter 12 we shall study the nuclear shell model which gives a picture of transitions between energy states rather like the atom case. A nuclear transition of the order of 0.1 MeV gives a recoil energy of the nucleus of the order 1 eV (see also Problem 15 in Chapter 11). A typical lifetime of an excited nuclear state may be 0.1 ns (an energy broadening of 10^{-5} eV). Thus the recoil shift of the emission line is not masked by the radiative linewidth. The emitted gamma ray in a gas of atoms with some excited nuclei cannot excite other nuclei in the ground state even though they have the same transition energy (i.e., there is no resonant excitation). If the nucleus is placed in a crystal, the bonding of the impurity to the host atoms

in the solid restricts the recoil of the impurity to small vibrations of all the atoms. The nuclear transitions in the impurity atom may involve the emission of a photon in combination with zero, one or more phonons. The removal of the recoil effect in the nuclear transition is known as the Mössbauer effect (see, for example, [10]).

2.6.2 Closed and open quantum systems

We treat a Hamiltonian system as a closed system with no interaction with the outside world. The evolution of a Hamiltonian system is unitary. On the contrary, the above examples involved systems which exhibit dissipative processes. The origin of such irreversible processes is the interaction with particles not included in the system. Such a system is called an open system.

We take the axiomatic view that the universe is a closed system. Then it is reasonable to assume that, without having to invoke the universe every time, we can isolate a sufficiently large portion of the universe outside the open system which together with the open system forms a closed system to a good approximation. To understand the microscopic origins of the dissipative phenomena, one way is to construct the larger Hamiltonian system and from its quantum dynamics extracts the behavior of the open system only. For example, to derive the relaxation of an excited hydrogen atom to the ground state with the emission of a photon, one may start with the Hamiltonian which contains the atom part, the quantized electromagnetic field and the atom-field interaction and then examine the time evolution of the atom. There is a subtlety in this route which we need to recognize right away. The evolution operator is unitary and, therefore, reversible. In a coupled system of two harmonic oscillators, the energy initially in one oscillator sloshes back and forth between the two. (For a more quantitative formulation of the sloshing, see Chapter 5). This oscillation cannot describe the decay of the excited state in the first oscillator, which is an irreversible process. However, if the second system is made up of a humongous number of oscillators, the destructive interference of the many states in coupling to the simple harmonic oscillator of the first system renders the process of energy transfer from the first to the second irreversible. In later chapters as we build up an arsenal of concepts and tools, we will carry out this program for a number of simple models which demonstrate the essential physics of the

dissipative processes.

A simpler method which accounts for the relaxation processes is the phenomenological approach, in which we add to the equation of quantum dynamics for the original open system (either in the Schrödinger or the Heisenberg approach) a term which gives rises to the dissipative process. The phenomenological model has to be treated with care and its legitimacy needs to be checked by the microscopic derivation whenever possible.

2.6.3 The product Hilbert space

Let the Hamiltonian of a large closed system be composed of three terms

$$H_T = H + H_R + V_I, \tag{2.6.1}$$

where H is the Hamiltonian of the open system which we will take to be microscopic (i.e., possessing a finite number of degrees of freedom), H_R is the Hamiltonian of a system with an infinite number of degrees of freedom known as the reservoir, and V_I the interaction between the two systems. Were there no interaction, the small system H would be a closed system and possess energy eigenstates $|n\rangle$ with energies E_n. Let the eigenstates of H_R be $|k\rangle$ with energy ε_k where k is a continuous variable. Without interaction V_I, the energy eigenstates of the whole system are

$$|n, k\rangle = |n\rangle \otimes |k\rangle, \tag{2.6.2}$$

with energies $E_n + \varepsilon_k$, where the symbol $\otimes$ is a reminder that the state of the whole system is a vector in the larger Hilbert space made up of a tensor product of two vectors from two separate Hilbert spaces. When there is no confusion, the symbol is understood. When there is interaction, the energy eigenstate of the whole system would not be the product states but they still form a possible basis, giving the energy eigenstates in the form

$$|\Psi\rangle = \sum_{nk} |n, k\rangle c_{nk}, \tag{2.6.3}$$

with scalar coefficients c_{nk}.

2.6.4 A simple model of particle escape

Problem 1.6 gives a phenomenological model for particle decay by the inclusion of an imaginary part to the potential. It is a very crude model. It can neither be extended to account for the relaxation processes which conserve the particle number in the system, nor does it explain the microscopic origin of the escape process.

Consider a particle in a potential $V(x)$ illustrated in Fig. 2.4. If the dike is sufficiently thick, there could be approximately a bound state in the central well at E_n. The wave function which decays exponentially through the barrier may emerge as a sinusoidally wave with a small amplitude outside. Thus the particle in the bound state is said to tunnel out. We shall now show how to arrive at the decay process in the two examples cited above: the electron ionization by an electric field and Gamow's model for the decay of alpha particles from a nucleus.

The Hamiltonian is separated into three parts as in Eq. (2.6.1) with the particle confined in the deep potential region being the open system H and the continuum states being the outside reservoir H_R. They are connected by the potential V, which, for simplicity, is assumed to have the matrix elements in the basis set $(|n\rangle, |k\rangle)$, n ranging over a set of integers and k over a continuous set of real numbers,

$$\begin{bmatrix} 0 & \langle n|V|k\rangle \\ \langle k|V|n\rangle & 0 \end{bmatrix}. \tag{2.6.4}$$

The time-dependent Schrödinger equation is

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = (H + H_R + V)|\Psi(t)\rangle. \tag{2.6.5}$$

We assume that the bound states inside the potential well are well separated in energy such that we can treat them one at a time. The time evolution of the state $|\Psi(t)\rangle$ may be expressed as a linear combination

$$|\Psi(t)\rangle = |n\rangle c(t) + \int dk|k\rangle b(k,t). \tag{2.6.6}$$

Substituting the state vector into Eq. (2.6.5), and taking matrix elements with the basis states, we obtain,

$$i\hbar\frac{\partial}{\partial t}c(t) \;\; = \;\; E_n c(t) + \int dk\; V_{nk} b(k,t), \tag{2.6.7}$$

$$i\hbar\frac{\partial}{\partial t}b(k,t) = V_{kn}c(t) + \varepsilon_k b(k,t), \tag{2.6.8}$$

$$\text{where } V_{nk} = \langle n|V|k\rangle. \tag{2.6.9}$$

The coupled set of differential equations may be simplified by the transformation,

$$c(t) = e^{-iE_nt/\hbar}\tilde{c}(t), \tag{2.6.10}$$

$$b(k,t) = e^{-i\varepsilon_k t/\hbar}\tilde{b}(k,t), \tag{2.6.11}$$

$$\text{where } \tilde{V}_{nk}(t) = \langle n|V|k\rangle e^{i(E_n-\varepsilon_k)t/\hbar}. \tag{2.6.12}$$

The substitution is known as the interacting representation (see Section 5.6). The resultant equations are

$$i\hbar\frac{\partial}{\partial t}\tilde{c}(t) = \int dk\ \tilde{V}_{nk}(t)\tilde{b}(k,t), \tag{2.6.13}$$

$$i\hbar\frac{\partial}{\partial t}\tilde{b}(k,t) = \tilde{V}_{kn}(t)\tilde{c}(t), \tag{2.6.14}$$

$$\text{where } \tilde{V}_{kn}(t) = [\tilde{V}_{nk}(t)]^*. \tag{2.6.15}$$

We make the first key assumption that initially $t = t_0$, the state of the whole system is given by the state $|n\rangle$ in the well with the reservior completely quiescent, i.e.,

$$c(t_0) = e^{-iE_nt_0/\hbar},$$

$$b(k,t) = 0. \tag{2.6.16}$$

Then, from Eq. (2.6.14), the coefficient $\tilde{b}(k,t)$ is an integral of $\tilde{c}(t)$, which may be substituted into Eq. (2.6.13), yielding

$$i\hbar\frac{\partial}{\partial t}\tilde{c}(t) = -\frac{i}{\hbar}\int_{t_0}^{t}dt'\int dk\ |V_{nk}|^2 e^{i(E_n-\varepsilon_k)(t-t')/\hbar}\tilde{c}(t'). \tag{2.6.17}$$

We now make the second assumption that the coupling matrix element V_{nk} is weak. Then the zeroth order solution of Eq. (2.6.13) has the rapidly oscillatory time dependence with a period of $2\pi\hbar/E_n$ and $\tilde{c}(t)$ is slowly varying in time compared with the time of $\hbar/E_n$. This enable us to carry out the integral on the right of Eq. (2.6.17),

$$\int_{t_0}^{t}dt'\int dk\ |V_{nk}|^2 e^{i(E_n-\varepsilon_k)(t-t')/\hbar}, \tag{2.6.18}$$

after replacing $\tilde{c}(t')$ with $\tilde{c}(t)$. The lower limit of the integral would lead to a rapidly oscillating term $e^{i(E_n-\varepsilon_k)(t-t_0)/\hbar}$, contrary to our ansatz of the slow time dependence of $\tilde{c}(t)$.

There are two ways to remove the influence of the initial time t_0. One way is to examine the origin of the ringing term. It comes from the sudden application of the coupling term $|V_{nk}|^2$. Our use of the initial state seems to suggest the physical picture that the particle appears suddenly in the well state $|n\rangle$ or, if it is there all the time, it starts interacting with the environment all of a sudden at time t_0. We may remedy the situation by either building up the state adiabatically (i.e., slowly) from the distant past or switching on the coupling term (or lowering the potential barrier) adiabatically from $t' = -\infty$. The adiabatic switching-on of the coupling term amount to extending the lower integration limit from $t' = t_0$ to $t' = -\infty$ and inserting a term $e^{\eta t'/\hbar}$ in the integral, where η is a small positive energy which will be taken to the zero limit after the integration. The slow build-up of the state will be given explicitly in Chapter 7 and shown to be equivalent to the adiabatic approximation. Thus,

$$i\hbar\frac{\partial}{\partial t}\tilde{c}(t) = -\frac{i}{\hbar}\tilde{c}(t)\int_{-\infty}^{t} dt' \int dk\ |V_{nk}|^2 e^{\eta t'/\hbar} e^{i(E_n-\varepsilon_k)(t-t')/\hbar}. \tag{2.6.19}$$

This leads to the equation for the bound state,

$$i\hbar\frac{\partial}{\partial t}\tilde{c}(t) = \int dk\ \frac{|V_{kn}|^2}{E_n + i\eta - \varepsilon_k}\tilde{c}(t). \tag{2.6.20}$$

The reduction of the dynamics of the whole system to that of the particle in the potential including the effect of decay via tunneling leads to the effective Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}c(t) \;\; = \;\; (E_n + \Sigma_n)c(t), \tag{2.6.21}$$

where the eigenenergy has been replaced by a complex energy, with the additional term, called the self-energy, given by

$$\Sigma_n = \int dk\ \frac{|V_{kn}|^2}{E_n + i\eta - \varepsilon_k}. \tag{2.6.22}$$

By using

$$\frac{1}{E + i\eta} = \left[\frac{1}{E}\right]_P - i\pi\delta(E), \tag{2.6.23}$$

where the subfix P denotes the taking of the principle value when this function is in an integral, we find the complex eigenenergy,

$$E = E_n + \Delta E_n - i\frac{\Gamma_n}{2}, \tag{2.6.24}$$

with a real shift

$$\Delta E_n = \int dk\ |V_{kn}|^2 \left[\frac{1}{E_n - \varepsilon_k}\right]_P, \tag{2.6.25}$$

and an imaginary part

$$\Gamma_n = 2\pi \int dk\ |V_{kn}|^2 \delta(E_n - \varepsilon_k) = 2\pi\rho(\varepsilon_{k_n})|V_{k_n n}|^2. \tag{2.6.26}$$

The last expression is related to the well-known Fermi Golden rule in terms of the density of states in the reservoir,

$$\rho(\varepsilon_{k_n}) = \int dk\ \delta(E_n - \varepsilon_k), \tag{2.6.27}$$

and the average of the matrix elements over the reservoir states k_n which have the same energy as E_n.

The solution of the reduced equation (2.6.20) for the motion inside the open system is

$$c(t) = e^{-i(E_n + \Delta E_n)t/\hbar - \Gamma_n t/2\hbar}. \tag{2.6.28}$$

The probability of finding the particle in the well decays exponentially with a characteristic relaxation time of

$$\tau = \frac{\hbar}{\Gamma_n}. \tag{2.6.29}$$

An alternate way to the adiabatic approximation is the Markovian approximation, which is the more common route of reasoning towards dissipation. This alternate third key assumption is to take the coupling term $|V_{nk}|^2$ as having a weak dependence on k in the neighborhood of the wave vector value given by $\varepsilon_k = E_n$. Then the k-integration in the integral (2.6.18) may be performed first,

$$\begin{aligned} \int dk\ |V_{nk}|^2 e^{i(E_n - \varepsilon_k)(t-t')/\hbar} &= \int d\varepsilon_k\ \rho(\varepsilon_k)|V_{nk}|^2 e^{i(E_n - \varepsilon_k)(t-t')/\hbar} \\ &= 2\pi\rho(\varepsilon_{k_n})|V_{nk_n}|^2 \delta(t - t'), \end{aligned} \tag{2.6.30}$$

by using the density of states in Eq. (2.6.27). The last result depends on neglecting entirely the k dependence of the prefactor to the exponential in the intergrand. The interaction process with the reservior is instanteous ($t = t'$) with no memory of past history. Such a process is said to be Markovian. Integration over t' then leads to the damping term with Γ_n. The delta function time dependence is equivalent to putting t_0 to $-\infty$. If the slow k dependence of $\rho(\varepsilon_k)|V_{nk}|^2$ is to be taken into account, the evaluation is carried out by integrating over t first and over then k, the process is the same as the adiabatic procedure, recovering both the ΔE_n and Γ_n terms.

In this example, the interaction V is a transfer operator between the open system and the reservoir and is simpler than the usual interaction. Nonetheless, it serves as an example of the reduction of the coupling of the system with the reservoir to demonstrate a simple dissipative process and to show how the escape rate may be calculated. The remarkable transformation from the reversible dynamics of the whole system to the irreversible decay of the population in the well depends on the third assumption, in terms of the adiabatic build-up or the Markovian approximation. Note that, were the energy levels of the reservoir system discrete, reversible dynamics would have been recovered. The example illustrates a key feature that the continuum of energy states in the reservoir is necessary for the irreversible process.

2.6.5 The reduced density matrix

The wave function method above cannot be easily extended to account for other types of dissipative processes such as the relaxation of a particle from an excited state to the ground state. The transition process is a probabilistic one so that the final result is most easily described by the density matrix. The density matrix of the open system is a reduced density matrix by the following construction. The open system plus its reservoir is a Hamiltonian system with a general density matrix of the form in terms of the eigenstates when there is no interaction between the system and the reservoir,

$$\rho_T = \sum_{n,n'} \int dk \int dk' \; |nk\rangle \rho_{T,nk,n'k'} \langle n'k'|. \tag{2.6.31}$$

By projecting out the reservoir states with the projection operator,

$$P_R = \int dk \; |k\rangle\langle k|, \tag{2.6.32}$$

and taking the trace, we obtain the reduced density matrix of the system,

$$\rho = \mathrm{Tr}[P_R \rho_T P_R] = \mathrm{Tr}[P_R \rho_T] = \sum_{nn'} |n\rangle \int dk \; \rho_{T,nk,n'k} \langle n'|. \tag{2.6.33}$$

The equation of motion for the density matrix of the whole system, the Liouville equation, assumes the simple form,

$$\frac{\partial}{\partial t}\rho_T = \mathcal{L}_T \rho_T, \tag{2.6.34}$$

if the linear operator, the Liouville operator, associated with a Hamiltonian, is defined generally by,

$$\mathcal{L}\rho = \frac{1}{i\hbar}[H, \rho]. \tag{2.6.35}$$

Following a procedure similar in spirit to the wave function method to eliminate the reservoir states in the preceding section, a Liouville equation for the reduced density matrix is commonly obtained in the Redfield form [3, 5],

$$\frac{\partial}{\partial t}\rho_{n,m}(t) = -i\omega_{nm}\rho_{n,m}(t) - \sum_{k\ell} R_{nmk\ell}\rho_{k\ell}(t), \tag{2.6.36}$$

where the transition frequency is given by

$$\omega_{nm} = \frac{E_n - E_m}{\hbar}. \tag{2.6.37}$$

The explanation of the relaxation coefficients $R_{nmk\ell}$ has to await the development of the microscopic theory in later chapters. Akin to the introduction of the adiabatic switching-on which leads to the irreversible decay in the last subsection, the Redfield result depends on the Born approximation (using weak coupling) and the Markovian approximation, which has the same effect as the adiabatic approximation in reducing the $t - t'$ dependence in the kernel of the integral in Eq. (2.6.19) to being an instantaneous response in Eq.(2.6.20). The weak coupling limit and the Markovian approximation are not necessary for the existence of an equation of motion for the reduced density matrix, known as the master equation.

The time evolution of the density matrix to describe the dissipative dynamics and the trace of the time-independent observable times the time-dependent density matrix as the mean value of the observable constitute the analog to the Schrödinger representation. In

the analog of the Heisenberg representation, the density matrix remains time independent and the equation of motion of a physical observable would include both a damping term involving the physical observable of the open system and a noise operator which is a function of the relevant operators of the reservoir, known as the quantum Langevin equation because of the correspondence with the classical Langevin equation used to treat classical dissipative dynamics such as the Brownian motion. An introductory treatment of the Heisenberg type approach will be given in later chapters.

2.6.6 Phenomenological approach to the relaxation dynamics

It is possible to add damping terms to the Liouville equation for the Hamilton of the system to simulate the dissipative forces. However, it may leads to certain undesirable results for the time development of the reduced density matrix. If the open system has only relaxation transitions within the system, while the total energy is not conserved, the total number of particles is conserved. Then the trace of the reduced density should remain unity. A general form of the Liouville operator [11] which preserves the trace of the reduce density matrix may be deduced by means of the concept of the dynamic semigroup in terms of its generators. (See Chapter 8 for the concept of the group, semigroup and generators [12].) Lindblad [13] has deduced a simple form,

$$\frac{\partial}{\partial t}\rho(t) = \frac{1}{i\hbar}[H,\rho] + \frac{1}{2}\sum_j \left\{[L_j\rho(t), L_j^\dagger] + [L_j, \rho(t)L_j^\dagger]\right\}, \tag{2.6.38}$$

where L_j is a set of damping operators which act on the state of the open system. For example, for linear coupling of a particle to a reservoir,

$$L = \alpha X + i\beta P, \tag{2.6.39}$$

where X and P are the position and momentum operators of the particle in an open system and α and β are scalars. For some simple models of the system plus reservoir, it is possible to derive the master equation and identify the Lindblad operators. It is clear from the form of the Lindblad equation that both the weak coupling and the Markovian approximation have been used.

An important example of the application of the Lindblad form of dissipative processes is given by the transitions in a two-state system, of which we shall have a lot to say in

Chapter 5. Let the ground state and excited state be $|0\rangle$ and $|1\rangle$. The Lindblad operator which simulates the decay from the excited to the ground state with the emission of a quantum of energy to the reservoir,

$$L_e = \sqrt{\hbar\gamma}|0\rangle\langle 1|, \tag{2.6.40}$$

leads to the relaxation rates,

$$\frac{d}{dt}\begin{bmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{bmatrix} = \begin{bmatrix} \gamma\rho_{11} & -\frac{1}{2}\gamma\rho_{01} \\ -\frac{1}{2}\gamma\rho_{10} & -\gamma\rho_{11} \end{bmatrix}. \tag{2.6.41}$$

Note that the decay rate of the excited state population is exactly offset by the increase in the ground state population. The interesting case of the off-diagonal elements ρ_{01}, ρ_{10} known as coherences will be studied in Chapter 5.

A second Lindblad operator which simulates the excitation from the ground state to the excited state by absorbing a quantum of energy from the reservoir,

$$L_a = \sqrt{\hbar\gamma'}|1\rangle\langle 0|, \tag{2.6.42}$$

leads to the relaxation rates,

$$\frac{d}{dt}\begin{bmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{bmatrix} = \begin{bmatrix} -\gamma'\rho_{00} & -\frac{1}{2}\gamma'\rho_{01} \\ -\frac{1}{2}\gamma'\rho_{10} & \gamma'\rho_{00} \end{bmatrix}. \tag{2.6.43}$$

A third one

$$L_f = \sqrt{2\hbar\gamma^*}|1\rangle\langle 1|, \tag{2.6.44}$$

leads only to the destruction of the phase coherence between the two states,

$$\frac{d}{dt}\begin{bmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{bmatrix} = \begin{bmatrix} 0 & -\gamma^*\rho_{01} \\ -\gamma^*\rho_{10} & 0 \end{bmatrix}. \tag{2.6.45}$$

The derivation of these results are left as problems. The emission term L_e and the absorption term L_a, in addition to altering the occupation numbers of the energy levels irreversibly, also contribute to the destruction of the phase coherence between two states, (ρ_{01} or ρ_{10}), known as dephasing. The term L_f might be viewed as the fluctuation of the energy state $|1\rangle$ because of the interaction with the reservoir and it contributes only to the dephasing, leading to the decreasing of ρ_{01} and ρ_{10} without affecting the populations of the energy levels. This type of dephasing is known as "pure" dephasing. Unlike the

dephasing rates $\gamma/2, \gamma'/2$ which is related to the transition rates γ, γ', the pure dephasing rate γ^* is not related to any decay rate.

A physical way to view this extension of the Liouville equation (2.6.34) to include dissipative terms is to extend the definition of the Liouville operator from Eq. (2.6.35) to accommodate the non-Hermitian Hamiltonian H_c as

$$\mathcal{L}\rho = \frac{1}{i\hbar}(H_c\rho - \rho H_c^\dagger). \tag{2.6.46}$$

If we take the complex Hamiltonian to be

$$H_c = H - \frac{i\hbar}{2}\sum_j L_j^\dagger L_j - iV_o, \tag{2.6.47}$$

where H is the Hamiltonian of the open system and L_j is the Lindblad operator and V_o is a Hermitian operator, the equation of motion of the density matrix becomes

$$\frac{\partial\rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] - \frac{1}{2}\sum_j\{L_j^\dagger L_j,\rho\} - \frac{1}{\hbar}\{V_o,\rho\}, \tag{2.6.48}$$

where $\{A,B\} \equiv AB + BA$ is the anticommutation bracket. Both the Lindblad terms and the imaginary potential term V_o lead to the decay of the particle number in the open system. The Lindblad terms above represent the scattering of the particles out of the open system into the reservoir. To preserve the particle number (i.e., $\mathrm{Tr}(\rho)$), a term $\sum_j L_j\rho L_j^\dagger$, representing the scattering of the particles into the open system, has to be added to the right-hand side of the new Liouville equation. This gives the form of the Lindblad equation (2.6.38).

The term V_o represents particle decay. In nuclear scattering, the phenomenological imaginary potential $-iV_o$ is known as the optical potential. For example, an elastic scattering experiment of a neutron against a target of He^3 atoms may be regarded as the potential scattering of a particle (see Chapter 7). However, it is possible for a He^3 atom to absorb a neutron (to become He^4). In principle, it is possible to construct a scattering theory with a conservative Hamiltonian for four particles (two neutrons and two protons) but it is more convenient to analyze the scattering data as a particle scattering in a complex potential, with the imaginary part simulating the decay of the one-particle open system. The simplification becomes more needed as the target atoms get heavier. For a reservoir with an Avogadro number of degrees of freedom, the use of the dissipative dynamics becomes necessary.

2.7 Quantum Measurement

The development of the measurements and associated theories utilizing quantum optics in the last two decades has greatly increased both the range of possible measurements and our understanding of the quantum processes associated with the measurement [14, 15]. The recent experiments and theories in the mesoscopic regime with atoms transfer between a scanning tunneling tip and a solid surface add to this body of knowledge [16]. We shall bypass the actual microscopic processes which lead to the "collapse" of the quantum state after a measurement. While it is somewhat analogous to the dissipative process, it is a still an actively researched and somewhat controversial subject and, therefore, beyond the scope of our purview. Instead, we follow the simplification of the measurement processes to a set of postulates and examine some consequences thereof.

2.7.1 Von Neumann's postulates

In Section 1.7.6, two postulates were made regarding the outcome of a measurement of a physical observable A as one of the eigenvalues with an assigned probability and the "collapse" of the state of the measured system to the associated eigenstate. Since the density matrix is often the more appropriate description of the system in the mixed state form, we describe the two postulates in terms of the development of the density matrix ρ:

1. The outcome of a measurement of the observable A is one of its eigenvalue, α, with the probability

$$P(\alpha) = \mathrm{Tr}(|\alpha\rangle\langle\alpha|\rho), \tag{2.7.1}$$

   where $|\alpha\rangle$ is the associated eigenstate.

2. At the end of the measurement, the density matrix describing the system becomes $\rho' = |\alpha\rangle\langle\alpha|$.

2.7.2 Back action noise of a measurement

By the second postulate, the result of a measurement makes a drastic change to the state. If repeated measurements of the same observable could be made instantly, then the same

value of the observable would be obtained. However, in reality the repeated measurement has to be made at a finite time later. Then the first measurement introduces noise (i.e., uncertainty) to the properties of the system which do not commute with the first observed property. After a finite time, the uncertainties in these observables may impart noise to a subsequent measurement of the first observable, i.e., the same eigenvalue which was measured the first time would not be reproduced.

A simple example is provided by measuring the position of a free particle. Suppose that, right after a measurement of the position coordinate x, instead of the system being in the position eigenstate, the state can be modeled by the Gaussian wave function given by Eq. (1.10.1). It has an amount of uncertainty $\Delta x(0)$ from the instrumental noise. Note that the uncertainty in momentum is the minimum allowed by the uncertainty principle, $\Delta p(0) = \hbar/2\Delta x(0)$. In practice the instrument noise could be much worse, caused by the correlation part in Eq. (1.9.15). In any case, a measurement of position gives rise to an uncertainty in momentum and therefore, an additional uncertainty in subsequent displacement which is proportional to the momentum. From Eq. (1.10.8), we have the uncertainty in position at time t after the measurement given by

$$[\Delta x(t)]^2 = [\Delta x(0)]^2 + \left(\frac{t}{m}\right)^2 [\Delta p(0)]^2. \tag{2.7.2}$$

The time evolution of the uncertainty in position for a general state is given in Problem 15. The above relation shows that, the more precise the initial measurement of position is, the larger the subsequent uncertain is through the Heisenberg uncertainty in momentum. Thus, the first measurement of position creates the uncertainty in momentum which acts back on the system. Hence,

$$\begin{aligned} [\Delta x(t)]^2 &= [\Delta x(0)]^2 \left[1 + \left(\frac{\hbar t}{2m\{\Delta x(0)\}^2}\right)^2\right] && (2.7.3) \\ &= [\Delta x(0)]^2 \left[\left(1 - \frac{\hbar t}{2m\{\Delta x(0)\}^2}\right)^2 + \frac{\hbar t}{m\{\Delta x(0)\}^2}\right] \\ &\geq \frac{\hbar t}{m}. && (2.7.4) \end{aligned}$$

Thus, a second measurement of X after a certain time will have a growing minimum uncertainty.

Such a quantum limitation as the uncertainty in position measurement is relevant to highly sensitive measurements, such as the attempt to detect gravitational radiation. Because of the weak interaction of gravitation with a measuring instrument (compared with the electromagnetic interaction), the detector has to be able to measure a displacement of the order 10^{-21} meter. The period of a gravitation wave is about a millisecond. The uncertainty increase between two measurements of position with a period must stay within 10^{-21} m. Thus, from Eq. (2.7.4), the mass whose displacement is affected by the gravitation wave must be

$$m \geq \frac{\hbar t}{\{10^{-21}\text{meter}\}^2} \approx 10^5 \text{ Kg}. \tag{2.7.5}$$

On the other hand, the momentum is a constant of the motion for the free particle and its uncertainty remains the same as the initial value caused by the contact with the measuring instrument. Thus, it can be limited by better design (see the discussion on the squeezed states in Chapter 14).

2.7.3 Quantum non-demolition measurement

A quantum non-demolition (QND) measurement means that the measurement can be performed repeatedly without the increase of the uncertainty of the measured quantity. Ideally, after one measurement, the results of further measurements of the same physical observable should be predictable. The behavior of the constant momentum uncertainty of a free particle gives us a clue to one requirement of a QND measurement, namely, for observable A,

$$[A(t), A(t')] = 0. \tag{2.7.6}$$

It follows that, while the state may evolve with time, the state remains an eigenstate of A and the eigenvalue of A measured remains constant. A constant of motion, i.e., if $[A, H] = 0$ for the system Hamiltonian H, is a QND observable.

The other requirement for QND is that the QND observable A should not be affected by the perturbation Hamiltonian H_I which couples the system to the measuring instrument, i.e., $[A, H_I] = 0$. In Chapter 10, the Kubo response function when a system is

subject to a probe is examined. Details of how the probe works in the quantum optics experiments on QND are beyond the scope of this book and interested readers are referred to references [9, 8].

We use now the two-level system described in Sec. 2.5.1 as an example to find QND observables. The position operator is, from Eq. (2.5.4),

$$X = \left[\begin{array}{cc} |+\rangle & |-\rangle \end{array} \right] \left[\begin{array}{cc} 0 & \xi \\ \xi & 0 \end{array} \right] \left[\begin{array}{c} \langle +| \\ \langle -| \end{array} \right]. \tag{2.7.7}$$

For brevity, we shall use the operator X as its matrix representation with the basis set understood without fear of confusion. Thus, the momentum operator is given by

$$P = \left[\begin{array}{cc} 0 & -i\varpi \\ i\varpi & 0 \end{array} \right], \tag{2.7.8}$$

$$\text{where the real number } \varpi = \hbar\langle +|\nabla|-\rangle. \tag{2.7.9}$$

The two observables, X and P, can be rendered dimensionless,

$$\sigma_x = X/\xi, \tag{2.7.10}$$

$$\sigma_y = P/\varpi. \tag{2.7.11}$$

Their combinations in the form

$$\sigma_\pm = \frac{1}{2}(\sigma_x \pm i\sigma_y), \tag{2.7.12}$$

have simple time evolution as can be seen by their Heisenberg representation,

$$\tilde{\sigma}_+(t) = e^{iHt/\hbar}\sigma_+ e^{-iHt/\hbar} = \sigma_+ \, e^{-i\omega t}, \tag{2.7.13}$$

$$\tilde{\sigma}_-(t) = e^{iHt/\hbar}\sigma_- e^{-iHt/\hbar} = \sigma_- \, e^{i\omega t}, \tag{2.7.14}$$

$$\text{where } \omega = (E_- - E_+)/\hbar, \tag{2.7.15}$$

in term of the energy difference between the two levels. Hence, the position and momentum operators in the Heisenberg representation are

$$\tilde{X}(t) = \xi(\sigma_+ e^{-i\omega t} + \sigma_- e^{i\omega t}) = X\cos\omega t + P\frac{\xi}{\varpi}\sin\omega t, \tag{2.7.16}$$

$$\tilde{P}(t) = -i\varpi(\sigma_+ e^{-i\omega t} - \sigma_- e^{i\omega t}) = P\cos\omega t - X\frac{\varpi}{\xi}\sin\omega t. \tag{2.7.17}$$

Note that the position and momentum operators in the Schrödinger representation are both time independent. From the requirement Eq. (2.7.6) that neither is a QND observable.

Now, in analogy with the harmonic oscillator case [9, 8], we define in the Schrödinger representation two *time-dependent* operators,

$$Q_r(t) = \xi(\sigma_+ e^{i\omega t} + \sigma_- e^{-i\omega t}), \tag{2.7.18}$$

$$Q_i(t) = -i\varpi(\sigma_+ e^{i\omega t} - \sigma_- e^{-i\omega t}). \tag{2.7.19}$$

They are related to the position and momentum with an important difference. Their explicit time dependence leads to their Heisenberg representation

$$\tilde{Q}_r(t) = e^{iHt/\hbar} Q_r(t) e^{-iHt/\hbar} = \xi(\sigma_+ + \sigma_-) = X, \tag{2.7.20}$$

$$\tilde{Q}_i(t) = e^{iHt/\hbar} Q_i(t) e^{-iHt/\hbar} = -i\varpi(\sigma_+ - \sigma_-) = P, \tag{2.7.21}$$

which are independent of time. They are QND observables.

The two "phase" operators are related to the position and momentum operators by

$$\tilde{Q}_r = \tilde{X}(t)\cos\omega t - \tilde{P}(t)\frac{\xi}{\varpi}\sin\omega t, \tag{2.7.22}$$

$$\tilde{Q}_i = \tilde{X}(t)\frac{\varpi}{\xi}\sin\omega t + \tilde{P(t)}\cos\omega t. \tag{2.7.23}$$

The two-level model is not robust since experimental disturbance may excite the particle out of the bound states. However, there are two-level models, such as the spin-1/2 particle (Chapter 5), which are robust under the action of the magnetic field. QND experiments with the above variables are in principle possible. A better (both conceptually and experimentally) example is the simple harmonic oscillator, which will be treated in Chapter 3. The simple harmonic oscillator is relevant in the sensitive measurement of gravitational waves and in quantum optics where many of the QND experiments are carried out [9, 8].

2.8 Examples

2.8.1 Ehrenfest's theorem

Let A be an observable not explicitly dependent on time. The time dependence of the expectation value of A for a system comes from the time dependence of the wave function of the system. Prove, using the Heisenberg representation that

$$\frac{d}{dt}\langle A\rangle = \frac{i}{\hbar}\langle [H, A]\rangle. \tag{2.8.1}$$

Solution — In the Heisenberg representation, Ψ is independent of t and the operator at time t is

$$A(t) = e^{iHt/\hbar}\, A\, e^{-iHt/\hbar}. \tag{2.8.2}$$

Thus,

$$\begin{aligned} \frac{d}{dt}\langle A\rangle &= \langle \frac{d}{dt}A\rangle \\ &= \frac{i}{\hbar}\langle [H, A]\rangle. \end{aligned} \tag{2.8.3}$$

2.8.2 A three-state system

A particle can have only three possible states, ψ_1, ψ_2, and ψ_3. In terms of these three states as the basis, the Schrödinger representation of the Hamiltonian H and the position operator x are given by matrices

$$H = \begin{pmatrix} E_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -E_0 \end{pmatrix}, \tag{2.8.4}$$

$$x = \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{pmatrix}, \tag{2.8.5}$$

where E_0 is an energy constant and a is a constant distance.

1. Find the vector representation of the energy eigenstates and the associated eigenvalues.

2. If a measurement of x is made, what are the possible measured values?

3. Say that the particle is found with the largest value for x. What are then the probabilities of finding the particle in each of the energy eigenstates?

4. If we define the momentum operator in the Heisenberg picture as

$$p(t) = m\frac{dx(t)}{dt} \tag{2.8.6}$$

where m is the mass of the particle and $x(t)$ is the position operator at time t, find the matrix representation for $p(t = 0)$.

5. Find $[x, p]$. Is the result a disaster?

6. The initial state (i.e. at time $t = 0$) is given by

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}. \tag{2.8.7}$$

Find the expectation value of x at time t.

Solution —

1. From the diagonal form of the Hamiltonian, it is obvious that the solutions to the eigen-equation

$$H\psi_n = E_n\psi_n \tag{2.8.8}$$

are given by

$$\psi_1, \psi_2, \psi_3 \;\; = \;\; \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \tag{2.8.9}$$

with the associated energy values E_0, 0, and $-E_0$ respectively.

2. The possible values of x is given by the eigenvalues λ of

$$x\phi = \lambda\phi, \tag{2.8.10}$$

i.e by the roots λ of the determinantal equation

$$|x - \lambda I| = 0, \tag{2.8.11}$$

where I denotes the 3×3 unit matrix, i.e.

$$\begin{vmatrix} -\lambda & 0 & a \\ 0 & -\lambda & 0 \\ a & 0 & -\lambda \end{vmatrix} = 0. \tag{2.8.12}$$

The possible values of x are $0, a, -a$.

3. The eigenstate of x with the eigenvalue a, i.e. the state ϕ given by

$$x\phi = a\phi, \tag{2.8.13}$$

is

$$\phi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}. \tag{2.8.14}$$

Thus, the probabilities of finding the energy value to be E_0, 0, and $-E_0$ are, respectively, $\frac{1}{2}$, 0, and $\frac{1}{2}$.

4. From the equation of motion

$$\frac{dx}{dt} = \frac{i}{\hbar}[H, x], \tag{2.8.15}$$

we obtain the relation for the momentum

$$p = \frac{im}{\hbar}[H, x]. \tag{2.8.16}$$

Evaluation of the commutation bracket then yields

$$\begin{aligned} p &= \frac{im}{\hbar} \left[\begin{pmatrix} E_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -E_0 \end{pmatrix} \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{pmatrix} \begin{pmatrix} E_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -E_0 \end{pmatrix} \right] \\ &= \frac{2maE_0}{\hbar} \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}. \end{aligned} \tag{2.8.17}$$

5. The commutator bracket

$$\begin{aligned} [x, p] &= \frac{2ma^2E_0}{\hbar} \left[\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \right] \\ &= -\frac{4imaE_0}{\hbar} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \end{aligned} \tag{2.8.18}$$

Since the factor in front of the matrix has the dimension of $\hbar$ and the commutation relation has the form

$$[A, B] = iC \tag{2.8.19}$$

with the uncertainty relation from Eq. (6.6.2)

$$\Delta x \, \Delta p \geq \left| \frac{2maE_0}{\hbar} \right|, \tag{2.8.20}$$

there is no disaster.

6. The state at time t is given by in terms of the energy eigenstates ψ_n

$$\begin{aligned} \Psi(t) &= \sum_n a_n \psi_n e^{-iE_n t/\hbar} \\ &= \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-iE_0 t/\hbar} \\ 0 \\ e^{iE_0 t/\hbar} \end{pmatrix}. \end{aligned} \tag{2.8.21}$$

The expectation of x at time t is given by

$$\begin{aligned} \langle x \rangle_t &= \langle \Psi(t) | x | \Psi(t) \rangle \\ &= \begin{pmatrix} e^{iE_0 t/\hbar} & 0 & e^{-iE_0 t/\hbar} \end{pmatrix} \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{pmatrix} \begin{pmatrix} e^{-iE_0 t/\hbar} \\ 0 \\ e^{iE_0 t/\hbar} \end{pmatrix} \\ &= a \cos\left(\frac{2E_0 t}{\hbar} \right). \end{aligned} \tag{2.8.22}$$

2.9 Problems

1. The Hamiltonian of a driven rotor about a fixed axis is given by

$$H = \omega L, \tag{2.9.1}$$

where ω is a constant frequency and L is the angular momentum operator.

(a) Find the energy eigenvalues and eigenstates.

(b) A state at time $t = 0$ has the wave function

$$\Psi(\phi, t = 0) = \frac{1}{\sqrt{\pi}} \cos\phi. \tag{2.9.2}$$

Find the wave function of the state at time t.

(c) Ehrenfest's theorem for the driven rotor. Find the time dependence of the expectation values of the angular momentum L and of the position ϕ for a state of the system.

2. A subspace of the rotor states. The collection of all states which are linear combinations of the two states

$$\psi_x(\phi) = \frac{1}{\sqrt{\pi}} \cos\phi,$$

$$\psi_y(\phi) = \frac{1}{\sqrt{\pi}} \sin\phi. \tag{2.9.3}$$

is called the subspace spanned by the basis of these two states.

(a) Find the vector representation of a state in this subspace.

(b) Find the matrix representation of the angular momentum operator L in this basis.

(c) Diagonalize the angular momentum matrix in part (b). What are the meanings of the resultant eigenvalues and eigenvectors?

(d) A new basis set is generated by the rotation operator $R(\alpha)$:

$$\psi_\xi = R(\alpha)\psi_x,$$

$$\psi_\eta = R(\alpha)\psi_y. \tag{2.9.4}$$

Find the transformation matrix.

(e) Show that the state

$$\psi(\phi) = \frac{1}{\sqrt{\pi}} \cos(\phi - \alpha), \tag{2.9.5}$$

with a constant α is a state in the subspace but not all states in the subspace is of this form.

3. Stranger than fiction. A baryon is a heavy elementary particle. Proton and neutron are baryons. A baryon is made up of three color quarks. Each quark can have one of three colors: red, green, and blue, but no two quarks in a baryon can have the same color. The six color states of a baryon are therefore: [rgb, brg, gbr, bgr, rbg, grb]. Use this basis set to represent a baryon state. A permutation is an operator which permutes the color arrangement of the three quarks. An exchange of the colors of the first two quarks, $P(xyz \rightarrow yxz)$ is an example of a permutation with a single pair exchange.

(a) Find the matrix representation of the exchange.

(b) Find the eigenvalues of the exchange.

(c) Show that the antisymmetric state with the vector representation

$$\frac{1}{\sqrt{6}} \begin{bmatrix} 1 \\ 1 \\ 1 \\ -1 \\ -1 \\ -1 \end{bmatrix} \tag{2.9.6}$$

is an eigenstate of the exchange with eigenvalue -1. Of the six eigenstates of the exchange operator, the antisymmetric state is the only one allowed for a baryon.

4. A stadium is divided from left to right into three sections: red, white and blue. The states ψ_r, ψ_w, and ψ_b form the basis set where ψ_r denotes the normalized state where Joe Fan is found with certainty in the red section, etc.

(a) Write down the vector representation of a state in which Joe Fan can be found with equal probability in each section.

(b) R is an operator which moves Joe Fan one section to the right, i.e.,

$$R\psi_r = \psi_w, \tag{2.9.7}$$

$$R\psi_w = \psi_b \tag{2.9.8}$$

except at the right end section,

$$R\psi_b = 0. \tag{2.9.9}$$

Find the matrix representation for R and its Hermitian conjugate.

(c) L is an operator which moves Joe Fan one section to the left, i.e.,

$$L\psi_b = \psi_w, \tag{2.9.10}$$

$$L\psi_w = \psi_r \tag{2.9.11}$$

except at the left end section,

$$L\psi_r = 0. \tag{2.9.12}$$

Find the matrix representation for L and its Hermitian conjugate.

(d) Are R and L observables?

(e) Let the Hamiltonian for Joe Fan be given by

$$H = R + L. \tag{2.9.13}$$

Is this valid ? (I.e., is the Hamiltonian Hermitian?)

(f) Find Joe Fan's energy eigenvalues.

(g) At the beginning of a game, Joe Fan was in the red section, find his state at time t after the start.

5. Quantum Beat. The Hamiltonian of an atom (or nucleus) which describes two excited states with closely spaced energy levels is given by

$$H = \begin{pmatrix} 0 & 0 & 0 \\ 0 & E_0 & 0 \\ 0 & 0 & E_0 + \Delta \end{pmatrix}, \tag{2.9.14}$$

where $0 < \Delta \ll E_0$. An electromagnetic field which excites the atom from its ground state with zero eigenenergy to an energy close to E_0 is represented by the raising operator

$$R = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \tag{2.9.15}$$

which raises the ground state to

$$\begin{aligned} \phi &= R \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}. \end{aligned} \tag{2.9.16}$$

If at time $t = 0$, the system is excited to the state ϕ, find the state of the system at time t. Hence find the probability at time t of finding the system at state ϕ. The oscillatory behavior of this probability is known as the quantum beat.

6. **The f sum rule.** For an electron with the Hamiltonian

$$H = \frac{P^2}{2m} + V(\vec{R}), \tag{2.9.17}$$

with discrete eigenenergies E_n and eigenstates $|n\rangle$, the absorption of the light of frequency ω is related to the ac conductivity,

$$\sigma(\omega) = 2e^2 \sum_n |\langle 0|X|n\rangle|^2 \delta(\hbar\omega + E_0 - E_n). \tag{2.9.18}$$

By evaluating the commutation bracket [X,[X,H]], prove the sum rule

$$\int_0^\infty d\omega\, \sigma(\omega)\omega = \frac{e^2}{m}. \tag{2.9.19}$$

7. Deduce the expression for the free particle propagator in Eq. (2.4.4). [Hint: Fourier transform the equation of motion for the propagator, (2.4.3), with respect to time and position.]

8. **The off-diagonal density matrix.** Consider a beam of photons flying in the z direction with two polarization states in the x and y directions , denoted by $|x\rangle$

and $|y\rangle$. Let the density matrix for the ensemble of photons in this basis set be diagonal,

$$\rho = \begin{bmatrix} \rho_1 & 0 \\ 0 & 1-\rho_1 \end{bmatrix}. \tag{2.9.20}$$

The most general unitary transformation of the basis set has the form,

$$S = \begin{bmatrix} e^{i\phi}\cos\theta & e^{-i\phi}\sin\theta \\ -e^{i\phi}\sin\theta & e^{-i\phi}\cos\theta \end{bmatrix}, \tag{2.9.21}$$

where the parameters ϕ and θ are real numbers. Below we study the off-diagonal density matrix element ρ_{12} for three different degrees of polarization of the ensemble of photons.

(a) Unpolarized beam: $\rho_1 = 1/2$. Show that the off-diagonal element of the density matrix in any transformed basis set is zero.

(b) Polarized beam: $\rho_1 = 1$ or 0. Show that $|\rho_{12}|$ may attain the maximum value of $1/2$ for some transformed basis sets.

(c) Partially polarized beam: $0 < \rho_1 < 1/2$ or $1/2 < \rho_1 < 1$. Show that $0 < |\rho_{12}| < 1/2$ for a non-trivial transformation of the basis.

9. **Population and coherence.** An ensemble of identical systems is described by the density matrix given by Eq. (2.5.10) where the basis set is chosen to be the energy eigenstates of each system. The eigenstate of an physical observable A associated with eigenvalue α_n is related to the chosen basis set by

$$|\psi_n\rangle = \sum_j |j\rangle c_{j,n} \ , n = 1, 2, \ldots. \tag{2.9.22}$$

(a) When A is measured on the ensemble, find the fraction of the systems showing the value α_n. The fraction is known as the population.

(b) When a single matrix element of A, $\langle\psi_m|A|\psi_n\rangle$ is measured, the outcome for the ensemble is determined by the density matrix element, $\langle\psi_n|\rho|\psi_m\rangle$, known as the coherence (between the two states). Find coherence in terms of probabilities w_j and the coefficients $c_{j,n}$.

(c) Find the time evolution of the population and the coherence above.

10. **The complex energy.** With the model in Section 2.6.4, take the energy eigenstate of the whole system to be given by

$$|\Psi\rangle = |n\rangle c + \int dk |k\rangle b(k). \tag{2.9.23}$$

(a) By making appropriate approximations and by inserting the small positive number η at the right step, can you find the eigenenergy to be the complex energy using Eq. (2.6.23)?

(b) Could you interpret the imaginary part of the self-energy found as the decay time?

(c) Since the total Hamiltonian is Hermitian, how do you reconcile the fact that the eigenenergy has to be real with the complex self-energy?

11. **Population decay and phase decoherence.** Consider the case of a two-state system in contact with a reservoir. With the Lindblad operators

$$L_1 = \sqrt{\hbar\gamma_1}|0\rangle\langle 1|, \tag{2.9.24}$$

$$L_2 = \sqrt{\hbar\gamma_2}|1\rangle\langle 1|, \tag{2.9.25}$$

show that the Bloch equations may be deduced from the Liouville equation,

$$\frac{d}{dt}\begin{bmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{bmatrix} = \begin{bmatrix} \frac{1}{T_1}\rho_{11} & \left(i\omega - \frac{1}{T_2}\right)\rho_{01} \\ \left(-i\omega - \frac{1}{T_2}\right)\rho_{10} & -\frac{1}{T_1}\rho_{11} \end{bmatrix}. \tag{2.9.26}$$

Relate the frequency ω and the relaxation times T_1 and T_2 to the energy and decay rate parameters of the open system.

12. **Einstein's theory of transitions in an atom.** Consider a two-level atom in contact with a blackbody at temperature T, with the Lindblad operators,

$$L_1 = \sqrt{\hbar(A + Bu)}|0\rangle\langle 1|, \tag{2.9.27}$$

$$L_2 = \sqrt{\hbar Bu}|1\rangle\langle 0|, \tag{2.9.28}$$

where the Einstein A and B coefficients are constants and independent of temperature, and u is the energy density of the radiation field per unit frequency range

obeying the Planck distribution,

$$u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} n(\omega), \tag{2.9.29}$$

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1}, \tag{2.9.30}$$

where ω is the transition frequency between the two state, c the speed of light, and k_B the Boltzmann constant.

(a) Deduce the rate equations including the damping terms,

$$\frac{d\rho_{11}}{dt} = -(A + Bu)\rho_{11} + Bu\rho_{00} = -\frac{d\rho_{00}}{dt}. \tag{2.9.31}$$

(b) If the atom is in thermal equilibrium with the blackbody, i.e.,

$$\rho_{11}/\rho_{00} = e^{-\hbar\omega/k_B T}, \tag{2.9.32}$$

show that the absorption rate is given by

$$Bu = n(\omega), \tag{2.9.33}$$

and the emission rate is given by

$$A + Bu = A[n(\omega) + 1], \tag{2.9.34}$$

13. **Quantum measurement of physicists' humor.** The source of the following Q&A is not known:

Q: How many quantum mechanicians does it take to change a light bulb?

A: None. Once the light bulb is observed to be out, it is changed.

The best way to kill a joke is to analyze it to death. Is the answer correct?

14. **QND Observable.** Consider a one-dimension system of a particle bound in a square well with only two bound states. Denote the ground state with ever parity by $|+\rangle$ and the excited state with odd parity by $|-\rangle$. Ensemble M of a large number N of identical copies of this system is made up of half of the systems in the even state $|+\rangle$ and half in the odd state $|-\rangle$. Ensemble P is made up of all systems in the same quantum state

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|+\rangle + i|-\rangle). \tag{2.9.35}$$

(a) Show that the expectation values of the position in both ensembles are the same.

(b) Find a dynamical property which behaves differently in the two ensembles.

(c) Show that, within the two-state model, $iPX = -iXP$ is a QND observable.

(d) Critique the restricted model of a particle in the presence of a square well, starting with the commutation relation between X and P and find the specific defects with the two-state model which lead to unphysical predictions.

15. **Uncertainty below the standard quantum limit.** Let δA denote the observable $A - \langle A \rangle$. Consider a free particle in one dimension.

(a) Show that

$$\langle [\delta X(t)]^2 \rangle = \langle [\delta X(0)]^2 \rangle + \left(\frac{t}{m}\right)^2 \langle [\delta P(0)]^2 \rangle + \left(\frac{t}{m}\right) \langle \{\delta X(0), \delta P(0)\} \rangle, \quad (2.9.36)$$

where the curly brackets $\{\}$ denote the anticommutation brackets.

(b) The wave function of a free particle at $t = 0$ is given by the Gaussian wave packet,

$$\Psi(x, 0) = (2\pi\sigma^2)^{-1/4} \exp\left(-\frac{x^2}{4\sigma^2} + iKx\right), \quad (2.9.37)$$

with the mean position at $x = 0$ and the uncertainty $\Delta x(0) = \sigma$ and $\Delta p(0) = \hbar/(2\sigma)$.

Show that, for the Gaussian wave packet, at $t = 0$,

$$\langle \{\delta X(0), \delta P(0)\} \rangle = 0. \quad (2.9.38)$$

(c) Can you find a wave packet such that, at $t = 0$,

$$\langle \{\delta X(0), \delta P(0)\} \rangle < 0? \quad (2.9.39)$$

Show then that the position uncertainty $\Delta x(t)$ can be less than the quantum limit in Eq. (2.7.3), (see Ref. [9], p. 541 and [8], p. 281).

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Chapter 3 Contents

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Chapter 3

Simple Harmonic Oscillator

But oh, beamish nephew, beware of the day,
If your Snark be a Boojum! For then
You will softly and suddenly vanish away,
And never be met with again!
—Lewis Carroll, The Hunting of the Snark.

3.1 Introduction

In quantum mechanics, the simple harmonic oscillator plays a very important role. As in classical mechanics, it deals with the physically important situation of motion near a potential minimum. The most familiar example of the harmonic oscillation is the small-amplitude vibrations of atoms or ions about their equilibrium positions in a molecule or in a solid. Another example is the electromagnetic wave which is composed of a number of normal modes each of which is a simple harmonic oscillator. As to the theory aspect, the simple harmonic oscillator provides an exactly soluble system. We shall not solve the Schrödinger equation as a partial differential equation with a power series solution [1]. We shall follow Dirac's operator method [2]. Its simplicity lies in the ease with which all relevant matrix elements can be constructed from first principles and, therefore, there are no complicated recurrence relations to remember. The methodology for diagonalization is also useful in the operator solution in diagonalizing the angular momentum operator, which is a stepping stone to the spin. It is also equivalent to the factorization method [3] for the solution of a family of second order differential equations, which we will explore further in Chapter 11 in connection with the radial equation for the hydrogen atom . The simple harmonic oscillator is also a wonderful system for delving deeper into the

density matrix, the coherent number states, the QND observable, and the time-dependent correlation functions.

3.2 The Operator Method

The aim is to find the eigenvalues and eigenstates of the Hamiltonian,

$$H = \frac{1}{2m}P^2 + \frac{1}{2}m\omega^2 X^2, \tag{3.2.1}$$

where P an X are the momentum and position operators, m is the mass of the oscillator, and ω its frequency.

3.2.1 Creation and annihilation operators

The position and momentum are first put in the dimensionless form

$$X = \left(\frac{2\hbar}{m\omega}\right)^{1/2}\Xi, \tag{3.2.2}$$

$$P = (2m\hbar\omega)^{1/2}\,\Pi. \tag{3.2.3}$$

Then the dimensionless Hamiltonian is

$$H/\hbar\omega = \Pi^2 + \Xi^2. \tag{3.2.4}$$

The commutation relation, $[X, P] = i\hbar$, becomes

$$[\Xi, \Pi] = \frac{i}{2}. \tag{3.2.5}$$

We wish to factorize the expression on the right for a reason which will be clear later:

$$\Pi^2 + \Xi^2 = (\Xi - i\Pi)(\Xi + i\Pi) + \frac{1}{2}. \tag{3.2.6}$$

The last term compensates the cross terms in the product of the two factors preceding it as a result of the noncommutative nature of the two operators Ξ and Π.

It is convenient to introduce the new operators,

$$c = \Xi + i\Pi, \tag{3.2.7}$$

$$c^\dagger = \Xi - i\Pi. \tag{3.2.8}$$

From the commutation relation (3.2.5) between Ξ and Π, the commutator between the new operators is

$$[c, c^\dagger] = 1. \tag{3.2.9}$$

The Hamiltonian has the simple expression

$$H = \hbar\omega \left(c^\dagger c + \frac{1}{2} \right). \tag{3.2.10}$$

The number operator $N = c^\dagger c$ is Hermitian and, therefore, a physical observable. From its relation to the Hamiltonian, it is evident that N and H share common eigenstates and their eigenvalues are simply related. We shall therefore find the eigenvalues and eigenstates of N first.

3.2.2 The ladder theorem

If $|\nu\rangle$ is an eigenstate of N with eigenvalue ν, then $c|\nu\rangle$ is an eigenstate with eigenvalue $\nu - 1$, and $c^\dagger|\nu\rangle$ is an eigenstate with eigenvalue $\nu + 1$.

Proof: The key is the commutation relations,

$$[c, N] = c\,, \tag{3.2.11}$$

$$\left[c^\dagger, N\right] = -c^\dagger\,, \tag{3.2.12}$$

which follows readily from Eq. (3.2.9). We are given

$$N|\nu\rangle = \nu|\nu\rangle. \tag{3.2.13}$$

Operating on both sides with c, we obtain

$$cN|\nu\rangle = \nu c|\nu\rangle. \tag{3.2.14}$$

Note that we have commuted the order of c and ν on the right side since ν is a number. The commutation relation between c and N, Eq. (3.2.11), leads to

$$N(c|\nu\rangle) = (\nu - 1)(c|\nu\rangle), \tag{3.2.15}$$

which means that $c\nu$ is an eigenstate of N with the eigenvalue $\nu - 1$. *Q.E.D.*

Similarly, it can be shown (really!) by Eq. (3.2.12) that

$$N(c^\dagger|\nu\rangle) = (\nu + 1)(c^\dagger|\nu\rangle). \tag{3.2.16}$$

3.2.3 The ground state and zero-point motion

Since for the normalized state $|\nu\rangle$

$$\nu = \langle\nu|N|\nu\rangle = \langle\nu|c^\dagger c|\nu\rangle \geq 0, \tag{3.2.17}$$

where the expression $\nu|c^\dagger c|\nu\rangle$ is the absolute square of the length of the state vector $c|\nu\rangle$, the smallest ν must be exactly zero, otherwise $\nu - 1$ would be a legitimate smaller eigenvalue. For $\nu = 0$, the same equation leads to

$$c|\psi_0\rangle = 0. \tag{3.2.18}$$

The state $|\nu = 0\rangle$ is the lowest energy state with energy

$$E_0 = \frac{1}{2}\hbar\omega. \tag{3.2.19}$$

It is possible to generate the ground state wave function by expressing the state as an expansion in the eigenstate $|\xi\rangle$ of the dimensionless position Ξ with the coefficient $\psi_0(\xi) = \langle\xi|0\rangle$, which is governed by Eq. (3.2.18),

$$0 = \langle\xi|c|\psi_0\rangle = \left(\xi + \frac{1}{2}\frac{\partial}{\partial\xi}\right)\psi_0(\xi), \tag{3.2.20}$$

using the definition of c in Eq. (3.2.7). The normalized solution is

$$\begin{aligned} \psi_0(\xi) &= \frac{2}{\pi}^{1/4} e^{-\xi^2}, \\ \text{or } \psi_0(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}. \end{aligned} \tag{3.2.21}$$

Since the ground state energy does not enter into the spectral distribution of the black-body radiation, there was no way for Planck to have known to include the zero point energy in his hypothesis. The existence of motion—the zero point motion—for the state of the lowest energy can be understood from the considerations of the uncertainty principle, as we have seen in Chapter 1. The Gaussian wave function shows that, although the particle is most likely to be at the origin, there is an uncertainty of position equal to $\sqrt{\hbar/2m\omega}$. Since the Fourier transform of a Gaussian is another Gaussian, the momentum wave function has a similar distribution.

One manifestation of the zero point motion is the fact that helium, both isotopes He^3 and He^4, remains a liquid down to the lowest temperatures reached (in the milli-degree Kelvin range), under one atmospheric pressure. In a solid made up of heavier elements, the atoms or ions are arranged in a regular array and oscillate about the mean equilibrium position. As the temperature approaches absolute zero, the oscillation is due to the zero point motion. If the amplitude of the zero point oscillation (roughly speaking, the uncertainty in position) is a small fraction of the inter-atomic distance, then the solid remains well ordered. For a helium atom, the mass is so small that the uncertainty in position is larger than the inter-atomic distance and the order of a solid is destroyed. It is possible to solidify liquid helium by applying pressure at sufficiently low temperatures. Even then the large zero point motion sets the solid helium apart from ordinary solids with properties of a "quantum solid".

The zero point motion of the electromagnetic field is known as the vacuum fluctuations, to be considered in Chapter 14.

3.2.4 The excited states

Once we know the ground state, we can obtain all the normalized higher number or energy eigenstates by using the ladder theorem repeatedly:

$$|n\rangle = \frac{1}{\sqrt{n!}}\,(c^\dagger)^n|0\rangle, \tag{3.2.22}$$

and the corresponding energies

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \tag{3.2.23}$$

where n is zero or a positive integer.

The ladder theorem relates two normalized adjacent number states by

$$c^\dagger|n\rangle = \gamma_n|n+1\rangle, \tag{3.2.24}$$

where γ_n is a number to be determined by:

$$\begin{aligned} |\gamma_n|^2\langle n+1|n+1\rangle &= \langle n|cc^\dagger|n\rangle \\ &= \langle n|(c^\dagger c+1)|n\rangle \\ &= n+1. \end{aligned} \tag{3.2.25}$$

In the last two steps, the commutation relation (3.2.9) and the number eigenstate property (3.2.13) are used. Hence,

$$\gamma_n = (n+1)^{1/2}, \tag{3.2.26}$$

aside from a multiplicative factor $e^{i\alpha}$ with an undetermined (real) phase α which by convention is set to zero. Thus,

$$c^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{3.2.27}$$

Similarly,

$$c|n\rangle = \sqrt{n}|n-1\rangle. \tag{3.2.28}$$

Eq. (3.2.22) is then obtained by induction.

The energy values of the energy eigenstates, i.e., the states with definite energies, are discrete. This is a common property of bound states. Since the potential for the harmonic oscillator rises quadratically without limit, all the states are bound. The energy values are separated by a regular spacing of $\hbar\omega$. This is the essential feature of the Planck hypothesis which is needed to derive the spectral distribution of the black-body radiation. It is very satisfying to have this as a consequence of quantum mechanics.

3.3 Quantum Non-Demolition Observables in a Simple Harmonic Oscillator

The example of a QND observable in a square well with two levels in the last chapter is a fine academic exercise but it is not a robust system since one has to be careful not to excite the particle out of the well. Now let us use the simple harmonic oscillator of frequency ω as an example to find QND observables. The position and momentum of the particle in one dimension are

$$X = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(c+c^\dagger), \tag{3.3.1}$$

$$P = \frac{1}{i}\left(\frac{m\hbar\omega}{2}\right)^{1/2}(c-c^\dagger), \tag{3.3.2}$$

The time evolution of the operators are given in the Heisenberg representation,

$$\tilde{c}(t) = c\, e^{-i\omega t}, \tag{3.3.3}$$

$$\tilde{c}^\dagger(t) = c^\dagger\, e^{i\omega t}. \tag{3.3.4}$$

To avoid later confusion, we denote an operator in the Heisenberg representation by the tilde over the symbol and the same operator in the Schrödinger representation by the same symbol without the tilde. Hence, the position and momentum operators are

$$\tilde{X}(t) = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(ce^{-i\omega t} + c^\dagger e^{i\omega t}) = X\cos\omega t + \frac{P}{m\omega}\sin\omega t, \tag{3.3.5}$$

$$\tilde{P}(t) = \frac{1}{i}\left(\frac{m\hbar\omega}{2}\right)^{1/2}(ce^{-i\omega t} - c^\dagger e^{i\omega t}) = P\cos\omega t - m\omega X\sin\omega t. \tag{3.3.6}$$

Note that the position and momentum operators in the Schrödinger representation are both time independent.

Now we define in the Schrödinger representation two *time dependent* operators,

$$Q_r(t) = \frac{1}{\sqrt{2}}(ce^{i\omega t} + c^\dagger e^{-i\omega t}), \tag{3.3.7}$$

$$Q_i(t) = \frac{1}{i\sqrt{2}}(ce^{i\omega t} - c^\dagger e^{-i\omega t}). \tag{3.3.8}$$

They are related to the position and momentum with a trivial difference and an important difference. The trivial difference is the factor which renders the new operators dimensionless. The important one is the time dependence which leads to their Heisenberg representation

$$\tilde{Q}_r = e^{iHt/\hbar}Q_r(t)e^{-iHt/\hbar} = \frac{1}{\sqrt{2}}(c + c^\dagger), \tag{3.3.9}$$

$$\tilde{Q}_i = e^{iHt/\hbar}Q_i(t)e^{-iHt/\hbar} = \frac{1}{i\sqrt{2}}(c - c^\dagger), \tag{3.3.10}$$

which are independent of time. They are called by Walls and Milburn [4] "quadrature phase amplitudes". "Quadrature" means that the two phases differ by $\pi/4$, as in "the first quarter moon is in quadrature with the sun", or closer to our example, "the two components of the two-phase ac current are in quadrature". Since these phase operators in the Heisenberg representation are independent of time, they are QND observables.

The two phase operators are related to the position and momentum operators by

$$\tilde{Q}_r = \left(\frac{m\omega}{\hbar}\right)^{1/2}\left[\tilde{X}(t)\cos\omega t - \frac{\tilde{P}(t)}{m\omega}\sin\omega t\right], \tag{3.3.11}$$

$$\tilde{Q}_i = \left(\frac{m\omega}{\hbar}\right)^{1/2}\left[\tilde{X}(t)\sin\omega t + \frac{\tilde{P}(t)}{m\omega}\cos\omega t\right]. \tag{3.3.12}$$

An observation useful for later use in the study of squeezed states is that the $\tilde{Q}_r - \tilde{Q}_i$ axis rotates relative to the $\tilde{X} - \tilde{P}$ axis with angular speed $-\omega$. A survey of experiments on QND is given in Ref. [4].

3.4 A system of many coupled oscillators

It is straightforward to generalize the foregoing work to a coupled set of harmonic oscillators. When the total Hamiltonian is quadratic in the momentum variables and the displacement from equilibrium positions of a number of particles, in classical mechanics it is possible to decouple them into a set of normal modes. If each normal mode is distinguished by a suffix j, the Hamiltonian may be written as

$$H = \sum_j \hbar\omega_j\left(c_j^\dagger c_j + \frac{1}{2}\right). \tag{3.4.1}$$

The commutation relations are

$$[c_j, c_{j'}] = 0, \tag{3.4.2}$$

$$\left[c_j, c_{j'}^\dagger\right] = \delta_{jj'}. \tag{3.4.3}$$

In Chapter 14, it will be shown that the quantization of the electromagnetic fields can be carried out in the same way, by determining the normal modes of the oscillations of the electromagnetic waves and quantizing the Hamiltonian of each independent oscillator. For a very large number of normal modes, this system is an important model for the reservoir in the study of dissipative dynamics of an open system.

3.4.1 Vibrations of atoms in a periodic lattice

Here we study an example of coupled harmonic oscillators originating from the oscillations of a linear chain of identical atoms with equally spaced equilibrium positions [5] moving along the chain. To use the periodic boundary condition, we imagine the atoms to be in

a necklace. The atoms are labeled by the integer $\ell = 0, 1, , \ldots, N-1$. Atom $\ell + N$ is the same as atom ℓ. The harmonic Hamiltonian is

$$H = \sum_{\ell} \left[\frac{P_\ell^2}{2m} + \frac{g}{2}(X_{\ell+1} - X_\ell)^2 \right], \tag{3.4.4}$$

where P_ℓ is the momentum operator of the ℓ-th atom along the chain, and X_ℓ its displacement operator from the equilibrium position ℓa.

For a periodic system, the translational symmetry may help in constructing the energy eigenstates. This will be done in Chapter 8 while the treatment here is analogous to the classical physics of small oscillations. The Heisenberg equations of motion for the coupled oscillators are

$$\frac{dX_\ell}{dt} = \frac{1}{m} P_\ell, \tag{3.4.5}$$

$$\frac{dP_\ell}{dt} = g(X_{\ell+1} - 2X_\ell + X_{\ell-1}). \tag{3.4.6}$$

The equations can be decoupled by the Fourier sum,

$$\begin{aligned} Q_k &= \frac{1}{\sqrt{N}} \sum_{\ell=0}^{N-1} e^{-ik\ell} X_\ell, \\ \Pi_k &= \frac{1}{\sqrt{N}} \sum_{\ell=0}^{N-1} e^{-ik\ell} P_\ell. \end{aligned} \tag{3.4.7}$$

where the "lattice wave vector" k is given by

$$k = \frac{2\pi n_k}{N}, \text{ with } n_k = 0, 1, \ldots, N-1. \tag{3.4.8}$$

We arrive at the equations for the normal mode harmonic oscillators,

$$\frac{dQ_k}{dt} = \frac{1}{m} \Pi_k, \tag{3.4.9}$$

$$\frac{d\Pi_k}{dt} = -m\omega_k^2 Q_k, \tag{3.4.10}$$

with the frequencies,

$$\omega_k = 2\sqrt{\frac{g}{m}} \sin\left(\frac{ka}{2}\right). \tag{3.4.11}$$

Each normal mode oscillator has the annihilation and creation operators given by,

$$Q_k = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (c_k + c_k^\dagger), \tag{3.4.12}$$

$$P_k = -i \left(\frac{m\hbar\omega}{2}\right)^{1/2} (c_k - c_k^\dagger). \tag{3.4.13}$$

These relations and the inverse Fourier transforms of Eq. (3.4.7) lead directly to the Hamiltonian (3.4.1) of N independent oscillators.

Extension to three dimensions is done first by permitting the atoms in the one dimension chain to oscillate normal to the chain. With a different (generally smaller) elastic constant g' for the transverse motion, there will be two transverse modes with lower frequencies than the vibration along the chain which is called the longitudinal mode. Next, the extension of the periodic structure to three dimensions can be done, for example, by a cubic lattice of atoms. The lattice wave vector is now a vector $\vec{k}$. For each $\vec{k}$, there are three normal modes in the case of a simple cubic lattice, but the direction of each normal mode is not necessarily parallel or perpendicular to $\vec{k}$. We may consider the index j in the Hamiltonian (3.4.1) as the collection of indices $\vec{k}, \nu$, where the number of normal modes per wave vector is three times the number of atoms per primitive unit cell of a periodic lattice. For details, consult a solid state book, e.g., [5, 6]. The essential point is the construction of the independent oscillators.

3.4.2 Second quantization - first look

We have seen how in terms of the annihilation and creation operators the Hamiltonian can be expressed in a factorizable form, and how the Schrödinger equation is then solved completely for the energy eigenvalues and their associated eigenstates. This method of solution affords us a graphic interpretation of the energy eigenstates of the harmonic oscillator. The nth level has energy $n\hbar\omega$ plus the zero point energy $\frac{1}{2}\hbar\omega$. Now imagine particles each of energy $\hbar\omega$. If the harmonic oscillator is an electromagnetic field, the particle is called the photon. If the harmonic oscillator is from the displacement of atoms in a solid or liquid, the particle of energy is called the phonon. Aside from the zero point energy, the nth state of the simple harmonic oscillator may be said to be a state containing n of these particles. The operator $c^\dagger$ acting on the nth state yields the $(n+1)$th state. $c^\dagger$ has created a particle of energy $\hbar\omega$ and is therefore called the creation operator. On the other hand, c acting on the nth state yields the $(n-1)$th state. c destroys a particle of energy $\hbar\omega$ and is therefore called the annihilation operator. These operators do more than just keeping count of the number of particles; they also provide the coherence between the two contiguous energy states since they keep the phase relation

between them.

For the system of N oscillators, we may think of $c_j^\dagger$ as the creation of a boson in state j. the commutation relations are

$$[c_j, c_{j'}^\dagger] = \delta_{jj'}. \tag{3.4.14}$$

In Chapter 13, the study of a system of identical particles leads to those with the commutation relations like the creation and annihilation operators which are called bosons. We could completely forget the original harmonic oscillators and their complicated wave functions and treat the system as a bunch of particles, photons or phonons, in different normal modes j. A general energy eigenstate of the system is

$$|n_0, n_1, \ldots\rangle = \prod_k \left[\frac{1}{\sqrt{n_k!}}(c_k^\dagger)^{n_k}\right]|0\rangle, \tag{3.4.15}$$

where the quantum numbers $\{n_j\}$ are given by the number of bosons in each normal mode j.

The first introduction of $\hbar$ into the commutation between the position and momentum is called the first quantization. The quantization of the multimode wave function into a system of Bose particles is called the second quantization.

3.5 Examples

The examples in this section are primarily for readers who have not encountered the quantum harmonic oscillator problem previously.

3.5.1 A harmonic oscillator subject to a constant force

A simple harmonic oscillator is restricted to move in one dimension. It has mass m and force constant $m\omega^2$. It carries a charge e and is placed in a uniform static electric field $\mathcal{E}$ in the line of direction of its motion. Find its energy eigenvalues and associated eigenstates. (Hint: Do not charge into the series solution of the Schrödinger equation. Ask yourself how you would solve the classical problem and ask if a similar procedure could not be adopted for the corresponding quantum case.)

Solution — The Hamiltonian is

$$H = \frac{P^2}{2m} + \frac{1}{2}\,kX^2 - e\mathcal{E}X. \tag{3.5.1}$$

Completing the square in X, we have

$$H = \frac{P^2}{2m} + \frac{1}{2}\,k(X - x_0)^2 - \frac{1}{2k}\,(e\mathcal{E})^2, \tag{3.5.2}$$

where $x_0 = e\mathcal{E}/k$. This is a harmonic oscillator with a displaced origin at $x = x_0$ and a shift in energy $-\frac{1}{2k}\,(e\mathcal{E})^2$. Hence, the energy eigenvalues are

$$E_n = (n + \frac{1}{2})\hbar\omega - \frac{(e\mathcal{E})^2}{2m\omega^2}, \tag{3.5.3}$$

where $n = 0, 1, 2, \ldots$ and

$$\omega = \sqrt{\frac{k}{m}}. \tag{3.5.4}$$

Th eigenstates are given by Eq. (3.2.22) with $c^\dagger$ defined by $X - x_0$ in placement of X.

3.5.2 Center of mass and relative motion

Two particles of masses m_1 and m_2 are confined to move in one dimension subject to an internal conservative force between the two particles.

1. Write down the Hamiltonian for the two particles.

   Solution — It is simplest to do the problem in the position representation. With the suffices 1 and 2 denoting the respective particles, the Hamiltonian for the system of two particles is

   $$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(x_1 - x_2). \tag{3.5.5}$$

2. Separate the Hamiltonian into two parts: one containing the center of mass motion only and one containing the relative motion only.

   Solution — Introduce the relative coordinate

   $$x = x_1 - x_2 \tag{3.5.6}$$

and the center of mass coordinate

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}. \tag{3.5.7}$$

To relate the relative and center-of-mass momentum operators to those of the individual particles, we use the chain rule for the differential operator

$$\frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} = \frac{\partial}{\partial x} - \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X}. \tag{3.5.8}$$

Repeating the operation once more and doing the same for the second particle, we eventually get

$$-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2(m_1+m_2)}\frac{\partial^2}{\partial X^2}, \tag{3.5.9}$$

where μ is the reduced mass given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}. \tag{3.5.10}$$

Thus, the Hamiltonian is divided into two terms:

$$H = H_c + H_r, \tag{3.5.11}$$

where the first is the center of mass motion

$$H_c = -\frac{\hbar^2}{2(m_1+m_2)}\frac{\partial^2}{\partial X^2} \tag{3.5.12}$$

and the second is the relative motion

$$H_r = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x). \tag{3.5.13}$$

3. If the force between the two particles is simple harmonic, solve the Schrödinger equation for the energy values and eigenstates for the system of two particles. (Do not forget to include both relative motion and center of mass motion, or equivalently, the coordinates of both particles.)

Solution — The wave function as a function of the center of mass coordinate and the relative coordinate is now separable:

$$\psi(X, x) = \psi_c(X)\psi_r(x), \tag{3.5.14}$$

with energy

$$E = E_c + E_r. \tag{3.5.15}$$

The center of mass motion is given by the Schrödinger equation

$$H_c\psi_c(X) = E_c\psi_c(x). \tag{3.5.16}$$

Therefore,

$$E_c = \frac{\hbar^2 K^2}{2(m_1 + m_2)} \tag{3.5.17}$$

and

$$\psi_c(X) = e^{iKX}. \tag{3.5.18}$$

The relative motion is simple harmonic and

$$E_{rn} = (n + \frac{1}{2})\hbar\omega, \tag{3.5.19}$$

where $\omega = \sqrt{k/\mu}$, and

$$\psi_{rn}(x) = \psi_n(x), \tag{3.5.20}$$

the harmonic oscillator wave function.

Putting the results together, we have for the system the eigenenergy

$$E_{K,n} = \frac{\hbar^2 K^2}{2(m_1 + m_2)} + (n + \frac{1}{2})\hbar\omega, \tag{3.5.21}$$

and the associated wave function

$$\psi_{K,n}(X, x) = e^{iKX}\psi_n(x). \tag{3.5.22}$$

3.5.3 Molecular vibration

Consider the vibrations of the two atoms along the line joining them in a diatomic atom. If r denotes the distance between the two atoms, their interaction potential is approximately given by the Morse potential

$$V(r) = V_0\left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right], e^{\alpha r_0} > 2. \tag{3.5.23}$$

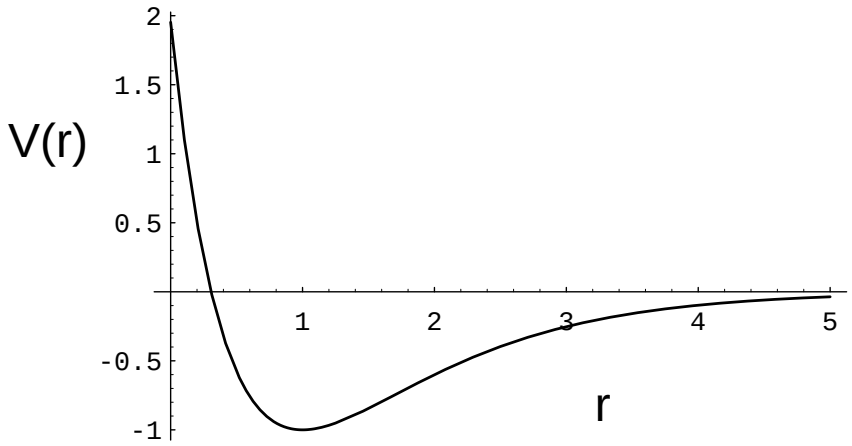

Figure 3.1: Morse potential with the potential in units of V_0 and distance in units of r_0 and $\alpha = 1/r_0$.

1. Sketch the potential for the range $0 < r < +\infty$ (pointing out the behavior of small r, large r, and any minimum or maximum).

   Solution — The Morse potential is plotted in Fig. 4.2.

   As easily verified analytically, the minimum occurs at $r = r_0$. As r decreases from infinity, the potential is attractive till it passes the minimum point. For small enough r, the potential is repulsive.

2. Approximate the potential near the minimum by a harmonic potential. If μ denotes the reduced mass of the two atoms, the kinetic energy due to their relative motion is the same as that of a particle of mass μ. Hence, find the energy levels for small oscillations about the equilibrium position of the molecule.

   Solution — Change the origin such that $x = r - r_0$. Expansion of the potential energy in small displacement x from the equilibrium position r_0 yields

   $$V(r) = V_0[-1 + \alpha^2 x^2 + O(x^3)]. \tag{3.5.24}$$

   The effective Hamiltonian for the relative motion of the two atoms along the line joining their positions is

   $$H_{eff} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V_0\alpha^2 x^2, \tag{3.5.25}$$

where μ is the reduced mass. The angular frequency is given by

$$\omega = \sqrt{\frac{2V_0\alpha^2}{\mu}}. \tag{3.5.26}$$

The energy levels are

$$E_n = (n + \frac{1}{2})\hbar\omega - V_0, \tag{3.5.27}$$

provided that n is not so large that the quadratic approximation for $V(r)$ breaks down.

3. For the hydrogen molecule, $V_0 = 5.07$ eV,

$$r_0 = 0.74\text{Å} \qquad , \alpha = 1.88\text{Å}^{-1}.$$

Compute the energy levels of the molecular vibration. (Caution: find the reduced mass for the hydrogen molecule.)

Solution — The reduced mass is

$$\mu = m_{proton}/2 = 8.35 \times 10^{-28} kg. \tag{3.5.28}$$

The frequency is

$$\begin{aligned} \omega &= \left[\frac{2 \times 5.07eV \times 1.60 \times 10^{-19}(J/eV)}{8.35 \times 10^{-28} kg}\right]^{1/2} \times 1.88 \times 10^{10}/m \\ &= 8.29 \times 10^{14}/s, \end{aligned} \tag{3.5.29}$$

and its energy is

$$\hbar\omega = 0.54eV. \tag{3.5.30}$$

The energy of the system is

$$E_n = (0.54n - 4.80)eV. \tag{3.5.31}$$

4. A better approximation for the energy levels of the Morse potential are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{\left[\left(n + \frac{1}{2}\right)\hbar\omega\right]^2}{4V_0} - V_0. \tag{3.5.32}$$

For the hydrogen molecule, comment on the accuracy of the harmonic approximation and on its correction.

Solution — The correction ratio is

$$\frac{\Delta E_n}{E_n} = \left(n + \frac{1}{2}\right) \frac{\hbar\omega}{V_0} = 0.11 \left(n + \frac{1}{2}\right). \tag{3.5.33}$$

For the lowest level, the correction is about 10%. The corrections becomes overwhelming at about $n = 10$. The tendency is to narrow the spacing between energy levels as n increases.

3.5.4 Pendulum motion

A particle of mass m is confined to move in a vertical circle of radius R in the earth's gravitational field. Its position is determined by θ, the angle of its radius vector with the downward vertical.

1. Establish the Schrödinger equation for the particle.

   Solution — Treat the motion as a rigid-body rotation. The Hamiltonian is given by

   $$H = \frac{L^2}{2I} + mgR(1 - \cos\theta), \tag{3.5.34}$$

   where the moment of inertia is $I = mR^2$ and L is the angular momentum operator

   $$L = \frac{\hbar}{i} \frac{\partial}{\partial\theta}. \tag{3.5.35}$$

   The time-dependent Schrödinger equation is

   $$H\Psi(\theta, t) = i\hbar \frac{\partial\Psi(\theta, t)}{\partial t}. \tag{3.5.36}$$

2. Show that the motion is simple harmonic if the wave function is concentrated near $\theta = 0$. Hence, write down the ground-state energy of the particle.

   Solution — For small angular displacement θ.

   $$1 - \cos\theta \approx \frac{\theta^2}{2}, \tag{3.5.37}$$

and the Hamiltonian is simple harmonic

$$H = -\frac{\hbar^2}{2mR^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{2}mgR\theta^2, \tag{3.5.38}$$

with frequency

$$\omega = \sqrt{\frac{g}{R}}. \tag{3.5.39}$$

The ground-state energy measured from the potential energy zero is

$$E_0 = \frac{\hbar}{2}\sqrt{\frac{g}{R}}. \tag{3.5.40}$$

3. Estimate the ground-state energy in electron volts if the radius R is 1 Å.

Solution —

$$\omega = \sqrt{\frac{10m/s}{10^{-10}m}} \approx 3 \times 10^5/s. \tag{3.5.41}$$

$$E_0 = 10^{-10}eV. \tag{3.5.42}$$

This shows that the gravitational force is unimportant in atoms.

4. Deduce the condition on R in order that the energy in part (b) is a good approximation to the ground, given that m is about 100 times the hydrogen atom mass.

Solution — Expand the power series for the potential energy in θ to one more term:

$$V(\theta) = mgR(1 - \cos\theta) = mgR\left(\frac{\theta^2}{2} - \frac{\theta^4}{24} + O(\theta^6)\right). \tag{3.5.43}$$

For the harmonic approximation to be valid, the fourth order term must be smaller than the second order:

$$\langle\theta^4\rangle \ll 12\langle\theta^2\rangle, \tag{3.5.44}$$

where the angular brackets denote the ground-state expectation value.

A sloppy way to proceed is to approximate $\langle\theta^4\rangle$ by $\langle\theta^2\rangle^2$. Then the condition Eq. (3.5.44) becomes

$$\langle\theta^2\rangle \ll 12. \tag{3.5.45}$$

From the next example we see that the potential energy expectation value for the harmonic oscillator is

$$\frac{1}{2}mgR\langle\theta^2\rangle = \frac{1}{4}\hbar\omega = \frac{1}{4}\hbar\sqrt{\frac{g}{R}}. \tag{3.5.46}$$

Thus, the condition for the validity of the harmonic approximation becomes

$$R \gg \left[\frac{\hbar^2}{576m^2g}\right]^{1/3} \approx 500\mathring{A}. \tag{3.5.47}$$

A more precise treatment of the condition is to evaluate $\langle\theta^4\rangle$. By the operator method, we obtain

$$\langle(c+c^\dagger)^4\rangle = 5, \tag{3.5.48}$$

which leads to the condition

$$R \gg \left[\frac{25\hbar^2}{576m^2g}\right]^{1/3} \approx 1500\mathring{A}. \tag{3.5.49}$$

3.5.5 Exercises using the operator method

1. The uncertainty in momentum for the oscillator in the ground state.

Solution — The momentum expectation value for the ground state is

$$\begin{aligned}
\langle P\rangle &= \langle 0|P|0\rangle \\
&= -i\left(\frac{m\hbar\omega}{2}\right)^{1/2}\langle 0|(c-c^\dagger)|0\rangle, \qquad \text{by Eq. (3.3.2)} \\
&= -i\left(\frac{m\hbar\omega}{2}\right)^{1/2}\langle 0|-c^\dagger|0\rangle, \qquad \text{by Eq. (3.2.18)} \\
&= i\left(\frac{m\hbar\omega}{2}\right)^{1/2}\langle 0|1\rangle, \qquad \text{by Eq. (3.2.27)} \\
&= 0,
\end{aligned} \tag{3.5.50}$$

by the orthogonality of the eigenstates.

From Eq. (3.3.1),

$$\begin{aligned}
P^2 &= -\frac{1}{2}m\hbar\omega(c-c^\dagger)(c-c^\dagger) \\
&= -\frac{1}{2}m\hbar\omega(c^2-c^\dagger c-cc^\dagger+c^{\dagger 2}) \\
&= -\frac{1}{2}m\hbar\omega(c^2-2c^\dagger c-1+c^{\dagger 2}), \\
&= \frac{1}{2}m\hbar\omega(1-c^{\dagger 2}-c^2+2c^\dagger c).
\end{aligned} \tag{3.5.51}$$

To evaluate the mean value, we need

$$\begin{aligned} \langle c^\dagger c\rangle &= \langle 0|c^\dagger c|\ 0\rangle = 0, \qquad \text{by Eq. (3.2.18)} \\ \langle c^2\rangle &= 0, \qquad \text{for the same reason,} \\ \text{and } \langle c^{\dagger 2}\rangle &= \langle c^2\rangle^* = 0. \\ \text{Hence, } \langle P^2\rangle &= \frac{1}{2}m\hbar\omega. \end{aligned} \tag{3.5.52}$$

The uncertainty is

$$\Delta p = \left(\frac{1}{2}m\hbar\omega\right)^{1/2}. \tag{3.5.53}$$

2. Ground state expectation value for the kinetic energy.

Solution —

$$\langle T\rangle = \langle (P^2/2m)\rangle = \frac{1}{4}\hbar\omega. \tag{3.5.54}$$

3. Ground state expectation value for the potential energy.

Solution —

$$\langle V\rangle = \langle H - T\rangle = \frac{1}{2}\hbar\omega - \frac{1}{4}\hbar\omega = \frac{1}{4}\hbar\omega. \tag{3.5.55}$$

4. Uncertainty for the position of the oscillator in the ground state.

Solution — Since $V = \frac{1}{2}m\omega^2 X^2$,

$$\langle X^2\rangle = \frac{\hbar}{2m\omega}. \tag{3.5.56}$$

Thus,

$$\Delta x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}. \tag{3.5.57}$$

For the ground state, we have

$$\Delta p \cdot \Delta x = \frac{\hbar}{2}. \tag{3.5.58}$$

3.5.6 Time evolution of the oscillator state

A simple harmonic oscillator of mass m and frequence ω has a wave function at $t = 0$ given by

$$|\Psi(t=0)\rangle = \frac{1}{\sqrt{2}}\left\{|0\rangle + |1\rangle\right\}, \tag{3.5.59}$$

in terms of the two lowest energy eigenstates.

1. Find the wave function at time t.

   Solution — By the procedure in Chapter 2, we obtain

   $$|\Psi(t)\rangle = \frac{1}{\sqrt{2}}\left\{|0\rangle e^{-iE_0 t/\hbar} + |1\rangle e^{-iE_1 t/\hbar}\right\}. \tag{3.5.60}$$

2. What is the probability of finding the oscillator with energy $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$, for n=0,1,2,...?

   Solution — If the expansion of the state in terms of the energy eigenstates is

   $$|\Psi(t)\rangle = \sum_n |n\rangle c_n e^{-iE_n t/\hbar}, \tag{3.5.61}$$

   then the probability of finding the particle in the state with energy E_n is

   $$P_n = |c_n|^2. \tag{3.5.62}$$

   Here, the probabilities are

   $$\begin{aligned} P_n &= \frac{1}{2} \quad \text{for} \quad n = 0, 1; \\ P_n &= 0 \quad \text{for} \quad n \geq 2. \end{aligned} \tag{3.5.63}$$

3. Find the mean energy and the uncertainty.

   Solution — The mean energy is

   $$\langle E\rangle = \sum_n P_n E_n = \frac{1}{2}\left(\frac{1}{2}\hbar\omega + \frac{3}{2}\hbar\omega\right) = \hbar\omega. \tag{3.5.64}$$

The mean square energy is

$$\langle E^2 \rangle = \sum_n P_n E_n^2 = \frac{1}{2}\left[\left(\frac{1}{2}\hbar\omega\right)^2 + \left(\frac{3}{2}\hbar\omega\right)^2\right] = \frac{5}{4}\left(\hbar\omega\right)^2. \tag{3.5.65}$$

The uncertainty in energy is

$$\Delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = \frac{1}{2}\hbar\omega. \tag{3.5.66}$$

This result could also be have been reached as the average is half-way between the only two admissible energy levels.

4. Find the mean position at time t.

Solution — By definition,

$$\langle x \rangle = \langle \Psi(t)|x|\Psi(t)\rangle. \tag{3.5.67}$$

Expanding out the energy eigenfunction series of the wave function and its complex conjugate, we obtain

$$\langle x \rangle = \frac{1}{2}\left[\langle 0|x|0\rangle + e^{i\omega t}\langle 1|x|0\rangle + e^{-i\omega t}\langle 0|x|1\rangle + \langle 1|x|1\rangle\right]. \tag{3.5.68}$$

Among the terms on the right, by inversion symmetry,

$$\langle n|x|n\rangle = 0, \tag{3.5.69}$$

and

$$\langle 1|x|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle 1|(c + c^\dagger)|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}. \tag{3.5.70}$$

Therefore,

$$\begin{aligned} \langle x \rangle &= \Re\left[e^{i\omega t}\langle 1|x|0\rangle\right] \\ &= \Re\left[\sqrt{\frac{\hbar}{2m\omega}}\, e^{i\omega t}\right] \\ &= \sqrt{\frac{\hbar}{2m\omega}}\, \cos(\omega t). \end{aligned} \tag{3.5.71}$$

5. Find the mean momentum at time t.

Solution — By a similar argument as for the position,

$$\langle p \rangle = \Re\left[e^{i\omega t}\langle 1|p|0\rangle\right]. \tag{3.5.72}$$

The matrix element of the momentum is

$$\langle 1|p|0\rangle = \frac{1}{i}\sqrt{\frac{m\hbar\omega}{2}}\langle 1|(c-c^\dagger)|0\rangle = i\sqrt{\frac{m\hbar\omega}{2}}. \tag{3.5.73}$$

The mean momentum at time t is

$$\Re\left[e^{i\omega t}\langle 1|p|0\rangle\right] = -\sqrt{\frac{m\hbar\omega}{2}}\sin(\omega t). \tag{3.5.74}$$

6. If at $t=0$, $|\Psi(t=0)\rangle = \frac{1}{\sqrt{2}}\{|0\rangle + i|1\rangle\}$, find the answers to (a)-(e). [Note: In the normalization constant for each eigenstate, we have chosen a real number, saying that a phase factor of $e^{i\delta}$ is immaterial to the physics. For $|\Psi(t)\rangle$, however, the factor of $i = e^{i\pi/2}$ is not an overall phase factor. (f) furnishes an example of the importance of the relative phase of the ψ_1 and ψ_0 terms.]

Solution — Similar to part (a), the wave function at time t is

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}}|0\rangle e^{-iE_0 t/\hbar} + \frac{i}{\sqrt{2}}|1\rangle e^{-iE_1 t/\hbar}, \tag{3.5.75}$$

The probability for finding each energy state and therefore the average energy and uncertainty are the same as in part (a). The change in coefficient, however, changes the mean position to

$$\begin{aligned}\langle x\rangle &= \frac{1}{2}\left[\langle 0|x|0\rangle - ie^{i\omega t}\langle 1|x|0\rangle + ie^{-i\omega t}\langle 0|x|1\rangle + \langle 1|x|1\rangle\right] \\ &= \Re\left[-i\sqrt{\frac{\hbar}{2m\omega}}\,e^{i\omega t}\right] \\ &= \sqrt{\frac{\hbar}{2m\omega}}\,\sin(\omega t).\end{aligned} \tag{3.5.76}$$

Note the change in phase of $-\pi/2$ in the oscillation of the mean position compared with part (d).

Similarly, the mean momentum is

$$\begin{aligned}\langle p\rangle &= \Re\left[-ie^{i\omega t}\langle\psi_1|p|\psi_0\rangle\right] \\ &= \sqrt{\frac{m\hbar\omega}{2}}\cos(\omega t). \end{aligned} \tag{3.5.77}$$

3.5.7 Matrix mechanics of the simple harmonic oscillator

We shall use the simple harmonic oscillator as an illustrative example of the matrix mechanics in Chapter 2. In the Schrödinger representation, the evolution operator is diagonal in the energy representation. It is, therefore, convenient to express the matrix representation of an operator in terms of the energy eigenstates as the basis set.

From Eq. (3.2.27,3.2.28), the matrix elements of the annihilation and creation operators follow:

$$c_{mn} = \delta_{m,n-1}\sqrt{n}\ , \tag{3.5.78}$$

$$c^\dagger_{mn} = \delta_{m,n+1}(n+1)^{1/2}. \tag{3.5.79}$$

Writing them out in matrix form, we have

$$c = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & . & . & . \\ 0 & 0 & \sqrt{2} & 0 & 0 & . & . & . \\ 0 & 0 & 0 & \sqrt{3} & 0 & . & . & . \\ 0 & 0 & 0 & 0 & \sqrt{4} & . & . & . \\ 0 & 0 & 0 & 0 & 0 & . & . & . \\ . & . & . & . & . & . & . & . \end{bmatrix}, \tag{3.5.80}$$

and

$$c^\dagger = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & . & . & . \\ 1 & 0 & 0 & 0 & 0 & . & . & . \\ 0 & \sqrt{2} & 0 & 0 & 0 & . & . & . \\ 0 & 0 & \sqrt{3} & 0 & 0 & . & . & . \\ 0 & 0 & 0 & \sqrt{4} & 0 & . & . & . \\ . & . & . & . & . & . & . & . \end{bmatrix}. \tag{3.5.81}$$

From the matrix forms, it is evident that $c^\dagger$ is the Hermitian conjugate of c.

The Hamiltonian has matrix elements

$$H_{nm} = \delta_{nm}\left(n+\frac{1}{2}\right)\hbar\omega, \tag{3.5.82}$$

i.e., diagonal:

$$H = \frac{1}{2}\hbar\omega \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & . & . & . \\ 0 & 3 & 0 & 0 & 0 & . & . & . \\ 0 & 0 & 5 & 0 & 0 & . & . & . \\ 0 & 0 & 0 & 7 & 0 & . & . & . \\ 0 & 0 & 0 & 0 & 9 & . & . & . \\ . & . & . & . & . & . & . & . \end{bmatrix}. \tag{3.5.83}$$

In the Heisenberg representation, the vector representation for a state of the oscillator is frozen at a fixed time, say, at $t = 0$. The equation for the time development of the operator c is

$$\frac{dc}{dt} = \frac{i}{\hbar}[H, c] = -i\omega c, \tag{3.5.84}$$

with the help of the commutation relation (3.2.12). Hence,

$$c(t) = c(0)\ e^{-i\omega t}. \tag{3.5.85}$$

Similarly,

$$c^\dagger(t) = c^\dagger(0) e^{i\omega t}. \tag{3.5.86}$$

3.6 Problems

1. A quantum one-dimensional harmonic oscillator has mass m, classical angular frequency ω, and the bottom of the potential at the origin of the coordinate axis. At time $t = 0$, it is in a state with (I) equal probability in the eigenstates with energies $(n + \frac{1}{2})\hbar\omega$ and $(n - \frac{1}{2})\hbar\omega$; (II) zero mean position; and (III) the mean momentum in the positive axis direction.

   (a) Find a state of the oscillator at time $t = 0$ satisfying all three conditions.

   (b) Find the mean values of its position and momentum at a subsequent time t.

   (c) Consider a classical oscillator with its total energy equal to the mean energy of the above quantum oscillator. Does the classical amplitude of oscillation agree with the largest mean value of the position of the quantum oscillator in (b)?

2. A one-dimensional harmonic oscillator is in its ground state. Suddenly, the attractive potential on the particle is switched off so that the particle is now under no external force. Describe what happens then by first finding the probability of the particle flying off with momentum $\hbar k$ (which can be either positive or negative) and then by a qualitative account. Contrast this with the classical harmonic oscillator in its ground state and with the oscillator in a state with energy equal to the zero-point energy.

3. **Parity.** The parity operator $\mathcal{P}$ transforms the position and momentum as

$$\mathcal{P}X\mathcal{P}^\dagger = -X, \tag{3.6.1}$$

$$\mathcal{P}P\mathcal{P}^\dagger = -P. \tag{3.6.2}$$

   (a) Show that the parity commutes with the harmonic oscillator Hamiltonian and, hence, that the energy eigenstates with even quantum number n are of even parity and that the eigenstates with odd quantum number are of odd parity. (Try to use the results of the operator method rather than the Weber functions.)

(b) A particle of mass m is restricted to move in one dimension. Its potential energy is

$$V(x) = \frac{1}{2}kx^2 \qquad \text{for } x > 0 \tag{3.6.3}$$

$$= +\infty \qquad \text{for } x < 0. \tag{3.6.4}$$

i. Find the energy and wave function of its ground state. (Hint: Do not solve the Schrödinger equation! Use the parity consideration.)

ii. Determine the uncertainties in position and momentum of the ground state. Is the uncertainty principle obeyed?

4. **Harmonic oscillator in two dimensions.** A particle of mass m is confined to move in a plane. If its position is denoted by the Cartesian coordinates (z, x), its potential energy is given by

$$V(z, x) = \frac{k}{2}\,(z^2 + x^2), \tag{3.6.5}$$

where k is the force constant.

(a) Find the energy eigenvalues and eigenstates (as state vectors) in terms of the solutions of the one-dimensional harmonic oscillator.

(b) Find the degeneracy (i.e. the number of states) of each energy level.

(c) Show that the angular momentum operator about the y-axis, $L_y = ZP_x - XP_z$ commutes with the Hamiltonian.

(d) For the three lowest energy levels, find the eigenvalues and eigenstates of L_y which remain energy eigenstates.

(e) Map the problem of finding the simultaneous eigenstates of H and L_y to the angular momentum problem.

5. **Correlation function of a harmonic oscillator.** For the simple harmonic oscillator of mass m with the Hamiltonian

$$H = \hbar\omega \left(c^\dagger c + \frac{1}{2}\right), \tag{3.6.6}$$

where c is the annihilation operator,

(a) find the time evolution of the Heisenberg operator $c(t)$ in terms of $c(0)$;

(b) find the evolution of $\langle c^\dagger(t)c(0)\rangle$ and $\langle c^\dagger(t)c(0)\rangle$, (i) for an energy eigenstate and (ii) for the oscillator in thermal equilibrium at temperature T;

(c) find the position correlation function $\langle X(t)X(0)\rangle$ for the same two cases as above. Explain why your results are not real and how you would fix them.

6. **Bose-Einstein Statistics.**

Statistic mechanics tells us that, in thermodynamic equilibrium, the probability of a system being found in a state n with energy E_n is proportional to $\exp(-E_n/kT)$ where T is the temperature and k the Boltzmann constant. For a simple harmonic oscillator, $c^\dagger c$ may be regarded as the number operator measuring the number of bosons in a state.

(a) If the system is in thermal equilibrium at temperature T, show that the expectation value $\langle\langle c^\dagger c\rangle\rangle$ is given by the well-known Bose-Einstein distribution function.

(b) Does the zero point energy play a role in this function? Why?

(c) Find the thermal average of e^{iqX} (the Debye-Waller factor) where q is a wave number and X is the position operator of a harmonic oscillator. Hint: Baker-Hausdorff theorem for two operators with $[[A,B],A] = 0 = [[A,B],B]$,

$$e^{A+B} = e^{-\frac{1}{2}[A,B]}e^A e^B. \tag{3.6.7}$$

7. **The coherent state** represents a coherent-phase state of macroscopic number of photons in a laser or a harmonic oscillator with a finite displacement. At time $t = 0$ the wave function of a simple harmonic oscillator of frequency ω is given by

$$|\Psi(t=0)\rangle = \exp\left\{-\frac{1}{2}(N+i\alpha)\right\} e^{\lambda c^+}|0\rangle \tag{3.6.8}$$

where $|0\rangle$ is the ground state, c^+ the creation operator and $\lambda = \sqrt{N}\, e^{-i\alpha}$. N is a very large integer and α is a real phase.

(a) Show that

$$|\Psi(t=0)\rangle = \sum_{n=0}^{\infty} e^{-i\left(n+\frac{1}{2}\right)\alpha} f_n^{1/2} |n\rangle \tag{3.6.9}$$

where $|n\rangle$ is the nth energy eigenstate and show that the probability of finding the system in state n is given by the Poisson distribution

$$f_n = \frac{N^n}{n!} e^{-N}. \tag{3.6.10}$$

Show that the state is normalized.

(b) Prove that the coherent state is an eigenstate of c with eigenvalue λ.

(c) Find the mean value and uncertainty of the number of bosons, c^+c, in this state. Show that as $N \to \infty$, the uncertainty is small compared with the mean value (central limit theorem).

(d) Show that the time development of the state at time t, $|\Psi(t)\rangle$ is equivalent to the phase α increasing as $\alpha(t) = \alpha + \omega t$.

(e) Show that

$$\langle \Psi(t)|c|\Psi(t)\rangle = \sqrt{N} e^{-i(\omega t+\alpha)}. \tag{3.6.11}$$

Hence, find the expectation value of the displacement of the harmonic oscillator at time t.

(f) Show that for this state

$$\Delta p \cdot \Delta x = \hbar/2. \tag{3.6.12}$$

8. **Transformation to normal modes.** From the transformation

$$\begin{aligned} X_\ell &= \frac{1}{\sqrt{N}} \sum_k e^{ik\ell} \left(\frac{\hbar}{2m\omega_k}\right)^{1/2} (c_k + c_k^\dagger), \\ P_\ell &= \frac{1}{\sqrt{N}} \sum_k e^{ik\ell} \left(\frac{m\hbar\omega_k}{2}\right)^{1/2} (-i)(c_k - c_k^\dagger), \end{aligned} \tag{3.6.13}$$

where k is given in Eq. (3.4.8), deduce the commutation relation $[c_k, c_k^\dagger]$ and the diagonal form of the coupled harmonic oscillator Hamiltonian, Eq. (3.4.4) in terms of c_k and $c_k^\dagger$. Deduce also the form of ω_k.

9. *Density of states.* Phonon density of states for each polarization is defined in terms of the frequency spectrum $\omega_{\vec{k},\nu}$ for wave vector $\vec{k}$ and polarization ν by

$$D_\nu(\omega) = \sum_{\vec{k}} \delta(\omega - \omega_{\vec{k},\nu}), \tag{3.6.14}$$

   (a) Evaluate the sum for a large system at low frequency where

$$\omega_{\vec{k},\nu} = s_\nu |\vec{k}|. \tag{3.6.15}$$

   (b) Hence, find the approximate expression for the zero point energy for the whole system and the total energys if one assumes that

      i. the linear dispersion holds for all $\vec{k}$;

      ii. there are one longitudinal branch and two transverse branches.

      iii. the allowable $\vec{k}$ lies in a sphere in $\vec{k}$ space for N atoms.

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Chapter 4

Angular Momentum and Spin

Sally go round the sun,
Sally go round the moon,
Sally go round the chimney-pots
On a Saturday afternoon.
— *Mother Goose.*

4.1 Angular Momentum and Spin

Angular momentum is one property which has very interesting quantum manifestations, which are subject to direct experimental verifications. One such experiment led to the discovery of electron spin. A theory of the angular momentum, which does not rely specifically on the orbital motion defining it, can be extended to describe spin which is an intrinsic property of the particle. It is as important (and interesting) to study the properties of spin itself as to understand the process of adding more degrees of freedom to the motion of a particle.

4.1.1 Definition of the Angular Momentum Operator

The operator which corresponds to the physical observable, a component of the angular momentum, is defined in the same way in terms of position and momentum as in classical mechanics:

$$\hbar\vec{L} = \vec{R} \times \vec{P}. \tag{4.1.1}$$

The Cartesian components are

$$\hbar L_x = YP_z - ZP_y$$

$$\hbar L_y = ZP_x - XP_z$$

$$\hbar L_z = XP_y - YP_x. \tag{4.1.2}$$

Since the components of position and momentum which form products in the angular momentum are never along the same axis and therefore commute (e.g., $YP_z = P_zY$), there is no ambiguity in the quantum mechanical definition of the angular momentum and it is not necessary to symmetrize the product of the position and momentum. Since $\hbar$ is a reasonable unit of angular momentum in quantum mechanics, we follow the convention of defining the angular momentum observable as a dimensionless operator as above.

4.1.2 Commutation Rules

In this section, we consider the commutation of the angular momentum with position, momentum, or itself.

Define the $\epsilon_{jk\ell}$ tensor as $= 1$ if j, k, ℓ form a cyclic permutation of x, y, z; $= -1$ if it is anticyclic; $= 0$ otherwise. Then,

$$[L_j, A_k] = i\epsilon_{jk\ell}A_\ell, \tag{4.1.3}$$

where $\vec{A}$ is $\vec{R}$, $\vec{P}$, or $\vec{L}$ and repeated indices are summed. We shall later give a very general proof from the transformation properties. Here is an elementary proof:

$$[\hbar L_z, X] = [XP_y - YP_x, X] = -Y[P_x, X] = i\hbar Y. \tag{4.1.4}$$

$$[\hbar L_z, Y] = [XP_y - YP_x, Y] = X[P_y, Y] = -i\hbar X. \tag{4.1.5}$$

$$[\hbar L_z, Z] = [XP_y - YP_x, Z] = 0. \tag{4.1.6}$$

The other six relations can be written down by cyclically permuting the Cartesian indices.

Similarly, for momentum,

$$[\hbar L_z, P_x] = [XP_y - YP_x, P_x] = [X, P_x]P_y = i\hbar P_y. \tag{4.1.7}$$

$$[\hbar L_z, P_y] = -i\hbar P_x. \tag{4.1.8}$$

$$[\hbar L_z, P_z] = 0. \tag{4.1.9}$$

The nine commutation relations of the angular momentum with itself can be succinctly summarized as

$$\vec{L} \times \vec{L} = i\vec{L}. \tag{4.1.10}$$

In components,

$$[L_x, L_x] = 0 \tag{4.1.11}$$

$$[L_x, L_y] = iL_z. \tag{4.1.12}$$

$$[L_x, L_z] = -iL_y. \tag{4.1.13}$$

The other six relations can be written down analogously.

4.1.3 Magnitude of the angular momentum

The square of the angular momentum is defined as

$$\vec{L}^{\,2} = L_x^2 + L_y^2 + L_z^2 \tag{4.1.14}$$

It commutes with all three components of the angular momentum,

$$[L_x, \vec{L}^{\,2}] = 0, \quad \text{etc.} \tag{4.1.15}$$

4.1.4 Physical implications

There exist states which are simultaneous eigenstates of $\vec{L}^{\,2}$ and only one of the three components of the vector $\vec{L}$, usually taken to be L_z. For these states, with wave functions given by the spherical harmonics, $\vec{L}^{\,2}$ and L_z can be measured simultaneously to arbitrary accuracy. Since the components do not commute with one another, they cannot be measured simultaneously to arbitrary accuracy.

4.2 Angular Momentum in Spatial Representation

In this section, we use the spatial representation of position and momentum operators for the angular momentum and summarize the results of the differential equation treatment of the eigenstate problem of L^2 and L_z.

4.2.1 The angular momentum operators

In the spatial representation, the angular momentum operator components are given in the Cartesian axes by

$$\begin{aligned} L_x[x,y,z] &= \frac{1}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ L_y[x,y,z] &= \frac{1}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_z[x,y,z] &= \frac{1}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \end{aligned} \tag{4.2.1}$$

The use of the square brackets including the position coordinates indicates the fact that the operator acts on a function of the coordinates. The functional dependence of the operator goes beyond the position to include differential operators with respect to the position coordinates.

The Cartesian coordinates and the spherical polars are related by

$$\begin{aligned} x &= r\sin\theta\cos\phi, \\ y &= r\sin\theta\sin\phi, \\ z &= r\cos\theta, \end{aligned} \tag{4.2.2}$$

or the inverse relations

$$\begin{aligned} r &= (x^2+y^2+z^2)^{1/2}, \\ \theta &= \cos^{-1}(z/r) = \cos^{-1}(z/\{x^2+y^2+z^2\}^{1/2}) \\ \phi &= \tan^{-1}(y/x). \end{aligned} \tag{4.2.3}$$

The first derivatives of the spherical polars with respect to the Cartesians are

$$\begin{array}{lll} \frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\cos\phi, & \frac{\partial r}{\partial y} = \frac{y}{r} = \sin\theta\sin\phi, & \frac{\partial r}{\partial z} = \frac{z}{r} = \cos\theta, \\ \frac{\partial \theta}{\partial x} = \frac{1}{r}\cos\theta\cos\phi, & \frac{\partial \theta}{\partial y} = \frac{1}{r}\cos\theta\sin\phi, & \frac{\partial \theta}{\partial z} = -\frac{1}{r}\sin\theta, \\ \frac{\partial \theta}{\partial x} = -\frac{1}{r}\,\frac{\sin\phi}{\sin\theta}, & \frac{\partial \phi}{\partial y} = \frac{1}{r}\,\frac{\cos\phi}{\sin\theta}, & \frac{\partial \phi}{\partial z} = 0. \end{array} \tag{4.2.4}$$

The chain rules are used to convert the partial derivatives with respect to x, y, z to the partial derivatives with respective to r, θ, ϕ, such as

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\,\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\,\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\,\frac{\partial}{\partial \phi}, \text{etc.} \tag{4.2.5}$$

Then, the Cartesian components of the angular momentum in terms of the spherical polars are

$$\begin{aligned} L_x[\theta,\phi] &= i\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right), \\ L_y[\theta,\phi] &= -i\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right), \\ L_z[\theta,\phi] &= -i\frac{\partial}{\partial\phi}. \end{aligned} \tag{4.2.6}$$

Although we are using the spherical polar coordinates, we have kept the components of the angular momentum along the Cartesian axes, i.e., along constant directions. The angular momentum vector is not resolved along the spherical polar coordinate unit vectors because these vary with position and are not convenient for the purpose of integration (which is much used in calculating expectation values, uncertainties and other matrix elements). The functional dependence of the angular momentum operators on only the two angular coordinates shows that it is redundant to use three position variables.

In Hamiltonian mechanics, if ϕ is chosen to be a generalized coordinate, then its conjugate momentum is the angular momentum $\hbar L_z$. By an extension of the rule of making the momentum conjugate of x to be the operator $-i\hbar\partial/\partial x$, L_z would have the expression in Eq. (4.2.6).

4.2.2 The magnitude squared of the angular momentum

From Eq. (4.2.6) one can work out the spatial representation for the angular momentum squared,

$$\vec{L}^{\,2}[\theta,\phi] = L_x^2 + L_y^2 + L_z^2 = -\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right]. \tag{4.2.7}$$

The θ and ϕ dependent part of the Laplacian in spherical polars is entirely represented by $\vec{L}^{\,2}$, yielding

$$\nabla^2 = \frac{1}{r^2}\,\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\vec{L}^{\,2}. \tag{4.2.8}$$

4.2.3 Eigenvalues and eigenfunctions of L^2 and L_z

The commutation rules (see Sec. 4.1.2) dictate that there are no simultaneous eigenstates of the components of the angular momentum but that it is possible to find simultaneous eigenstates of one component and the square of the angular momentum. As a review of the wave mechanics treatment of the angular momentum [1], we record here the simultaneous eigenfunctions of $\vec{L}^{\,2}$ and L_z as spherical harmonics $Y_{\ell m}(\theta, \phi)$:

$$\vec{L}^{\,2} Y_{\ell m} = \ell(\ell+1) Y_{\ell m}, \tag{4.2.9}$$

$$L_z Y_{\ell m} = m Y_{\ell m}. \tag{4.2.10}$$

The z component of the angular momentum $\hbar L_z$ is quantized into integral multiples of $\hbar$ with $|m|$ less than or equal to ℓ. The magnitude of the angular momentum is $\hbar\sqrt{\ell(\ell+1)}$. Note that the integer values of m are a direct consequence of the requirement that the wave function is the wave function is unchanged by a 2π rotation about the z axis.

The spherical harmonics are determined in terms of the generalized Legendre functions P_ℓ^m:

$$Y_{\ell m}(\theta, \phi) = N_{\ell m} P_\ell^m(\cos\theta) e^{im\phi}, \tag{4.2.11}$$

with the constant

$$N_{\ell m} = \left[\frac{(2\ell+1)\cdot(\ell-|m|)!}{4\pi(\ell+|m|)!}\right]^{1/2} \times \begin{cases} (-1)^m & \text{if } m > 0 \\ 1 & \text{if } m \leq 0 \end{cases} \tag{4.2.12}$$

The normalization constants $N_{\ell m}$ are so chosen that the spherical harmonics form an orthonormal set:

$$\int_0^\pi d\theta \int_0^{2\pi} d\phi \sin\theta Y^*_{\ell' m'}(\theta, \phi) Y_{\ell m}(\theta, \phi) = \delta_{\ell\ell'}\delta_{mm'}. \tag{4.2.13}$$

Note that $\sin\theta d\phi d\theta$ is the solid angle part of the volume element $r^2 dr \sin\theta d\theta d\phi$ in the spherical polars representation.

Table 4.2.3 gives the explicit expressions for the more commonly used spherical harmonics.

Table 4.1: Spherical harmonics

$$
\begin{aligned}
\ell = 0 \quad & Y_{0\ 0} = \tfrac{1}{\sqrt{4\pi}} \\
\ell = 1 \quad & Y_{1\pm1} = \mp\sqrt{\tfrac{3}{8\pi}}\sin\theta e^{\pm i\phi} \\
& Y_{1\ 0} = \sqrt{\tfrac{3}{4\pi}}\cos\theta \\
\ell = 2 \quad & Y_{2\pm2} = \sqrt{\tfrac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi} \\
& Y_{2\pm1} = \mp\sqrt{\tfrac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi} \\
& Y_{2\ 0} = \sqrt{\tfrac{5}{16\pi}}(3\cos^2\theta - 1) \\
\ell = 3 \quad & Y_{3\pm3} = \mp\sqrt{\tfrac{35}{64\pi}}\sin^3\theta e^{\pm 3i\phi} \\
& Y_{3\pm2} = \sqrt{\tfrac{105}{32\pi}}\sin^2\theta\cos\theta e^{\pm 2i\phi} \\
& Y_{3\pm1} = \mp\sqrt{\tfrac{21}{64\pi}}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi} \\
& Y_{3\ 0} = \sqrt{\tfrac{7}{16\pi}}[5\cos^3\theta - 3\cos\theta] \\
\ell = 4 \quad & Y_{4\pm4} = 105\sqrt{\tfrac{9}{(4\pi)(8!)}}\sin^4\theta e^{\pm 4i\phi} \\
& Y_{4\pm3} = \mp 105\sqrt{\tfrac{9}{(4\pi)(7!)}}\sin^3\theta\cos\theta e^{\pm 3i\phi} \\
& Y_{4\pm2} = \tfrac{15}{2}\sqrt{\tfrac{9}{(2\pi)(6!)}}\sin^2\theta(7\cos^2\theta - 1)e^{\pm 2i\phi} \\
& Y_{4\pm1} = \mp\tfrac{5}{2}\sqrt{\tfrac{9}{80\pi}}\sin\theta\cos\theta(7\cos^2\theta - 3)e^{\pm i\phi} \\
& Y_{4\ 0} = \tfrac{1}{8}\sqrt{\tfrac{9}{4\pi}}(35\cos^4\theta - 30\cos^2\theta + 3)
\end{aligned}
$$

The angular dependence of the probability density is contained in the factor

$$F_{\ell m}(\theta) = |Y_{\ell m}(\theta, \phi)|^2 = N_{\ell m}^2 |P_\ell^m(\cos\theta)|^2. \tag{4.2.14}$$

It is independent of the angle ϕ. To get a feel for the θ dependence of the probability, polar plots for a few $F_{\ell m}$ are given in Fig. 4.2.3. A polar plot for $F_{\ell m}(\theta)$ is a plot of the radial distance from the origin in the direction of θ equal to the function,

$$r = F_{\ell m}(\theta). \tag{4.2.15}$$

These plots also give an indication of the directional dependence of the wave functions, which is important in the consideration of chemical bonding.

4.2.4 Vector model

Since we are used to thinking in terms of classical mechanics, it is useful to represent the quantum angular momentum in a semi-classical picture. Caution is given here that if the picture is taken too literally it could be very misleading [2]. The angular momentum is represented by a vector with a fixed magnitude $\hbar[\ell(\ell+1)]^{1/2}$ and a fixed component $\hbar m$ along the z direction, precessing about the z-axis. Figure 4.2 shows the example of $\ell = 1$. There are three vectors with magnitude $\hbar\sqrt{2}$, having, respectively, $\hbar$, 0, $-\hbar$ as the z components.

The vector has to be taken as precessing about the z-axis because the L_x and L_y components are not well defined. Their mean values are zero. Their uncertainties are given by

$$\begin{aligned} \hbar^2(\langle L_x^2\rangle + \langle L_y^2\rangle) &= \hbar^2(\langle L^2\rangle - \langle L_z^2\rangle) \\ &= [\ell(\ell+1) - m^2]\hbar^2 \geq \ell\hbar^2 \end{aligned} \tag{4.2.16}$$

4.2.5 Arbitrariness of the z direction

We could have chosen a component of the angular momentum along any direction. How does one relate the eigenfunctions of $\vec{L}^{\,2}$ and the component along this direction to the $Y_{\ell m}$ for $\vec{L}^{\,2}$ and L_z? Suppose we rotate the Cartesian axes in some fashion and label the new axes x', y', z'. The eigenfunctions of the new component $L_{z'}$ and $\vec{L}^{\,2}$, denoted by

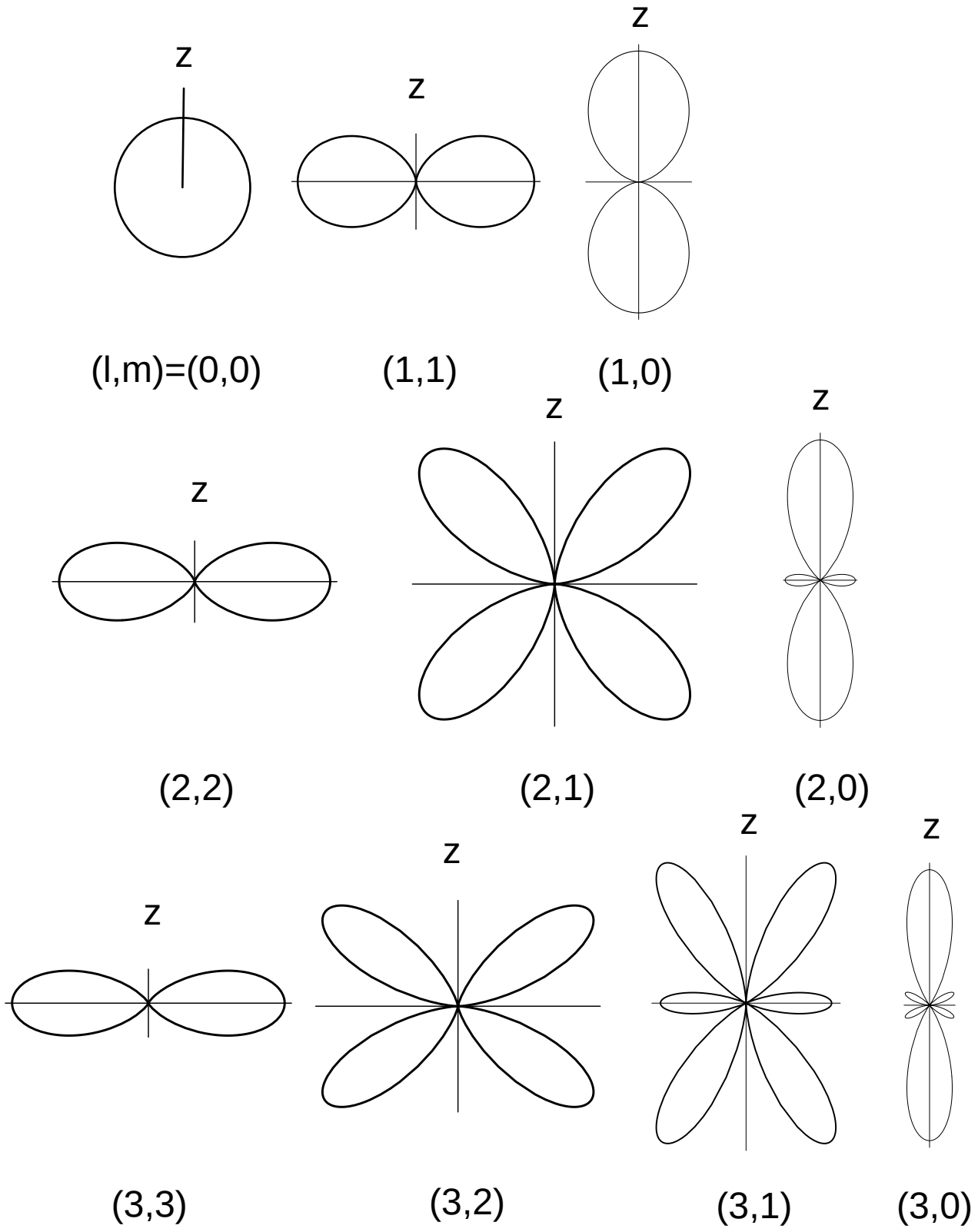


Figure 4.1: Polar plots of the angular dependent part of the probability density

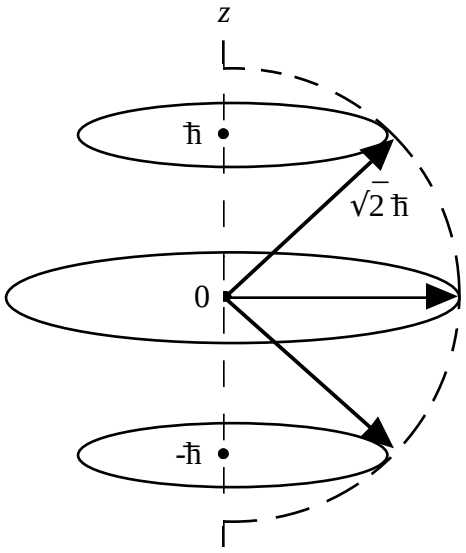


Figure 4.2: Vector diagram of the angular momentum

$Z_{\ell m}$, must be the spherical harmonics in the new coordinates. Since $\vec{L}^{\,2}$ is unchanged by the rotation of the axes, the eigenvalues of $\vec{L}^{\,2}$ are the same. For a given ℓ, the eigenstates of L^2 in the new coordinates, $Z_{\ell m}$, must be linear combinations of the eigenstates of L^2 in the old coordinates, $Y_{\ell m}$. Thus, the transformation is given by

$$Y_{\ell m} = \sum_m Z_{\ell m'} S_{m' m}(\ell). \tag{4.2.17}$$

In a later chapter, we will study the general theory of rotations and treat the transformation S as a representation of the rotation operator. Right now, I wish to present a seat-of-the-pants type solution for the transformation matrix S. Of course, my greatest fear in life is that one day you would be stranded on a desert island without proper tools to reconstruct the general theory of rotations. However, stick and sand would be available for a down-to-earth calculation of the simple rotations which you might need.

The transformation S which relates the Z's to the Y's has zero elements connecting different ℓ's since $\langle Z_{\ell m} | Y_{\ell' m'} \rangle = 0$ as eigenstates of L^2 with different eigenvalues when $\ell \neq \ell'$. The blocks of non-zero matrices connecting states with the same ℓ are the ones with elements $S_{mm'}(\ell)$. A straightforward, though inelegant, method of finding the transformation matrix is based on the principle that, Z's as spherical harmonics in the x', y', z' coordinates, have the same functional dependence on the primed coordinates as the Y's on the unprimed coordinates, which is a homogeneous polynomial of order ℓ. Express the unprimed oordinates in each $Y_{\ell,m}$ in the primed x',y',z' coordinates and

then regroup the terms into a number of $Z_{\ell,m'}$'s enabling one to identify the coefficients as $S_{m'm}(\ell)$ in Eq. (4.2.17).

Let us illustrate the procedure with the p states ($\ell = 1$). The eigenstates of L^2 and L_z are,

$$Y_{1,1} = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} = \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{r}\,\frac{1}{\sqrt{2}}(-x - iy) \tag{4.2.18}$$

$$Y_{1,0} = \left(\frac{3}{4\pi}\right) \cos\theta = \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{r} z \tag{4.2.19}$$

$$Y_{1,-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi} = \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{r}\,\frac{1}{\sqrt{2}}(x - iy) \tag{4.2.20}$$

Suppose that we wish to find the common $\ell = 1$ eigenstates of L^2 and L_x in terms of the basis set of the above spherical harmonics. Set up the new axes with z' along the x-axis, x' along the y-axis and y' along the z-axis. For $\ell = 1$, there are three eigenstates of $L_{z'}$ and L^2:

$$Z_{1,1} = f(r')\sqrt{\frac{1}{2}}\,(-x' - iy') \tag{4.2.21}$$

$$Z_{1,0} = f(r')z' \tag{4.2.22}$$

$$Z_{1,-1} = f(r')\sqrt{\frac{1}{2}}\,(x' - iy') \tag{4.2.23}$$

where,

$$f(r') = \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{r'}. \tag{4.2.24}$$

In terms of the original coordinates,

$$Z_{1,1} = f(r)\sqrt{\frac{1}{2}}\,(-y - iz) \tag{4.2.25}$$

$$Z_{1,0} = f(r)x \tag{4.2.26}$$

$$Z_{1,-1} = f(r)\sqrt{\frac{1}{2}}\,(y - iz). \tag{4.2.27}$$

The 3×3 matrix governing the transformation is given by

$$(Y_{1,1}Y_{1,0}Y_{1,-1}) = (Z_{1,1}Z_{1,0}Z_{1,-1}) \begin{bmatrix} S_{1,1} & S_{1,0} & S_{1,-1} \\ S_{0,1} & S_{0,0} & S_{0,-1} \\ S_{-1,1} & S_{-1,0} & S_{-1,-1} \end{bmatrix} \tag{4.2.28}$$

Here is a systematic way of using matrices to evaluate the transformation matrix.

(1) Express the spherical harmonics in terms of the appropriate coordinates:

$$\begin{aligned} (Y_{1,1}Y_{1,0}Y_{1,-1}) &= (xyz) \begin{bmatrix} -1/\sqrt{2} & 0 & 1/\sqrt{2} \\ -i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & 1 & 0 \end{bmatrix} \\ (Z_{1,1}Z_{1,0}Z_{1,-1}) &= (x'y'z') \begin{bmatrix} -1/\sqrt{2} & 0 & 1/\sqrt{2} \\ -i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & 1 & 0 \end{bmatrix}. \end{aligned} \tag{4.2.29}$$

A common factor of $(3/4\pi)^{1/2}/r$ is understood.

(2) Coordinate transformation

$$(xyz) = (x'y'z') \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}. \tag{4.2.30}$$

(3) Inverse relations of (1)

$$(x'y'z') = (Z_{1,1}Z_{1,0}Z_{1,-1}) \begin{bmatrix} -1/\sqrt{2} & i/\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 1/\sqrt{2} & i/\sqrt{2} & 0 \end{bmatrix}. \tag{4.2.31}$$

(4) Put them all together: substituting (4.2.31) into (4.2.30) and the latter into (4.2.29) and comparing (4.2.28):

$$\begin{bmatrix} S_{1,1} & S_{1,0} & S_{1,-1} \\ S_{0,1} & S_{0,0} & S_{0,-1} \\ S_{-1,1} & S_{-1,0} & S_{-1,-1} \end{bmatrix} = \begin{bmatrix} -\frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \sqrt{\frac{1}{2}} & i\sqrt{\frac{1}{2}} & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} -\sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} \\ -i\sqrt{\frac{1}{2}} & 0 & -i\sqrt{\frac{1}{2}} \\ 0 & 1 & 0 \end{bmatrix}$$

$$= \begin{bmatrix} \frac{1}{2}i & i\sqrt{\frac{1}{2}} & i\frac{1}{2} \\ -\sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} \\ -i\frac{1}{2} & i\sqrt{\frac{1}{2}} & -i\frac{1}{2} \end{bmatrix}. \tag{4.2.32}$$

An alternative way, which is perhaps more physical, is to examine each state on the right side of Eq. (4.2.28). For example,

$$Y_{1,1} = Z_{1,1}S_{1,1} + Z_{1,0}S_{0,1} + Z_{1,-1}S_{-1,1}. \tag{4.2.33}$$

Substituting Eqs. (4.2.18, 4.2.25-4.2.27),

$$-\sqrt{\frac{1}{2}}\,(x+iy) = -\sqrt{\frac{1}{2}}\,(y+iz)S_{1,1} + xS_{0,1} + \sqrt{\frac{1}{2}}\,(y-iz)S_{-1,1}. \tag{4.2.34}$$

Since this equality holds for all x, y and z, we can equate their coefficients on both sides:

$$\begin{aligned} S_{0,1} &= -\sqrt{\frac{1}{2}} \\ -S_{1,1} + S_{-1,1} &= -i \\ -S_{1,1} - S_{-1,1} &= 0. \end{aligned} \tag{4.2.35}$$

Thus,

$$\begin{aligned} S_{1,1} &= i/2 \\ S_{0,1} &= -\sqrt{\frac{1}{2}} \\ S_{-1,1} &= -i/2. \end{aligned} \tag{4.2.36}$$

The other six elements of the transformation matrix can be found in a similar way. Because the spherical harmonics are normalized wave functions, S must be a unitary matrix. We verify that

$$|S_{1,1}|^2 + |S_{0,1}|^2 + |S_{-1,1}|^2 = 1. \tag{4.2.37}$$

Suppose that a system is prepared in the state represented by the wave function $Y_{1,1}$ with respect to a chosen z axis. Since this state is the eigenstate of L^2 and L_z with eigenvalues 2 and 1, respectively, measurement of L^2 and L_z will definitely yield the same values. If a measurement of L_x is made on this system, what will be the outcome? The eigenstates of L_x are $Z_{1,1}$, $Z_{1,0}$, $Z_{1,-1}$ with eigenvalues 1, 0, -1, respectively. The initial state of the system, $Y_{1,1}$, is a linear combination of the eigenstates of L_x given by Eq. (4.2.33). The possible outcomes of the measurement of L_x are 1, 0, -1 with probabilities $|S_{1,1}|^2$, $|S_{0,1}|^2$, $|S_{-1,1}|^2$, i.e. $\frac{1}{4}$, $\frac{1}{2}$, $\frac{1}{4}$, respectively.

The mean value of L_x is

$$\begin{aligned} \langle L_x \rangle &= \langle Y_{1,1}|L_x|Y_{1,1}\rangle = |S_{1,1}|^2 \cdot (1) + |S_{0,1}|^2 \cdot (0) + |S_{-1,1}|^2 \cdot (-1) \\ &= 0. \end{aligned} \tag{4.2.38}$$

The uncertainty is given by

$$\begin{aligned} (\Delta L_x)^2 &= \langle L_x^2 \rangle \\ &= |S_{1,1}|^2 \cdot (1)^2 + |S_{0,1}|^2 \cdot (0)^2 + |S_{-1,1}|^2 \cdot (-1)^2 \\ &= \frac{1}{2}. \end{aligned} \tag{4.2.39}$$

Hence,

$$\Delta L_x = \frac{1}{\sqrt{2}}. \tag{4.2.40}$$

4.3 Orbital Magnetic Moment

In Sec. 4.2.3, the z-component of the angular momentum is quantized. Loosely speaking, the orientation of the angular momentum vector in space is quantized. This phenomenon is known as the space quantization. How does one measure the angular momentum and verify space quantization? Direct measurements of mechanical properties on microscopic systems are usually very difficult. Fortunately, the electron is charged. Linear motion of an electron creates a current. Periodic motion of an electron creates a magnetic dipole. Electronic motion is, therefore, measured by electromagnetic means.

4.3.1 Angular momentum and magnetic dipole moment

A classical derivation is given here for the relation between the angular momentum and the magnetic dipole moment. A quantum mechanical derivation which yields the same relation will be given later. For simplicity, consider the electron moving in a circular orbit with speed v. (Refer to an electromagnetism text [3] for the case of a general motion.) The angular momentum of the electron with respect to the center of the orbit is

$$L = mvr, \tag{4.3.1}$$

where r is the radius of the orbit and m is the electron mass.

The current I is the amount of charge passing a point of the orbit per unit time:

$$I = (-e)v/2\pi r, \tag{4.3.2}$$

where e denotes the charge of a proton.

The magnetic dipole moment created by the current I is

$$\mu = I\pi r^2 = -evr/2 = (-e/2m)L. \tag{4.3.3}$$

The magnetic dipole moment is in the same direction as the angular momentum vector. Hence,

$$\vec{\mu} = (-e/2m)\vec{L}. \tag{4.3.4}$$

In an external magnetic field $\vec{B}$, the energy of the magnetic dipole moment is

$$E = -\vec{\mu} \cdot \vec{B}. \tag{4.3.5}$$

4.3.2 Magnetic dipole moment in quantum mechanics

The operator representing the magnetic moment is given by the same relation (4.3.4) with the angular momentum. Since a component of the angular momentum is quantized in units of $\hbar$, it is convenient to write the magnetic dipole moment of the electron as

$$\vec{\mu} = -\mu_B \vec{L}, \tag{4.3.6}$$

where

$$\mu_B = e\hbar/2m, \tag{4.3.7}$$

is called the Bohr magneton. Thus, the z-component of the magnetic dipole moment of the electron is quantized in units of the Bohr magneton.

In the presence of an external magnetic field $\vec{B}$, the angular momentum of the electron creates an additional term in the Hamiltonian,

$$H = -\vec{\mu} \cdot \vec{B} = \mu_B \vec{L} \cdot \vec{B}. \tag{4.3.8}$$

Note that in a field of 1 Tesla (10^4 Gauss), one Bohr magneton has an energy of about 6×10^{-5} eV. A field of 16 Tesla or 160 kilo-Gauss is now readily available in a laboratory superconducting magnet.

In Eq. (4.3.7) if the electron mass is replaced by a proton mass m_p and the sign of the charge is reversed, the quantity

$$\mu_N = e\hbar/2m_p, \tag{4.3.9}$$

is known as the nuclear magneton, and is approximately 3×10^{-8} eV/T, about 2000 times smaller than the Bohr magneton.

4.4 The Stern-Gerlach Experiment

4.4.1 Principle of the experiment

In a magnetic field $\vec{B} = (0, 0, B)$ which is non-uniform with a gradient of $\partial B/\partial z$, the force on a magnetic dipole is

$$(\vec{\mu} \cdot \nabla)\vec{B} = \left(0, 0, \mu_z \frac{\partial B}{\partial z}\right). \tag{4.4.1}$$

A dipole moving normal to the magnetic field will be deflected by this force. The amount of deflection of the path of the dipole can be used to deduce the force and, therefore, the component of the dipole moment along the field if the field gradient is known.

4.4.2 The Stern-Gerlach experiment

The cross-section of the magnet is shown in Fig. 4.3(a). The convergent magnetic line of force creates a field gradient. The arrangement of the apparatus is shown in Fig. 4.3(b). Neutral atoms are used in this experiment so that there is no net Lorentz force acting on

the atoms. A beam of neutral atoms is generated in the oven and passed through a slit and then between the poles of the magnet normal to the magnetic field. Any deflection from the origin path is recorded on a glass plate or some other kind of detector plate.

4.4.3 Prediction of classical mechanics

The possible values of the z-component of the angular momentum and, therefore, the z-component of the magnetic dipole moment are continuous. Hence, the deposit of atoms on the detector plate is expected to be a smeared blot.

4.4.4 Prediction of quantum mechanics

For a given ℓ, L_z has discrete values m, where $m = -\ell, -\ell+1, -\ell+2, \ldots, -1, 0, 1, 2, \ldots, \ell$. μ_z has discrete values $m\mu_B$. Thus, there should be $2\ell + 1$ lines on the detector plate.

4.4.5 Experimental findings

In this type of experiment, indeed a discrete number of lines are found on the detector plate. It proves the existence of "space quantization." However, using the neutral noble atoms (silver, copper, and gold), Stern and Gerlach [4] actually found only two lines on the screen. This means that $\ell = 1/2$. Phipps and Taylor [5] repeated the experiment with neutral hydrogen atoms in their ground states, i.e., $\ell = 0$ and $m = 0$. The Stern-Gerlach apparatus still splits the atomic beam into two beams only. Since the electron has no orbital angular momentum in the ground state of hydrogen, the splitting is attributed to an intrinsic angular momentum carried by the electron regardless of its orbital motion. We shall study this property in detail in the next section.

4.4.6 Measurement of L_x

In Sec. 4.2.5 we studied the problem of the outcome of a measurement of L_x on a system with the initial state $Y_{1,1}$. Such measurements can in principle be made with the Stern-Gerlach apparatus. Imagine a beam of neutral particles with states in $\ell = 1$ and $m = 1, 0$ or -1, passed through a Stern-Gerlach apparatus with the magnetic field in the z direction. The particle beam is split into three beams, each being in a different eigenstate of L_z. Now let only the $m = 1$ beam through another Stern-Gerlach apparatus which has the

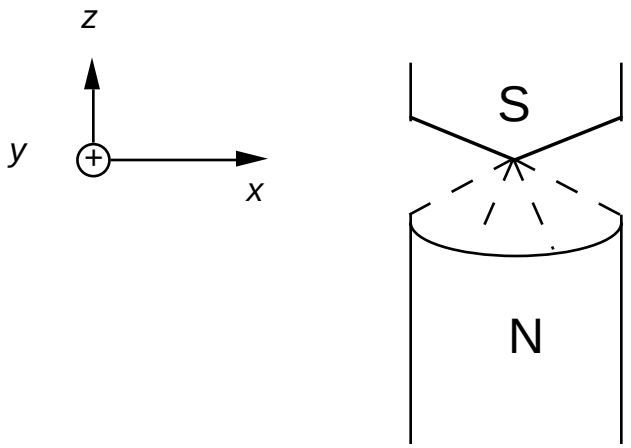


Figure 4.3: (a) Cross-section of the magnet.

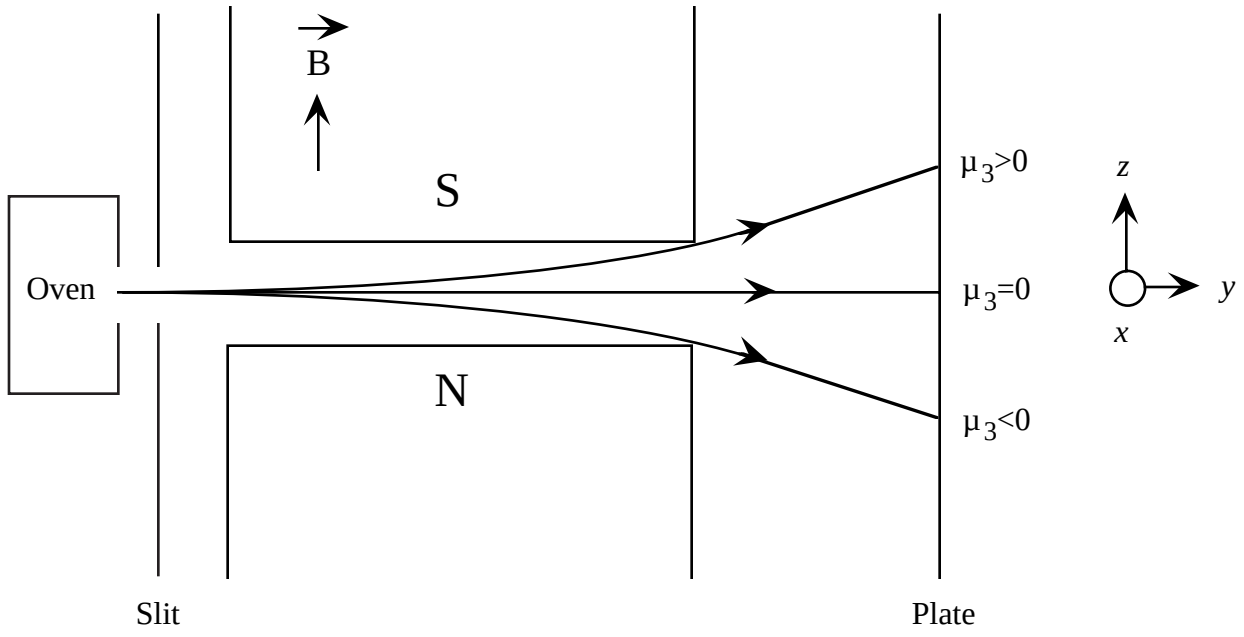


Figure 4.3: (b) Apparatus arrangement for the Stern-Gerlach experiment.

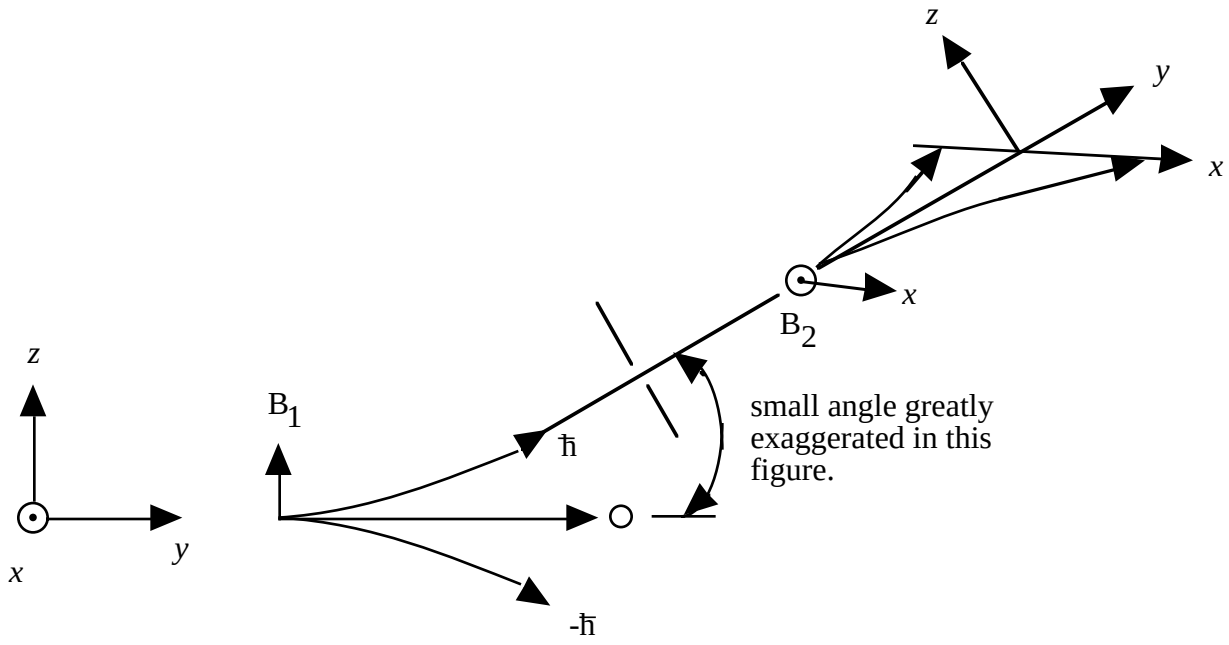


Figure 4.4: Measuring L_x on a beam in the state $Y_{1,1}$.

magnetic field along the x direction (see Fig. 4.4). Before entering the second apparatus, the particles must already be in the $Y_{1,1}$ state. This beam will be split by the second apparatus into three beams with eigenvalues 1, 0, -1 for L_x. From the probability amplitudes (4.2.36), the intensity of the three beams should be in the ratio of 1:2:1. These predictions can in principle be experimentally tested. However, we have to make sure that the particles do not possess additional angular momentum besides the $\ell = 1$ component.

4.5 Spin of a Particle

4.5.1 Operator representation of the spin

Quantization of orbital angular momentum of a particle leads to an odd number $(2\ell+1)$ of possible values of one component in a fixed direction for a given "magnitude" ℓ of the angular momentum. However, the Stern-Gerlach experiment, with either the silver atoms or the hydrogen atoms, yields only two possible values of the magnetic moment in the direction of the magnetic field. This forces us to ascribe the magnetic moment to an intrinsic angular momentum of an elementary particle. In the non-relativistic quantum theory, we are naturally led to a representation of the angular momentum due to the orbital motion of the electron around the nucleus by analogy with classical mechanics.

The problem now is how to construct an operator corresponding to the intrinsic angular momentum of a particle which is independent of the position and momentum of the particle.

Let us postulate that we may define three physical observables as the Cartesian components of the spin vector $\vec{S}$ such that $\hbar\vec{S}$ is the intrinsic angular momentum of a particle. That the intrinsic angular momentum obeys the same commutation rules as the orbital angular momentum leads to

$$\vec{S} \times \vec{S} = i\vec{S}. \tag{4.5.1}$$

Of course, $\vec{S}$ must be Hermitian, i.e.,

$$\vec{S}^{\,\dagger} = \vec{S}. \tag{4.5.2}$$

We cannot insist on the $\vec{r} \times \vec{p}$ representation for $\vec{S}$; otherwise, $\vec{S}$ is not different from $\vec{L}$ and we cannot explain the two beam result of the Stern-Gerlach experiment. Thus, the spin $\vec{S}$ has no classical counterpart.

4.5.2 Magnitude of spin

The square of the magnitude of the spin is given by

$$S^2 = S_x^2 + S_y^2 + S_z^2. \tag{4.5.3}$$

It follows from the commutation rules (4.5.1) that, just like the orbital angular momentum,

$$[\vec{S}, S^2] = 0. \tag{4.5.4}$$

4.5.3 The eigen-problem of S^2 and S_z

We cannot use the spatial representation of $\vec{L}$ and solve the differential equations to find the eigenvalues and eigenfunctions of S^2 and S_z. Let us try an alternative operator method, in analogy with the simple harmonic oscillator problem. Since the method relies only on the commutation relations which $\vec{S}$ and $\vec{L}$ share, part of the solutions for the general spin must be solutions of the orbital angular momentum.

Since S^2 and S_z commute with each other, we define their common eigenstate as $|\psi_{\alpha\beta}\rangle$ with eigenvalues α and β, respectively, i.e.,

$$S^2|\psi_{\alpha\beta}\rangle = \alpha|\psi_{\alpha\beta}\rangle \tag{4.5.5}$$

$$S_z|\psi_{\alpha\beta}\rangle = \beta|\psi_{\alpha\beta}\rangle. \tag{4.5.6}$$

The eigenstate $|\psi_{\alpha\beta}\rangle$ can no longer represented by a wave function of position of the particle. We shall, however, be able to find out enough properties about these states and their matrix representations that predictions about measurements of the spin can still be made.

4.5.4 The raising and lowering operators

By analogy with the harmonic oscillator, we wish to factorize S^2,

$$\begin{aligned} S^2 &= S_x^2 + S_y^2 + S_z^2 \\ &= (S_x + iS_y)(S_x - iS_y) - S_z + S_z^2, \end{aligned} \tag{4.5.7}$$

where the cross terms in the product of two brackets are cancelled out by the $-S_z$ term. Thus, we can also define the raising and lowering operators:

$$\begin{aligned} S_+ &= S_x + iS_y \\ S_- &= S_x - iS_y. \end{aligned} \tag{4.5.8}$$

Since S_x and S_y are Hermitian operators, S_+ and S_- are not Hermitian but they are Hermitian conjugates of each other. Then various useful expressions for S^2 are:

$$\begin{aligned} S^2 &= S_+S_- - S_z + S_z^2 \\ &= S_-S_+ + S_z + S_z^2 \\ &= \frac{1}{2}(S_+S_- + S_-S_+) + S_z^2 \end{aligned} \tag{4.5.9}$$

4.5.5 Commutation relations of $S_\pm$

(1)
$$[S_z, S_\pm] = \pm S_\pm. \tag{4.5.10}$$

Proof:

$$\begin{aligned}[S_z, S_+] &= [S_z, S_x + iS_y] \\ &= [S_z, S_x] + i[S_z, S_y] \\ &= iS_y + i(-i)S_x \\ &= (S_x + iS_y).\end{aligned}$$

(2)
$$[S_\pm, S^2] = 0 \tag{4.5.11}$$

(3)
$$[S_+, S_-] = 2S_z. \tag{4.5.12}$$

4.5.6 Effects of the raising and lowering operators

If $|\psi_{\alpha\beta}\rangle$ is an eigenstate of S^2 with eigenvalue α and of S_z with eigenvalue β, then $S_\pm|\psi_{\alpha\beta}\rangle$ are eigenstates of S^2 with the same eigenvalue α and eigenstates of S_z with eigenvalues $(\beta \pm 1)$.

Proof: The proof that $S_\pm|\psi_{\alpha\beta}\rangle$ are eigenstates of S^2 with the same eigenvalue as $|\psi_{\alpha\beta}\rangle$ is left as an exercise.

$$\begin{aligned}S_z(S_+|\psi_{\alpha\beta}\rangle) &= (S_zS_+)|\psi_{\alpha\beta}\rangle \\ &= (S_+S_z + S_+)|\psi_{\alpha\beta}\rangle \\ &= (\beta + 1)(S_+|\psi_{\alpha\beta}\rangle).\end{aligned} \tag{4.5.13}$$

A similar proof can be constructed for S_-.

Thus, S_+ raises the eigenvalue of S_z by one; and S_- lowers the eigenvalue of S_z by one. Their functions are analogous to the creation and annihilation operators for a harmonic oscillator.

4.5.7 Theorem: β is bounded if the value of α is fixed.

Since $\langle\psi_{\alpha\beta}|S^2|\psi_{\alpha\beta}\rangle \geq \langle\psi_{\alpha\beta}|S_z^2|\psi_{\alpha\beta}\rangle$, we have,

$$\alpha \geq \beta^2. \tag{4.5.14}$$

4.5.8 The eigenvalues

Since for a given α, β is bounded, there must exist a smallest value for β, which is denoted by β_1, and a largest value of β, which is denoted by β_2. For a fixed α, β_1 is the smallest eigenvalue of S_z and β_2 is the largest eigenvalue. Therefore,

$$S_-|\psi_{\alpha\beta_1}\rangle = 0, \tag{4.5.15}$$

$$S_+|\psi_{\alpha\beta_2}\rangle = 0, \tag{4.5.16}$$

otherwise, these two states would be eigenstates of S_z with eigenvalues $(\beta_1 - 1)$ and $(\beta_2 + 1)$, contrary to the definitions of β_1 and β_2.

A useful equation is

$$\begin{aligned}
\langle S_+\psi_{\alpha\beta}|S_+\psi_{\alpha\beta}\rangle &= \langle\psi_{\alpha\beta}|(S_+)^\dagger S_+|\psi_{\alpha\beta}\rangle \\
&= \langle\psi_{\alpha\beta}|S_-S_+|\psi_{\alpha\beta}\rangle \qquad (4.5.17)\\
&= \langle\psi_{\alpha\beta}|S^2 - S_z - S_z^2|\psi_{\alpha\beta}\rangle \text{ using Eq. (4.5.9)}, \\
&= (\alpha - \beta - \beta^2)\langle\psi_{\alpha\beta}|\psi_{\alpha\beta}\rangle. \qquad (4.5.18)
\end{aligned}$$

Since for the largest β state, raising it cannot yield another state, Eq. (4.5.16) leads to

$$\begin{aligned}
\langle S_+\psi_{\alpha\beta_2}|S_+\psi_{\alpha\beta_2}\rangle &= 0, \\
\text{i.e.,}\quad \alpha - \beta_2 - \beta_2^2 &= 0. \qquad (4.5.19)
\end{aligned}$$

Similarly,

$$\langle S_-\psi_{\alpha\beta}|S_-\psi_{\alpha\beta}\rangle = (\alpha + \beta - \beta^2)\langle\psi_{\alpha\beta}|\psi_{\alpha\beta}\rangle. \tag{4.5.20}$$

So,

$$\alpha + \beta_1 - \beta_1^2 = 0. \tag{4.5.21}$$

Subtracting Eq. (4.5.21) from Eq. (4.5.19),

$$\begin{aligned}
\beta_1^2 - \beta_1 &= \beta_2^2 + \beta_2, \\
\text{or}\qquad (\beta_1 + \beta_2)(\beta_1 - \beta_2 - 1) &= 0. \qquad (4.5.22)
\end{aligned}$$

Since β_2 is greater than β_1, the second bracket cannot vanish. Hence,

$$\beta_2 = -\beta_1. \tag{4.5.23}$$

If the raising operator is used repeatedly on the state $|\psi_{\alpha\beta_1}\rangle$, we obtain the eigenstates of S_z

$$|\psi_{\alpha\beta_1}\rangle, S_+|\psi_{\alpha\beta_1}\rangle, S_+^2|\psi_{\alpha\beta_1}\rangle, \ldots, S_+^n|\psi_{\alpha\beta_1}\rangle, \tag{4.5.24}$$

with eigenvalues,

$$\beta_1, (\beta_1+1), (\beta_1+2), \ldots, (\beta_1+n). \tag{4.5.25}$$

There must exist an integer n such that after n steps the maximum value β_2 is reached. Thus,

$$\beta_1 + n = \beta_2. \tag{4.5.26}$$

Using this in conjunction with Eq. (4.5.23), we obtain

$$\beta_1 = -\frac{n}{2}, \tag{4.5.27}$$

$$\beta_2 = \frac{n}{2}, \tag{4.5.28}$$

where n is zero or a positive integer. From Eq. (4.5.19),

$$\alpha = \frac{n}{2}\left(\frac{n}{2}+1\right). \tag{4.5.29}$$

To summarize, we have

$$S^2|\psi_{sm}\rangle = (s+1)s|\psi_{sm}\rangle, \tag{4.5.30}$$

$$S_z|\psi_{sm}\rangle = m|\psi_{sm}\rangle, \tag{4.5.31}$$

where, s is a half-integer or integer, i.e.

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots \tag{4.5.32}$$

and for a given s,

$$m = -s,\ -s+1,\ -s+2,\ \ldots, s-1, s. \tag{4.5.33}$$

4.5.9 Recurrence relations between eigenstates

If the eigenstates $|\psi_{sm}\rangle$ are normalized, then

$$S_+|\psi_{s,m}\rangle = |\psi_{s,m+1}\rangle\{s(s+1)-m(m+1)\}^{1/2}, \tag{4.5.34}$$

$$S_-|\psi_{s,m}\rangle = |\psi_{s,m-1}\rangle\{s(s+1)-m(m-1)\}^{1/2}. \tag{4.5.35}$$

Proof: Since we know that $S_+|\psi_{s,m}\rangle$ is an eigenstate of S_z with eigenvalue $(m+1)$, from Eq. (4.5.13), it must be proportional to $|\psi_{s,m+1}\rangle$. So, let

$$S_+|\psi_{s,m}\rangle = \gamma|\psi_{s,m+1}\rangle. \tag{4.5.36}$$

Then, from Eq. (4.5.18),

$$\begin{aligned} |\gamma|^2\langle\psi_{s,m+1}|\psi_{s,m+1}\rangle &= \langle S_+\psi_{s,m}|S_+\psi_{s,m}\rangle \\ &= \{s(s+1)-m-m^2\}. \end{aligned} \tag{4.5.37}$$

There is some arbitrariness in the phase of the wave function of each eigenstate $|\psi_{s,m}\rangle$. We assume that the phases are chosen in such a way that γ is a real number. Then Eq. (4.5.34) follows. The proof for Eq. (4.5.35) is similar.

4.5.10 Matrix elements of $\vec{S}$ and S^2

$$\langle\psi_{s'm'}|S^2|\psi_{sm}\rangle = s(s+1)\delta_{ss'}\delta_{mm'} \tag{4.5.38}$$

$$\langle\psi_{s'm'}|S_z|\psi_{sm}\rangle = m\delta_{ss'}\delta_{mm'} \tag{4.5.39}$$

$$\langle\psi_{s'm'}|S_+|\psi_{sm}\rangle = \{(s-m)(s+m+1)\}^{1/2}\delta_{ss'}\delta_{m'm+1} \tag{4.5.40}$$

$$\langle\psi_{s'm'}|S_-|\psi_{sm}\rangle = \{(s+m)(s-m+1)\}^{1/2}\delta_{ss'}\delta_{m'm-1}. \tag{4.5.41}$$

The matrix elements of S_x and S_y can be deduced with the help of Eq. (4.5.8).

Note that all the matrix elements connecting different s's vanish. Thus, we often work with submatrices with a given s.

$s = 0$.

$$\langle\psi_{00}|S^2|\psi_{00}\rangle = 0. \tag{4.5.42}$$

$$\langle\psi_{00}|\vec{S}|\psi_{00}\rangle = 0. \tag{4.5.43}$$

$s = 1/2$. See Problem 7.

$s = 1$.

$$\langle \psi_{1m'} | S^2 | \psi_{1m} \rangle = \begin{bmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{bmatrix}. \tag{4.5.44}$$

The rows follow the ranking of $m' = 1, 0, -1$; and the columns follow the ranking of $m = 1, 0, -1$.

$$\langle \psi_{1m'} | S_z | \psi_{1m} \rangle = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{4.5.45}$$

$$\langle \psi_{1m'} | S_+ | \psi_{1m} \rangle = \begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix} \tag{4.5.46}$$

$$\langle \psi_{1m'} | S_- | \psi_{1m} \rangle = \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix} \tag{4.5.47}$$

$$\langle \psi_{1m'} | S_x | \psi_{1m} \rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{4.5.48}$$

$$\langle \psi_{1m'} | S_y | \psi_{1m} \rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix} \tag{4.5.49}$$

4.5.11 Conclusion

The spin, which is assumed to be Hermitian and to have the same commutation relations between its components as the angular momentum, is found to possess eigenstates $|\psi_{sm}\rangle$ with eigenvalues $(s+1)s$ for S^2 and with eigenvalues m for S_z. s assumes values of positive integers divided by two (including zero). m assumes the $2s+1$ values between

$-s$ and s. Thus, if s is an integer, there are an odd number of eigenstates of S_z. If s is an integer plus a half, there are an even number of eigenstates of S_z.

If the spin is independent of position and momentum of a particle, then the eigenstate is not expressible as a wave function of position. However, since the matrix elements of the spin and the square of the spin are known, prediction of measurements can be made.

The orbital angular momentum, which is a vector product of position and momentum, has the same commutation rules as the spin and ought to have eigenstates and eigenvalues behaving the same way. However, because of its spatial dependence, a wave function of position (or of momentum) is defined. A one-valued-ness condition is imposed on the wave function and, consequently, the eigenstates with non-integral values of s have to be excluded.

4.6 Electron Spin

Passing a beam of hydrogen atoms in their ground state through a Stern-Gerlach apparatus results in two beams. Since the magnetic dipole moment is inversely proportional to the mass of a particle [see Eq. (4.3.4)], the electronic dipole moment is at least a thousand times larger than the nuclear magnetic dipole moment for the same angular momentum. It is safe to assume that the Stern-Gerlach measurement is dominated by the electron contribution. Since the ground state of the hydrogen atom is the $\ell = 0$, $m = 0$ eigenstate of the angular momentum, there is no contribution to the magnetic dipole moment in the applied magnetic field direction from the electron orbital angular momentum. Yet, the splitting of the beam implies the existence of a magnetic dipole moment carried by the electron. One is forced to postulate that the electron carries an intrinsic angular momentum independent of its orbital motion, which is called spin, to distinguish it from the orbital angular momentum. The spin also conjures up a mental picture of the electron being a ball of finite extent which spins about its own axis. Such a classical picture of the electron spin can mislead us to several fruitless inferences, such as the radius of the electron sphere (the electron is an elementary particle and is therefore a point particle), the analogy of spin to the classical angular momentum, etc.

Furthermore, that the beam splits into *two* beams implies that the electron spin is in

an $s = \frac{1}{2}$ state. The electron is said to have spin "one-half."

If the hydrogen is not in an s-state, then the magnitude of the orbital angular momentum is no longer zero. The Stern-Gerlach apparatus measures the total angular momentum which is the sum of the orbital angular momentum and the spin of the electron.

4.6.1 Anomalous magnetic moment of electron spin

From the measurements of the deflections of the split beams, the force on the magnetic dipole moment can be deduced. Equation (4.4.1) then yields the component of the magnetic dipole moment along the magnetic field direction, μ_z, if the field gradient is known. It turns out that

$$\mu_z = \pm\mu_B. \tag{4.6.1}$$

The relation between magnetic dipole moment and orbital angular momentum, Eq. (4.3.6), has to be modified for the spin,

$$\vec{\mu} = -2\mu_B\vec{S}, \tag{4.6.2}$$

since the eigenvalues of S_z are $\frac{1}{2}$ and $-\frac{1}{2}$. The factor of two change in the relation causes the magnetic moment of the spin to be called anomalous.

In general, when an electron possesses both spin and orbital angular momentum, its magnetic dipole moment is

$$\vec{\mu} = -\mu_B(g_s\vec{S} + g_\ell\vec{L}). \tag{4.6.3}$$

g is known as the gyromagnetic ratio, or simply as the g-factor. For the electron spin,

$$g_s = 2. \tag{4.6.4}$$

For the orbital motion,

$$g_\ell = 1. \tag{4.6.5}$$

4.6.2 Origin of the electron spin

In the non-relativistic treatment of the electron motion by either the Schrödinger wave mechanics or the Heisenberg matrix mechanics, the spin property of the electron has to be grafted on. In the next chapter, we shall introduce the view that, for the double degeneracy of the ground state found in the Stern-Gerlach experiment, the electron spin is a natural consequence. Dirac has shown that, if the classical motion of the electron is treated by the special relativity theory, and if the Schrödinger procedure of quantization is followed, then the spin $\frac{1}{2}$ property of the electron arises naturally in the non-relativistic limit. This theory will be studied in Chapter 15.

4.6.3 Electron dynamics including spin

The electron properties now include not only functions of position $\vec{r}$ and momentum $\vec{p}$, but also of spin $\vec{S}$. Since the spin is independent of position and momentum, it commutes with both $\vec{r}$ and $\vec{p}$. To specify the wave function of an electron, we require, in addition to the three degrees of freedom given by the position $\vec{r}$ (or the momentum $\vec{p}$), the spin degrees of freedom. The experiments show that the electron spin is always one half. Thus, any electron state satisfies

$$S^2|\Psi\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)|\Psi\rangle = \left(\frac{3}{4}\right)|\Psi\rangle. \tag{4.6.6}$$

The square of the spin operator is a constant of motion. The only additional spin variable is s_z, the eigenvalues of S_z. The other two components S_x and S_y do not commute with S_z and cannot be used in the wave function, just as $\vec{p}$ is not used once $\vec{r}$ is chosen, or vice versa. In general, the electron wave function is

$$\langle \vec{r}, s_z|\Psi(t)\rangle = \Psi(\vec{r}, s_z, t). \tag{4.6.7}$$

4.6.4 Spin degeneracy

If the Hamiltonian of an electron is independent of its spin, then the energy eigenstates are at least doubly degenerate.

Proof: Let S_χ be the component of $\vec{S}$ with spin $\frac{1}{2}$ along some direction χ and the eigen-

states of S_χ be denoted by $|\chi_\pm\rangle$, such that

$$S_\chi|\chi_+\rangle = \frac{1}{2}|\chi_+\rangle \tag{4.6.8}$$

$$S_\chi|\chi_-\rangle = -\frac{1}{2}|\chi_-\rangle. \tag{4.6.9}$$

The states χ_+ and χ_- are often referred to as the spin-up state and the spin-down state.

Since the Hamiltonian is assumed to be independent of the spin variables, the energy eigenfunctions can be found as functions of positions only as before:

$$H\psi(\vec{r}) = E\psi(\vec{r}). \tag{4.6.10}$$

Now let the electron state including spin be

$$|\Psi\rangle = |\psi, \chi_\sigma\rangle, \tag{4.6.11}$$

with the wave function,

$$\Psi(\vec{r}, s_z) = \langle \vec{r}, s_z|\psi, \chi_\sigma\rangle = \psi(\vec{r})\chi_\sigma(s_z), \tag{4.6.12}$$

being a simultaneous eigenstate of H and S_χ. With the choice of $\sigma = \pm$, there are two states with energy eigenvalues E.

4.6.5 Hydrogen atom

The Hamiltonian of the hydrogen atom derived from classical mechanics (Chapter 11) is independent of spin. There are four quantum numbers n, ℓ, m, σ specifying the energy eigenstates, when the spin degree of freedom is included. The wave function is

$$\psi_{n\ell m\sigma}(\vec{r}, s_z) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)\chi_\sigma(s_z). \tag{4.6.13}$$

The energy is unchanged:

$$E_{n\ell m\sigma} = -(1/n^2)Ryd. \tag{4.6.14}$$

The number of states with this energy is $2n^2$. The doubling comes from the added possibility of spin up and down states.

4.7 Nucleon Spin

Nucleon is the name given to the nuclear particles which include both proton and neutron. The charge state of a nucleon gives the distinction between a proton and a neutron. A nucleon has spin one-half. If $\vec{S}$ denotes the spin of a nucleon and $\vec{L}$ its orbital angular momentum in a nucleus, then its magnetic moment is given by

$$\vec{\mu} = \mu_N(g_\ell \vec{L} + g_s \vec{S}) \ , \tag{4.7.1}$$

where g_ℓ and g_s are the orbital and spin g-factors. In the table below, we list the empirical values of the g-factors:

	g_ℓ	g_s
proton	1	5.6
neutron	0	-3.8

The orbital g-factor values are as expected for the charged proton and uncharged neutron but the expected spin g-factors are respectively 2 and 0. The explanation of the measured values of the spin g-factors is given in terms of the internal structure of the nucleon, being composed of three quarks.

4.8 Addition of Angular Momenta

4.8.1 Total angular momentum

An electron in an atom carries an orbital angular momentum $\vec{L}$ as well as spin $\vec{S}$. The total angular momentum is

$$\vec{J} = \vec{L} + \vec{S}. \tag{4.8.1}$$

It is important to be able to express the eigenstates of the angular momentum L^2 and L_z and the spin S^2 and S_z in terms of the total angular momentum J^2 and J_z (as well as of L^2 and S^2) because of the conservation of the total angular momentum in the presence of internal spin-orbit interaction. (See Sec. 4.10.7.) Let us consider the more general case of the addition of two angular momentum operators $\vec{L}$ and $\vec{S}$, both of which can take on either integer or half integer values of the "magnitude" ℓ and s.

4.8.2 Commutation rules

We start with

$$\vec{L} \times \vec{L} = i\vec{L} \tag{4.8.2}$$

$$\vec{S} \times \vec{S} = ih\vec{S} \tag{4.8.3}$$

$$[\vec{L}, \vec{S}] = 0. \tag{4.8.4}$$

It follows that

$$[\vec{L}, L^2] = 0 \tag{4.8.5}$$

$$[\vec{S}, S^2] = 0 \tag{4.8.6}$$

$$[\vec{L}, S^2] = 0 \tag{4.8.7}$$

$$[\vec{S}, L^2] = 0. \tag{4.8.8}$$

For the sum of the angular momenta,

$$\vec{J} \times \vec{J} = i\vec{J} \tag{4.8.9}$$

$$[\vec{J}, J^2] = 0. \tag{4.8.10}$$

Since

$$J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}, \tag{4.8.11}$$

$$[J^2, S^2] = 0, \tag{4.8.12}$$

$$\text{and} \quad [J^2, L^2] = 0. \tag{4.8.13}$$

Thus, we have two sets of four commutative operators:

$$(1) \qquad L^2, L_z, S^2, S_z; \tag{4.8.14}$$

$$(2) \qquad J^2, J_z, L^2, S^2. \tag{4.8.15}$$

We may choose either set and find the simultaneous eigenstates of the four operators in the same set.

4.8.3 Relationship between the two sets of eigenstates and eigenvalues

(1) The eigenstates of the first set of operators are easy to find. Let $|Y_{\ell m_\ell}\rangle$ be the eigenstate of L^2 and L_z with eigenvalues $\ell(\ell+1)$ and m_ℓ, and let $|\chi_{sm_s}\rangle$ be the eigenstate of S^2 and S_z with eigenvalues $s(s+1)$ and m_s. Then, the simultaneous eigenstate of all four operators is

$$|\psi(\ell m_\ell s m_s)\rangle = |Y_{\ell m_\ell}\chi_{sm_s}\rangle. \tag{4.8.16}$$

Since ℓ is not confined to the integral values, $|Y_{\ell m_\ell}\rangle$ here is not restricted to the spherical harmonics. Given ℓ and s, there are $(2\ell+1)(2s+1)$ eigenstates.

(2) Since $\vec{J}$ is an angular momentum operator satisfying the usual commutation rules, the eigenstates of J^2 and J_z can be defined as usual. In addition, however, these states must be eigenstates of L^2 and S^2. Each state is characterized by four quantum numbers j, m_j, ℓ, s, such that

$$J^2|\Psi_{jm_j\ell s}\rangle = j(j+1)|\Psi_{jm_j\ell s}\rangle \tag{4.8.17}$$

$$J_z|\Psi_{jm_j\ell s}\rangle = m_j|\Psi_{jm_j\ell s}\rangle \tag{4.8.18}$$

$$L^2|\Psi_{jm_j\ell s}\rangle = \ell(\ell+1)|\Psi_{jm_j\ell s}\rangle \tag{4.8.19}$$

$$S^2|\Psi_{jm_j\ell s}\rangle = s(s+1)|\Psi_{jm_j\ell s}\rangle. \tag{4.8.20}$$

The problem is how to relate the eigenstates $|\Psi_{jm_j\ell s}\rangle$ and their eigenvalues of the second set of operators to those of the first set given by Eq. (4.8.16).

We note that $|\psi(\ell m_\ell s m_s)\rangle$ is already an eigenstate of L^2 and S^2. Given ℓ and s, we only need to take linear combinations of the $(2\ell+1)(2s+1)$ states $|\psi(\ell m_\ell s m_s)\rangle$ to make eigenstates of J^2 and J_z. Now,

$$\begin{aligned} J_z|\psi(\ell m_\ell s m_s)\rangle &= (L_z+S_z)|\psi(\ell m_\ell s m_s)\rangle \\ &= (m_\ell+m_s)|\psi(\ell m_\ell s m_s)\rangle. \end{aligned} \tag{4.8.21}$$

This shows that $|\psi(\ell m_\ell s m_s)\rangle$ is already an eigenstate of J_z with eigenvalue $(m_\ell+m_s)$, i.e. the sum of eigenvalues for L_z and S_z. It is in general not an eigenstate of J^2. The

possible values of m_j are

$$m_j = m_\ell + m_s. \tag{4.8.22}$$

We shall now find, given ℓ and s, what are the values of j. The largest value of m_j is

$$(m_j)_{max} = \ell + s. \tag{4.8.23}$$

Since m_j ranges from $-j$ to j, the largest possible value of j is

$$j_{max} = \ell + s. \tag{4.8.24}$$

Since there is only one such state $|\psi(\ell\ell ss)\rangle$, this state must be an eigenstate of J^2 and J_z, i.e. $|\Psi_{\ell+s\,\ell+s\,\ell s}\rangle$. This statement can easily be verified directly by operating

$$J^2 = J_- J_+ + J_z + J_z^2 \tag{4.8.25}$$

on the state $|\psi(\ell\ell ss)\rangle$, since J_+ annihilates the state and each J_z produces a factor of $\ell + s$.

The second largest value of m_j is

$$m_j = \ell + s - 1. \tag{4.8.26}$$

There are two such $|\psi(\ell m_\ell s m_s)\rangle$ states with

$$m_\ell = \ell - 1 \qquad \text{and } m_s = s \tag{4.8.27}$$

$$\text{and} \quad m_\ell = \ell, \qquad m_s = s - 1. \tag{4.8.28}$$

Two suitable linear combinations of these two states will be eigenstates $|\Psi_{jm_j\ell s}\rangle$, with

$$j = \ell + s, \quad m_j = \ell + s - 1, \tag{4.8.29}$$

$$j = \ell + s - 1, \quad m_j = \ell + s - 1. \tag{4.8.30}$$

The former is a state of $j = \ell + s$ with the second largest m_j. The latter is a state of $j = \ell + s - 1$ with the largest m_j.

In the same way, the next value of m_j is $\ell + s - 2$ with three possible combinations of m_ℓ and m_s. They yield three states with the same m_j but three different j values: $\ell + s$, $\ell + s - 1$, $\ell + s - 2$.

We can keep going in this manner. The smallest value of j, which must be positive, is $|\ell - s|$ because the total number of possible product states $|\psi(\ell m_\ell s m_s)\rangle$ for given ℓ and s is exhausted:

$$\begin{aligned}\sum_{j=|\ell-s|}^{\ell+s}(2j+1) &= (\ell+s-|\ell-s|+1)(\ell+s+|\ell-s|+1)\\ &= (2\ell+1)(2s+1).\end{aligned} \tag{4.8.31}$$

This yields just the right number of combinations for the unitary transformation:

$$|\Psi_{jm_j\ell s}\rangle = \sum_{m_\ell}\sum_{m_s}|Y_{\ell m_\ell}\chi_{sm_s}\rangle\langle Y_{\ell m_\ell}\chi_{sm_s}|\Psi_{jm_j\ell s}\rangle, \tag{4.8.32}$$

where,

$$\langle Y_{\ell m_\ell}\chi_{sm_s}|\Psi_{jm_j\ell s}\rangle = C^{jm_j}_{\ell m_\ell, sm_s} = \begin{pmatrix} j & \ell & s \\ m_j & m_\ell & m_s \end{pmatrix} \tag{4.8.33}$$

denoted by the Clebsch-Gordan coefficient, or the $3j$ symbol. We shall delay the study of the general theory for these coefficients but for now work out only a couple of specific examples in the next section.

There is an alternative way to obtain the largest value of j (say, j_{max}) and the smallest value of j (say, j_{min}). The total number of states with ℓ and s is on the one hand

$$\begin{aligned}\sum_{j=j_{min}}^{j_{max}}(2j+1) &= \frac{1}{2}(2j_{max}+1+2j_{min}+1)(j_{max}-j_{min}+1)\\ &= (j_{max}+j_{min}+1)(j_{max}-j_{min}+1),\end{aligned} \tag{4.8.34}$$

and on the other hand $(2\ell+1)(2s+1)$. If $\ell > s$, the solution is

$$\begin{aligned}j_{max}+j_{min} &= 2\ell,\\ j_{max}-j_{min} &= 2s,\end{aligned} \tag{4.8.35}$$

yielding

$$\begin{aligned}j_{max} &= \ell+s,\\ j_{min} &= \ell-s.\end{aligned} \tag{4.8.36}$$

4.8.4 Example

Let us illustrate the above procedure with an example. Let $\ell = 1$ and $s = \frac{1}{2}$. For instance, we wish to find the total angular momentum of the electron (carrying a spin $\frac{1}{2}$) in a p state of the hydrogen atom. There are 6 eigenstates of L^2, L_z, S^2 and S_z with m_ℓ and m_s chosen from

$$\begin{aligned} m_\ell &= 1, 0, -1 \\ m_s &= \frac{1}{2}, -\frac{1}{2}. \end{aligned}$$

From Eq. (4.8.22), the possible values of m_j are

$$\begin{array}{cccc} \frac{3}{2}, & \frac{1}{2}, & -\frac{1}{2}, & -\frac{3}{2}. \\ \left(1, \frac{1}{2}\right) & \left(1, -\frac{1}{2}\right) & \left(0, -\frac{1}{2}\right) & \left(-1, -\frac{1}{2}\right) \\ & \left(0, \frac{1}{2}\right) & \left(-1, \frac{1}{2}\right) & \end{array}$$

Under each value of m_j is a column of combinations of (m_ℓ, m_s). Thus, the possible values of j and m_j are

$$\begin{aligned} j &= \frac{3}{2},\ m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}; \\ \text{and}\ \ j &= \frac{1}{2},\ m_j = \frac{1}{2}, -\frac{1}{2}. \end{aligned}$$

They correspond to exactly 6 states. The $(m_\ell, m_s) = \left(1, \frac{1}{2}\right)$ state is the only one with $m_j = \frac{3}{2}$ and, thus, it must be an eigenstate of J^2 with $j = \frac{3}{2}$. The two states $(m_\ell, m_s) = \left(1, -\frac{1}{2}\right)$ and $\left(0, \frac{1}{2}\right)$ have $m_j = \frac{1}{2}$ and suitable linear combinations can be made from them to yield an eigenstate of J^2 with $j = \frac{3}{2}$ and one with $j = \frac{1}{2}$.

4.8.5 The vector model

In Section 4.2.4, a semi-classical picture of the angular momentum is described in which it is represented by a vector precessing about the z-axis with a fixed z component equal to the eigenvalue of the z component of the angular momentum operator. Now, all three angular momenta, $\vec{L}$, $\vec{S}$ and their sum $\vec{J}$ can be represented by three precessing vectors. The vector $\vec{J}$ is given in terms of $\vec{L}$ and $\vec{S}$ by the usual vector addition rule. For the example above, the three possible orientations of the vector $\vec{L}$ are illustrated in

Fig. 4.5(a), and the two possible states of the vector $\vec{S}$ are illustrated in Fig. 4.5(b). The z-component of the vector $\vec{J}$ must be the sum of the z components of $\vec{L}$ and $\vec{S}$. Figures 4.5(c) and (d) show the possible combinations of vector additions of the precessing vectors $\vec{L}$ and $\vec{S}$.

4.9 A Composite of Two Spin $\frac{1}{2}$ Particles

Besides the electron, there are other particles with spin $\frac{1}{2}$, e.g. the neutron and the proton. Consider a system of two spin $\frac{1}{2}$ particles, either identical, such as two protons in the hydrogen molecule, or dissimilar, such as the electron and proton in the hydrogen atom or the neutron and proton in the deuteron. We shall work out this example of two spins not only for the eigenvalues but also eigenstates of the total spin J^2 and J_z.

Using the notations of the last section, let $\vec{L}$ and $\vec{S}$ be the spin operators of the two particles. Then

$$\ell = \frac{1}{2}, \quad \text{and } s = \frac{1}{2}. \tag{4.9.1}$$

For simplicity, denote the eigenstates of L_z with eigenvalues $\pm\frac{1}{2}$ by $|\phi_\pm\rangle$ and those of S_z by $|\chi_\pm\rangle$. The four eigenstates of L^2, L_z, S^2, and S_z are $|\phi_+\chi_+\rangle$, $|\phi_+\chi_-\rangle$, $|\phi_-\chi_+\rangle$, $|\phi_-\chi_-\rangle$.

4.9.1 Total spin

The possible values of j, m_j are

$$\begin{aligned} j &= 0, \quad m_j = 0; \\ \text{and} \quad j &= 1, \quad m_j = 1, 0, -1. \end{aligned} \tag{4.9.2}$$

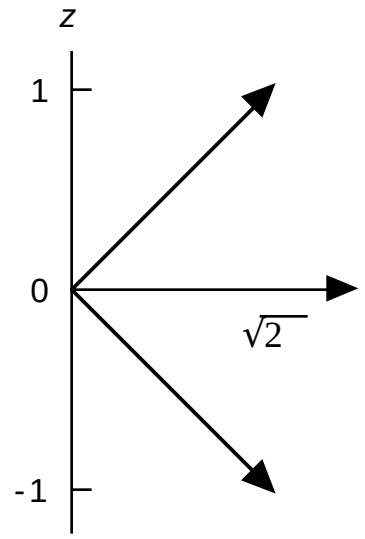
Denote the eigenstates of J^2 and J_z by $|\Psi_{jm_j}\rangle$, with the quantum numbers ℓ and s understood to be a half.

From Eq. (4.8.21), $|\phi_+\chi_+\rangle$ is an eigenstate of J_z with eigenvalue

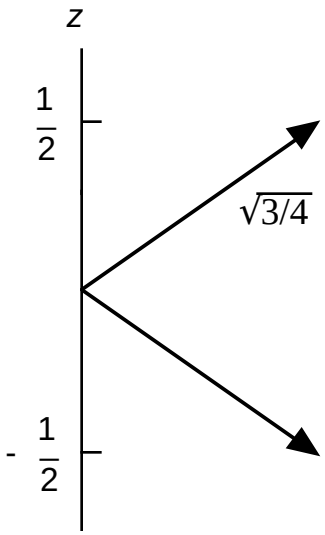
$$m_j = m_\ell + m_s = 1. \tag{4.9.3}$$

Since there is only one such state, the $j = 1$ $m_j = 1$ state must be

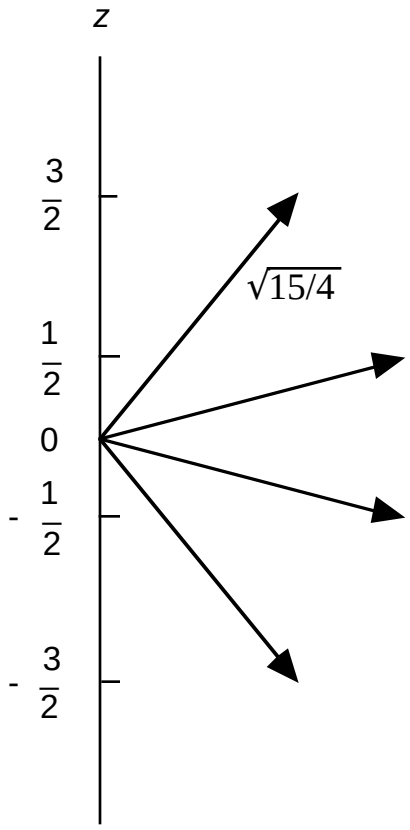
$$|\Psi_{1,1}\rangle = |\phi_+\chi_+\rangle. \tag{4.9.4}$$



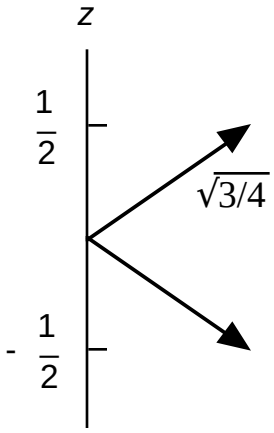
(a) $l = 1$



(b) $s = 1/2$



(c) $j = 3/2$



(d) $j = 1/2$

Figure 4.5: Vector model for the addition of angular momentum.

For the same reason, the $j = 1$, $m_j = -1$ state is

$$|\Psi_{1,-1}\rangle = |\phi_-\chi_-\rangle. \tag{4.9.5}$$

The remaining two states $|\phi_+\chi_-\rangle$ and $|\phi_-\chi_+\rangle$ are both eigenstates of J_z with $m_j = 0$. Neither is an eigenstate of J^2. Hence, we need to make up new combinations:

$$|\Psi_{1,0}\rangle = |\phi_+\chi_-\rangle a + |\phi_-\chi_+\rangle b, \tag{4.9.6}$$

$$|\Psi_{0,0}\rangle = |\phi_+\chi_-\rangle c + |\phi_-\chi_+\rangle d. \tag{4.9.7}$$

The determination of the four coefficients a, b, c d will be left as an exercise for the reader.

We proceed with an alternative method of finding $|\Psi_{1,0}\rangle$ and $|\Psi_{0,0}\rangle$. From Eq. (4.5.35),

$$J_-|\Psi_{1,1}\rangle = \sqrt{2}|\Psi_{1,0}\rangle. \tag{4.9.8}$$

From Eq. (4.9.4),

$$\begin{aligned} J_-|\Psi_{1,1}\rangle &= (L_- + S_-)|\phi_+\chi_+\rangle \\ &= |(L_-\phi_+)\chi_+\rangle + |\phi_+(S_-\chi_+)\rangle \\ &= |\phi_-\chi_+\rangle + |\phi_+\chi_-\rangle, \quad \text{using Eq. (4.5.34)}, \\ &= |\phi_-\chi_+\rangle + |\phi_+\chi_-\rangle. \end{aligned} \tag{4.9.9}$$

Hence,

$$|\Psi_{1,0}\rangle = \frac{1}{\sqrt{2}}(\|\phi_-\chi_+\rangle + |\phi_+\chi_-\rangle). \tag{4.9.10}$$

The state $|\Psi_{0,0}\rangle$ must be orthogonal to $|\Psi_{1,0}\rangle$ and, therefore,

$$|\Psi_{0,0}\rangle = \frac{1}{\sqrt{2}}(|\phi_-\chi_+\rangle - |\phi_+\chi_-\rangle). \tag{4.9.11}$$

It can be checked by direct verification that these states are eigenstates of J^2.

The eigenstates of two spin $\frac{1}{2}$ particles are summarized in the following table:

j	m_j	state	spin orientation	
1	1	$\|\phi_+\chi_+\rangle$	$\uparrow\uparrow$	
1	0	$\sqrt{1/2}(\|\phi_-\chi_+\rangle + \|\phi_+\chi_-\rangle)$	$(\uparrow\downarrow + \downarrow\uparrow)\sqrt{1/2}$	triplets
1	-1	$\|\phi_-\chi_-\rangle$	$\downarrow\downarrow$	
0	0	$\sqrt{1/2}(\|\phi_-\chi_+\rangle - \|\phi_+\chi_-\rangle)$	$(\uparrow\downarrow - \downarrow\uparrow)\sqrt{1/2}$	singlet

These combination states of two spin $\frac{1}{2}$ particles have many applications. We shall later use them in atomic physics. Another interesting application is in the nuclear motion of a diatomic molecule. Consider, for example, the hydrogen molecule, consisting of two protons and two electrons. Concentrate on the protons' motion. The spin states are grouped into three $j = 1$ states (triplets) and one $j = 0$ (singlet) state. Hydrogen molecules with the former proton states are called ortho-hydrogen; those with the latter proton state are called para-hydrogen. The $j=1$ states are three-fold degenerate and the $j=0$ states are non-degenerate. This difference shows up in the intensity of the rotational spectra of the hydrogen molecules. The intensity of the lines from ortho-hydrogen is three times that of the lines from para-hydrogen. The difference in degeneracy also is manifest in the thermodynamic properties, such as the specific heat.

4.10 Examples

4.10.1 Exercise in commutation relations

(a) If $[A, B] = C$, show that $[A^2, B] = AC + CA$.

Solution —

$$\begin{aligned}[A^2, B] &= A^2B - BA^2 = A^2B - ABA + ABA - BA^2 \\ &= A[A, B] + [A, B]A = AC + CA. \end{aligned} \tag{4.10.1}$$

(b) Evaluate $[L_x^2, L_z]$.

Solution — Using Eq. (4.10.1) and $[L_x, L_z] = -iL_y$, we obtain

$$[L_x^2, L_z] = -i(L_xL_y + L_yL_x). \tag{4.10.2}$$

4.10.2 Spherical harmonics and homogeneous polynomials

(a) Show that the d-orbitals, xy, yz, zx, $3z^2 - r^2$, and $x^2 - y^2$, are eigenstates of L^2 with $\ell = 2$.

Solution — From Table 4.2.3, the spherical harmonics with $\ell = 2$ are

$$\begin{aligned} Y_{2,\pm 2}(\theta,\phi) &= \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi} = \frac{f(r)}{2}[(x^2-y^2) \pm i\, 2xy]\,, \\ Y_{2,\pm 1}(\theta,\phi) &= \mp\sqrt{\frac{15}{8\pi}}\sin\theta\,\cos\theta\, e^{\pm i\phi} = \mp f(r)[(x \pm iy)z]\,, \\ Y_{2,0}(\theta,\phi) &= \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) = \frac{f(r)}{\sqrt{6}}(3z^2 - r^2)\,, \end{aligned} \tag{4.10.3}$$

where

$$f(r) = \sqrt{\frac{15}{8\pi}}\,\frac{1}{r^2}\,. \tag{4.10.4}$$

Therefore, we have

$$\begin{aligned} xy &= \frac{1}{if(r)}[Y_{2,2} - Y_{2,-2}], \\ yz &= \frac{1}{2if(r)}[Y_{2,1} - Y_{2,-1}], \\ zx &= \frac{1}{2f(r)}[Y_{2,1} + Y_{2,-1}], \\ 3z^2 - r^2 &= \frac{\sqrt{6}}{f(r)}Y_{2,0}, \\ x^2 - y^2 &= \frac{1}{f(r)}[Y_{2,2} + Y_{2,-2}]. \end{aligned} \tag{4.10.5}$$

(b) Any wave function which is a product of a homogeneous polynomial of second degree in (x, y, z) and a function of r is a linear combination of $\ell = 2$ and $\ell = 0$ spherical harmonics with coefficients as functions of r.

Solution — A homogeneous polynomial of second degree is a linear combination of $x^2, y^2, z^2, xy, yz, yz$. It is, therefore, also a linear combination of the d-orbitals $xy, yz, zx, 3z^2-r^2, x^2-y^2$ and the s-orbital r^2. From part (a), the assertion follows.

4.10.3 Rotational operator

(a) Show that a rotational operator, which rotates any wave function rigidly through an angle α about the z-axis, can be express as

$$R(\alpha, z) = e^{-i\alpha L_z}. \tag{4.10.6}$$

Solution — See Problem 12 in Chapter 1. The effect of the operator on a wave function is

$$\begin{aligned} R(\alpha, z)\psi(r, \theta, \phi) &= \psi(r, \theta, \phi - \alpha) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\alpha \frac{\partial}{\partial \phi}\right)^n \psi(r, \theta, \phi) \\ &= e^{-\alpha \frac{\partial}{\partial \phi}} \psi(r, \theta, \phi) \\ &= e^{-i\alpha L_z} \psi(r, \theta, \phi). \end{aligned} \tag{4.10.7}$$

(b) Is $R(\alpha, z)$ a Hermitian operator?

Solution — No, its Hermitian conjugate is

$$R^{\dagger}(\alpha, z) = e^{i\alpha L_z}, \tag{4.10.8}$$

which is not equal to $R(\alpha, z)$ except in the trivial case of $\alpha = 0$.

(c) Find the transformation matrix which connects the $\ell = 1$ spherical harmonics to the eigenstates of $\ell = 1$ of $L_{x'}$ where x' is obtained by rotating the x-axis through an angle α about the z-axis.

Solution — By using the rotation operator, we obtain the new eigenstates

$$\begin{aligned} Z_{1,1} = R(\alpha, z)Y_{1,1} &= Y_{1,1}e^{-i\alpha}, \\ Z_{1,0} = R(\alpha, z)Y_{1,0} &= Y_{1,0}, \\ Z_{1,-1} = R(\alpha, z)Y_{1,-1} &= Y_{1,-1}e^{i\alpha}. \end{aligned} \tag{4.10.9}$$

The transformation S, which is given by

$$Y_{1,m} = \sum_{m'=-1}^{1} Z_{1,m'} S_{m',m}, \tag{4.10.10}$$

is, therefore, a diagonal matrix

$$S = \begin{bmatrix} e^{i\alpha} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\alpha} \end{bmatrix}. \tag{4.10.11}$$

(d) What is the most general expression for a rotation operator?

Solution — A rotation may be expressed as through an angle α about an axis in the direction of the unit vector $\vec{n}$. Thus, from part (a), it can be represented by

$$R(\alpha, \vec{n}) = e^{-i\alpha \vec{n}\cdot\vec{L}}. \tag{4.10.12}$$

4.10.4 Stern-Gerlach experiment for spin 1/2 particles

Platt [7] complained that most textbook treatments of the Stern-Gerlach experiment were based on semiclassical quantum mechanics. Indeed, the account in this chapter is also based on the semiclassical orbital argument. He gave a quantum treatment. Here is a simplified version of his paper for the spin 1/2 particles in a Stern-Gerlach apparatus.

(a) Wave function representation of the spin 1/2 particle in three dimensions.

Solution — If $|\Psi\rangle$ represents the state of the particle, and $|\vec{r}, \pm\rangle$ represents the eigenstate of position at $\vec{r}$ and spin state in the z direction $\pm 1/2$, then

$$\Psi(\vec{r}, \pm) = \langle \vec{r}, \pm | \Psi \rangle \tag{4.10.13}$$

is the two-component wave function.

(b) The time-dependent Schrödinger equation.

Solution — The time-dependent Schrödinger equation is given by

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = H |\Psi\rangle \tag{4.10.14}$$

with the Hamiltonian given by

$$H = \frac{P^2}{2m} - g\mu_B \vec{S} \cdot \vec{B}, \tag{4.10.15}$$

in a non-uniform magnetic field $\vec{B} = (0, 0, \beta z)$. Applying $\langle \vec{r}, \pm|$ to Eq. (4.10.14) yields the two-component Schrödinger equation for the wave functions:

$$i\hbar \frac{\partial \Psi(\vec{r}, \pm)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, \pm) \mp \frac{1}{2} g\mu_B \beta z \Psi(\vec{r}, \pm). \tag{4.10.16}$$

(c) The particle paths and their interpretation.

Solution — If we apply the Ehrenfest theorem separately to each spin component of the wave function, we obtain the equations of motion for the separate expectation values $\langle \vec{r} \rangle_\pm = \langle \Psi(\pm) | \vec{r} | \Psi(\pm) \rangle$

$$\begin{aligned} \frac{d\langle \vec{r} \rangle_\pm}{dt} &= \frac{\langle \vec{p} \rangle_\pm}{m}, \\ \frac{d\langle \vec{p} \rangle_\pm}{dt} &= \pm \frac{1}{2} g\mu_B \beta z \hat{k}, \end{aligned} \tag{4.10.17}$$

where $\hat{k}$ is the unit vector in the z direction.

While the equations no doubt give us two mathematical paths, one for each spin state, the interpretation for the prediction of experimental outcome requires care. Suppose that spatially each particle is prepared as a wave packet. Remember that if the state wave function is normalized at a given time, then

$$\langle \Psi(+) | \Psi(+) \rangle + \langle \Psi(-) | \Psi(-) \rangle = 1. \tag{4.10.18}$$

This reminds us that $\langle \Psi(\pm) | \Psi(\pm) \rangle$ for the wave packet are measures of the probabilities of the particle being in either path. Thus, if we set up the detector screen as in Fig. 4.3, the two intersects of the paths with the screen give us the positions for the spin up and down states and their intensities give us the probabilities in these spin states. A single particle can end up in either point, with its associated probability.

4.10.5 Zeeman splitting

A hydrogen atom in its ground state is placed in a uniform magnetic field of 200 Tesla. Calculate the energy difference of the two-spin states to two significant figures in electron volts and the frequency of the electromagnetic wave which would cause resonance absorption between the two levels.

Solution — The Hamiltonian for the spin in magnetic field B along the z direction is

$$H = -\, g_s \mu_B \, S_z B. \tag{4.10.19}$$

The energy difference for the two states with S_z given by $\pm\frac{1}{2}$ is

$$\begin{aligned} \Delta E &= -\, g_s \mu_B \, B \left(\frac{-1}{2} - \frac{1}{2} \right) \\ &= g_s \mu_B B \\ &= 2 \times 5.79 \times 10^{-5} \text{ eV/T} \times 200 \text{ T} \\ &= 0.023 \text{ eV}. \end{aligned} \tag{4.10.20}$$

We have used the g-factor of the electron spin to be 2 and the value of the Bohr magneton from the table of Fundamental Physical Constants. Note that it agrees with the energy on the last but one line of the table.

Thus, from the same line of the table, the corresponding frequency for the electromagnetic wave is

$$\begin{aligned} \nu &= 0.028 \text{ THz/T} \times 200 \text{ T} \\ &= 5.6 \text{ THz}. \end{aligned} \tag{4.10.21}$$

4.10.6 Matrix representation of the angular momentum

(a) Evaluate the matrix elements of $\vec{L}$ for the $\ell = 2$ states.

Solution — In the basis set of the common eigenstates of L_z and L^2, $Y_{\ell,m}$, all the matrix elements of $\vec{L}$ and L^2 connecting states of different ℓ's vanish. Thus, we can

consider the matrices for different ℓ's in isolation. The matrix representation for L_z in the descending order of m is

$$L_z = \begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{bmatrix}. \tag{4.10.22}$$

(4.10.23)

By using Eq. (4.5.41), we obtain the matrix representation for L_+

$$L_+ = \begin{bmatrix} 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}. \tag{4.10.24}$$

(4.10.25)

Its Hermitian conjugate (i.e. complex conjugate and transpose) is L_-

$$L_- = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{6} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \end{bmatrix}. \tag{4.10.26}$$

(4.10.27)

The relation $S_x = (S_+ + S_-)/2$ gives

$$L_x = \frac{1}{2}\begin{bmatrix} 0 & 2 & 0 & 0 & 0 \\ 2 & 0 & \sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & \sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & 2 \\ 0 & 0 & 0 & 2 & 0 \end{bmatrix}, \tag{4.10.28}$$

(4.10.29)

and similarly $S_y = (S_+ - S_-)/2i$ yields

$$L_y = \frac{1}{2}\begin{bmatrix} 0 & -2i & 0 & 0 & 0 \\ 2i & 0 & -i\sqrt{6} & 0 & 0 \\ 0 & i\sqrt{6} & 0 & -i\sqrt{6} & 0 \\ 0 & 0 & i\sqrt{6} & 0 & -2i \\ 0 & 0 & 0 & 2i & 0 \end{bmatrix}. \tag{4.10.30}$$

(4.10.31)

(b) For the eigenstate of L_z with eigenvalue 2, find its expectation value of L_x and its uncertainty.

Solution — The vector representation of the eigenstate is

$$\Psi = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}. \tag{4.10.32}$$

(4.10.33)

The expectation value of L_x is

$$\langle L_x \rangle = \langle \Psi | L_x | \Psi \rangle = 0 \tag{4.10.34}$$

by matrix multiplication of the row vector of $\Psi^\dagger$, the matrix of L_x, and the column vector of Ψ, the product of the two latter terms being

$$L_x \cdot \Psi = \frac{1}{2}\begin{bmatrix} 0 & 2 & 0 & 0 & 0 \\ 2 & 0 & \sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & \sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & 2 \\ 0 & 0 & 0 & 2 & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}. \tag{4.10.35}$$

(4.10.36)

The uncertainty is given by

$$\begin{aligned}(\Delta L_x)^2 &= \langle\Psi|L_x^2|\Psi\rangle = \langle L_x\Psi|L_x\Psi\rangle \\ &= [0\ 1\ 0\ 0\ 0]\begin{bmatrix}0\\1\\0\\0\\0\end{bmatrix} = 1.\end{aligned} \tag{4.10.37}$$

Thus,

$$\Delta L_x = 1. \tag{4.10.38}$$

(c) Justify the vector model in this case.

Solution — Either from symmetry consideration or by a similar matrix multiplication procedure as in part (b), we have

$$\langle L_y\rangle \quad = \quad = 0,$$

$$\Delta L_y = 1 \tag{4.10.39}$$

Thus, a vector with a component 2 along the z-axis and a component of magnitude $\sqrt{2}$ normal to the z-axis and precessing about it will have at all times $L_z = 2$ and L_x and L_y varying between $\pm\Delta L_x$ and $\pm\Delta L_y$ with average values 0.

(d) Find the eigenstates of L_x.

Solution — The eigenstate Φ is given by

$$L_x\Phi = m\Phi, \tag{4.10.40}$$

that is, we have to diagonalize the matrix L_x. In the matrix representation, from

the symmetric structure of L_x we note that Φ must be of the form

$$\Phi = \begin{bmatrix} a \\ b \\ c \\ \pm b \\ \pm a \end{bmatrix}. \tag{4.10.41}$$

(4.10.42)

For the symmetric states, the 5×1 equation is the reduced to a 3×1 equation

$$\begin{bmatrix} -m & 1 & 0 \\ 1 & -m & \sqrt{\frac{3}{2}} \\ 0 & \sqrt{6} & -m \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = 0. \tag{4.10.43}$$

(4.10.44)

Since we already know that the values of m, for $m = 0$ this set of equations is easily solved to yield the normalized eigenstate

$$\Phi_{2,0} = \begin{bmatrix} \sqrt{\frac{3}{8}} \\ 0 \\ -\frac{1}{2} \\ 0 \\ \sqrt{\frac{3}{8}} \end{bmatrix}. \tag{4.10.45}$$

(4.10.46)

The secular equation (4.10.43) is readily solved for the two eigenvalues ± 2 with eigenstates

$$\Phi_{2,\pm 2} = \begin{bmatrix} \frac{1}{4} \\ \pm\frac{1}{2} \\ \sqrt{\frac{3}{8}} \\ \pm\frac{1}{2} \\ \frac{1}{4} \end{bmatrix}. \tag{4.10.47}$$

(4.10.48)

A check is provided by the evaluation

$$\langle \Phi_{2,\pm 2} | L_z^2 | \Phi_{2,\pm 2} \rangle = 1 \,. \tag{4.10.49}$$

The secular equation (4.10.40) for the antisymmetric states is reduced to a 2×2 set

$$\begin{bmatrix} -m & 1 \\ 1 & -m \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0. \tag{4.10.50}$$

$$\tag{4.10.51}$$

Solution leads to the eigenstates for $m = \pm 1$

$$\Phi_{2,\pm 1} = \begin{bmatrix} \frac{1}{2} \\ \pm\frac{1}{2} \\ 0 \\ \mp\frac{1}{2} \\ -\frac{1}{2} \end{bmatrix}. \tag{4.10.52}$$

$$\tag{4.10.53}$$

(e) Check the eigenstate of L_x, $\Phi_{2,0}$, using the spatial representation in Sec. 8.10.2.

Solution — From

$$Y_{2,0} = \frac{f(r)}{\sqrt{6}}(3z^2 - r^2), \tag{4.10.54}$$

we write down the eigenstate of L_x by changing the coordinates

$$\Phi_{2,0} = \frac{f(r)}{\sqrt{6}}(3x^2 - r^2), \tag{4.10.55}$$

which can be rewritten as

$$\begin{aligned} \Phi_{2,0} &= \frac{f(r)}{\sqrt{6}} \left[\frac{3}{2}(x^2 - y^2) - \frac{1}{2}(3z^2 - r^2) \right] \\ &= \sqrt{\frac{3}{8}} \left(Y_{2,2} + Y_{2,-2} \right) - \frac{1}{2} Y_{2,0}. \end{aligned} \tag{4.10.56}$$

The coefficients give the correct column vector for $\Phi_{2,0}$.

4.10.7 Spin-orbit interaction

We give here a reason why sometimes the eigenstates of J^2, J_z, L^2, and S^2 are preferred to those of L^2, L_z, S^2, and S_z. Later, we shall establish the interaction between the magnetic dipole moment due to the orbital motion and the spin magnetic dipole moment. Here we argue that the interaction between $\vec{L}$ and $\vec{S}$ must have spherical symmetry since there is no reason for a special direction. The invariants are L^2, S^2 and $\vec{L}\cdot\vec{S}$. The first two depend only on the individual properties. The interaction must involve the last one. The Hamiltonian is of the form

$$H_{so} = 2\zeta\,\vec{L}\cdot\vec{S}, \tag{4.10.57}$$

where ζ is independent of the angular and spin coordinates. The spin-orbit interaction may be rewritten as

$$H_{so} = \zeta\,(J^2 - L^2 - S^2). \tag{4.10.58}$$

It is evident then that an eigenstate of J^2, J_z, L^2, and S^2 is also an eigenstate of H_{so}, with the eigenvalue $\zeta[j(j+1) - \ell(\ell+1) - s(s+1)]$. That eigenvalue of the interaction has a $2j+1$-fold degeneracy.

4.10.8 Hydrogen 4f states

(a) If the electron of a hydrogen atom is in the $4f$ state, list by appropriate quantum numbers the eigenstates of the z-components of the electron orbital angular momentum and spin. By using the vector model or otherwise, list by appropriate quantum numbers the eigenstates of J^2 and J_z of the total angular momentum (spin plus orbital).

Solution — Let $\vec{L}$ denote the orbital angular momentum and $\vec{S}$ the spin. For the $4f$ level, $\ell = 3$. Thus, the additional quantum numbers in this level are given by (m_ℓ, m_s), with m_ℓ in integers ranging from -3 to 3 and $m_s = \pm 1/2$. There are in total 14 states.

The total angular momentum, $\vec{J} = \vec{L} + \vec{S}$, has quantum numbers for J^2 and J_z denoted by (j, m_j). The possible values of j range from $|\ell - s|$ in unit increments

to $\ell + s$. Thus,

$$j = 3 \pm \frac{1}{2} = \frac{5}{2} \text{ or } \frac{7}{2}. \tag{4.10.59}$$

For $j = \frac{5}{2}$,

$$m_j = -\frac{5}{2},\ -\frac{3}{2}\ , -\frac{1}{2},\ \frac{1}{2},\ \frac{3}{2},\ \frac{5}{2}\,; \tag{4.10.60}$$

for $j = \frac{7}{2}$,

$$m_j = -\frac{7}{2}, \ldots, \frac{7}{2}. \tag{4.10.61}$$

There are again 14 states.

(b) Find the component of the magnetic dipole moment along the z-direction in units of the Bohr magneton of the eigenstate of J^2 and J_z with the largest eigenvalues for a $4f$ electron.

Solution — The largest eigenvalues of J^2 and J_z are $(j, m_j) = (\frac{7}{2}, \frac{7}{2})$. The associated state is

$$\Psi_{\frac{7}{2},\frac{7}{2}} = Y_{3,3}\psi_{\frac{1}{2},\frac{1}{2}}, \tag{4.10.62}$$

where the terms on the right side are the eigenstates of the orbital angular momentum and spin respectively.

The z component of the magnetic dipole moment is given by

$$\mu_z = -\,\mu_e(L_z + 2S_z). \tag{4.10.63}$$

Acting on the $(\frac{7}{2}, \frac{7}{2})$ state yields

$$\begin{aligned}
\mu_z \Psi_{\frac{7}{2},\frac{7}{2}} &= -\,\mu_B(L_z + 2S_z) Y_{3,3}\psi_{\frac{1}{2},\frac{1}{2}} \\
&= -\,\mu_B[(L_z Y_{3,3})\psi_{\frac{1}{2},\frac{1}{2}} + Y_{3,3}(2S_z\psi_{\frac{1}{2},\frac{1}{2}})] \\
&= -\,\mu_B[(3Y_{3,3})\psi_{\frac{1}{2},\frac{1}{2}} + Y_{3,3}(\psi_{\frac{1}{2},\frac{1}{2}})] \\
&= -4\mu_B \Psi_{\frac{7}{2},\frac{7}{2}}.
\end{aligned} \tag{4.10.64}$$

This shows that the state is also an eigenstate of μ_z with eigenvalue $-4\mu_B$.

4.11 Problems

1. From the definition of the orbital angular momentum, deduce the commutation relations:

$$\vec{L} \times \vec{L} = i\vec{L},$$

$$[\vec{L}, L^2] = 0.$$

2. Let the three components of $\vec{K}$ be Hermitian operators with the commutation relations:

$$[K_y, K_z] = iK_x, \quad [K_z, K_x] = iK_y, \quad [K_x, K_y] = -iK_z. \tag{4.11.1}$$

No, the minus sign in the last equation is not a typo. (For a more detailed discussion of these generators of the SO(2,1) group, see [6]).

(a) Establish the following relations:

$$[K_z, K_\pm] = \pm K_\pm \text{ for } K_\pm = K_x \pm iK_y; \tag{4.11.2}$$

$$[K_-, K_+] = 2K_z; \tag{4.11.3}$$

$$\text{if} \qquad M = K_z^2 - K_x^2 - K_y^2, \text{ then } M = K_z^2 - K_z - K_+K_-; \tag{4.11.4}$$

$$\left[M, \vec{K}\right] = 0. \tag{4.11.5}$$

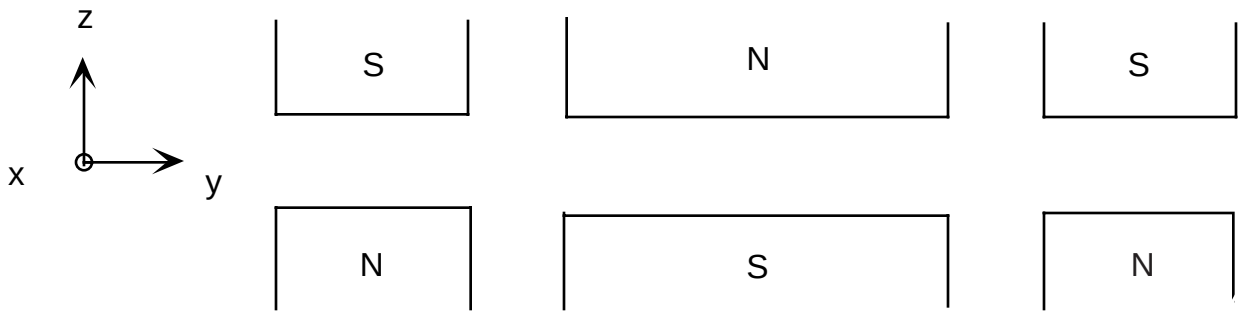
(b) Hence use the raising and lower operators on the common eigenstates of K_z and M to find the possible values of their eigenvalues.

3. The unnormalized wave function of a particle at some instant of time is

$$\Psi(\vec{r}) = (x + y + z)F(x^2 + y^2 + z^2),$$

where F is a given function. Find all the possible outcomes and their associated probabilities that a measurement of the square of the magnitude of the angular momentum L^2 and the z component L_z will yield. Is the state an eigenstate of $\hat{n} \cdot \vec{L}$, where $\hat{n}$ is a unit vector to be determined?

4. In a modified arrangement of the Stern-Gerlach apparatus, three magnets with high field gradients are placed in sequence along the y-axis, as shown in the diagram.



The outer ones are identical. The middle one has the same cross-section in the x-z plane as the others but twice as long in the y direction and reversed in polarity.

(a) Describe the paths of a beam of neutral atoms (neglecting spins) injected along the y direction from the left with $\ell = 1$ for the magnitude of the angular momentum. (See [8]).

(b) Is this apparatus as described above a measuring instrument? (What does it measure?) What is the final state of an atom emerging from the apparatus? What minor additions would you make to the apparatus in order to measure the z component of the magnetic dipole moment distribution among the atoms?

(c) Two identical apparati of the type described above are placed in series with one N-S direction rotated by an angle α about the y-axis relative to the other. A beam of $\ell = 1$ neutral hydrogen atoms (neglecting spin) is injected into the first apparatus. A diaphragm is placed in the middle magnet of the first set such that only one beam of a particular L_z momentum state is allowed through the first apparatus at a time. For each of the three beams, find the probability amplitude in the eigenstates of the momentum component along the N-S direction of the second apparatus. (For a computation of the probability amplitude for a general ℓ, see [2]).

5. **Just to keep the topic of angular momentum physical:**

(a) Compute the field gradient of a meter-long Stern-Gerlach magnet necessary to produce a 1 mm separation at the end of the magnet between the components of a beam of neutral atoms with no spin and with orbital angular momentum $\ell = 1$ incident with kinetic energy of 1000 K.

(b) The ground state of ^{57}Fe (a favorite nucleus for the Mössbauer experiment) has a spin 1/2 ground state. Nuclear magnetic resonance (more about that in the next chapter) gives a change of the resonance frequency of 1.38 MHz at an additional magnetic field of 1 T. Deduce the g-factor for ^{57}Fe.

6. If $\vec{S}$ denotes the spin angular momentum and $S_\pm = S_x \pm iS_y$, show that

$$[S_\pm, S^2] = 0,$$

and hence, show that if $\psi_{\alpha\beta}$ is an eigenstate of S^2 and S_z, then $S_\pm\psi_{\alpha\beta}$ are also eigenstates of S^2 with the same eigenvalue as $\psi_{\alpha\beta}$.

7. Exercises in angular momentum.

(a) Evaluate the matrix elements $\langle\psi_{sm}|\vec{S}|\psi_{sm'}\rangle$ of all three components of the angular momentum for s =1, $\frac{1}{2}$, and $\frac{3}{2}$.

(b) For the eigenstate of L_z with eigenvalue 1 and of L^2 with $\ell = 1$, find its expectation value of L_x and its uncertainty.

(c) Find the eigenstates of L_x with $\ell = 1$ from its matrix representation.

(d) Check the eigenstate of L_x with eigenvalue 1, using the spatial representation in Eq. (4.2.29).

8. For the orbital angular momentum $\vec{L}$, find the expressions for the raising and lowering operators $L_\pm = L_x \pm iL_y$ in terms of the spherical polar coordinates. Use the properties of these raising and lowering operators to find the $\ell = 2$ normalized eigenfunctions for L_z and L^2, given one of them:

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \propto P_2(\cos\theta).$$

9. If the electron of a hydrogen atom is in the $3d$ state, list by appropriate quantum numbers the eigenstates of the z-components of the electron orbital angular momentum and spin. By using angular momentum addition, list by appropriate quantum numbers the eigenstates of J^2 and J_z of the total angular momentum (spin plus orbital).

   Find the component of the magnetic dipole moment along the z-direction in units of the Bohr magnetons of the eigenstate of J^2 and J_z with the largest eigenvalues for a $3d$ electron.

10. In a system of two spin one-half particles, $|\phi_\pm\rangle$ and $|\chi_\pm\rangle$ denote the spin-up and spin-down states of the two particles respectively.

    (a) Show that $|\phi_+\chi_-\rangle$ and $|\phi_-\chi_+\rangle$ are eigenstates of the z-component of the total spin J_z but not of the square of the total momentum J^2.

    (b) Find the 2×2 matrix of J^2 with respect to the two states $|\phi_+\chi_-\rangle$ and $|\phi_-\chi_+\rangle$ and diagonalize it to find the eigenvalues and eigenstates of J^2.

    (c) Why is it not necessary in (b) to consider the matrix elements of J^2 connecting the state $|\phi_+\chi_-\rangle$ or the state $|\phi_-\chi_+\rangle$ to either $|\phi_+\chi_+\rangle$ or $|\phi_-\chi_-\rangle$?

11. A deuteron (^2H) is composed of a proton and a neutron. Let us think of the state of the deuteron as due to the two spin one-half constituent particles moving around each other with a central potential. Let the total angular momentum be

$$\vec{I} = \vec{S}_p + \vec{S}_n + \vec{L},$$

    being the sum of the proton spin, neutron spin and the orbital angular momentum.

    (a) The measured total angular momentum of the deuteron is $i = 1$. Show that the four possible states are:

        i. S_{pz} and S_{nz} parallel with $\ell = 0$,

        ii. S_{pz} and S_{nz} antiparallel with $\ell = 1$,

        iii. S_{pz} and S_{nz} parallel with $\ell = 1$,

iv. S_{pz} and S_{nz} parallel or antiparallel with $\ell = 2$.

(b) The spatial parity of deuteron is determined by studying nuclear reactions involving deuterons to be even. Show that this eliminates the $\ell = 1$ states.

(c) The experimentally measured magnetic dipole moment of the deuteron is $0.8574\mu_N$. By calculating the maximum magnetic dipole moment for the $\ell = 0$ and the maximum magnetic dipole moment $\ell = 2$ states, show that the state of deuteron is $\ell = 0$.

12. Consider angular momentum addition $\vec{J} = \vec{L} + \vec{S}$. $|\ell, s; j, m\rangle \equiv |j, m\rangle$ is an eigenstate respectively of L^2, S^2, J^2, and J_z; while $|\ell, s; m_\ell, m_s\rangle \equiv |m_\ell, m_s)$ denotes an eigenstate respectively of L^2, S^2, L_z, and S_z.

(a) Find the eigenstate $|j = \ell+s, m = \ell+s\rangle$ in terms of $|m_\ell, m_s)$. By means of the lowering operator $J_- = L_- + S_-$ find the eigenstate $|j = \ell + s, m = \ell + s - 1\rangle$ in terms of $|m_\ell, m_s)$.

(b) Hence, find the eigenstate $|j = \ell + s - 1, m = \ell + s - 1\rangle$ in terms of $|m_\ell, m_s)$.

(c) Explain briefly how to use the lowering operator J_- to construct in principle the eigenstate $|j, m\rangle$ in terms of $|m_\ell, m_s)$.

13. Find the eigenvalues and eigenstates of J^2 and J_z of the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ for $\ell = 1$ and $s = \frac{1}{2}$ in terms of the eigenstates of L^2, S^2, L_z and S_z. This problem has a number of applications, e.g. the "holes" in the valence band of a III-V semiconductor [9].

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Chapter 5 Contents

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Chapter 5

Two-State Systems

> *. . . wherever the road divided, there were sure to be two finger posts pointing the same way, one marked 'to Tweedledum's House,' and the other 'to the House of Tweedledee.'*
>
> *"I do believe," said Alice at last, "that they live in the same house!. . . "*
>
> — Through the Looking-Glass *by Lewis Carroll.*

5.1 The general two-state system

A thorough study of the most general case of a two-state system is an excellent application of the quantum theory presented in the first two chapters. Because the most general two-state system is isomorphous to the simplest case of the angular momentum states, $s = \frac{1}{2}$, the study of the dynamics can be very explicit. It also means that the theory of spin $\frac{1}{2}$ dynamics can be applied to a long list of important systems, even though quite frequently the two-state system is just an approximation to the complete system. The quantum physics revealed has a truly amazing reach. The study yields a graphic description of the quantum dynamics and the salient features of the dissipation. This is an invaluable aid to understanding the quantum phenomena.

5.1.1 States and observables

Consider a quantum system any of whose properties on measurement yields only two values (which could be equal) with two associated eigenstates. Take any pair of such states as an orthonormalized basis set, denoted by $|+\rangle$ and $|-\rangle$. Or, if two energy eigenstates of a system are well isolated from the rest of the states for some relevant properties, we may consider only these two states as the basis set for a model system.

A physical observable A is represented by a 2×2 matrix:

$$\begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix}. \tag{5.1.1}$$

Since the observable and, therefore, its matrix representation must be Hermitian, the diagonal elements A_{11} and A_{22} are real and the off-diagonal elements are related by

$$A_{12} = A_{21}^*. \tag{5.1.2}$$

The observable is completely determined by four real numbers. The matrix of A can be rearranged as

$$\begin{aligned} A &= \begin{bmatrix} \frac{1}{2}(A_{11}+A_{22}) & 0 \\ 0 & \frac{1}{2}(A_{11}+A_{22}) \end{bmatrix} + \begin{bmatrix} \frac{1}{2}(A_{11}-A_{22}) & 0 \\ 0 & -\frac{1}{2}(A_{11}-A_{22}) \end{bmatrix} \\ &+ \begin{bmatrix} 0 & \Re\{A_{21}\} \\ \Re\{A_{21}\} & 0 \end{bmatrix} + \begin{bmatrix} 0 & -i\Im\{A_{21}\} \\ i\Im\{A_{21}\} & 0 \end{bmatrix}. \end{aligned} \tag{5.1.3}$$

Thus any observable can be expressed as a linear combination of four 2×2 matrices:

$$\begin{aligned} A &= \alpha_0 I + \alpha_x \sigma_x + \alpha_y \sigma_y + \alpha_z \sigma_z \\ &= \alpha_0 + \vec{\alpha} \cdot \vec{\sigma}. \end{aligned} \tag{5.1.4}$$

The unit matrix and three Pauli spin matrices are defined as:

$$I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{5.1.5}$$

The unit matrix I is frequently replaced by a scalar with the multiplication of a unit matrix understood, as in Eq. (5.1.4). The four real numbers α_0, α_x, α_y, α_z can then equally well be used to characterize the observable A.

5.1.2 The spin one-half language

An electron state represents both orbital and spin motion. Let us ignore the spatial dependence and concentrate on the spin dependence for now. Then, for the electron, or any other spin $\frac{1}{2}$ particle, there are two possible eigenstates of S^2 and S_z: the spin-up state $|+\rangle$ and the spin-down state $|-\rangle$. Thus,

$$S^2|\pm\rangle = \frac{3}{4}|\pm\rangle, \tag{5.1.6}$$

$$S_z|\pm\rangle = \pm\frac{1}{2}|\pm\rangle. \tag{5.1.7}$$

With $|\pm\rangle$ as the basis set, the matrix representation of the spin in the $s = 1/2$ subspace is:

$$\vec{S} = \frac{1}{2}\vec{\sigma}, \quad S^2 = \frac{3}{4}I. \tag{5.1.8}$$

Thus, by accepting the results of the Stern-Gerlach experiment with the neutral atoms as giving two possible states for an intrinsic dynamic observable for the electron, we can construct the spin operators as the only possible observables. To relate the spin to an angular-momentum like property, the electron spin further possesses, unlike other two-state systems, the relation of the spin to the magnetic dipole momentum, and, hence, similar dynamics to the orbital angular momentum in the presence of a magnetic field.

5.1.3 Properties of the Pauli matrices

Some simple properties of the Pauli matrices are:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1. \tag{5.1.9}$$

$$\sigma^2 = \begin{bmatrix} 3 & 0 \\ 0 & 3 \end{bmatrix}. \tag{5.1.10}$$

$$\vec{\sigma} \times \vec{\sigma} = 2i\vec{\sigma} \tag{5.1.11}$$

$$\sigma_x\sigma_y = -\sigma_y\sigma_x = i\sigma_z, etc. \tag{5.1.12}$$

$$\sigma_x\sigma_y\sigma_z = i. \tag{5.1.13}$$

On the right-hand side of the last equation, we have used the convention that the scalar is understood to represent the scalar times the unit matrix. We have also adopted the notation convention of the lazy: we use the symbols for the operator and for its matrix representation in the eigenstates of S_z.

5.1.4 Mapping the two-state system to the spin one-half particle

In any two-state system, two orthogonal states are sufficient to form a complete basis set. Any state of the system is a linear combination of the two states forming the basis. The state vector is a vector in a two dimensional vector space. Any physical observable of

the system is represented by a 2×2 matrix. The two-state systems all have the unifying features of the same formal structure of the matrix algebra of the two dimensional vector space for the vector representation of the state and the matrix representation of the physical observable. Thus, all the two-state systems are said to be isomorphic to the spin 1/2 system. The physical differences among the various two-state systems have to be found in their basis states or in the coupling of their observables to external stimuli, such as the electromagnetic fields. Quite commonly, the spin description and terminology are used for other two-state systems whose properties may have nothing to do with angular momentum at all. The distinction from the true spin is often made by the term "pseudo-spin". The importance of this chapter lies not only in the simplicity which gives us a graphic illustration of the theory of quantum mechanics, but also in the unified study of the prototype of many important physical and chemical phenomena.

The most general form of the two-state Hamiltonian is, by Eq. (5.1.4),

$$H = E_0 + \vec{B}' \cdot \vec{\sigma}, \tag{5.1.14}$$

completely determined by four real numbers E_0, B'_x, B'_y, B'_z. For the spin $\frac{1}{2}$ particle, E_0 could be the energy of due to its orbital motion. The physical meaning of $\vec{B}'$ is gleaned from the extension of the classical Hamiltonian of the magnetic dipole moment to the spin $\frac{1}{2}$ case:

$$H = E_0 - \vec{B} \cdot \vec{\mu}, \tag{5.1.15}$$

where $\vec{B}$ is the external magnetic field. Thus, $B' = \mu B$, where μ is the magnetic dipole moment of spin 1/2 from $\vec{\mu} = \mu\vec{\sigma}$. For a nucleon spin, μ is positive,

$$\mu = \frac{g_s \mu_N}{2}, \tag{5.1.16}$$

with $\mu_N = e\hbar/2m_p$ for the proton mass m_p. For the electron spin, μ is negative,

$$\mu = -\mu_B, \tag{5.1.17}$$

where we have taken the g-factor to be 2.

5.1.5 Spin-1/2 Hamiltonian in a magnetic field – redux

In the non-relativistic limit of a particle, the classical kinetic energy is given by

$$T = \frac{p^2}{2m}. \tag{5.1.18}$$

The quantization procedure consists in replacing $\vec{p}$ by the momentum operator $\vec{P}$ with a spatial representation $-i\hbar\nabla$ acting on a wave function $\psi(\vec{r})$. To include the spin-1/2 dynamics, the state vector is written in the basis set of the eigenstates of the spin component S_z:

$$\psi = \begin{bmatrix} \psi_+ \\ \psi_- \end{bmatrix}. \tag{5.1.19}$$

The operator equation,

$$(\vec{\sigma}\cdot\vec{P})^2 = P^2, \tag{5.1.20}$$

can be established by choosing the z-axis to be along the momentum vector $\vec{P}$, leading to the kinetic energy operator,

$$\begin{aligned} T &= \frac{P^2}{2m}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \frac{1}{2m}P_z\sigma_z\sigma_z P_z \\ &= (\vec{P}\cdot\vec{\sigma})\frac{1}{2m}(\vec{\sigma}\cdot\vec{P}), \end{aligned} \tag{5.1.21}$$

from the vector product invariance. Alternatively, it follows from the relation [see Problem 5.1 (c)]

$$(\vec{A}\cdot\vec{\sigma})(\vec{B}\cdot\vec{\sigma}) = \vec{A}\cdot\vec{B} + i(\vec{A}\times\vec{B})\cdot\vec{\sigma}, \tag{5.1.22}$$

where $\vec{\sigma}$ is a vector of the three Pauli matrices and $\vec{A}$ and $\vec{B}$ are two vectors of three operators.

In the presence of a vector potential $\vec{A}$, the momentum $\vec{P}$ is replaced by $\vec{P} - q\vec{A}$ for the particle with charge q. The kinetic energy operator becomes

$$\begin{aligned} T &= \vec{\sigma}\cdot(\vec{P}-q\vec{A})\frac{1}{2m}\vec{\sigma}\cdot(\vec{P}-q\vec{A}) \\ &= \frac{1}{2m}(\vec{P}-q\vec{A})^2 + \frac{i}{2m}\vec{\sigma}\cdot(\vec{P}-q\vec{A})\times(\vec{P}-q\vec{A}) \\ &= \frac{1}{2m}(\vec{P}-q\vec{A})^2 - \frac{q\hbar}{2m}\vec{\sigma}\cdot\vec{B}, \end{aligned} \tag{5.1.23}$$

where we have used the relation (5.1.22), $\nabla \times \vec{A} = \vec{B}$, and

$$[\vec{P}, f(\vec{R})] = -i\hbar \nabla f(\vec{r}). \tag{5.1.24}$$

Notice that, for the electron, this gives the correct g factor of 2 for the energy of the spin magnetic moment in a magnetic field. This is a consequence of the spin transformation properties and not of relativity.

5.1.6 Examples of two-state systems

We list here examples, besides the electron spin states, and discuss some of them in the following sections and some in the problems:

1. All spin $\frac{1}{2}$ particles such as neutron and proton.

2. The proton mass is 938.3 MeV/c^2 and neutron 939.6 MeV/c^2, differing by about 1 part in 10^3. In the consideration of the nuclear structure consisting of protons and neutrons, it is convenient to think of the proton and the neutron as two possible charged states of a particle called the nucleon: when it is charged, it is a proton; when it is uncharged, it is a neutron. This property of the nucleon is called the isotopic spin (isospin in short). This terminology is an example of analogy with the spin $\frac{1}{2}$ system because of the two level nature and not because of any other spin or angular momentum property. The strong interaction between the two nucleons conserves the total isospin. This leads to some useful applications, e.g., Problems 14 and 15. Why, then, does one find a mixed neutron and proton state in nature? The weak electromagnetic interaction breaks the isospin symmetry leading to two stable charged states and slightly different masses.

3. The dynamics of an atom under the influence of a monochromatic and coherent radiation field resonant with two levels in the atom is essentially represented by the two-level atom model. Thus, quantum optics was stimulated by a flow of concepts from spin resonance.

4. Molecular and solid-state systems which have two low-lying energy states close to each other but far away from the other excited states. Then, a two-state system

is an excellent approximation for the low-energy properties involving mostly these two states. For instance,

(a) The covalent bond in the ionized hydrogen molecule, H_2^+. The molecule consists of two protons and one electron. Neglect the motion of the heavier protons. If the protons are very far apart, the electron can be in the ground state of the hydrogen atom provided by either proton, slightly modified by the presence of the other Coulomb potential. Thus, the electron is in a two-state system. As the protons move closer towards their equilibrium separation, the ground state wave function of the electron around one proton begins to overlap substantially with the other. The number of possible states remains two, but the lowest state is lower in energy than the ground state of the atom, thus providing binding of the molecule. This is a simple prototype of the covalent bond provided by two electrons binding two atoms into a diatomic molecule.

(b) An atom in a potential with two equilibrium positions, such as the hydrogen bond and the nitrogen atom in the ammonia molecule, NH_3. The nitrogen atom can be at either the position N_1 or N_2 indicated in Fig. 5.1.

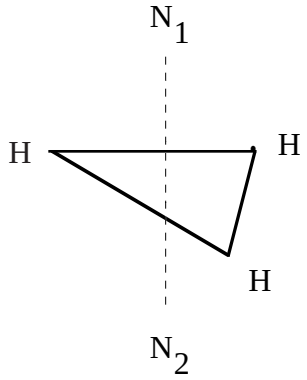

Figure 5.1: The ammonia molecule.

5. The polarization states of a photon. In a classical electromagnetic wave, the propagation vector $\vec{k}$, the electric vector $\vec{E}$, and the magnetic vector $\vec{B}$ form a right-handed orthogonal triad. The electric field can thus be used to specify the polarization state of the wave. It is a linear combination of two orthogonal vectors (say, along the x and y axis) normal to $\vec{k}$ (along the z-axis). When the intensity

of the electromagnetic wave is so low that it represents a photon, the polarization state of the photon is then a linear combination of the two states corresponding to polarization in the x and y direction respectively. Experiments can be carried out with polaroid films and birefringence crystals.

6. The "strangeness oscillation" of kaons was an important step in the history of elementary particles and can be understood by the two-state quantum theory without relativity. From the decay of the long-lived state, the CP violation (breach of the charge-conjugation and parity invariance) was first found.

5.2 Energy Eigenstates of Spin $\frac{1}{2}$ Particle

5.2.1 Magnetic field splitting

Recall that in the spin $\frac{1}{2}$ system, the basis set chosen consists of the spin up state χ_+ and the spin down state χ_- which are the eigenstates of σ_z with eigenvalues +1 and -1, respectively. In the absence of a magnetic field, these two states are also energy eigenstates with the same energy E_0. In the presence of a magnetic field $\vec{B}$, choose, for convenience, the z-axis along the field direction. From Eq. (5.1.14), the Hamiltonian is

$$H = E_0 + \mu_B B_z \sigma_z = \begin{bmatrix} E_0 + \mu_B B & 0 \\ 0 & E_0 - \mu_B B \end{bmatrix}. \tag{5.2.1}$$

Since the matrix is already diagonal, it means that $\chi_\pm$ remain the energy eigenstates with energy values $E_0 \pm \mu_B B$. The magnetic field splits the doubly degenerate spin states into two energy levels with a spacing $2\mu_B B$.

5.2.2 Magnetic field in a general direction

Sometimes it is necessary not to choose the z-axis along the direction of the magnetic field $\vec{B}$. Then, the Hamiltonian is

$$H = \begin{bmatrix} E_0 + \mu_B B_z & \mu_B(B_x - iB_y) \\ \mu_B(B_x + iB_y) & E_0 - \mu_B B_z \end{bmatrix}. \tag{5.2.2}$$

The diagonalization of this 2×2 matrix is straightforward. Nonetheless we record here a method with which the eigenvalues and eigenstates of a general two-state Hamiltonian can be easily found. Expressing the magnetic field in the spherical polar coordinates. Let

the magnetic field $\vec{B}$ be in the direction at an angle θ with the z-axis and its projection in the x-y plane be at an angle ϕ with the x-axis. Then,

$$\begin{aligned} B_x &= B\sin\theta\cos\phi, \\ B_y &= B\sin\theta\sin\phi, \\ B_z &= B\cos\theta. \end{aligned} \tag{5.2.3}$$

The Hamiltonian becomes

$$H = E_0 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \mu_B B \begin{bmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{bmatrix}. \tag{5.2.4}$$

We need only diagonalize the second matrix on the right and add E_0 to the eigenvalues. The energy values are

$$E = E_0 \pm \mu_B B, \tag{5.2.5}$$

independent of the direction of the z-axis, as they should be. The corresponding eigenstates $\psi_\pm$ are given by

$$[|\psi_+\rangle\ |\psi_-\rangle] = [|\chi_+\rangle\ |\chi_-\rangle] \begin{bmatrix} a_{++} & a_{+-} \\ a_{-+} & a_{--} \end{bmatrix}, \tag{5.2.6}$$

with the coefficients a_{ij} given by,

$$\begin{aligned} \frac{a_{++}}{a_{-+}} &= \frac{\sin\theta e^{-i\phi}}{1-\cos\theta} = \frac{2\sin\frac{1}{2}\theta\cos\frac{1}{2}\theta e^{-i\phi}}{2\sin^2\frac{1}{2}\theta} \\ &= \frac{\cos\frac{1}{2}\theta}{\sin\frac{1}{2}\theta} e^{-i\phi}. \end{aligned} \tag{5.2.7}$$

Let us choose the phase of the wave function ψ_+ such that

$$a_{++} = \cos\frac{1}{2}\theta e^{-i\frac{1}{2}\phi}. \tag{5.2.8}$$

Then,

$$a_{-+} = \sin\frac{1}{2}\theta e^{+i\frac{1}{2}\phi}. \tag{5.2.9}$$

Similarly,

$$a_{+-} = -\sin\frac{1}{2}\theta e^{-i\frac{1}{2}\phi}, \tag{5.2.10}$$

$$a_{--} = \cos\frac{1}{2}\theta e^{+i\frac{1}{2}\phi}. \tag{5.2.11}$$

In the presence of a magnetic field $\vec{B}$ in the direction (θ, ϕ), the energy eigenstates are related to the spin states along the z-axis by the unitary matrix

$$a = \begin{bmatrix} \cos\frac{\theta}{2}e^{-i\frac{\phi}{2}} & -\sin\frac{\theta}{2}e^{-i\frac{\phi}{2}} \\ \sin\frac{\theta}{2}e^{i\frac{\phi}{2}} & \cos\frac{\theta}{2}e^{i\frac{\phi}{2}} \end{bmatrix}. \tag{5.2.12}$$

5.2.3 Transformation matrix

The energy eigenstates $\psi_\pm$ are also the spin-up and spin-down states of $S_{z'}$. They are related to the eigenstates of S_z by Eq. (5.2.6). By the definition of the transformation in Sec. 2.2,

$$S[|\psi_+\rangle\ |\psi_-\rangle] = [|\psi_+\rangle\ |\psi_-\rangle] \begin{bmatrix} S_{++} & S_{+-} \\ S_{-+} & S_{--} \end{bmatrix}, \tag{5.2.13}$$

the transformation matrix is $S = a^\dagger$. In other words, the old spin states are related to the new ones by

$$[|\chi_+\rangle\ |\chi_-\rangle] = [|\psi_+\rangle\ |\psi_-\rangle] \begin{bmatrix} \cos\frac{\theta}{2}e^{i\frac{\phi}{2}} & \sin\frac{\theta}{2}e^{-i\frac{\phi}{2}} \\ -\sin\frac{\theta}{2}e^{i\frac{\phi}{2}} & \cos\frac{\theta}{2}e^{-i\frac{\phi}{2}} \end{bmatrix}. \tag{5.2.14}$$

Here is a case where the operator S and the matrix representation S_{mx} occur in the same equation and have to be distinguished. The representation of a state $|\Psi\rangle$ in the old and new basis given by

$$|\Psi\rangle = [|\chi_+\rangle\ |\chi_-\rangle] \begin{bmatrix} c_+ \\ c_- \end{bmatrix} = [|\psi_+\rangle\ |\psi_-\rangle] \begin{bmatrix} c'_+ \\ c'_- \end{bmatrix}, \tag{5.2.15}$$

has the coefficients related by the transformation matrix as $a' = Sa$ or:

$$\begin{bmatrix} c'_+ \\ c'_- \end{bmatrix} = \begin{bmatrix} \cos\frac{\theta}{2}e^{i\frac{\phi}{2}} & \sin\frac{\theta}{2}e^{-i\frac{\phi}{2}} \\ -\sin\frac{\theta}{2}e^{i\frac{\phi}{2}} & \cos\frac{\theta}{2}e^{-i\frac{\phi}{2}} \end{bmatrix} \begin{bmatrix} c_+ \\ c_- \end{bmatrix}. \tag{5.2.16}$$

5.3 Transformation and rotation

We have a couple of agenda in this section. One is to find the basis transformation when more than just the new direction of the z axis is specified. The other is to examine the relation between the rotation of the basis and the rotation of a state. This issue is general but can be treated explicitly in the two-state case.

Note that in the transformation matrix in the last section, there is an arbitrariness due to the arbitrary choice of the overall phase for the coefficients of either energy eigenstate. For example, an equally valid choice for the eigenstates is

$$a = \begin{bmatrix} \cos\frac{1}{2}\theta & -\sin\frac{1}{2}\theta e^{-i\phi} \\ \sin\frac{1}{2}\theta e^{i\phi} & \cos\frac{1}{2}\theta \end{bmatrix}. \tag{5.3.1}$$

This arbitrariness can be removed if the new field direction is achieved by a rotation from the field direction along z, thus specifying also the directions of the other two axes.

In Section 4.2.4, a procedure is given for constructing the transformation matrix relating the angular momentum eigenstates for one set of Cartesian axes to the eigenstates for a rotated set of axes. Such a procedure, valid for integer values of ℓ cannot be used for the half-integer spin states since the latter cannot be expressed in terms of the position coordinates and do not transform like the spherical harmonics. We consider here an evaluation of the rotation matrix for the spin 1/2 system and leave the general case till a later chapter.

A deeper subtext is the development of the rotational operators as symmetry operations on the states whose generators are Hermitian and, therefore, possible observables. This gives us a method to construct new observables on different systems which have the same transformation properties. The two-state system is a clear example, where the Paul matrices will be shown to be the generators of the rotations and are related to the physical properties which can be unrelated to the position and momentum variables.

5.3.1 Transformation matrix in terms of rotational matrices

From Sec. 4.10.3 (d), the rotation operator through an angle α about an axis along the unit vector $\vec{n}$ is $\exp(-i\alpha\vec{n}\cdot\vec{L}/\hbar)$. It was derived from the wave-function representation. We now extend its validity from the orbital angular momentum $\vec{L}$ to the general spin $\vec{S}$. For spin one-half, the rotation operator is

$$R(\alpha,\vec{n}) = e^{-i\frac{\alpha}{2}\vec{n}\cdot\vec{\sigma}}. \tag{5.3.2}$$

From Problem 1 (c),

$$(\vec{n}\cdot\vec{\sigma})^2 = 1. \tag{5.3.3}$$

The infinite series expansion of the rotational operator leads to

$$\begin{aligned} R(\alpha,\vec{n}) &= \sum_{k=0}^{\infty}\frac{1}{k!}(-i\frac{\alpha}{2})^k(\vec{n}\cdot\vec{\sigma})^k \\ &= \sum_{k=0}^{\infty}\frac{1}{(2k)!}(-i\frac{\alpha}{2})^{2k}(\vec{n}\cdot\vec{\sigma})^{2k}+\sum_{k=0}^{\infty}\frac{1}{(2k+1)!}(-i\frac{\alpha}{2})^{(2k+1)}(\vec{n}\cdot\vec{\sigma})^{(2k+1)} \\ &= \sum_{k=0}^{\infty}\frac{1}{(2k)!}(-i\frac{\alpha}{2})^{2k}+\sum_{k=0}^{\infty}\frac{1}{(2k+1)!}(-i\frac{\alpha}{2})^{(2k+1)}(\vec{n}\cdot\vec{\sigma}) \\ &= \cos\left(\frac{\alpha}{2}\right)-i\sin\left(\frac{\alpha}{2}\right)(\vec{n}\cdot\vec{\sigma}), \end{aligned} \tag{5.3.4}$$

where we have split the exponential series into an even power series and an odd power series, used Eq. (5.3.3), and then re-summed the two series to cosine and sine. The matrix representation of the rotation operator in the basis of the eigenstates of S_z and S^2 is

$$\mathcal{D}(R(\alpha,\vec{n})) = \begin{bmatrix} \cos(\frac{\alpha}{2})-in_z\sin(\frac{\alpha}{2}) & -i(n_x-in_y)\sin(\frac{\alpha}{2}) \\ -i(n_x+in_y)\sin(\frac{\alpha}{2}) & \cos(\frac{\alpha}{2})+in_z\sin(\frac{\alpha}{2}) \end{bmatrix}. \tag{5.3.5}$$

One rotation which brings the z-axis to point in the (θ,ϕ) direction is a combination of a rotation about the z-axis through the azimuthal angle ϕ and then the rotation through an angle θ about an axis normal to the plane containing the two field axes, i.e., in the xy-plane at an angle $\frac{\pi}{2}+\phi$ from the x-axis, or,

$$\vec{n_2} = (-\sin\phi, \cos\phi, 0). \tag{5.3.6}$$

Thus, the first rotation is given by

$$\mathcal{D}(R(\phi,\hat{z})) = \begin{bmatrix} e^{-i\phi/2} & 0 \\ 0 & e^{i\phi/2} \end{bmatrix}, \tag{5.3.7}$$

and the second rotation is given by

$$\mathcal{D}(R(\theta,\vec{n_2})) = \begin{bmatrix} \cos\frac{\theta}{2} & -\sin\frac{\theta}{2}e^{-i\phi} \\ \sin\frac{\theta}{2}e^{i\phi} & \cos\frac{\theta}{2} \end{bmatrix}. \tag{5.3.8}$$

Note that the matrix (5.3.1) corresponds to the second rotation alone. The resultant rotation is the product

$$\mathcal{D}(R) = \mathcal{D}(R(\theta,\vec{n_2}))\mathcal{D}(R(\phi,\hat{z})) = \begin{bmatrix} \cos\frac{\theta}{2}e^{-i\frac{\phi}{2}} & -\sin\frac{\theta}{2}e^{-i\frac{\phi}{2}} \\ \sin\frac{\theta}{2}e^{i\frac{\phi}{2}} & \cos\frac{\theta}{2}e^{i\frac{\phi}{2}} \end{bmatrix}. \tag{5.3.9}$$

This result is the same as the matrix a in Eq. (5.2.12).

Since the rotation operator rotates the spin-up and down states from the z-axis to the (θ, ϕ) direction, the states become the spin-up and down states along the new direction:

$$[|\psi_+\rangle \ |\psi_-\rangle] = R[|\chi_+\rangle \ |\chi_-\rangle] = [|\chi_+\rangle \ |\chi_-\rangle]\mathcal{D}(R). \tag{5.3.10}$$

The transformation matrix for the state vector is

$$S(R) = \mathcal{D}^\dagger(R) = a^\dagger = S, \tag{5.3.11}$$

the same as the transformation matrix in Eq. (5.2.14).

Note that in the case just considered the state vector is kept fixed. The transformation matrix gives the relation between its coefficients in the transformed basis set to those in the old basis set. Because the state vector is not changed, the transformation is sometimes said to be passive. Now we ask a different question: what is the state vector after it has been rotated by R, i.e., find in terms of the fixed basis set $|\chi_+\rangle, |\chi_-\rangle$

$$|\Psi^r\rangle = R|\Psi\rangle. \tag{5.3.12}$$

The transformation is said to be active. In order to avoid confusion, we shall refer to the former (passive transformation) as the transformation of the basis set and refer to the latter (active transformation) as the symmetry operation on the state or, in this case, the rotation of the state. Then, the representation of the rotated state about the original basis set is, from Eq. (5.3.12),

$$|\Psi^r\rangle = [|\chi_+\rangle \ |\chi_-\rangle]\mathcal{D}(R) \begin{bmatrix} \langle\chi_+|\Psi\rangle \\ \langle\chi_-|\Psi\rangle \end{bmatrix}. \tag{5.3.13}$$

The coefficients are related by

$$\begin{bmatrix} \langle\chi_+|\Psi^r\rangle \\ \langle\chi_-|\Psi^r\rangle \end{bmatrix} = \mathcal{D}(R) \begin{bmatrix} \langle\chi_+|\Psi\rangle \\ \langle\chi_-|\Psi\rangle \end{bmatrix} = \begin{bmatrix} \cos\frac{1}{2}\theta e^{-i\frac{1}{2}\phi} & -\sin\frac{1}{2}\theta e^{-i\frac{1}{2}\phi} \\ \sin\frac{1}{2}\theta e^{i\frac{1}{2}\phi} & \cos\frac{1}{2}\theta e^{i\frac{1}{2}\phi} \end{bmatrix} \begin{bmatrix} \langle\chi_+|\Psi\rangle \\ \langle\chi_-|\Psi\rangle \end{bmatrix} \tag{5.3.14}$$

Note the difference between the transformation matrix (5.2.16) and the rotation matrix (5.3.14), one being the Hermitian conjugate of the other.

5.3.2 Some special rotations

(1) It takes a 4π rotation to bring a state back to its original self. Suppose that the z-axis is kept fixed and that the x and y-axes are rotated through 360°. Then, $\theta = 0$ and

$\phi = 2\pi$. From Eq. (5.3.1) or Eq. (5.2.12),

$$|\psi_\pm\rangle = -|\chi_\pm\rangle. \tag{5.3.15}$$

The spin $\frac{1}{2}$ wave functions change sign, but the probability is the same. The sign change may be regarded as a phase change of π. This is an example where the overall phase of a wave function cannot be measured. However, if it is made to interfere with another part of the wave function, such as in the neutron interference setup of Problem 17, the phase difference between a part which is not changed and a part which is changed may be detected. The experiment was first suggested by Herbert J. Bernstein and performed by S.A. Werner et al.

(2) The z′-axis points opposite the z-axis. Then, $\theta = \pi$ and $\phi = 0$. From Eq. (5.3.8),

$$|\psi_+\rangle = |\chi_-\rangle, \tag{5.3.16}$$

$$|\psi_-\rangle = -|\chi_+\rangle. \tag{5.3.17}$$

The spin-up and down states are interchanged as expected but one of the states also changes sign.

5.4 Spin Precession

When a spin $\frac{1}{2}$ particle is placed in a magnetic field, the energy eigenstates are the spin-up and spin-down states in the direction of the field. If the particle is in one of these states, it will stay in the same state forever, provided it is well isolated. Now we wish to find the time development of the spin state if the initial state is known and is not necessarily in one of the energy eigenstates.

For convenience, consider the electron and measure energy from E_0. Let the z-axis be along the magnetic field $\vec{B}$. The spin up and down states $\chi_\pm$ are also the energy eigenstates. Suppose that at $t = 0$, the spin points in the θ, ϕ direction with respect to the chosen axes. This is putting it in a picturesque way. To be precise, we mean that the initial state of the particle is in the spin-up eigenstate of the component of spin $\vec{S}$ along the θ, ϕ direction. From Eq. (5.2.6) and Eq. (5.2.12) the spin state of the electron is at

$t = 0$,

$$|\Psi(0)\rangle = |\chi_+\rangle \cos\frac{\theta}{2} e^{-i\frac{\phi}{2}} + |\chi_-\rangle \sin\frac{\theta}{2} e^{i\frac{\phi}{2}}. \tag{5.4.1}$$

Since $\chi_\pm$ are also energy eigenstates in the presence of the field $\vec{B}$, the state at time t is

$$|\Psi(t)\rangle = |\chi_+\rangle \cos\frac{\theta}{2} e^{-i\frac{\phi}{2} - i\mu_B Bt/\hbar} + |\chi_-\rangle \sin\frac{\theta}{2} e^{i\frac{\phi}{2} + i\mu_B Bt/\hbar}, \tag{5.4.2}$$

where $\pm\mu_B B$ are the energy values of $\chi_\pm$. Notice that the wave function at time t has exactly the same form as at $t = 0$ if ϕ is changed to $\phi + \omega_0 t$, where

$$\omega_0 = 2\mu_B B/\hbar. \tag{5.4.3}$$

Thus, the state of the particle, $|\Psi(t)\rangle$, is the spin-up state along the direction θ, $\phi + \omega_0 t$.

When the particle is in the spin-up state of the component of the spin along a certain direction, as a shorthand and as a helpful mental picture we say and think that the spin vector of the particle is pointing in that direction. Thus, the dynamics of the spin 1/2 state may be traced on the unit sphere, known as the Bloch sphere, in honor of Felix Bloch's pioneering work on spin dynamics, which included the Bloch equation in Problem 4. Note that this is not at all the same picture as the one described in the vector model. If the spin initially points at an angle θ from the z-axis, the angle of the spin vector remains the same at all times. The angle ϕ, which its (classical) projection makes with the x-axis, will increase at a constant rate ω_0. The spin vector precesses about the z-axis, which is the direction of the magnetic field, with a constant angular frequency ω_0.

$$\begin{aligned} 2\mu_B/\hbar &= 1.8 \times 10^{11}\text{sec}^{-1}\text{tesla}^{-1} \\ &= 2.8 \times 10^{10}\text{hertz tesla}^{-1} \\ &= 1.8 \times 10^{7}\text{sec}^{-1}\text{gauss}^{-1}. \end{aligned} \tag{5.4.4}$$

For a field of about 100 gauss, the precession frequency is $2 \times 10^9 \text{sec}^{-1}$ or about 10^8 Hz, which is in the range of the microwave frequencies.

5.4.1 Spin flip

If we know the direction of a spin, we can in principle flip it through 180° (changing it from a spin-up state in that direction to a spin-down state) by turning on a field B at right angles to the spin for a time π/ω_0, i.e., half a precession cycle, and then turning the field off (known as the π-pulse).

5.5 Magnetic Resonance

A uniform static magnetic field B_0 along the z-axis will split the spin-up and spin-down states' energy apart with a gap $2\mu_B B_0$. At low enough temperatures, the electron will stay in the lower energy state, i.e., the spin-down state. Now supply the system with energy from an electromagnetic wave of frequency ω. If ω is equal to the precession frequency, i.e.,

$$\omega = \omega_0 = 2\mu_B B_0/\hbar, \tag{5.5.1}$$

the electron can absorb a photon of energy $\hbar\omega$ and get excited to the higher energy state, i.e., the spin-up state. This absorption of the electromagnetic energy at a particular frequency is called the magnetic resonance.

The magnetic resonance can also be described in terms of the time dependent picture developed in the last two sections. When the field B_0 is applied to the system, the electron spin will in general be at an angle with the field direction. The spin will, therefore, precess about the field with frequency ω_0. Now apply a small circularly polarized rf field with the magnetic field in the plane at right angles to the static field B_0. If the frequency of the rf field is in resonance with the precession rate, the rf magnetic field vector is fixed in the rotating frame of the spin vector. The rf field can then rotate the spin vector. How this secondary precession leads to a transition between two spin states is studied next.

5.5.1 Transition probability

We have a qualitative picture of magnetic resonance and also the resonance condition (5.5.1). In principle, we know how to obtain the time dependence of the transition of the spin-1/2 particle from the spin-down state to the spin-up state. In this subsection,

we study the case of the weak perturbing field (compared to the static field producing the energy splitting) with a broad bandwidth which yields a quantitative account of the probability of transition. In the next section, we shall study by contrast the case of a strong perturbing oscillating field with a narrow frequency spectrum.

Let the oscillating magnetic field be perpendicular to the static field $\vec{B}_0$, thus:

$$\begin{aligned} B_x &= b\cos\omega t, \\ B_y &= b\sin\omega t, \\ B_z &= B_0. \end{aligned} \tag{5.5.2}$$

We have chosen the oscillating field to be right-handed circularly polarized for clarity of exposition. The justification of this term being dominant in near-resonance condition is given below. The oscillating field which supplies energy to the electron is assumed to be small compared with the static field: $b \ll B_0$.

The Hamiltonian of the electron in the presence of the static field $\vec{B}_0$ is

$$H_0 = \begin{bmatrix} \mu_B & B_0 & 0 & \\ 0 & & -\mu_B & B_0 \end{bmatrix}. \tag{5.5.3}$$

The oscillating field provides a perturbation on the Hamiltonian,

$$H_1 = \begin{bmatrix} 0 & \mu_B b e^{-i\omega t} \\ \mu_B b e^{i\omega t} & 0 \end{bmatrix}. \tag{5.5.4}$$

The total Hamiltonian of the electron is the sum

$$H = H_0 + H_1. \tag{5.5.5}$$

The matrix representations above refer to the basis set of the spin up and down states $|\chi_\pm\rangle$ along the z-axis, i.e., the direction of the static field $\vec{B}_0$.

Let the state of the electron spin at time t be

$$|\Psi(t)\rangle = |\chi_+\rangle a_+(t) + |\chi_-\rangle a_-(t). \tag{5.5.6}$$

The Schrödinger equation

$$i\hbar\frac{\partial|\Psi\rangle}{\partial t} = H|\Psi\rangle, \tag{5.5.7}$$

can easily be written in matrix form by noting that $|\Psi(t)\rangle$ is represented by a column vector and H by a matrix, and, thus,

$$i\hbar\frac{da_+}{dt} = H_{++}a_+ + H_{+-}a_-, \tag{5.5.8}$$

$$i\hbar\frac{da_-}{dt} = H_{-+}a_+ + H_{--}a_-. \tag{5.5.9}$$

The solution of the Schrödinger equation in either form is facilitated by the transformation to the interaction representation for the state,

$$|\Psi(t)\rangle = e^{-iH_0t/\hbar}|\Phi(t)\rangle, \tag{5.5.10}$$

and for the observable A,

$$\hat{A}(t) = e^{iH_0t/\hbar}\, A\, e^{-iH_0t/\hbar}. \tag{5.5.11}$$

If there were no perturbation ($H_1 = 0$), then $|\Phi(t)\rangle$ would be time independent and the observable would be in the Heisenberg representation. The interaction representation simplifies the Schrödinger equation in the presence of the perturbation to

$$i\hbar\frac{\partial|\Phi(t)\rangle}{\partial t} = \hat{H}_1(t)|\Phi(t)\rangle, \tag{5.5.12}$$

In the matrix representation, if $c_\pm(t)$ denotes the coefficients of $|\Phi(t)\rangle$, then

$$a_+(t) = c_+(t)e^{-iE_+t/\hbar} \tag{5.5.13}$$

$$a_-(t) = c_-(t)e^{-iE_-t/\hbar}, \tag{5.5.14}$$

where,

$$E_\pm = \pm\mu_B B_0, \tag{5.5.15}$$

are the energies of the spin states in the presence of the static field B_0 only. The Schrödinger equation in the interaction representation becomes

$$i\hbar\frac{dc_+}{dt} = \mu_B b e^{-i(\omega-\omega_0)t}c_-, \tag{5.5.16}$$

$$i\hbar\frac{dc_-}{dt} = \mu_B b e^{i(\omega-\omega_0)t}c_+, \tag{5.5.17}$$

where ω_0 is the precession frequency

$$\omega_0 = (E_+ - E_-)/\hbar = 2\mu_B B_0/\hbar. \tag{5.5.18}$$

The two equations are coupled by the rf field b. Suppose that the application of the rf field starts at $t = 0$ when the electron is in the lower energy state, i.e., the spin-down state:

$$\begin{aligned} c_+(0) &= 0, \\ c_-(0) &= 1. \end{aligned} \tag{5.5.19}$$

Since the rf field is weak compared with the static field B_0, as the time goes on, the change of the probability amplitudes $c_+(t)$ and $c_-(t)$ will be of the order b/B_0.

The smallness of b/B_0 enables us to solve Eqs. (5.5.16) - (5.5.17), approximately. Since $c_+(t)$ will be of the order of b/B_0, we may substitute for $c_-(t)$ on the right-hand side of Eq. (5.5.16) its initial value of unity with an error on the right of $O(b/B_0)^2$.

$$i\hbar \frac{dc_+}{dt} = \mu_B b e^{-i(\omega-\omega_0)t}. \tag{5.5.20}$$

Hence,

$$\begin{aligned} c_+(t) &= \frac{\mu_B b/\hbar}{\omega - \omega_0}[e^{-i(\omega-\omega_0)t} - 1] \\ &= -\frac{\mu_B b/\hbar}{\omega - \omega_0} e^{-i\frac{1}{2}(\omega-\omega_0)t} 2i \sin\left[\frac{1}{2}(\omega - \omega_0)t\right]. \end{aligned} \tag{5.5.21}$$

The probability of transition from the spin-down state χ_- to the spin-up state χ_+ at time t is

$$\begin{aligned} P_{-+}(\omega) &= |c_+(t)|^2 \\ &= (\mu b t/\hbar)^2 \left[\frac{\sin\frac{1}{2}(\omega - \omega_0)t}{\frac{1}{2}(\omega - \omega_0)t}\right]^2. \end{aligned} \tag{5.5.22}$$

For a given time t, the transition probability as a function of the exciting field frequency ω is sharply peaked at the resonance frequency ω_0, as shown in Fig. 5.2. For a field B_0 of about 100 gauss, the resonance frequency ω_0 is $2 \times 10^9 \text{sec}^{-1}$. If we use a reasonable time scale of 10^{-2} sec, the width of the resonance peak is about

$$\Delta\omega = \pi/t \simeq 3 \times 10^2 \text{sec}^{-1}. \tag{5.5.23}$$

The Q of the resonance is

$$Q = \omega_0/\Delta\omega = 10^7, \tag{5.5.24}$$

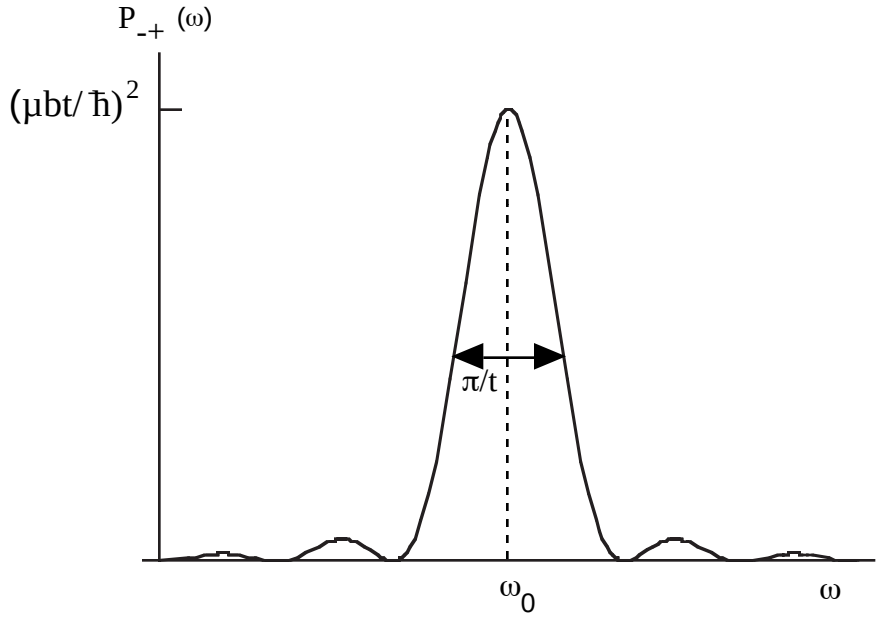

Figure 5.2: Transition probability dependence on frequency.

indicative of very sharp resonance.

While in the optical frequency regime, it is a simple matter to produce a circularly polarized light, at the microwave range it is not a practical matter. However, a plane-polarized oscillating field can be resolved into a right-handed and a left-handed circularly polarized field, e.g.,

$$\vec{b} = (2b\cos\omega t,\ 0,\ 0) = \vec{b}_+ + \vec{b}_- \tag{5.5.25}$$

$$\vec{b}_+ = b(\cos\omega t,\ \sin\omega t,\ 0)$$

$$\vec{b}_- = b(\cos\omega t,\ -\sin\omega t,\ 0).$$

In Eq. (5.5.21) for the coefficient c_+, the left-handed field causes an additional term with the resonance factor $\omega - \omega_0$ being replaced by $\omega + \omega_0$. If the applied frequency ω close to the resonance frequency ω_0, the perturbation effect of the left-handed component is negligible. This approximation is sometimes known as the rotative wave approximation.

In an actual magnetic resonance experiment, the oscillating magnetic field is provided by a microwave cavity, which means that the frequency ω of the oscillating field is fixed. The resonance is achieved by varying the static field B_0 and hence the precession

frequency ω_0. Knowing the g-factor of the electron spin, this experiment gives a more accurate measurement of the Bohr magneton than the Stern-Gerlach experiment.

The microwave cavity has a finite band width, which is easily greater than the natural width π/t of the resonance given by Eq. (5.5.22). Let the intensity of the microwave per unit frequency range ω be $\hbar b^2 I(\omega)$, where $I(\omega)$, the density of states for a unit magnetic field, is a much more slowly varying function of ω than the transition probability (5.5.22). Then, the total probability over all frequencies for the transition from the spin-down state to the spin-up state at time t is

$$\begin{aligned} P_{-+} &= \int_0^\infty d\omega (\mu_B b t/\hbar)^2 \hbar I(\omega) \left[\frac{\sin \frac{1}{2}(\omega-\omega_0)t}{\frac{1}{2}(\omega-\omega_0)t}\right]^2 \\ &= \frac{2\pi}{\hbar}(\mu_B b)^2 I(\omega_0) t, \end{aligned} \tag{5.5.26}$$

where we have replaced $I(\omega)$ under the integral by $I(\omega_0)$ since it varies negligibly over the range of π/t around the resonance frequency ω_0.

The transition probability per unit time is, therefore,

$$Q_{-+} = \frac{2\pi}{\hbar}|\langle \chi_- | H_1 | \chi_+ \rangle|^2 I(\omega_0), \tag{5.5.27}$$

where we have used Eq. (5.5.4) for the perturbation H_1. This formula is known as the Fermi golden rule. It has the form of the general formula for the transition probability per unit time between two states due to a perturbation H_1. A small but important difference with the more common formula lies in the density of states of the system in place of the cavity intensity distribution. The difference in physics comes from the assumption here that the two unperturbed energy states are infinitely sharp (or have infinite life-time) whereas the usual derivation makes use of the broad energy distribution. A derivation of more general validity will be given in the chapter on perturbation theory.

The resonance phenomenon is not restricted to the spin $\frac{1}{2}$ states of the electron. Clearly, any two level system can have resonance. In particular, the magnetic resonance due to the spin of nuclear particles is possible (known as the nuclear magnetic resonance), even though compared with the electron spin resonance the transition probability per unit time is down by a factor of at least 10^6 because of the dependence on the square of the magnetic dipole moment. Also, any magnetic dipole moment, whether it comes

from the spin or orbital angular momentum, precesses about a static magnetic field and, therefore, has resonance if excited by an oscillating field. For any angular momentum, spin or orbital, greater than a half, there are more than two states and there is more than one resonance between two adjacent energy levels.

5.5.2 The Rabi oscillations

Actually, the equations of motion reduced to Eqs. (5.5.16) and (5.5.17) can be solved exactly for any strength of the ac field b in the circular polarization. This solution will give us not only the phenomenon of Rabi oscillation which is of importance to nuclear magnetic resonance, quantum optics, and quantum computing, but also gives us a perspective to the perturbation theory of quantum transitions by examining an exact solution of a nontrivial model problem.

Let us introduce two quantities which help to make the physics of the solution more transparent. One is the detuning,

$$\delta = \omega_0 - \omega, \tag{5.5.28}$$

the difference between the frequency of the driving field and the characteristic frequency of the two-level system. The other is the Rabi frequency

$$\Omega_R = 2\mu_B b/\hbar \tag{5.5.29}$$

which is also a measure of the strength of the driving field. Eqs. (5.5.16) and (5.5.17) become

$$\begin{aligned} i\frac{dc_+}{dt} &= \frac{\Omega_R}{2} e^{-i\delta t} c_-, \\ i\frac{dc_-}{dt} &= \frac{\Omega_R}{2} e^{i\delta t} c_+. \end{aligned} \tag{5.5.30}$$

A transformation of the coefficients of the state

$$c_+ = b_+ e^{-i\delta t/2}, \quad c_- = b_- e^{i\delta t/2}, \tag{5.5.31}$$

eliminates the explicit time dependence in the equations,

$$i\frac{d}{dt}\begin{bmatrix} b_+ \\ b_- \end{bmatrix} = \frac{1}{2}\begin{bmatrix} \delta & \Omega_R \\ \Omega_R & -\delta \end{bmatrix}\begin{bmatrix} b_+ \\ b_- \end{bmatrix}. \tag{5.5.32}$$

The transformation (5.5.31) may be viewed as one into a rotating frame with relative angular velocity δ as can be deduced from Eq. (5.4.2). The resultant equation (5.5.32) has the same form as the Schrödinger equation with a constant potential. The time evolution of the transformed state can be solved in the standard way in terms of the eigenstates. We use the spin analogy to diagonalize the pseudo-Hamiltonian in the rotating frame on the right side of Eq. (5.5.32) and let

$$\begin{aligned} \Omega &= \sqrt{\delta^2 + \Omega_R^2} \\ \cos\theta &= \delta/\Omega. \end{aligned} \tag{5.5.33}$$

The eigenstates associated with the eigenvalues $\pm\Omega/2$ are, respectively,

$$\begin{aligned} \vec{\psi}_+ &= \begin{bmatrix} b_{++} \\ b_{+-} \end{bmatrix} = \begin{bmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{bmatrix} \\ \vec{\psi}_- &= \begin{bmatrix} b_{-+} \\ b_{--} \end{bmatrix} = \begin{bmatrix} -\sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{bmatrix}. \end{aligned} \tag{5.5.34}$$

The initial condition of the system being in the lower state leads to the time evolution,

$$\begin{bmatrix} b_+ \\ b_- \end{bmatrix} = \vec{\psi}_+ \sin\frac{\theta}{2} e^{-i\Omega t/2} + \vec{\psi}_- \cos\frac{\theta}{2} e^{i\Omega t/2}. \tag{5.5.35}$$

The state in the interaction representation is

$$\begin{bmatrix} c_+ \\ c_- \end{bmatrix} = \begin{bmatrix} -i\sin\theta\sin(\Omega t/2)e^{-i\delta t/2} \\ \{\cos(\Omega t/2) + i\cos\theta\sin(\Omega t/2)\}e^{i\delta t/2} \end{bmatrix}. \tag{5.5.36}$$

We have deliberately adopted an elementary mathematical procedure to solve the Rabi oscillation problem here. In Problem 7, a more concise approach is used to yield a geometrical description of the spin dynamics in terms of an rf-field driven rotation in a precessing frame caused by the static magnetic field.

After applying the right-handed circularly polarized field to the spin in its ground state, the probability of find the spin in the spin-up state at time t is

$$P_{-+}(t) = |c_+|^2 = \frac{1}{2}\sin^2\theta\left[1 - \cos(\Omega t)\right], \tag{5.5.37}$$

oscillating with the Rabi frequency. When there is a finite detuning ($\sin^2\theta < 1$), even at maximum transition probability the state is not entirely in the spin-up state. The

expectation value of the longitudinal component of the dipole moment

$$\langle \mu_z \rangle = -\mu_B \langle \Psi(t)|\sigma_z|\Psi(t)\rangle = -\mu_B(|c_+|^2 - |c_-|^2) = \mu_B[\cos^2\theta + \sin^2\theta\cos(\Omega t)]. \quad (5.5.38)$$

In the case of laser action, this is a measure of the population inversion. The transverse magnetization may be obtained from

$$\begin{aligned} \langle \mu_+ \rangle &= \langle \mu_x + i\mu_y \rangle = -\mu_B \langle \Psi(t)|\sigma_+|\Psi(t)\rangle = -2\mu_B a_+^* a_- \\ &= -2\mu_B \sin\theta \sin\frac{\Omega t}{2}\left(\cos\theta \sin\frac{\Omega t}{2} + i\cos\frac{\Omega t}{2}\right) e^{i\omega t}. \end{aligned} \quad (5.5.39)$$

The factor $e^{i\omega t}$ shows the interesting fact that the transverse magnetization can be phase-locked with the driving field. The Rabi oscillation opens up the possibility of making an arbitrary combination of the two states (not just making the transition from one state to another with a finite probability). This is a fundamental requirement for quantum computation and quantum information processing.

5.5.3 Irreversible transitions versus oscillations between states

We now address the fundamental difference between the Fermi golden rule and the Rabi oscillation. The exact solution in Eq. (5.5.36) does contain the weak field limit in Eq. (5.5.21). To reach the Fermi rule, we then include the contribution of the driving fields with frequencies in the neighborhood of the resonance frequency (or alternately include the finite lifetime of the final state or the finite state distribution around it). In the long-time limit, the destructive interference of the neighboring nonresonant contributions converts the oscillations into an irreversible transition. The requirement of the Rabi oscillations is that the driving frequency is sharp and the level life-time is so long that the coherent effects of the oscillations are visible. Eventually, in a realistic system, the decoherence effects (treated in the next section) will diminish the Rabi oscillations. Thus, the apparent contradiction between the appearance of the abrupt jumps in the Fermi golden rule and the seemingly deterministic motion of the Rabi oscillations is resolved as the two limits of frequency resolution of the driving field.

5.6 Dissipative Dynamics for an Ensemble of Two-Level Systems

The density matrix for an ensemble of two-level systems is the tool for describing the state in dynamics with dissipation. As we have seen above, there are many important two-level systems, and thus the density matrix for the two-level systems has applications in many areas, particularly the electron and nuclear spin resonance and quantum optics in which the two-level atom model is basic. For convenience and for historical reasons, the terminology for the general two-level system is still couched in terms of the spin 1/2 system.

5.6.1 The Bloch equations

The Hamiltonian of the two-state system consists of two parts,

$$H = H_0 + H_1, \tag{5.6.1}$$

where H_0 is the conservative part with the form (5.5.3) containing the static field B_0 chosen to be in the z direction and H_1 is driven by a time-dependent field $\vec{b} = (b_x, b_y, b_z)$, not necessarily of the circularly polarized transverse field (5.5.4). When the influence of the environment is included, the description of the dissipative dynamics, from Section 2.6.6, is given by the master equation for the density matrix,

$$\frac{d}{dt}\rho(t) = \frac{1}{i\hbar}[H, \rho] + \left.\frac{d}{dt}\rho(t)\right|_{\text{relax}}, \tag{5.6.2}$$

where the relaxation terms have the form

$$\frac{d}{dt}\begin{bmatrix} \rho_{++} & \rho_{+-} \\ \rho_{-+} & \rho_{--} \end{bmatrix}_{\text{relax}} = \begin{bmatrix} \Gamma_a\rho_{--} - \Gamma_e\rho_{++} & -\left\{\frac{1}{2}(\Gamma_a + \Gamma_e) + \Gamma^*\right\}\rho_{+-} \\ -\left\{\frac{1}{2}(\Gamma_a + \Gamma_e) + \Gamma^*\right\}\rho_{-+} & -\Gamma_a\rho_{--} + \Gamma_e\rho_{++} \end{bmatrix} \tag{5.6.3}$$

in the spin basis set $(|+\rangle, |-\rangle)$, with the $|-\rangle$ being the ground state. The absorption rate and emission rate are, respectively, Γ_a, Γ_e and the pure dephasing rate Γ^*.

The 2×2 density matrix still obeys the unit trace constraint. It can, therefore, be put in the form

$$\rho = \frac{1}{2}(I + \vec{P} \cdot \vec{\sigma}), \tag{5.6.4}$$

where $\vec{P}$ is a vector of three numbers known as the spin polarization in a spin system or simply polarization in a general two-state system such as the atom model (in which case it should not be confused with the polarization vector of the photon). The ensemble average of the spin vector is given by $\vec{S} = \vec{P}/2$.

In the most general construction of the density matrix which is determined by the fractions $\frac{1}{2}(1+P)$ and $\frac{1}{2}(1-P)$ for the spin up and down states in the (θ, ϕ) direction, the density matrix in the basis of the spin up and down states along the z direction is

$$\rho = \frac{1}{2}\begin{bmatrix} 1+P\cos\theta & P\sin\theta e^{-i\phi} \\ P\sin\theta e^{i\phi} & 1-P\cos\theta \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1+P_z & Px - iP_y \\ Px + iP_y & 1-P_z \end{bmatrix}. \tag{5.6.5}$$

The parameters (P, θ, ϕ) and (P_x, P_y, P_z) are just the polar and Cartesian coordinates of the vector $\vec{P}$.

From the above master equation of the density matrix, it is possible to derive the equation of motion for the spin polarization $\vec{P}$, known as the Bloch equation, (see Problem 4),

$$\frac{d\vec{P}}{dt} = \gamma\vec{P} \times \vec{B} - \frac{1}{T_1}\left(\vec{P}_\parallel - \vec{P}_0\right) - \frac{1}{T_2}\vec{P}_\perp, \tag{5.6.6}$$

where $\gamma = \mu/\hbar$ is the gyromagnetic ratio. $\vec{P}_\parallel = (0, 0, P_z)$ is the longitudinal component of the polarization at time t and $\vec{P}_\perp = (P_x, P_y, 0)$ is the transverse component. The time-independent $\vec{P}_0$ is the steady state value when H_1 is zero, given by $(0, 0, P_0)$ where,

$$P_0 = -\frac{\Gamma_e - \Gamma_a}{\Gamma_e + \Gamma_a}. \tag{5.6.7}$$

The decay time T_1, given by

$$\frac{1}{T_1} = \Gamma_e + \Gamma_a, \tag{5.6.8}$$

is known as the longitudinal relaxation time. It is a measure of the relaxation time of the longitudinal component of the polarization $\vec{P}_\parallel$ to $\vec{P}_0$. The decay time T_2, given by,

$$\frac{1}{T_2} = \frac{1}{2}(\Gamma_e + \Gamma_a) + \Gamma^*, \tag{5.6.9}$$

is the transverse relaxation time (or the decoherence time). It is a measure of the relaxation time of the transverse component of the polarization $\vec{P}_\perp$.

Thus, the physical picture of spin precession about a magnetic field and spin flipping, etc, applies not only to a pure spin state but also to the average spin vector of an ensemble of spins or other two-level systems. Problem 3 derives a number of these properties.

5.6.2 Relaxation times due to transitions between states

We have obtained the form of the decay terms from the Lindblad form. Here we shall examine the physical origin of the Γ_a and Γ_e terms in the damping or relaxation rates. We choose the example where the two-state atom is driven by an oscillating field (see Problem 9) and is coupled to the reservoir of the ambient electromagnetic fields. While the radiative transition is important to the decaying processes in a two-level atom, it is not the dominant relaxation mechanism for an electron spin situated in a vibrating lattice, where the phonons or the random interaction with other spins are generally more important. The treatment is meant to be illustrative rather than exhaustive of the microscopic relaxation mechanisms.

From the Lindblad generator $\sqrt{\Gamma_a}|+\rangle\langle -|$, we identify the process as the transition of the system from the ground state absorbing a photon or electromagnetic energy from the electromagnetic reservoir. Similarly, Γ_e is identified as the emission rate. There are two ways to derive formulas for these two rates. One way is to treat the electromagnetic field in the reservoir quantum mechanically as photons. The other is to treat the fields as classical quantities, except that the energy density obeys Planck's law. The second method, coupled with the quantum treatment of the system, is known as the semiclassical method.

The quantum treatment will be given in Chapter 14. The essence of the physics lies in quantizing the electromagnetic field into the photons the same way the harmonic oscillator is quantized into phonons. From the well-known transition relations between the harmonic oscillator states, $c^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ and $c|n\rangle = \sqrt{n}|n-1\rangle$, the absorption process from the ground state to the excited state of the two-level atom will take a photon away from the reservoir with the probability proportional to n (the relevant matrix element squared) while the emission process from the excited state to the excited state of the two-level atom will give a photon to the reservoir with the probability proportional to $n+1$. The thermal average of n at frequency ω in a thermodynamic equilibrium at temperature T is given by (see Problem 3.6)

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_BT} - 1}, \tag{5.6.10}$$

where k_B is the Boltzmann constant. The two relaxation rates may be calculated by the

Fermi Golden Rule. Since the transition matrix elements for the system part are the same for emission and absorption,

$$\frac{\Gamma_e}{\Gamma_a} = \frac{n(\omega)+1}{n(\omega)}. \tag{5.6.11}$$

Hence, the emission rate may be considered as composed of a stimulated term (proportion to the number of relevant photons in the reservoir, $n(\omega)$) and a spontaneous term,

$$\Gamma_s = \Gamma_e - \Gamma_a. \tag{5.6.12}$$

With the formula for the spontaneous emission rate Γ_s, Eq. (14.8.9), the absorption and emission rates are

$$\Gamma_a = \Gamma_s n(\omega), \tag{5.6.13}$$

$$\Gamma_e = \Gamma_s\{n(\omega)+1\}. \tag{5.6.14}$$

The semiclassical treatment is due to Einstein. It is included here because the physical argument is illuminating. The essence of the physics is to use the thermal equilibrium of the reservoir to relate the emission rate and the absorption rate to temperature. If the system with the steady state polarization $(0, 0, P_0)$ is in thermal equilibrium with the reservoir at temperature T, then the Boltzmann law says that the ratio of the probabilities being in states $|+\rangle$ and $|-\rangle$ is

$$\frac{\rho_{++}}{\rho_{--}} = \frac{1+P_0}{1-P_0} = e^{-\hbar\omega/k_BT}. \tag{5.6.15}$$

If we let $\Gamma_s = \Gamma_e - \Gamma_a$, the relation Eq. (5.6.7) of P_0 to Γ_a and Γ_e yields the formulas,

$$\Gamma_a = \Gamma_s n(\omega) \tag{5.6.16}$$

$$\Gamma_e = \Gamma_s[n(\omega)+1], \tag{5.6.17}$$

where the thermal distribution of photons $n(\omega)$, as defined by Eq. (5.6.10), is a result of the Einstein argument.

Section (5.5.1) gives the transition rate from the ground state to the excited state in Eq.(5.5.27). For the electrical field excitation, the formula is

$$\Gamma_a = \frac{2\pi}{\hbar}|\langle+|H_1|-\rangle|^2 I(\hbar\omega), \tag{5.6.18}$$

where $\hbar\omega$ is the energy difference between the two states and the transition matrix element is $\langle +|H_1|-\rangle = \vec{\mu}\cdot\vec{\mathcal{E}}$, with the electric dipole moment μ and the density of states per unit energy per polarization for the photon reservoir is, from Problem 3.9, given by

$$I(\hbar\omega) = \frac{\omega^2}{2\pi^2\hbar c^3}. \tag{5.6.19}$$

To relate Γ_a to the transition rate, we average the latter over all possible directions of the polarization vector so that the matrix element squared yields a factor of $\frac{1}{3}\mu^2\mathcal{E}^2$. By Planck's theory, we replace the classical energy density by the phonon one,

$$\epsilon_0\mathcal{E}^2 I(E) = \hbar\omega n(\omega)\frac{\omega^2}{\hbar\pi^2 c^3}. \tag{5.6.20}$$

Thus, the semiclassical treatment of the decay rate Γ_a leads to

$$\Gamma_s = \frac{\mu^2\omega^3}{3\pi\epsilon_0\hbar c^3}. \tag{5.6.21}$$

If we calculate the transition rate from state $|+\rangle$ to $|-\rangle$ driven by the oscillating electric field by the same perturbative method as the absorption process, we would get the same decay rate as Γ_a. This is known as the principle of microscopic balance. The extra term Γ_s in the emission rate Γ_e, Eq. (5.6.17), is independent of the applied electric field and is known as the spontaneous emission rate. By contrast, the $\Gamma_s n(\omega)$ is known as the stimulated emission rate. Although Γ_s comes of the semiclassical argument, its true physical origin derives from the quantization of the electromagnetic field yielding a vacuum field.

5.6.3 A physical origin of pure dephasing

The Lindblad term $\sqrt{2\Gamma^*}|+\rangle\langle +|$ leads to a decay rate Γ^* only of the coherence term of the density matrix ρ_{+-} or the transverse component of the spin polarization. Because of the process disrupting the phase coherence, it is known as pure dephasing. By contrast, the emission and absorption processes contribute both to the change of the population density ρ_{++} or ρ_{--} and to the decay of the coherence terms. Returning to the spin system, we consider a microscopic cause of pure dephasing where the reservoir provides a small component of fluctuating magnetic field $(0, 0, b(t))$ in addition to the static field

$(0, 0, B_0)$. The magnetic field does not drive the longitudinal component P_z but does drive the transverse component,

$$\frac{dP_-}{dt} = -i(\omega_0 + \gamma b)P_-(t), \tag{5.6.22}$$

where $P_- = P_x - iP_y$ and $\omega_0 = \gamma B_0$. In the interaction representation,

$$P_-(t) = \tilde{P}_-(t)e^{-i\omega t}, \tag{5.6.23}$$

$$\text{and} \quad \frac{d\tilde{P}_-}{dt} = -i\gamma b(t)\tilde{P}_-(t). \tag{5.6.24}$$

For the weak fluctuating field, we integrate the last equation from the initial time t_0 to obtain,

$$\tilde{P}_-(t) = \tilde{P}_(t_0) - i\gamma \int_{t_0}^{t} dt' b(t')\tilde{P}_-(t') \tag{5.6.25}$$

and then iterate the equation once to arrive at

$$\frac{d\tilde{P}_-}{dt} = -i\gamma b(t)\tilde{P}_-(t_0) - i\gamma^2 \int_{t_0}^{t} dt' b(t)b(t')\tilde{P}_-(t'). \tag{5.6.26}$$

Now we average over the classical distribution of the set of random variables $\{b(t)\}$ and obtain

$$\frac{d\langle\tilde{P}_-\rangle}{dt} = -\gamma^2 \int_{t_0}^{t} dt' \langle b(t)b(t')\rangle\langle\tilde{P}_-(t')\rangle, \tag{5.6.27}$$

denoting the classical average by $\langle \ldots \rangle$. We choose the mean of each field $\langle b(t)\rangle = 0$. On the right hand side, we have used the decoupling approximation,

$$\langle b(t)b(t')\tilde{P}_-(t')\rangle \approx \langle b(t)b(t')\rangle\langle\tilde{P}_-(t')\rangle \tag{5.6.28}$$

The decoupling result on the right side may be seen from the decoupling of the infinite series solution from repeated iterations. It follows from the zero average of b that all odd order terms in b vanish on averaging. All even order terms survive the averaging and are sums of products of the second order correlation functions under the decoupling scheme. For example, the four-time correlation function may be decoupled as

$$\begin{aligned}\langle b(t_1)b(t_2)b(t_3)b(t_4)\rangle &\approx \langle b(t_1)b(t_2)\rangle\langle b(t_3)b(t_4)\rangle + \langle b(t_1)b(t_3)\rangle\langle b(t_2)b(t_4)\rangle \\ &+ \langle b(t_1)b(t_4)\rangle\langle b(t_2)b(t_3)\rangle.\end{aligned} \tag{5.6.29}$$

The decoupling approximation is equivalent to the restriction that the true three-time or higher order correlation is negligible. It is true, for example, for weak fluctuating fields. The two-time correlation function is given by

$$C(t-t') = \gamma^2 \langle b(t) b(t') \rangle. \tag{5.6.30}$$

The time dependence comes from the time invariance of the fluctuation field. Now, we impose the Markovian approximation,

$$C(t-t') = 2\Gamma^* \delta(t-t'). \tag{5.6.31}$$

From the relation,

$$\int_{-\infty}^{0} dt \delta(t) = \frac{1}{2}, \tag{5.6.32}$$

we establish the pure dephasing term

$$\frac{d\langle \tilde{P}_- \rangle}{dt} = -\Gamma^* \langle \tilde{P}_-(t) \rangle. \tag{5.6.33}$$

The fluctuation of the magnetic field is called "noise". The stochastic variable $b(t)$ is the mathematical representation of the classical noise which drives the spin system. Since the off-diagonal density matrix element varies with time as $e^{-i\Delta E t/\hbar}$ where ΔE is the energy between the two states, the fluctuating field smears out the energy and, therefore, the phase.

5.7 Methods of Measuring the Spin Resonance

As examples of connecting the microscopic system to the macroscopic world, we describe briefly two methods for measuring the spin resonance.

5.7.1 Free induction decay

The physics behind the measurement comes from an application of the Bloch equations. Consider an ensemble of independent spins. Let us consider the proton spins for a change from the electron spins as well as a nod towards the important applications of nuclear magnetic resonance (NMR) such as determination of structures in molecules, liquids, and solids, and magnetic resonance imaging (a euphemism to avoid the word "nuclear"). Since

the magnetic moment of the proton is positive, the spin-up state $|+\rangle$ is now the ground state and $|-\rangle$ the excited state. The relaxation terms in the master equation (5.6.3) are changed by exchanging Γ_a and Γ_e. The equilibrium spin polarization now points along the static field direction. The transverse field is made left-handed to follow the clockwise direction of the spin precession, resulting in the change of the familiar magnetic field configuration to $(b\cos(\omega t), -b\sin(\omega t), B_0)$. In practice, the oscillating field $\vec{b}$ is in the x direction and the theory needs only to neglect the component of the circularly polarized field counter to the spin precession — the rotating wave approximation, *cf.* Eq. (5.5.25).

We shall describe the qualitative features of the solution to the Bloch equations, leaving the general construction to Problem 7. The polarization $\vec{P}$ precesses clockwise with the frequency $\omega_0 = \mu_N B_0$ driven by the static field. It is simpler to describe the motion of the polarization in the rotating frame with the same angular velocity. The oscillating field $\vec{b}(t)$ at resonance would be static along the x axis in the rotating frame. It creates a Rabi rotation of the spin polarization in the $y-z$ plane. If an induction coil is placed with its axis along the y axis (Fig. 5.3), the oscillation of the magnetization in the y direction will induce a current in the induction coil whose resistance change can be measured. The name "free induction method" refers to being "free" from the rf field b.

5.7.2 Spin and photon echo

In the rotating frame, the rf field b which drives the Rabi rotation of the polarization $\vec{P}$ may be stopped in time at any point of the circle. Thus, the equilibrium polarization may be rotated through a chosen angle by a pulse of the rf field. For example, a $\pi/2-$pulse of duration t given by $\Omega_R t = \pi/2$ where Ω_R is the Rabi frequency would drive the state from spin-up to an equal combination of spin-up and spin-down states and, therefore, would rotate $\vec{P}$ about the x axis through an angle of $\pi/2$ from the equilibrium along the positive z axis to pointing along the negative y axis, as indicated in Fig. 5.3(a). If the magnetization is measured by induction as a function of time, it will suffer "free induction decay". However, if another pulse of rf field is applied at time τ after the first pulse, a signal is echoed at another lapse of time. This is known as the spin echo.

An ensemble of spins in a liquid or solid commonly experience an inhomogeneous distribution of magnetic field B_0 and, therefore, would have a distribution of precession

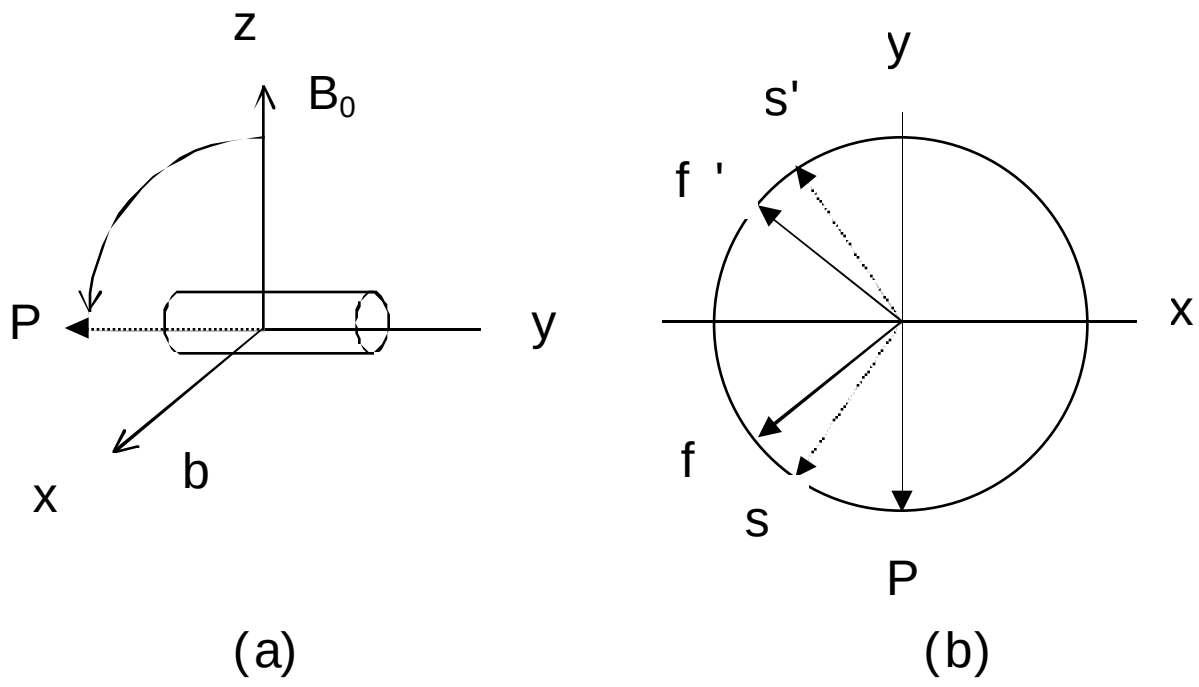

Figure 5.3: Dynamics of the spin polarization: (a) The magnetic field and the induction coil configuration; (b) illustration of the spin echo (see text).

frequencies, say with width of $\Delta\omega$. Fig. 5.3(b) shows the precession of spins from the initial point P resulting in a spread of points between the fastest f and the slowest s. The interference of the frequency spread will lead to a decay of the induction signal in a time of the order $1/\Delta\omega$, known as the inhomogeneous relaxation time. If a $\pi-$pulse is applied at a delay time τ after the first pulse, the spread-out polarization vectors would be rotated through π about the x axis to a distribution between f' and s' in the upper half plane as shown. Note that the order of the spin with different precession rates is now reversed in the clockwise direction of the precession. After another lapse of time τ, they would regroup and form a strong enough polarization for the induction signal to reappear. The echo signal would be weaker because of the intrinsic (or homogeneous) transverse relaxation time T_2. Clearly the delay between the two pulses τ must be shorter than T_2. The spin echo may be used to measure T_2 even though the inhomogeneity dephasing time $1/\Delta\omega$ is shorter.

It is impressive but not surprising that the same echo phenomenon happens to the coherence term in the density matrix describing the two-level model for an ensemble of

atoms in the presence of inhomogeneity influence on the energy level spacing. It is known as the photon echo.

5.7.3 The Rabi Molecular Beam Method

In the Stern-Gerlach experiment, the limiting accuracy for the measurement of the magnetic dipole moment is due to the measurement of the small separation of the split beams. Rabi's method combines the resonance effect with the Stern-Gerlach arrangement into an extremely sensitive instrument for the measurement of the magnetic dipole moment.

The arrangement of the apparatus is shown in Fig. 5.4(a). Consider only spin $\frac{1}{2}$ systems. For example, the oven supplies only silver atoms, which carry electronic spin $\frac{1}{2}$. Magnet #1 is a Stern-Gerlach-type magnet producing a field with a large gradient (in the up direction, say). An atom in the spin up state will be bent towards the N pole and an atom in the down state will be bent towards the S pole. Magnet #2 produces a uniform field B_0 which does not deflect the paths of the atoms. Magnet #3 is identical to magnet #1 except for the reversed polarity. It bends the path of an atom in the opposite way to magnet #1. Thus, the spin-up atom will be deflected upwards and the spin-down atom will be deflected downwards. The fields are adjusted so as to allow atoms in both spin states through the final slit to the detector screen.

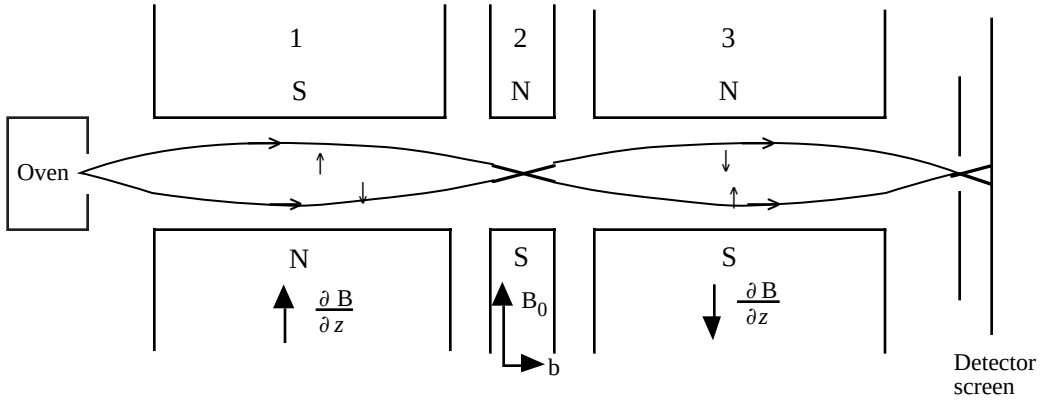

Figure 5.4: (a) The Rabi molecular beam apparatus.

A weak oscillating field b is applied in the region of magnet #2 at right angles to the uniform and static field B_0. If the frequency ω of the oscillating field is not near the resonance frequency ω_0, the spin states of the atoms are not much affected and the paths

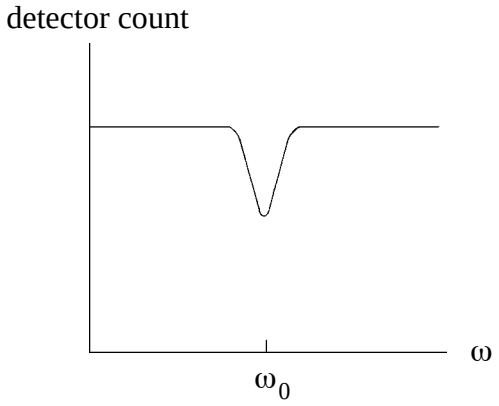

Figure 5.4: (b) Resonance shown by the detector count.

of the atoms are hardly disturbed and the detector count remains constant. If ω is equal to ω_0, the atoms on reaching the region of magnet #2 will have a strong probability of changing their states from spin-up to down or vice versa. Once an atom has its spin reversed in magnet #2, it cannot follow its former path to reach the detector screen. The number of atoms reaching the detector will be sharply reduced. The resonance frequency is therefore easily measured. See Fig 5.4(b).

5.8 Bonding of the Ionized Hydrogen Molecule

For each two-state system, the basis set of $|u_1\rangle$ and $|u_2\rangle$ is chosen for its particular physical reasons. Let us consider here the example of the ionized hydrogen molecule (H_2^+). Treat the protons as classical particles fixed in position. Take the basis states $|u_1\rangle$ and $|u_2\rangle$ to be the ground-state wave functions of the electron centered on one of the protons alone. They are then made orthogonal to each other. By the symmetry of the two protons, the matrix elements H_{11} and H_{22} are equal and are approximately the ground-state energy of the hydrogen atom, E_0:

$$H_{11} = H_{22} = E_0. \tag{5.8.1}$$

Since $|u_1\rangle$ and $|u_2\rangle$ have, in this case, real wave functions, all the four matrix elements of the Hamiltonian are real numbers. Also by symmetry, the off-diagonal elements H_{12} and H_{21} are equal. They are negative because in the ground state of the atom, the potential

energy overwhelms the kinetic energy. Thus,

$$H_{12} = H_{21} = -V, \tag{5.8.2}$$

where V is a real and positive number, of the order 1 eV.

5.8.1 The covalent bond

The lower energy state is

$$|\psi_1\rangle = 2^{-1/2}(|u_1\rangle + |u_2\rangle), \tag{5.8.3}$$

and the energy

$$E_1 = E_0 - V. \tag{5.8.4}$$

The molecule is symmetric about the plane perpendicular bisecting the line joining the protons. The lower state wave function is of even parity, and is said to be *gerade* (mostly by theoretical chemists) which is just the German way of saying symmetric, and which is usually denoted by a subscript g.

The higher energy state is

$$|\psi_2\rangle = 2^{-1/2}(|u_1\rangle - |u_2\rangle), \tag{5.8.5}$$

and energy

$$E_2 = E_0 + V. \tag{5.8.6}$$

The higher state wave function is of odd parity, and is also said to be *ungerade*, denoted by a subscript u.

By sharing the electron between the two protons symmetrically, the system lowers its energy by an amount of V. Thus, the electron binds the molecule and is said to be in a bonding state (or orbital). The higher energy state is an antibonding orbital and does not bind the molecule.

5.8.2 Time evolution of the electron in the bonding state

Suppose that we bring together very quickly a hydrogen atom and a hydrogen ion (i.e., a proton) to form the molecular ion, such that initially the electron is in the ground state of one of the protons, say u_1. How does the electron state develop in time?

According to the Schrödinger theory, the electron state has the time dependence given in terms of the energy eigenstates by

$$\Psi(t) = \psi_1 c_1 e^{-iE_1 t/\hbar} + \psi_2 c_2 e^{-iE_2 t/\hbar}. \tag{5.8.7}$$

Initially, i.e., at $t = 0$, it is given that

$$\Psi(0) = u_1. \tag{5.8.8}$$

From Eq. (5.8.7) it follows that

$$c_1 = c_2 = 2^{-1/2}. \tag{5.8.9}$$

Hence, in terms of the basis set u_1 and u_2,

$$\begin{aligned} \Psi(t) &= \frac{1}{2}[(u_1 + u_2)e^{-i(E_0 - V)t/\hbar} + (u_1 - u_2)e^{-i(E_0+V)t/\hbar}] \\ &= u_1 e^{-iE_0 t/\hbar} \cos\left(\frac{Vt}{\hbar}\right) + u_2 i e^{-iE_0 t/\hbar} \sin\frac{Vt}{\hbar}. \end{aligned} \tag{5.8.10}$$

The probability of the electron being in state $|u_1\rangle$, roughly speaking in the atomic ground state around proton #1, is

$$P_1 = [\cos(Vt/\hbar)]^2. \tag{5.8.11}$$

Probability of the electron being in state $|u_2\rangle$, i.e., around proton #2, is

$$P_2 = [\sin(Vt/\hbar)]^2. \tag{5.8.12}$$

These probabilities are plotted as functions of t in Fig. 5.5. The electron oscillates between the two protons with frequency $\omega = 2V/\hbar$.

There is a classical analogue of this phenomenon. If two identical tuning forks are placed on top of a resonance box and one fork is plucked, then the sound energy will slosh back and forth from one fork to the other. By analogy with this classical phenomenon, Pauling called the hopping back and forth of the electron from one proton to the other a "resonance". Thus, the chemical bond can be described either in the time independent picture as the splitting of the two states of equal energy E_0 into a bonding state with energy $E_0 - V$ and an antibonding state with energy $E_0 + V$ due to the overlap of the atomic wave functions or in the time dependent picture as due to the electron going back and forth from one ion to another with a resonance frequency $2V/\hbar$.

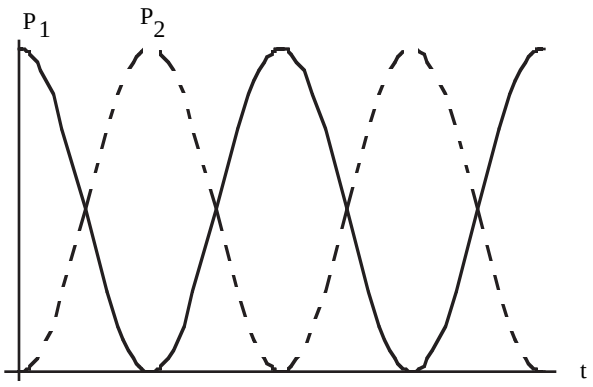

Figure 5.5: $P_1(t)$ solid line, and $P_2(t)$ dashed line.

5.9 The Ammonia Maser

The ammonia maser is the first device of this type (masers and lasers) made, by Gordon, Zieger and Townes in 1954. We briefly survey the working principles of this device which has wider applications.

(1) The maser material used is the ammonia molecule. As was indicated in Sec. 5.1.6, the nitrogen atom has two possible positions. These form the two states of the systems. Because the nitrogen atom can tunnel from one position to the other, the Hamiltonian has off-diagonal elements.

(2) When the nitrogen atom is in one of the two equilibrium positions, the arrangement of the molecule is asymmetric. Even when there is no external electric field, the electrons are polarized, i.e., the centroid of the electron charge distribution does not coincide with the nuclear charge distribution centroid. Hence, the ammonia molecule carries a net electric dipole moment μ along the N_1N_2 line joining the two nitrogen positions. When an electric field E is applied along the line N_1N_2 towards N_1, say, there is an additional term in the Hamiltonian,

$$H_1 = -\vec{E} \cdot \vec{\mu}. \tag{5.9.1}$$

If the nitrogen is in position N_1, the molecule has electric dipole moment $-\mu$ and the system has an additional energy μE. If the nitrogen is in position N_2, the molecule has electric dipole moment μ and therefore an additional energy $-\mu E$. Thus, the two states of the ammonia molecule are no longer equivalent.

(3) An electrical analogue of the Stern-Gerlach set-up is used to split a beam of ammonia molecules into two beams one in each of the two energy states described above. The higher energy state molecules are passed into a microwave cavity. In thermal equilibrium, the ammonia molecules are distributed between the energy states according to the Boltzmann law. This process of getting a larger portion into the upper energy level than the thermal distribution is known as the population inversion.
(4) The excited ammonia molecules in the microwave cavity can lose energy in the form of a photon (of microwave frequency) either by spontaneous emission or by stimulated emission which has a probability proportional to the photon distribution of that frequency already present in the cavity. The cavity serves as a resonator which builds up the number of photons of the same frequency into a coherent beam of microwave radiation.

The advantages of this device are: (i) An output of narrow frequency range. The limitation due to the molecule de-excitation process is $\Delta\omega/\omega \simeq 10^{-12}$. (ii) The operation is very stable, about 1 in 10^{10} drift over long periods. Thus, an important use of the maser is as an atomic clock. The deviation from true periodicity is about 1 sec in a century.

The disadvantages of the ammonia maser are: (i) The frequency is fixed. It is equal to $\frac{2}{\hbar}\sqrt{(\mu E)^2 + V^2}$ which can be changed by adjusting the electric field. (For a way to define V, see Problem 10). However, the microwave cavity is of fixed dimension and therefore fixed resonance frequency which is not tunable. (ii) The width of the frequency distribution $\Delta\omega = 4$ kHz is relatively large in this business. (iii) The power output of 10^{-9} watt is weak.

When the emitted radiation has frequency in the range of light, the device is called a laser. The operating principles are the same:
(1) Two energy levels are needed. There are, by now, an enormous range of materials. A common example is ruby which is just Al_2O_3 with C^{3+} impurities (substituting aluminum ions). The electronic states in the chromium ion impurity have three energy levels. The two upper levels are closer in energy. The highest energy level has a very short life-time. When the Cr ion is excited from the lowest energy level to the highest energy level, it relaxes very fast to the middle level where it is de-excited to the lowest level

by stimulating emission of photons. Other systems include CO_2, YIG, and various dyes. Dyes have a broad distribution of energy levels being large molecules with lots of closely spaced electronic energy levels which provide the possibility of tuning (variable frequency output).

(2) A mechanism for population inversion. More common than the Stern-Gerlach type arrangement are optical pumping or atom bombardment. For the three level system in ruby, the excitation from the lowest level to the highest is done by light input with a higher frequency than the coherent output.

(3) A resonator for stimulated emission is needed. In lasers, the microwave cavity is replaced by a Fabry-Perot type mirror arrangement to allow the emitted radiation to oscillate back and forth to build up its intensity.

Lasers have many applications. One of the most fascinating from the point of view of applying the principles of quantum physics is the separation of isotopes by lasers. Isotopes of an element differ only by the number of neutrons in the nucleus. They are difficult to distinguish chemically. The electronic energy levels differ only by minute amounts due to the difference in the reduced mass. Laser light has such a narrow frequency distribution that it can excite one isotope without exciting another with a slightly different excitation energy. The excited atoms have very different magnetic or electric dipole moments from their isotopic brethren which were not excited by the laser light. The two different isotopes can then be separated by an inhomogeneous magnetic or electric field as in a Stern-Gerlach experiment.

5.10 Strangeness Oscillations of the Kaons

To demonstrate the ubiquitous nature of the two-state systems, we now apply it to the strange particles. To understand how a two-state system may be extracted from a larger number of mesons, we describe briefly the background in elementary particle physics.

There is a bewildering variety of elementary particles, leading to the quip that all particles are elementary though some are more elementary than others. They are now generally classified into four families.

1. Field particles (gauge particle) such as photons, the $W^{\pm}$ and Z^0 particles and the

gluons. They are exchanged during the interaction between two particles. For example, the electromagnetic interaction between two charged particles may be viewed as exchange of a photon.

2. Leptons: the family of particles which interact with only weak and electromagnetic interaction includes the electron, neutrino, and μ meson (muon).

3. Hadrons: those interacting with strong interaction. There are two families of such particles:

   (a) Mesons. Particles of integer spins (bosons) which include the pions (π mesons) and the kaons (K mesons).

   (b) Baryons. Particles of integer-plus-half spins (fermions) which include the stable nucleons. The baryons are distinguished from the mesons by the baryon number (± 1). The assignment of the baryon number explains the occurrence and non-occurrence of certain decays and reactions since all of them obey baryon number conservation.

Consider now only the meson family. The kaons and the pions are distinguished by a property known as the strangeness. The law of conservation of strangeness which correlates the decay events of the particles stipulates that

1. The total strangeness must remain constant if the processes involve strong or electromagnetic interaction.

2. The total strangeness may remain constant or change by ± 1 if only the weak interaction (without the electromagnetic interaction) is involved.

For particles with strong interaction (of the order 10 MeV), the decay processes are expected to take place within 10^{-22} s by the energy-time uncertainty relation. Yet, some of these decay processes take place on a much longer time scale of 10^{-10} s, characteristic of the weak interaction. The introduction of the additional quantum number called strangeness to the particles and of the conservation of strangeness in particle reactions by the strong interaction would then forbid certain decay processes if the weak interaction is

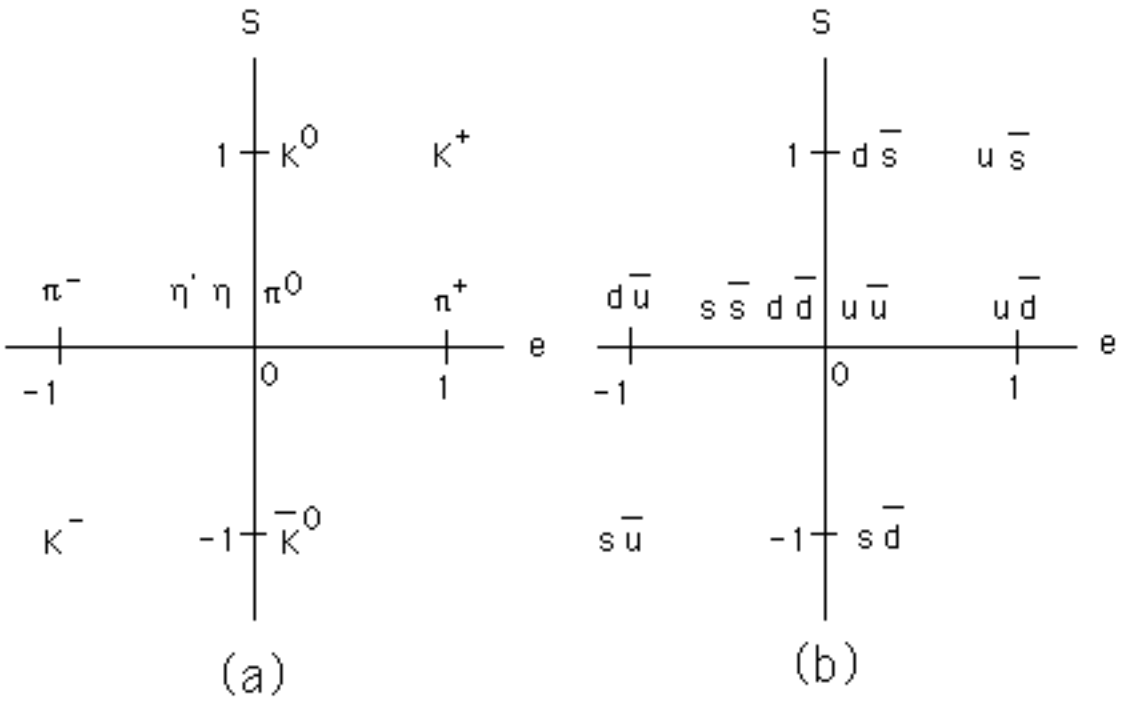

Figure 5.6: Spin-zero mesons (a) and as combinations of quarks (b).

neglected. Fig. 5.6(a) shows the charge and strangeness of the spin-zero mesons. Because strangeness is a good quantum number in the strong interaction, the strong interaction produces particles with definite strangeness. For example, the reaction

$$\pi^- + p^+ \rightarrow \Lambda^0 + K^0 \tag{5.10.1}$$

combines a meson (π^-) and a baryon (p^+), both with zero strangeness, to produce a hyperon Λ^0 (a baryon) with strangeness -1 and the meson K^0 with strangeness $+1$. This is a good source of pure K^0.

Hadrons may be considered as composite particles of quarks, whose introduction greatly simplifies the structure of the hadrons. There are of the order 100 known hadrons. The following table summarizes the key quarks and anti-quarks and their properties:

Name	quark	charge(e)	spin	baryon#	strangeness(S)
Up	u	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	0
Down	d	$-\frac{1}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	0
Strange	s	$-\frac{1}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	-1

Name	antiquark	charge(e)	spin	baryon#	strangeness(S)
Up	$\overline{u}$	$-\frac{2}{3}$	$\frac{1}{2}$	$-\frac{1}{3}$	0
Down	$\overline{d}$	$\frac{1}{3}$	$\frac{1}{2}$	$-\frac{1}{3}$	0
Strange	$\overline{s}$	$\frac{1}{3}$	$\frac{1}{2}$	$-\frac{1}{3}$	1

Figure 5.6(b) shows the combinations of quarks and antiquarks which would yield mesons of the same characteristics.

The particles K^0 and $\overline{K}^0$ have strangeness ± 1 and, therefore, by strong interaction alone which conserves strangeness, cannot convert into each other. However, by weak interaction, they can convert into each other through their coupling to pions which have zero strangeness. The two particle states K^0 and $\overline{K}^0$ can be considered as a two-state system if the intermediate pion states are eliminated and their influence is replaced by an effective matrix element of the Hamiltonian connecting the two states, $A\hbar$, where A is real. As we have seen earlier, because of the weak interaction, A is of the order $10^{10}\ s^{-1}$ and $A\hbar$ is of the order 10^{-5} eV. The diagonal matrix element connecting K^0 or $\overline{K}^0$ to itself is also $A\hbar$ if it is also via the same two-pion intermediate state. The Hamiltonian is

$$H = \begin{bmatrix} A & A \\ A & A \end{bmatrix} \hbar. \tag{5.10.2}$$

In the diagonal terms of the Hamiltonian we have left out the equal energy (mass) of the K^0 and $\overline{K}^0$ particles of 500 MeV, which is enormous compared with the other terms. The qualitative description of the reduction of the Hamiltonian to the two-state system given above is illustrated quantitatively in Problem 11.

The energy difference of the two energy eigenstates, the symmetric state being called K_L^0 and the antisymmetric state K_S^0, is $2A\hbar$. It is measured to be $0.5 \times 10^{10}\ \hbar s^{-1}$, in good agreement with the theoretical anticipation of it being "second order" weak interaction.

If the particle is initially a K^0 particle, then the probability of it converting to a $\overline{K}^0$ at time t is

$$P(t) = \sin^2(At). \tag{5.10.3}$$

This is called the "strangeness oscillations". The deduction of this result is left as a problem. If we wish to include phenomenologically the fact that each particle can decay into something else than the other particle, we replace the real number A by a complex number $A - i\Gamma$, where Γ is positive. Then, the Hamiltonian is not Hermitian and Γ measures the rate of disappearance of the particle from the two-state system. (See

Problem 1.13). The probability of a K^0 converting to a $\overline{K}^0$ at time t is

$$P(t) = \frac{1}{4}[1 + e^{-4\Gamma t} - e^{-2\Gamma t} 2\cos(2At)]. \tag{5.10.4}$$

The strangeness oscillations have been observed experimentally by producing a beam of K^0 using the strong-interaction reaction process in Eq. (5.10.1) and monitoring the intensity of $\overline{K}^0$ by measuring the hyperons produced by the strong-interaction reaction

$$\overline{K}^0 + p^+ \to \Lambda^0 + \pi^+ . \tag{5.10.5}$$

Notice that strangeness is conserved in the reaction because Λ^0 and $\overline{K}^0$ both have strangeness -1.

Actually, the two energy eigenstates K_L and K_S have different decay times, $\tau_L \sim 10^{-7}\, s$ and $\tau_S \sim 10^{-10}\, s$. Because of the difference in the CP (charge conjugation and parity) symmetry, K_S can decay into two pions (π^+ and π^-) but K_L can only decay into three pions, leading to the difference in decay times.

Pais and Piccioni suggested an experiment to observe the mixing of the K^0 and $\overline{K}^0$ states into K_L and K_S, known as the K^0 regeneration. If a pure K^0 beam is allowed to move in vacuum for a time about $100\tau_S$, the constituent state K_S will decay, leaving only a beam of K_L. Now pass the beam through a slab of material. The strong interaction between the $\overline{K}^0$ component in K_L and protons p in the slab will produce hyperons, as in Eq. (5.10.5), which can be measured. This was experimentally confirmed a year later by Fry *et al.* The regeneration is an illustration of the quantum phenomenon of two-state mixing, analogous to passing the spin 1/2 particles through a series of Stern-Gerlach apparati, arranged as in the Problem 16.

Study of the decay of the long-lived kaon K_L led to the discovery of the violation of the CP symmetry. Denote the eigenstates of Eq. (5.10.2) as

$$|K_\pm\rangle = \frac{1}{\sqrt{2}}(|K^0\rangle + |\overline{K}^0\rangle). \tag{5.10.6}$$

The states K^0 and $\overline{K}^0$ are related by the CP operation,

$$CP|K^0\rangle = |\overline{K}^0\rangle. \tag{5.10.7}$$

Then, the mixed states $K_\pm$ are eigenstates of CP with eigenvalues ± 1. Above, the K_- and K_+ states were identified respectively as the long- and short-lived kaons K_L and K_S.

In 1964, Cronin, Fitch, *et al.* found that the long-lived K_L also had a small probability in decaying into two pions like the short-lived K_S. In other words, they are not pure $K_\pm$:

$$\begin{aligned} |K_L\rangle &= |K_-\rangle + \epsilon |K_+\rangle \\ |K_L\rangle &= |K_+\rangle - \epsilon |K_-\rangle. \end{aligned} \tag{5.10.8}$$

where $\epsilon \approx 2 \times 10^{-3}$. CP violation has serious implications for the particle theory. Intense pursuit is being conducted to seek additional examples of CP violation. B quarks are being viewed as another likely candidate.

5.11 Isospin of nucleons

Proton and neutron are regarded as two states of a nucleon. Thus, we can write the two charge states as the spin-up and down states of the z-component of a pseudo-spin operator of spin 1/2, know as the isospin, denoted by $\vec{T}$, which are dimensionless observables obeying the same commutation relations as the spin vector but with $\hbar$ removed. This pseudo-spin vector can be used to construct a representation of the charge property of the nucleon.

The three components of the isospin vector $\vec{T}$ are usually denoted by the suffices (1,2,3) instead of (x,y,z). The proton state and neutron state which are eigenstates of T_3 have the vector representation

$$\begin{aligned} p &= \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \\ n &= \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \end{aligned} \tag{5.11.1}$$

The charge operator is

$$Q = \frac{e}{2}(1 + T_3) = \quad = \begin{bmatrix} e & 0 \\ 0 & 0 \end{bmatrix}, \tag{5.11.2}$$

where e is the proton charge. The proton and neutron states are the eigenstates of Q:

$$\begin{aligned} Q|p\rangle &= e|p\rangle, \\ Q|n\rangle &= 0|n\rangle, \end{aligned} \tag{5.11.3}$$

with the correct charges for the eigenvalues.

In nuclear binding, the dominant interaction between the nucleons is much stronger than the electromagnetic interaction and is referred above as the strong interaction. We examine the structure of the strong interaction Hamiltonian in the isospin space of one nucleon and of two nucleons. The Hamiltonian H of a single nucleon is, in the absence of the electromagnetic interaction, independent of the charge of the nucleon and thus commutes with Q and T_3:

$$[H, T_3] = 0. \tag{5.11.4}$$

The eigenvalue of H for an energy eigenstate is unchanged if a proton state in it is changed into a neutron state or vice versa. Thus, H commutes with T_+ and T_- and, therefore,

$$[H, T_1] = 0 \quad \text{and} \quad [H, T_2] = 0. \tag{5.11.5}$$

Thus, H has a diagonal representation in the isospin space with equal elements in the diagonal.

For two nucleons, the Hamiltonian is a function of both isospin vectors $\vec{T}^{(j)}$, $j = 1, 2$. Since the Hamiltonian cannot depend on the specific orientation of either one or the other, it can only depend on their relative orientation. Apart from two single nucleon terms, the interaction term has the form $\vec{T}^{(1)} \cdot \vec{T}^{(2)}$, or equivalently, $(\vec{T}^{(1)} + \vec{T}^{(2)})^2$. With these simple constructions, we can illustrate by problems 14 and 15 a physical understanding of the nuclear structure of the pr-deuterons and of the series of nuclei, ^{6}He, ^{6}Li, and ^{6}Be.

5.12 Examples

5.12.1 An operator which commutes with the Pauli matrices

An operator has a 2×2 matrix representation in the spin 1/2 space, denoted by A. It commutes with the three components of the Pauli matrices, $[A, \vec{\sigma}] = 0$. Show that A must a scalar times the unit matrix and give an example for A.

Solution — From Sec. 5.1 or Problem 1, A has the form

$$A = \alpha_0 + \vec{\alpha} \cdot \vec{\sigma}, \tag{5.12.1}$$

with four coefficients α_0 and $\vec{\alpha}$ which commute with the Pauli matrices and the unit matrix multiplying α_0 understood. Thus,

$$\begin{aligned} [A, \sigma_x] &= [\alpha_0 + \vec{\alpha} \cdot \vec{\sigma}, \sigma_x] \\ &= \alpha_y [\sigma_y, \sigma_x] + \alpha_z [\sigma_z, \sigma_x] \\ &= -2i\alpha_y \sigma_z + 2i\alpha_z \sigma_y, \end{aligned} \tag{5.12.2}$$

whose vanishing leads to the zero coefficients:

$$\begin{aligned} \alpha_y &= 0, \\ \alpha_z &= 0. \end{aligned} \tag{5.12.3}$$

Similarly, commutation brackets with the other components lead to the additional

$$\alpha_x = 0. \tag{5.12.4}$$

Therefore, A is α_0 times the unit matrix. An example is S^2, which is $\frac{3}{4}$ times the unit matrix.

5.12.2 Neutron spin precession

In the experimental setup illustrated by Fig. 5.7, a beam of neutrons along the y direction is polarized (how?) to have all the spins lined up in the positive x direction. The neutrons then travel through a uniform magnetic field B pointing in the z direction and enter a detector at a distance L, which can be varied. The detector measures the neutron spin in the x direction.

(a) As the distance L between the detector and the polarizer is varied, the measured spin in the x direction will vary sinusoidally. Find the change in the distance ΔL which corresponds to one period of change in the measured spin in terms of the magnetic field B and the neutron wavelength λ.

Solution — The neutron speed is

$$v = \frac{h}{\lambda m_N}, \tag{5.12.5}$$

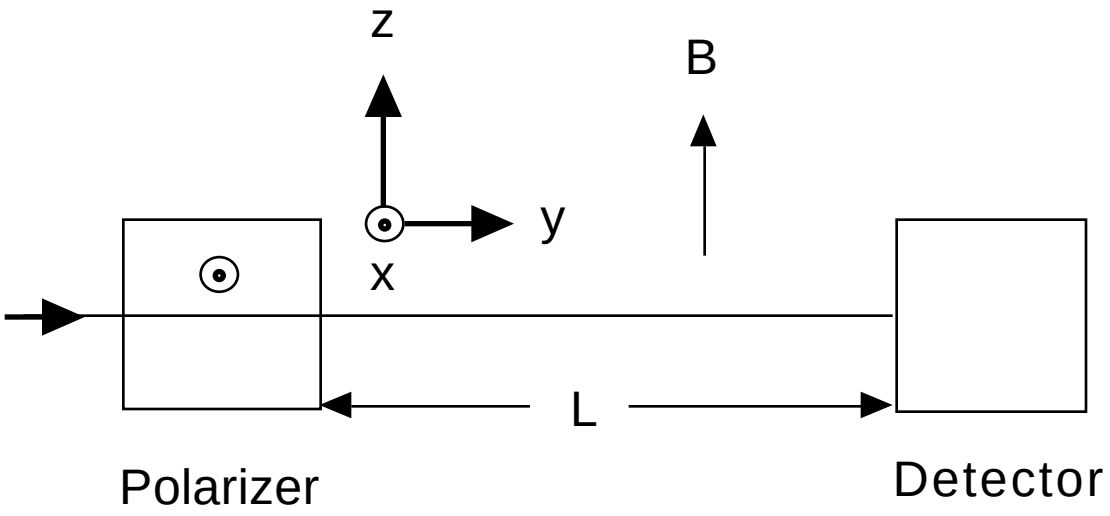

Figure 5.7: Experimental arrangement for measuring spin precession of neutrons

where m_N is the neutron mass. Thus, the time to traverse a distance of ΔL is

$$T = \frac{\Delta L}{v} = \frac{\Delta L \lambda m_N}{h}$$

$$= \frac{2\pi}{\omega}, \tag{5.12.6}$$

where we have related it to the period of the neutron spin precession with angular frequency

$$\omega = \frac{g_s \mu_N}{\hbar} B. \tag{5.12.7}$$

Thus,

$$\Delta L = \frac{(h^2/\lambda m_N)}{g_s \mu_N B}. \tag{5.12.8}$$

(b) With the neutron wavelength $\lambda = 1.55\ \mathring{A}$ in a magnetic field $B = 1.55 \times 10^{-3}\ T$, ΔL is found to be 5.56 mm. Determine the g-factor g_s for the neutron spin.

Solution — The neutron speed is

$$v = \frac{h}{\lambda m_N}$$

$$= \frac{2\pi \times 1.0546 \times 10^{-34}\text{`Js}}{1.55 \times 10^{-10}\ \text{m} \times 1.6726 \times 10{-}27\ \text{kg}}$$

$$= \quad 2.556 \times 10^3 \text{ m/s} \,, \tag{5.12.9}$$

so that the frequency is

$$\frac{1}{T} = \frac{v}{\Delta L} = 4.601 \times 10^4 \text{ Hz} \tag{5.12.10}$$

corresponding to an energy of

$$\frac{h}{T} = 1.904 \times 10^{-7} \text{ meV}. \tag{5.12.11}$$

The energy corresponding to the resonance frequency is

$$\begin{aligned} g_s \mu_N B &= g_s \; 3.1525 \times 10^{-5} \text{ meV/T} \;\times\; 1.55 \times 10^{-3} \text{ T} \\ &= g_s \; 4.886 \times 10^{-8} \text{ meV}. \end{aligned} \tag{5.12.12}$$

Equating the two energies yields the g-factor

$$g_s = 3.90 \tag{5.12.13}$$

which is quite close to the accepted value.

5.12.3 An application of the transformation matrix

A beam of particles of spin $\frac{1}{2}$ is sent through a Stern-Gerlach apparatus. One of the resulting beams is sent through another similar apparatus with the magnetic field at an angle α with respect to that of the first apparatus. What are the relative numbers of particles that appear in the two beams leaving the second apparatus?

Solution — Let the magnetic field in the first Stern-Gerlach apparatus be along the z-axis and the particle beam be along the y-axis. The corresponding directions in the second apparatus will be denoted by the z'-axis and y'-axis respectively. The new axes are obtained from the old ones by rotation through an angle α about the y-axis. Thus, y and y' axes are the same. The spin-up and down states along the z'-axis are related to those along the z-axis by Eq. (5.2.6):

$$[\psi_+ \; \psi_-] \;=\; [\chi_+ \; \chi_-] \begin{bmatrix} \cos\frac{\alpha}{2} & -\sin\frac{\alpha}{2} \\ \sin\frac{\alpha}{2} & \cos\frac{\alpha}{2} \end{bmatrix}, \tag{5.12.14}$$

where we have put $\theta = \alpha$ and $\phi = 0$. If a state has the vector representations

$$\begin{bmatrix} a_+ \\ a_- \end{bmatrix} \text{ and } \begin{bmatrix} a'_+ \\ a'_- \end{bmatrix}, \tag{5.12.15}$$

in the basis sets along z-axis and z'-axis respectively, then from the relation

$$\Psi = [\chi_+ \; \chi_-] \begin{bmatrix} a_+ \\ a_- \end{bmatrix} = [\psi_+ \; \psi_-] \begin{bmatrix} a'_+ \\ a'_- \end{bmatrix}, \tag{5.12.16}$$

the coefficients are related by the Hermitian conjugate of the transformation relating the basis states in Eq. (5.12.14):

$$\begin{bmatrix} a'_+ \\ a'_- \end{bmatrix} = \begin{bmatrix} \cos\frac{\alpha}{2} & \sin\frac{\alpha}{2} \\ -\sin\frac{\alpha}{2} & \cos\frac{\alpha}{2} \end{bmatrix} \begin{bmatrix} a_+ \\ a_- \end{bmatrix}. \tag{5.12.17}$$

Thus, if we pick the spin-up beam after it leaves the first apparatus, the relative intensities of the particles in the spin-up and down beams leaving the second apparatus are $\cos^2\frac{\alpha}{2}$ and $\sin^2\frac{\alpha}{2}$ respectively. If the spin-down beam emerging from the first apparatus, the relative intensities after the second one are $\sin^2\frac{\alpha}{2}$ and $\cos^2\frac{\alpha}{2}$. The neutron spin precession experiment in Sec. 5.12.2 is due to [10].

5.13 Problems

1. **Properties of Pauli Matrices**

   Prove the essential properties of the Pauli matrices and a useful identity:

   (a) Any 2×2 matrix A (which does *not* have to be Hermitian) can be expressed as $A = \alpha_0\, 1 + \vec{\alpha} \cdot \vec{\sigma}$. Find α_0 and $\vec{\alpha}$ in terms of the matrix elements of A.

   (b) $\sigma_x \sigma_y = -\sigma_y \sigma_x = i\sigma_z$, etc.

   (c) $\sigma_x^2 = 1$, etc.

   (d) For any two vectors of operators $\vec{A}$ and $\vec{B}$ which commute with $\vec{\sigma}$,

   $$(\vec{A} \cdot \vec{\sigma})(\vec{B} \cdot \vec{\sigma}) = \vec{A} \cdot \vec{B} + i(\vec{A} \times \vec{B}) \cdot \vec{\sigma}. \tag{5.13.1}$$

2. By diagonalizing the Pauli matrices σ_x and σ_y, find the spin up and down states in the x and y directions in terms of the basis set of the eigenstates of σ_z.

3. **Density matrix of two-level systems**

   (a) Find the density matrix for an ensemble of spin-1/2 systems with a fraction $\frac{1}{2} + p$ in the spin-up states along the (θ, ϕ) direction and a fraction $\frac{1}{2} - p$ in the spin-down states.

   (b) Relate the density matrix elements to the coefficients a_0, a_x, a_y, a_z of the form

   $$\rho = a_0 I + \vec{a} \cdot \vec{\sigma}, \tag{5.13.2}$$

   and, hence, show that the ensemble average of the spin $\vec{S}$ completely determines the density matrix of an ensemble of spin 1/2 particles.

   (c) Show that an unpolarized ensemble (half in spin-up and half in spin-down states along a chosen direction) remains unpolarized in any direction.

   (d) All the spins of an ensemble of spin-1/2 particles point in the plane bisecting the angle between the zx and yz plane. The probability distribution of the angle θ of the spin state about the z axis is proportional to $\sin\theta$. Is this a coherent ensemble?

4. **The Bloch Equations with dissipation**

   (a) For a time-dependent field $\vec{b}$ perturbing a conservative Hamiltonian system of spin $\frac{1}{2}$, establish the equation of motion for the expectation values for the spin vector in the form

   $$\frac{d}{dt}\langle\vec{S}\rangle = \gamma\langle\vec{S}\rangle \times \vec{B}.$$

   Find an expression for γ, know as the gyromagnetic ratio. This equation is valid for any spin, not just spin 1/2.

   (b) Let the total magnetic field be in the form $\vec{B} = (b\cos\omega t, b\sin\omega t, B_0)$, where b, ω, and B_0 are constants. Deduce from the Lindblad form of the master equation the dissipative terms for the Bloch equation in terms of the longitudinal relaxation time T_1 and the transverse relaxation time T_2.

5. **Transverse magnetic susceptibility.** Obtain from the Bloch equations in Problem 4 the magnetization (or the polarization) to first order in the transverse magnetic field b as a function of the resonance frequency.

6. **Spin Precession via the Bloch equations**

   Another way of demonstrating spin precession in a magnetic field. Let the static magnetic field $\vec{B}$ be along the z-direction. A spin $\frac{1}{2}$ particle with a magnetic dipole moment μ is initially in a state with expectation values of the spin $(m_x, 0, m_z)$.

   (a) From the Bloch equations neglecting the damping terms, show that the expectation values of the spin at time t is given by,

   $$\begin{aligned}\langle S_x\rangle &= m_x\cos(\omega t),\\ \langle S_y\rangle &= m_x\sin(\omega t),\\ \langle S_z\rangle &= m_z.\end{aligned}$$

   Find ω, the magnetic resonance frequency in relation to the energy eigenstates of the spin in the magnetic field.

(b) Find the effect of the damping terms on the precession.

7. **Rabi rotation** The aim of this problem is to establish explicitly the rotational operation from the time evolution of the Rabi oscillation. Take the Hamiltonian given by Eqs. (5.5.3,5.5.4). Assume the relaxation times to be infinitely long.

   (a) By the unitary transform of the spin state $|\Psi\rangle = T|\Phi\rangle$, where

   $$T = \begin{bmatrix} e^{-i\omega t} & 0 \\ 0 & e^{i\omega t} \end{bmatrix}, \tag{5.13.3}$$

   show that $|\Phi\rangle$ obeys the Schrödinger equation with an effective Hamiltonian which is time independent. Hence, find its time evolution operator as a rotation operator, identifying the rotational axis and the angle of rotation.

   (b) Find the corresponding rotation of the spin polarization vector derived from the density matrix in this "rotational frame".

   (c) Hence, derive the rotations explained in Secs. 5.7.1 and 5.7.2.

8. A particle is initially in the ground state of a potential well W_1.

   (a) If a second identical well W_2 is placed close to W_1 for a long time, the energy separation between the two lowest states in the double well is $2V$. Find the relevant Hamiltonian for the double well.

   (b) Now suppose the wells are initially well separated. The well W_2 is brought up suddenly close to W_1. The object of the experiment is to capture the particle in W_2 by suddenly removing W_1. Calculate the best time of removal.

9. **The two-level atom model.** The system consists of the (100) and (210) states of the hydrogen atom. It is driven by an external oscillating electric field $\mathcal{E}\cos(\omega t)$ along the z direction.

   (a) Construct the Hamiltonian matrix of the two-level system. Take the perturbing Hamiltonian to be $H_1 = -\vec{\mu}\cdot\vec{\mathcal{E}}$, where $\vec{\mu} = -e\vec{r}$ is the electron dipole moment.

(b) The atom is initially in the ground state. State the rotating wave approximation in this context. For the driving frequency equal to the resonance frequency, solve the time evolution of the state of the system *without* limiting to the case of a weak driving field.

(c) Deduce the formula for the Rabi frequency in this case.

(d) Describe the motion in the spin picture.

(e) Explain how you would put the system from the ground state into the excited state.

(f) Express your own thoughts concerning the fact that your results above seem to be inconsistent with the Fermi golden rule even if you take the driving field to be weak.

(g) Include the dissipative effects in the dynamics by establishing the analog Bloch equation, known as the optical Bloch equation.

10. **The Ammonia Maser**

(a) Approximate the potential energy of the nitrogen atom in the ammonia molecule by two square wells of the same shape shown in Fig. 5.8a. Define the states of the two stable positions of nitrogen by the ground states of the wells. Obtain the Hamiltonian matrix with respect to these two states and give a physical interpretation of the matrix elements.

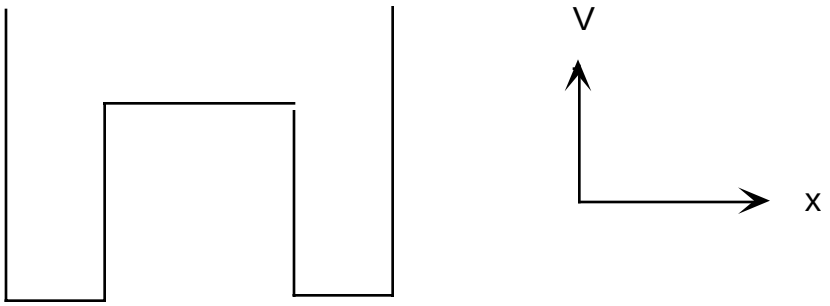

Figure 5.8: Potential for the nitrogen atom in the ammonia molecule.

(b) Show that the Hamiltonian in Part (a) may be expressed in the form $E_0 - \vec{B}\cdot\vec{\sigma}$ in terms of the Pauli and unit matrices. Hence, find the coefficients.

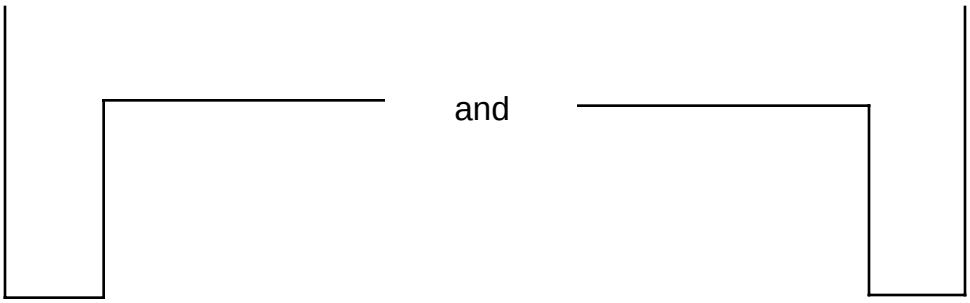

Figure 5.9: Separation of the double well.

(c) Diagonalize the Hamiltonian obtained in Part (a) to obtain the energy eigenstates and the associated eigenvalues.

(d) If the nitrogen atom is initially known to be on one side of the hydrogen triangle, show that subsequently the nitrogen atom oscillates back and forth. Find the frequency of oscillation. Explain why the nitrogen atom, having lower energy than the barrier between the two positions, can nevertheless oscillate back and forth.

(e) The ammonia molecule carries an electric dipole with moment μ. If it is placed in a uniform static electric field, find the eigenenergies as functions of the electric field and sketch the dependence.

(f) Given a source of ammonia molecules, explain how the electrical analogue of the Stern-Gerlach apparatus may be used to separate the molecules in one energy eigenstate of Part (c), from the molecules in another energy eigenstate.

(g) If the ammonia molecule in one of the energy eigenstates is placed in an AC electric field (along the axis of the nitrogen atom motion) with frequency ω, calculate the transition probability of the ammonia into the other eigenstate as a function of time and the electric field frequency. If the electric field has a fairly broad band with intensity $I(\omega)$, calculate the transition probability per unit time.

(h) The resonance frequency of oscillation for the ammonia molecule is 2.387×10^{10} Hz.

i. Calculate the off-diagonal Hamiltonian matrix element in electron volts.

ii. Is it also possible to find the diagonal element? Does it matter to the operation of the ammonia maser?

iii. Estimate the size of the microwave cavity used as a resonator for the ammonia molecules.

iv. If the operating time of the microwave cavity is about 10^{-3} seconds, what is the line-width (full width at half maximum in percentage frequency) of the ammonia molecule power output?

11. **The effective Hamiltonian of the neutral kaons.** Take as the basis states the states of strangeness 1, 0, and -1 for K^0, one of the neutral particles with $S = 0$ in Fig. 5.6, and $\overline{K}^0$, respectively. The Hamiltonian may be taken in the form,

$$H = \begin{bmatrix} K & W & 0 \\ W & K+\Delta & W \\ 0 & W & K \end{bmatrix}. \tag{5.13.4}$$

The diagonal terms represent the strong and electromagnetic interactions yielding K the masses of the two neutral kaons and Δ the mass difference with the intermediate particle. The off-diagonal terms W represent the weak interaction (not including the electromagnetic terms). To second order in the small parameter $\eta = W/\Delta$, find a unitary transformation leading to the effective Hamiltonian, Eq. (5.10.2).

12. **The neutral kaon oscillations**

(a) Justify on phenomenological ground the introduction of damping in the effective Hamiltonian Eq. (5.10.2) by replacing A with $A - i\Gamma$. Does the resulting equation fit the Lindblad form?

(b) Deduce Eq. (5.10.3) and (5.10.4).

(c) Find also the probability of the particle remaining a K^0 at time t in each case.

13. **Photon polarization**

Later in the course, we shall quantize the electromagnetic field into photons. Here is a warm-up exercise on the polarization of the photon. To construct the polarization

states of a photon, we adopt the following rules of correspondence:

Rule 1: Take the propagation direction of the corresponding classical electric field along the z axis. For the linearly polarized light along the x axis and along the y-axis given, respectively, by

$$\vec{E} = \hat{x}E\Re[e^{i(kz-\omega t)}], \tag{5.13.5}$$

$$\vec{E} = \hat{y}E\Re[e^{i(kz-\omega t)}], \tag{5.13.6}$$

where $\hat{x}$ denotes the unit vector along the x direction, the time-independent quantum polarization states of the photon corresponding to the above fields are denoted by $|0,\hat{z}\rangle$ and $|\pi/2,\hat{z}\rangle$. Use these two states as the basis set.

Rule 2: The quantum state corresponding to the phase-shifted classical field

$$\vec{E} = \hat{x}E\Re[e^{i(kz-\omega t-\theta)}], \tag{5.13.7}$$

is given by $e^{-i\theta}|0,\hat{z}\rangle$.

(Baym [2] uses the polarization states of the classical electromagnetic field to build up the quantum theory for two states.)

(a) Find the quantum state $|\phi,\hat{z}\rangle$ of the photon propagating along the z axis and linearly polarized along a vector in the xy-plane at an angle ϕ from the x-axis (with the phase $\theta = 0$).

(b) Under the rotation operator $R(\alpha,\hat{z})$, the state $|\phi,\hat{z}\rangle$ is moved to

$$R(\alpha,\hat{z})|\phi,\hat{z}\rangle = |\phi+\alpha,\hat{z}\rangle. \tag{5.13.8}$$

Let the generator G_z of the rotation operator be given by

$$R(\delta\alpha,\hat{z}) = 1 - i\delta\alpha G_z + O((\delta\alpha)^2). \tag{5.13.9}$$

Find the matrix representation of G_z in the basis set of $|0,\hat{z}\rangle$ and $|\pi/2,\hat{z}\rangle$.

(c) Find the eigenstates of G_z and *deduce* their physical meaning using the rules given above.

(d) Let $|\varepsilon_j\rangle,\ j = x, y, z$ be three linearly polarized states along the Cartesian axes. Define the three generators G_j as in Eq. (5.13.9). Show that

$$S_j|\varepsilon_j\rangle = i\epsilon_{jk\ell}|\varepsilon_\ell\rangle, \tag{5.13.10}$$

where the summation over the repeated index ℓ is understood. (See a similar operator defined in Ref. [16], p. 72.) Show that the components of $\vec{G}$ satisfy the commutation relations of the angular momentum vector

$$[G_i, G_j] = i\epsilon_{ijk}G_k. \tag{5.13.11}$$

From two of the eigenstates of G_z and G^2, argue that the photon has spin 1.

(e) Find the third eigenstate of G_z and G^2 and discuss its physical meaning if any.

(f) Even though the photon has two polarization states, why is it not a spin-1/2 Fermion?

14. **Stability of a nucleus with two nucleons**

The interaction which binds the nucleons, including protons and neutrons, is called the strong interaction, which is much stronger than the electromagnetic interaction. The two charge states of a nucleon may be simulated by using the analogous spin 1/2 states, called the isospin, $\vec{T}$. The 3-component of the isospin, T_3, (analogous to S_z) has two eigenstates, isospin-up state assigned by convention to proton and isospin-down state to neutron. (See Sec. 5.11). Now consider a nucleus with two nucleons. By neglecting the weaker electromagnetic interaction, we expect that the energy of the nucleus to depend on the magnitude of the sum of the two isospins (characterized by the quantum number u) but not on the quantum number of the 3-component of the total isospin. In fact, the $u = 0$ state is bound and the $u = 1$ states are unbound. Hence, explain (a) why the stable two-particle nucleus must be composed of a proton and a neutron, (b) why a two-proton or two-neutron nucleus is always unstable (a stable helium atom contains two protons and one or two neutrons), (c) why a proton-neutron pair may be unstable and how this state is different from the stable nucleus in (a).

15. **Isospin and nuclear structure**

    Consider the three nuclei, ^{6}He, ^{6}Li, and ^{6}Be as members of a family composed of two nucleons plus an inert core of ^{4}He which has zero isospin. If the strong interaction is invariant under the isospin rotations, sketch qualitatively the masses (energy levels) of these three nuclei. If there is an energy spacing of 2 MeV between two states of ^{6}Li, write down an effective Hamiltonian in terms of the isospin vectors of the two additional nucleons in the outer shell which reproduces the energy scheme.

16. A beam of particles of spin $\frac{1}{2}$ is sent through a Stern-Gerlach apparatus. One of the two resulting beams is sent through another similar apparatus with the magnetic field at right angles to the field of the first apparatus. One of the two beams emerging from the second apparatus is passed through to a third apparatus which is identical to the first, including the field orientation. What are the relative intensities of the two particle beams leaving the third apparatus?

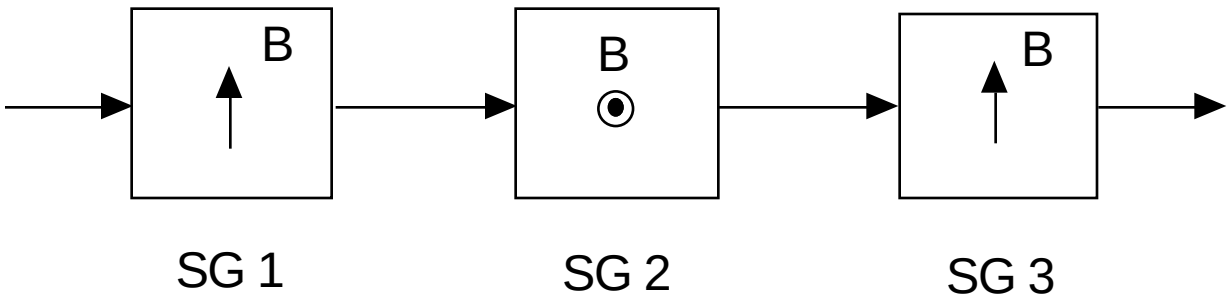

Figure 5.10: An arrangement of Stern-Gerlach magnets for Problem 16.

17. **Rotation by 2π of a spin-1/2 state**

    In the neutron interferometer by Werner *et al.* [23] sketched in Fig. 17, the circle region has a uniform magnetic field B. Incoming neutrons are monoenergetic and unpolarized. They are diffracted at the four points using crystal Bragg diffraction.

    (a) Is it necessary to polarize the neutron beam first? Why?

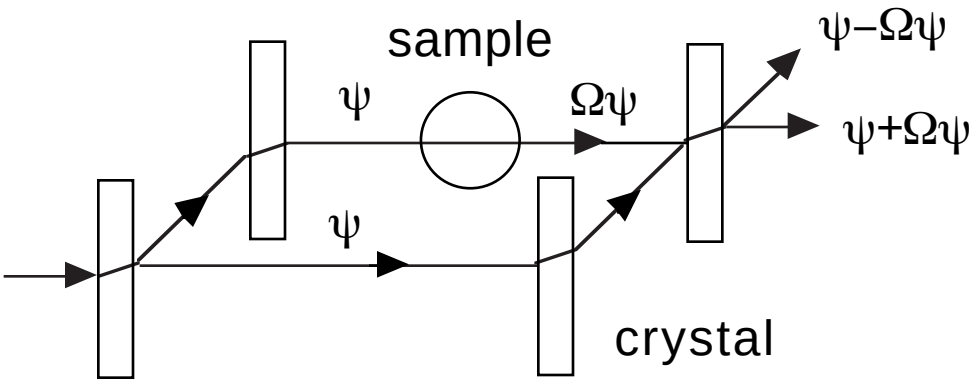

Figure 5.11: A neutron interferometer.

(b) If L is the distance taken by the neutron to traverse the magnetic field B with speed v, show that the phase difference between the two beams is

$$\phi = \frac{\mu B L}{v},$$

where $\mu = \mu_N g_N$ is the magnetic moment of the neutron.

(c) Hence, find the separation between the inference fringes as the amount ΔB through which the magnetic field must change.

(d) If the wavelength of the neutrons is 1.55 Åand $L = 1$ cm, find the magnetic field change ΔB for the separation between two adjacent interference fringes.

(e) In the above experiment, should you make allowance for the earth's magnetic field?

(f) Instead of the above, find a partner and read the papers by Bernstein and by Werner et al. and prepare a 10-minute talk on the topic.

18. **Non-linearity in Quantum Mechanics.** [22]

Consider a two-state system with the state vector

$$\Psi = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \tag{5.13.12}$$

satisfying the Schrödinger equation

$$i\hbar \frac{d}{dt}\Psi = H\Psi, \tag{5.13.13}$$

where the Hamiltonian is given by

$$H = \begin{bmatrix} E_1 - \frac{\lambda}{2} f_2^2 & 0 \\ 0 & E_2 - \frac{\lambda}{2} f_2^2 + \lambda f_2 \end{bmatrix} \tag{5.13.14}$$

containing a small non-linear term with $\lambda \ll E_2 - E_1$ dependent on the fractional occupation of the

$$\begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

state, f_2, given by

$$f_2 = \frac{|a_2|^2}{|a_1|^2 + |a_2|^2}. \tag{5.13.15}$$

(a) Show that homogeneity is preserved, i.e., if Ψ is a solution of the Schrödinger equation, so is any constant times Ψ.

(b) Show that H is time independent.

(c) Find the wave function at time t given that at $t = 0$,

$$\Psi = \begin{bmatrix} \sqrt{1 - b^2} \\ b \end{bmatrix}, \tag{5.13.16}$$

b being a constant.

Describe the relation of Ψ to the eigenstates of the Hamiltonian with no non-linear terms ($\lambda = 0$).

(d) If the system is initially at the lower energy state E_1, (i.e., $b = 0$) and a broad-band electromagnetic wave is used to excite the system, describe what would happen to the resonance frequency for absorption.

(e) Describe briefly how you would design an experiment to measure the size of the non-linear term.

5.14 Source Material and Further Reading

This chapter was inspired by the elegant introduction to quantum mechanics by Feynman [5]. Books which I have consulted for examples of the two-state systems include spin dynamics [19], isospins [7], quantum optics [1, 4, 11, 18, 21], the covalent bond [14], They would provide good reading for further study.

The kinetc energy of spin 1/2 particle is due to van der Waerden [20, 17]. For a discussion of the relation between the Fermi golden rule and the Rabi oscillation, see Ref. [4], p. 10 or [11], p. 356. An elementary account of the theory and experiment of the polarization of light to illustrate quantum theory in the beautifully off-beat but informative book [9]. The polarization of light has also been used by Baym [2] to construct the quantum theory of the two-state system. The first maser paper is [6]. For many interesting details in isotope separation, refer to the article [24]. The neutron experiment used in Problem 17 is carried out by Werner et al. [23] and described in a popular account in Ref. [3]. The kaon oscillations was originally suggested by Pais and Piccioni [12]. Readable accounts of the kaons can be found in [5, 8, 15] and CP violation in [7],

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Chapter 6 Contents

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Chapter 6

Quantum Reality, Information and Computation

Cyber space, unlike real space, is not bound by physical concepts.
— John H. Minan, Professor of Law,
Opinion Page, San Diego Union, November 25, 1999.

Information is physical!
— Rolf Landauer, Physics Letters A **217**, 188 (1996).

6.1 Introduction

For a complete quantum theory, it is not sufficient to calculate the wave function of the state and the eigen-properties of the physical observables using the rules of quantum mechanics. The theoretical results have to be correctly correlated with the output of the experimental measurements. This stems from the nature of the measurement of a quantum system. A measurement causes an abrupt change of a microscopic system to a pure eigenstate, according to von Neumann's postulates. These postulates are adopted because so far no experiments have been found to contradict them. They are necessary because the alternate of using the microscopic theory including dissipative dynamics of the macroscopic measurement instrument in each case involves prohibitive labor. This chapter deals with some salient features of the theory of the measurement processes, namely the description of the consequences of measurement on the system as well on the macroscopic measuring system. This part of the theory is formally known as the interpretation of quantum mechanics. In the vast majority of the measurements of quantum systems, the properties are averaged over a macroscopic ensemble or the measurement is a one-shot affair. And so following the von Neumann postulates and interpreting the

results in terms of probabilities of the eigenstates is adequate. However in the last two decades or so, the rapid advances of the measuring techniques and of the preparation of microscopic and mesoscopic (in size somewhere between microscopic and macroscopic systems) have made it possible to examine the microscopic properties more directly and to repeatedly measure the microscopic system. This means that the dynamics of the microscopic system has to be followed including intrusions of the measuring instrument. A basic knowledge of the measurement theory becomes an essential part of the quantum theory.

The most far reaching fundamental issues are brought out by two famous problems, the so called EPR paradox, put forward by A. Einstein, B. Podolsky and N. Rosen and the life and death of Schrödinger's cat. We shall study not only the posed problem but also the resolution: in the EPR case, the Bell theorem and associated experiments and in the Schrödinger's cat problem, the phenomenon of decoherence.

Remarkable advances were made recently in the theory of information processing and computation based on quantum dynamics of the information coded in quantum systems. Quantum information processing and computation are expected and shown in theory to supersede the classical ways currently employed in a number of interesting cases. Although the electronic processes in a transistor are quantum in nature, the binary number coded depends on two values of the voltage built upon the charge of a large number of electrons without regard to their quantum properties. Thus, the extant computation processes are based on the concepts of classical physics. The theory effort in quantum information and computation has stimulated blossoming research programs for the physical realization of such quantum devices. Since consideration of such applications may depend crucially on a thorough understanding of the consequences of quantum theory, it is educational to examine some of the basic notions here.

6.2 The EPR Paradox and Bell's Inequalities

EPR stands for A. Einstein, B. Podolsky and N. Rosen who questioned whether quantum theory was a complete description of physical reality. J. S. Bell found that the paradox posed by the EPR definition of physical reality against quantum theory could be formu-

lated as a set of inequalities of measured quantities subjected to experimental testing. Experiments have shown that the results are consistent with quantum theory and not with the Einstein's requirement of physical reality. (See, for example,). D. Bohm [5] changed the EPR illustrative example of a two-particle system to a two-spin system. Following the chapter on the two-state systems, this then serves very well as a vehicle for us to delve a little deeper into the predictions of quantum theory.

6.2.1 Measurement of the Two-Spin System

In Chapter 4, we have worked out the eigenstates of the total spin in a system of two spin-1/2 particles. For example, the singlet state with zero total momentum and zero z-component is given by

$$|\Psi_{0,0}\rangle = \sqrt{\frac{1}{2}}\,(|+z,-z\rangle - |-z,+z\rangle), \tag{6.2.1}$$

where we have used the first $\pm z$ to denote the spin-up and down states along the z-axis of the first particle and the second placed $\pm z$ to denote the states of the second particle. This state is an example of an entangled states, that is, while it is the sum of products of states of two (for example) particles which cannot be expressed as a product of a state of one particle times another state of the second. If the spin of the first particle is measured along the z direction after the composite is prepared in the singlet state, then we know for certain the outcome of a subsequent measurement of the spin of the second particle along the z axis. For example, if the result of measuring the first leads to the spin-up state, then the system has collapsed to the state $|+z,-z\rangle$ and the second particle is definitely in the spin-down state. If we rotate the axis of measurement to the x-direction, since the singlet state must be isotropic, i.e., independent of the axis direction,

$$|\Psi_{0,0}\rangle = \sqrt{\frac{1}{2}}\,(|+x,-x\rangle - |-x,+x\rangle). \tag{6.2.2}$$

We can verify this direction by the transformation for each spin:

$$|+z\rangle = \sqrt{\frac{1}{2}}\,(|+x\rangle - |-x\rangle). \tag{6.2.3}$$

Again a measurement of the first spin along the x direction leads to the second particle being in a definite spin direction along x. However, if a measurement of S_z is now made on the second, there would be only a fifty-fifty chance of finding the spin-up state.

Now imagine that the singlet state of the composite particle is prepared when the constituents are in close proximity of each other. Then an internal explosion between the two particles is rigged such that the two particles fly apart without changing the total momentum or angular momentum of the system. One of the aforesaid spin measurements on the first particle is made after the two particles are so far apart that there could be no interaction potential between the two particles. Quantum theory predicts that the spin of the second is opposite that of the outcome of the first in any direction measured. This is just good old fashion conservation of angular momentum which nobody disputes. However, quantum theory also predicts that measurement of a spin component of one particle can influence the outcome of a subsequent measurement of a spin component of the other. For example, if either S_{1z} or S_{1x} is measured on the first particle and only S_{2z} is later measured on the second particle, then the second result depends on whether the first one measures S_{1z} or S_{1x}. The results of a sequence of such measurements when both S_{1z} and S_{2z} are measured may take the form:

$$\begin{array}{rccccccc} \text{First:} & + & - & + & + & - & - & - & \ldots \\ \text{Second:} & - & + & - & - & + & + & + & \ldots \end{array} \tag{6.2.4}$$

where $\pm$ are short for $\pm 1/2$. They are perfectly correlated. On the other hand, if S_{1x} and S_{2z} are measured, the results may take the form:

$$\begin{array}{rccccccc} \text{First:} & + & - & + & + & - & - & - & \ldots \\ \text{Second:} & - & - & - & + & + & - & + & \ldots \end{array} \tag{6.2.5}$$

The second row is completely random with respect to the first. That the nature of the two sets (6.2.4) and (6.2.5) is correlated with whether the z-components of both spins are measured or the x-component of the first and the z-component of the second are measured is known as quantum nonlocal correlation. Since during the measurements the two particles so far apart that there could be no interaction between them, this prediction of quantum theory is rather counterintuitive and has been labeled as "action at a distance". It certainly bothered Einstein as evidenced by his letter to to E. Schrödinger May 31, 1928:

> *The Heisenberg-Bohr tranquilizing philosophy—or religion?—is so delicately contrived that, for the time being, it provides a gentle pillow for the true*

believer from which he cannot very easily be aroused. So let him lie there.

6.2.2 EPR Paradox and Einstein's Locality Hypothesis

The key points of the EPR arguments are:

1. They gave a definition for an element of physical reality:

   > *If, without in any way disturbing a system, we can predict with certainty (i.e, with probability equal to unity) the value of physical quantity, then there exists an element of physical reality corresponding to this physical quantity.*

2. For two noncommuting observables, such S_{2z} and S_{2x}, knowing the value of one precisely means the values of the other is not known. EPR would describe it as when the z-component of the spin is known, the x-component has no physical reality. It follows that either that two physical properties represented by two noncommuting operators "cannot have simultaneous reality" or that "the quantum mechanical description of reality ... is not complete."

3. Now take the entangled spin state of two particles. Measurement of S_{1z} yields, say, the value of $+1/2$. Then the observable S_{2z} of the second particle would have the value $-1/2$ without any measurement. If then S_{2x} is measured, say, with a value $+1/2$, then the second particle has a definite value. EPR asserted what has become known as Einstein's locality principle. When the two particles are far apart, there is no interaction. Therefore the experiments on the first particle cannot influence the properties of the second. Thus, the physical quantities represented by the noncommuting observables S_{2z} and S_{2x} are shown to "have simultaneous reality". This eliminates the first of the two alternatives in statement No. 2, leading to the s conclusion that the quantum mechanical description of reality given by the original wave function is not complete.

The latter conclusion led to attempts to find "hidden variables" to supplement the quantum theory.

Niels Bohr's rebuttal invoked the concept of complementarity for a complete description of two noncommuting observables.

6.2.3 Bell's Inequalities

The EPR paradox indicates a choice between the quantum nonlocal correlation and the Einstein locality hypothesis. A Bell's inequality is derived from a model observing the Einstein locality. It can then be compared the quantum prediction. For cases in which the two results disagree, experiment can then falsify one of the two assertions. Consider a model which is consistent with the Einstein locality. Let ϕ and χ be two particles of spin 1/2, each of which is given two physical attributes mz and $m'x$ of spin directions along z and x, where $m, m' = \pm$. Each one of the four possible states of ϕ is $\phi(mz, m'x)$ and similarly for χ. A composite of ϕ and χ of total spin zero has four possible states, $\phi(mz, m'x)\chi(\bar{m}z, \bar{m}'x)$, where $\bar{m} = -m$. We make an ensemble of a large number of replicas of the composite particles, with a quarter of them in each state. The statistical average of the measurements in either z or x direction for either particle will be consistent with the quantum theory. The model is consistent with the Einstein locality in the sense that the outcome of a measurement on one particle is independent of the measurements which have been done on the other particle.

Now consider making measurements in three different directions along unit vectors $\hat{a}, \hat{b}, \hat{c}$ (which should not be mutually orthogonal). Let the fraction of the composite particles in the ensemble in the state $\phi(\ell a, mb, nc)\chi(\bar{\ell}a, \bar{m}b, \bar{n}c)$ be $f(\ell, m, n)$, where $\ell, m, n = \pm$. The eight fractions sum to unity. Suppose that Alice measures one of the three directions on the ϕ particle and Bob measures a different direction on the χ particle. The probabilities of the ϕ particle having the same spin up or down in any two directions are given by

$$\sum_{m=\pm} P_\phi(ma, mb) = f(+,+,+) + f(+,+,-) + f(-,-,+) + f(-,-,-); \quad (6.2.6)$$

$$\sum_{m=\pm} P_\phi(mb, mc) = f(+,+,+) + f(-,+,+) + f(+,-,-) + f(-,-,-); \quad (6.2.7)$$

$$\sum_{m=\pm} P_\phi(mc, ma) = f(+,+,+) + f(+,-,+) + f(-,+,-) + f(-,-,-). \quad (6.2.8)$$

Thus, the sum of the conditional probabilities that the spin states of ϕ in any two

directions are both up or down is given by

$$P_\phi(\text{same}) = 1 + 2f(+,+,+) + 2f(-,-,-) \geq 1. \tag{6.2.9}$$

This is one of the Bell inequalities. This is a consequence of the model which satisfies the Einstein locality.

What does the quantum theory predict for $P_\phi(\text{same})$? The probability $P_\phi(+a,+b)$ is the same as that of Alice obtaining spin-up in the a-direction for ϕ and Bob obtaining spin-down in the b-direction for χ,

$$\begin{aligned} P_\phi(+a,+b) &= |\langle \phi_{+a}\chi_{-b}|\Psi_{0,0}\rangle|^2 \\ &= |\langle \phi_{+a}\chi_{-b}|\sqrt{\frac{1}{2}}\left(|\phi_{+a}\chi_{-a}\rangle - |\phi_{-a}\chi_{+a}\rangle\right)|^2 \\ &= \frac{1}{2}|\langle \phi_{+a}\chi_{-b}|\phi_{+a}\chi_{-a}\rangle|^2 \\ &= \frac{1}{2}|\langle \chi_{-b}|\chi_{-a}\rangle|^2. \end{aligned} \tag{6.2.10}$$

using the singlet expression, Eq. (6.2.1) in the a-direction. If we align $\hat{a}$ with the z-axis and $\hat{b}$ at an angle θ_{ab} from the z axis, the transformation matrix yields the matrix element $\langle \chi_{-b}|\chi_{-a}\rangle$ and thus,

$$P_\phi(+a,+b) = \frac{1}{2}\cos^2\left(\frac{\theta_{ab}}{2}\right). \tag{6.2.11}$$

In the same manner, we can obtain the same expression for $P_\phi(-a,-b)$ and, hence,

$$P_\phi(\text{same}) = \cos^2\left(\frac{\theta_{ab}}{2}\right) + \cos^2\left(\frac{\theta_{bc}}{2}\right) + \cos^2\left(\frac{\theta_{ca}}{2}\right). \tag{6.2.12}$$

That the quantum prediction is different from the locality result can be seen from the fact that Eq. (6.2.12) does not always obey the Bell inequality (6.2.9), e.g., when the three directions are coplanar and the angle between each pair is $2\pi/3$:

$$P_\phi(\text{same}) = 3/4. \tag{6.2.13}$$

The two distinct consequences of Einstein's locality and of quantum nonlocal correlation can then be subjected to experimental tests. As mentioned above, experimental results favor the quantum conclusion (see Problem 2).

6.3 Rudiments of Quantum Information

The discussion on EPR and the Bell inequalities also brings out the concept of the entangled states which are the underpinning of the processing of quantum information and which are also useful in quantum computation.

Rolf Landauer illustrated the cornerstone of his study of the energy and entropy of classical computation processes by the succinct sentence that information is physical. Each piece of information has to be expressed as a physical state. So you may take comfort in the fact that the famous information highway cannot be built without physics. As the physical system storing a bit of information gets smaller and smaller, quantum effects come into play. As the ultimate quantum system, the two-state system seems to be ideal for the storage of a bit, know as the qubit (quantum bit). The trick is then to be able to isolate it from the uncontrolled environment effects. As the amount of information (number of bits) becomes enormous, the qubits have to be well isolated from one another and from the environment or else rapid decoherence will set in and the system will obey the laws of thermodynamics. The remarkable development in the last decade has been to show how in principle quantum effects may be used to advantage in the science of information. In this section, we give a flavor of the concepts involved as rather novel and fun applications of the theory of two-state systems which we have just examined.

6.3.1 Quantum Cryptography

On hearing the EPR experiment, "Aha", you say,"Alice can now communicate with Bob at a rate faster than the speed of light." Suppose Alice goes to Anchorage and Bob to Barbados. Calvin in California sends at periodic intervals from each singlet composite of two particles a particle to Alice and a particle to Bob. It has been prearranged that both of them will measure the spin in the same z direction. It is true that if Alice finds a spin-up state, Bob will find a spin-down state. However, Alice gets an up or down state randomly. So all Bob will get is a photo-negative copy of the random sequence, Eq. (6.2.4), which contains no information.

Let us modify the information transmission protocol somewhat. Alice measures either S_z or S_x without telling Bob which but she emails Bob her data as a sequence of pluses

and minuses. Bob then does his measurements of S_z and compare his sequence with Alice's. If they are exactly opposite (except for a few errors), then he can deduce that she measured S_z. If the results correlate only half of the time, then she measured S_x. This seems a very clumsy way to communicate: not only is it no longer faster than the speed of light but Alice has to send Bob many bits of information to convey just one bit. However, if we think of it not as a means for communication but as a means for cryptography, it is rather robust. Anyone who intercepts the email message has no means to decode the message of which direction Alice has measured unless the person possesses the "key", i.e., the particles which are sent to Bob. How to discover if the particles have been intercepted and then resent to Bob will be left as an exercise for the reader.

The above is an example of a quantum public key distribution in the public key cryptography. For an accessible discussion, see [18].

6.3.2 A Qubit

The fundamental unit of information is a bit which is a state such as 0 or 1 in a classical two-state system. The state of a quantum bit, now called a qubit, is a state in the Hilbert space of all possible states in a quantum two-state system. For the sake of familiarity, we shall use the two basis states to be $|\pm\rangle$, or the spin-up and down states along a specified direction. For definiteness, we shall take the basis set $|+\rangle, |-\rangle$ to represent $1, 0$ respectively. A qubit represents more than just the possibility of one of these two states to include any superposition of them. The restriction of normalization and the removal of an overall phase yield two real numbers (p, θ) to characterize a qubit:

$$|\psi\rangle = |+1\rangle p e^{i\theta} + |-1\rangle \sqrt{1-p^2}. \tag{6.3.1}$$

To "read" the qubit (to retrieve the information) requires measurements on this state, the outcome of which we have examined.

6.3.3 Entangled States and Quantum Operations

As in the classical information processing, the quantum counterpart also requires logical operations involving two qubits. The composite system of two spin-1/2 particles has four states. As eigenstates of the total angular momentum J^2 and J_z, two of the triplet

states, $|+,+\rangle$ and $|-,-\rangle$, are unentangled product states. Measurement of spin on one does not disturb the state of the other. One may also say that the spin states of the two particles are uncorrelated. By contrast, the triplet state $\Psi_{1,0}$ and the singlet state $\Psi_{0,0}$ are sums of product states, i.e., entangled states. We have seen that, in an entangled state, measurement on one spin can affect the outcome of the subsequent measurement of the other spin. This property provides the important distinction between classical and quantum information.

Consider coding two classical bits of information in two qubits. The straightforward way is to store the information in four unentangled states:

$$|\pm,\pm\rangle \equiv |\pm\rangle|\pm\rangle. \tag{6.3.2}$$

It is sometimes advantageous to encode the information in four entangled states, known as the Bell states or EPR pairs,

$$\begin{aligned} |\Psi_\pm\rangle &= \frac{1}{\sqrt{2}}(|+,-\rangle \pm |-,+\rangle) \\ |\Phi_\pm\rangle &= \frac{1}{\sqrt{2}}(|+,+\rangle \pm |-,-\rangle). \end{aligned} \tag{6.3.3}$$

We have seen one example in quantum cryptography and we shall see more presently.

To find a transformation from the unentangled states to the Bell states, we consider first a useful single-spin transformation known as the Hadamard transform

$$H = \frac{1}{\sqrt{2}}(\sigma_x + \sigma_z) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}. \tag{6.3.4}$$

It transform the basis states $|m\rangle, m = \pm 1$ into two superposition states $(|+\rangle + m|-\rangle)/\sqrt{2}$. It is convenient to introduce a quantum circuit diagram to depict the operation (Fig. 6.1(a)).

A most important transformation involving two qubits is the logic operation, XOR or controlled-NOT (C-NOT) (Fig. 6.1(b)),

$$C_N|m,n\rangle = |m,\bar{m}n\rangle. \tag{6.3.5}$$

The first bit may be regarded as the source or control, whose spin direction determines how the second bit (known as the target) is changed. Thus, if the source is $-$, the target state is unchanged and if the source is $+$, the target is flipped ($|n\rangle \to |\bar{n}\rangle$).

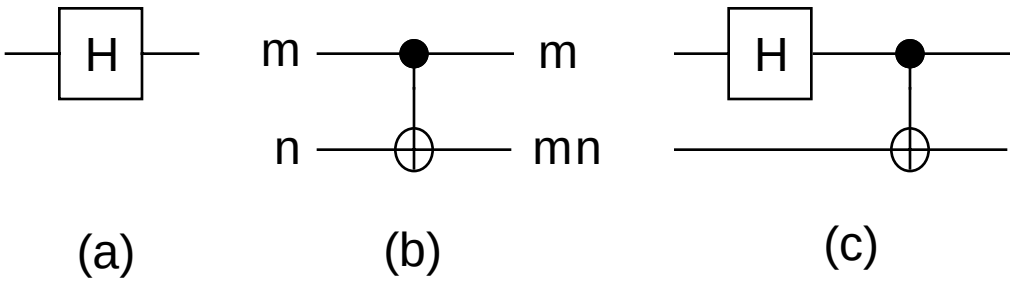

Figure 6.1: Quantum circuit elements: (a) The Hadamard transform on a single qubit. (b) Controlled-NOT operation on two qubits, where $m, n = \pm 1$. (c) In order from left to right is the Hadamard transformation followed by C-NOT.

Its importance derives from the fact that any other logic function of two qubits is a combination of C-NOT and single qubit operations. Moreover, it can be shown that any unitary transformation can be broken down into a product of unitary transformations involving the changes of only two components of the basis set. Then a combination of the C-NOT gate and all possible single qubit operations can be used to form any unitary transformation for n qubits. The set of the C-NOT gate and all possible single qubit operations is said to be universal for quantum computation.

Although the Hadamard transformation and C-NOT are widely used in the theory literature, they involve rotation about the z-axis. For some means of physical realization the Rabi rotation about x and y may be more convenient. For optical excitation about two energy levels, if the pseudo-magnetic field along the (pseudo-)z-axis is used to simulate the splitting of the two levels, the electromagnetic fields which generate the transitions or Rabi oscillations are about the (pseudo-)x or y axis. The rotation which serves the purpose as well as the Hadamard transformation is the $\pi/2$ rotation about the y-axis,

$$R(\pi/2, y) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}. \tag{6.3.6}$$

Note that the determinant of the Hadamard transformation is -1 which makes it an improper rotation, in contrast to the $\pi/2$ rotation. The Hadamard is equivalent to the combination of σ_z and then the rotation. The logic gate, C-NOT, with the first qubit as control can be replaced by a controlled π-rotation, C-ROT, i.e., a π-rotation of the second qubit as the target conditional on the first qubit being spin up or leaving the second qubit unchanged if the first qubit is spin down. The matrix representation in the

basis set of $[|+,+\rangle \;\; |+,-\rangle \;\; |-,+\rangle \;\; |-,-\rangle]$ is

$$C_2(\pi, y) = \begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \tag{6.3.7}$$

The combination of H followed by C_N (Fig. 6.1(b)) transforms the unentangled states $[|+,+\rangle \;\; |+,-\rangle \;\; |-,+\rangle \;\; |-,-\rangle]$ in order to the Bell states in Eq. (6.3.3), $[\Psi_+ \;\; \Phi_+ \;\; \Psi_- \;\; \Phi_-]$ (see Problem 5). Since the Bell states are of the form $|m,n\rangle + p|\bar{m},\bar{n}\rangle$, we may regard the two-qubit system made up of the four Bell states with the first bit as having been coded as the phase bit p and the second bit as the parity bit mn. Both H and C_N are their own inverse. It is then easy to reverse the operation and disentangle the Bell states and then measure the phase bit and parity bit contained in the Bell states.

A spin operator of one particle acting on one of the Bell states (i.e. measuring a spin property of one particle) transforms it to another Bell state. The transformation may be said to be local. There are four such operations: the identity, σ_x, σ_y, and σ_z. (See Problem 6.)

Of course the idea of entangled states is not limited to two particles. In fact, the three-particle GHZ state, Eq. (6.6.3), is a coherent superposition of two states which represent 0 and 7 in binary form. In Problem 3, we see its power.

6.3.4 Beam me up, Scottie!

A basic quantum teleportation consists in sending a state $|\Psi\rangle$ from A to B by deconstructing the state at A to obtain classical information about the state which is sent to B where the information is used to reconstruct the state. The key ingredients in the deconstruction and reconstruction are a particle at A and one at B which form an EPR pair or a Bell state. In general, it is not possible to make copies of a quantum state (see Problem 7)

Figure 6.2 shows the circuit diagram necessary to send a state $|\Psi\rangle$ of a spin-1/2 particle from A to B, given by

$$|\Psi\rangle = c_+|+\rangle + c_-|-\rangle. \tag{6.3.8}$$

A and B share the two spin-1/2 particles ϕ and χ respectively of a Bell state or EPR pair,

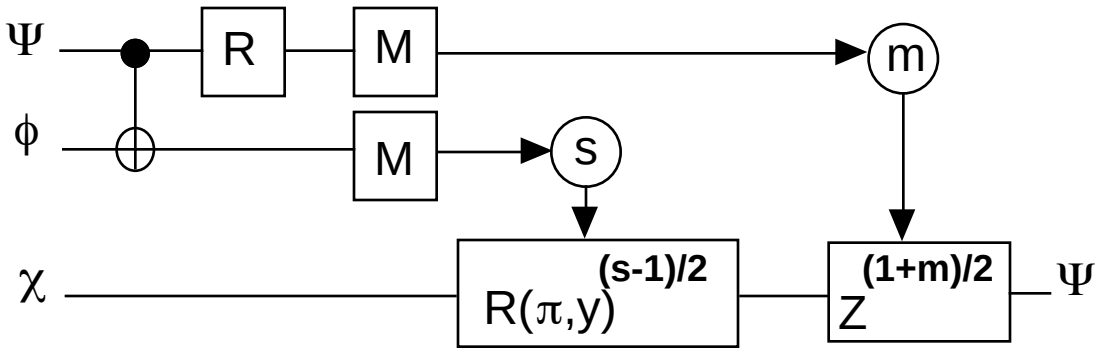

Figure 6.2: A quantum circuit for teleportation (after Fig. 1.13 of Ref. [24]).

$|\Psi_-\rangle$, in Eq. (6.3.3) – the singlet. The three horizontal lines shows the time evolution from left to right of the three qubits in order: the top qubit carrying the state to be teleported, the middle qubit at A the first particle of the EPR pair, and the bottom qubit at B the second particle of the EPR pair. Thus the initial state is

$$\begin{aligned} |\psi_i\rangle &= |\Psi\rangle|\Psi_-\rangle \\ &= (c_+|+\rangle + c_-|-\rangle)\frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle). \end{aligned} \tag{6.3.9}$$

We take care to preserve the order from left to right in which the first state is that of the message qubit, the second the A qubit and the third the B qubit, no matter how they are bracketed, e.g.,

$$|+--\rangle = |+\rangle|-\rangle|-\rangle = |+\rangle|--\rangle = |+-\rangle|-\rangle. \tag{6.3.10}$$

In this problem, we have no occasion to bracket the first and third qubits together. Hence, the initial state can be expanded as

$$|\psi_i\rangle = \frac{1}{\sqrt{2}}(c_+|++-\rangle - c_+|+-+\rangle + c_-|-+-\rangle - c_-|--+\rangle). \tag{6.3.11}$$

The first operation in the circuit diagram is a C-ROT, denoted by $C_2(\pi, y)$ in Eq. (6.3.7), depicted in the diagram as connected dot (control) and circle (target), acting on the first two qubits. Thus, if the first qubit is $+$, the second qubit undergoes a π rotation and if the first is $-$, the second remains unchanged. Then,

$$C_2(\pi, y)|\psi_i\rangle = \frac{1}{\sqrt{2}}(c_+|+--\rangle + c_+|+++\rangle + c_-|-+-\rangle - c_-|--+\rangle). \tag{6.3.12}$$

Note that the middle qubit in the first and second terms on the right are changed.

The second operation is the $\pi/2$ rotation about the y-axis denoted by R acting on the first qubit:

$$\begin{aligned} R|+\rangle &= \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle), \\ R|-\rangle &= \frac{1}{\sqrt{2}}(-|+\rangle + |-\rangle). \end{aligned} \tag{6.3.13}$$

The result of the second operation is

$$\begin{aligned} RC_N|\psi_i\rangle &= \frac{1}{2}[c_+(|+--\rangle + |--+\rangle + |++-\rangle + |-+-\rangle) \\ &\quad +c_-(-|++-\rangle + |-+-\rangle + |+--\rangle - |--+\rangle)] \\ &= \frac{1}{2}[|++\rangle(c_+|+\rangle - c_-|-\rangle) + |+-\rangle(c_-|+\rangle + c_+|-\rangle) \\ &\quad +|-+\rangle(c_+|+\rangle + c_-|-\rangle) + |--\rangle(-c_-|+\rangle + c_+|-\rangle)]. \end{aligned} \tag{6.3.14}$$

In the last step, we have expressed the state in terms of the spin states of the first two qubits. If their spin states (S_z) are measured, as indicated by the boxes M, the state will end up in one of the states $|ms\rangle$, where m and s are the spin directions of the message bit and the sender's bit. The receiver qubit will end up in the corresponding state in the last step of Eq. (6.3.14). For example, if the measured result is $(m, s) = (-, +)$, then the qubit at the receiver's end B becomes the state $|\Psi\rangle$. In general, if the measured state is $|ms\rangle$, the single-qubit operations $Z^{(m+1)/2}R(\pi, y)^{(s-1)/2}$ will bring the third qubit at B to the state $|\Psi\rangle$, where Z is the operator σ_z.

Since the state at B cannot be measured without destroying it, the classical information (m, s) from the sender is indispensable in reconstructing the teleported state. This message sending keeps the whole teleportation speed below that of light. Note that a way to view the teleportation is that a shared EPR pair and two classical bits of information are equivalent to one qubit of communication.

6.3.5 You've Got Mail

Although we have craftily turned the failure of the first attempt at quantum communication into quantum cryptography, the question of how Alice and Bob can communicate

with entangled states remains. Here is an example of applying entanglement to communication. As before, Calvin prepares two spins in a standard Bell state and send ϕ to Alice and χ to Bob. Alice can perform on ϕ one of the four local operations and thereby changes the Bell state Calvin of CalComm prepared into one of the four possible Bell states. Now, she sends her particle to Bob who is, thus, in possession of the two particles in the new Bell state. A C-NOT followed by a Hadamard operation will give Bob one of the unentangled states which he can determine by spin measurements on both particles. Thus, he knows the new Bell state and, hence, the two (classical) bits of information Alice sends him (cf. Sec. 6.3.3). The company CalComm which sells the communication equipment and protocol advertises that Alice can send two bits of information to Bob with one photon (utilizing its polarization states – see Problem 10 in Chapter 5). This is an example of "dense coding". Consumer Advocate points out that, of course, Bob also needs the photon CalComm sends him. Nonetheless, Alice's information may be sent to Bob regardless of the information content of the photons sent out by CalComm. The added bonus is that the information is interception-proof.

6.4 A Brief Introduction to Quantum Computation

A knowledge of quantum computing is timely, but more important to the learning of quantum theory is the fact that quantum computing provides a wonderful framework to understand how quantum theory works in the microscopic components of the computer and the consequence of their interaction with the macroscopic world, in the preparation of the initial state, in the dissipative and dephasing effects of the environment, and in the measurement of the finite state of the quantum computation.

Richard Feynman noted the rapid increase of steps required to simulate the time evolution of a quantum system as the number of particles in the system rises. He suggested using an analog quantum computer to simulate the dynamics of a whole class of quantum systems. P. Benioff introduced the notion of building a universal computer (a Turing machine) based on the quantum system. In this section, we introduce the key ideas of quantum computation. First, we illustrate the power of quantum computation through "parallel processing" by studying the Deutsch-Josza algorithm. Then we discuss

the basic components for a universal computer. An examination of the dephasing effects of the environment on the quantum computer leads to the concept of decoherence, which we will examine more generally in the following section.

6.4.1 The Deutsch-Josza algorithm

David Deutsch [11] pointed out that the potential of quantum computing lies in "quantum parallelism". He posed the following problem of conditional branching. Suppose we have already a program which computes $f(x)$ if x is given. In the simple example of two bits, $(x = \pm 1, f(x) = \pm 1)$, there are four possible functions to produce $f(+1)$ and $f(-1)$. Deutsch's problem is how to use quantum theory to arrange the evaluation of $f(x)$ to determine if the function is constant $(f(+1) = f(-1))$ or balanced (the function yields the ± 1 values equally). The classical way takes two evaluations and then comparison of the two results. Now consider a quantum program for $f(x)$ using a transformation which is a relative of C-NOT:

$$U_f|m, n\rangle = |m, f(m)n\rangle. \tag{6.4.1}$$

A state is first prepared in the ground state $|-,-\rangle$. A Hadamard transform is used on the second bit, to yield

$$|-x\rangle = \frac{1}{\sqrt{2}}(|+\rangle - |-\rangle). \tag{6.4.2}$$

Then the Hadamard transform is used on the first bit of the state $|+,-\rangle$):

$$|+x\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle). \tag{6.4.3}$$

The result is a mapping from $|-,-\rangle$ to $|+x,-x\rangle$. Then the operation U_f is used on the rotated product state, resulting in

$$U_f|+x,-x\rangle = \frac{1}{\sqrt{2}}\left[(-1)^{[f(+1)-1]/2}|+1,-x\rangle + (-1)^{[f(-1)-1]/2}|-1,-x\rangle\right]. \tag{6.4.4}$$

If the function f is constant, the resultant state is $|+x,-x\rangle$ and, if not, it is the resultant state is $|-x,-x\rangle$. Which of these states can be determined by measuring the x component of the spin of the first bit.

The contrast between the classical program and the quantum one is in the use of the subroutine for evaluation of the function $f(x)$. The classical program submits each value

of x for a separate evaluation of the function. The power of the quantum computation comes from the use of the linear superposition of two states in both the input and output qubits for one linear transformation. It means that the information can be spread into both states of the same bit and that parallel processing is possible. The implementation of the Deutsch-Jozsa algorithm by nuclear magnetic resonance has been carried out.

6.4.2 Requirements for quantum computation

We describe a simple conceptual quantum computer and its operations. There are ingenious alternatives but we are contented with illustrating the essential ideas. The physical components of a quantum computer are a set of subsystems in which the qubit can be coded. The simplest example is a system of spin 1/2 particles. There should be negligible interaction between any two qubits except under control of the program when it is desired to run a logic gate operation between two qubits. There should be as little interaction as possible with the environment since irreversible processes are deleterious to the ideal quantum computing process consisting of a series of linear, reversible transformations. The only exceptions are the initialization of the state of the quantum computer and the measurement at the end of the computing process where the macroscopic instrument must intervene. The initialization may be as simple as cooling the computer to the ground state. Note that this is an irreversible process and would take a very long time if the temperature is not sufficiently low compared with the energy spacing between the two qubit states.

A computation on a quantum computer consists in applying a single unitary operation on the n qubits of this system. In order that the computer is flexible and not just for a single purpose, one scenario is to render the operations on the qubits as composed of controlled single qubit dynamics and two-qubit conditional dynamics described above. A computing process could consist of a controlled sequence of such operations. It is sufficient to have at hand a set of arbitrary one qubit rotations and the CNOT logic gate in order to make up a sequence of operations which result in any desired unitary operation of the n qubits. This is known as universal computation. This greatly simplifies the design of physical operations to implement quantum computation.

A classical computation procedure involves processing information stored in bits us-

ing a sequence of elementary logic operations on two bits. The corresponding elementary quantum gate performs an elementary operation on two qubits, which is just a unitary transformation. The C-NOT is an example. Such an operation has been demonstrated recently in experiments using trapped atoms, cavity quantum electrodynamics, and nuclear magnetic resonance. More generally, a quantum computation for n qubits involves a sequence of unitary transformations. Thus, every operation has an inverse and is reversible. In classical computation, there are also reversible gates. However, unlike the quantum case, not all gates have to be reversible. A logic gate like NAND combines the input of two bits into a one-bit result. The procedure cannot be reversed.

The algorithm to solve the Deutsch problem and to illustrate the aspect of parallel processing in quantum computation can be generalized to any number of qubits. A physical system which can implement a generalization to a large number of qubits is said to be scalable. In the quantum procedure, the initial information has to be coded and the final outcome measured. So at these stages, it has no advantage over the classical procedure. However, the intermediate transformations handle the bits in parallel and possess a much higher efficiency. In theory, the power of quantum computing was first demonstrated dramatically by Peter Shor in factorizing a large integer. It is commonly believed (but not proven) that to factorize an integer of N digits by a classical algorithm requires the number of steps exponential in N. Shor showed that a quantum algorithm requires the number of steps which is a polynomial in N. Since the best current encryption schemes depend on the near impossibility of factorization, this has vast implication on cryptography, much used in electronic banking and other online commerce. The key in the quantum factorization scheme is the quantum Fourier transform, which has a number of other applications. Another famous quantum algorithm was constructed by L.K. Grover for searching an unsorted list. A classical search mechanism takes $O(N)$ steps for a long list of N items. Grover's algorithm takes $O(\sqrt{N})$ steps.

The requirement of weak interaction between the qubits and the environment stems from the fact that the dephasing dynamics causes the final state to deviate from the ideal design. This requirement brings into sharp relief the decoherence effect. Since the phenomenon is of importance to the general quantum theory in the interplay between the

dynamics of the microscopic and macroscopic systems, we shall devote the next section to it.

One major development not touched upon is the quantum error correction. The error in the intermediate states which occurs because either of the environment dephasing or of unintended dynamics due to the intrusion of the states in the system not designed for the qubits can be corrected by making replicates of each qubit and by designing quantum operations which automatically change the state of the set of all replicas of a qubit to the one assumed by the majority. The error correction is not sure fire but can have a very high success rate.

We have only given a flavor of the excitement of the recent development in this group of applications of quantum mechanics. There are major efforts devoted to the quantum algorithms as well as to the implementation of these ideas in real physical systems.

6.5 Decoherence

6.5.1 Dephasing and decoherence

It is shown in Section 5.6 that a two-state system in contact with a reservoir develops irreversible dynamical processes which can be separated into dissipation and dephasing. Dissipation is present in the transition from one state to another, represented by the damping terms in the diagonal part of the density matrix, known as the population terms. Dephasing refers to the loss of phase coherence between the two states, represented by the decay of the off-diagonal term of the density matrix, also known as the coherence term. The dephasing varies over a wide range of values for different systems, depending on the strength of interaction with the environment. For the nuclear spins in a liquid or solid, it could be seconds or much longer; for the electron spins, of the order of milliseconds; for two levels in an atom which suffers radiative recombination, 10 ns; and, for two levels in a semiconductor quantum dot, 100 ps.

The question before us now is what is the dephasing time between two states of a macroscopic system, i.e., one with the number of degrees of freedom closer to the Avogadro's number A than to unity. The question is posed most starkly as the problem of Schrödinger's cat. The system consists of a single atom with two states, a Geiger

counter which can measure the single photon emitted by the atom, a hammer which can be triggered by the Geiger counter to break a glass vial containing cyanide gas, which can kill the cat in a sealed box (with an ample supply of air to satisfy the kindly volunteer from ASPCA who oversees the experiment). If the initial state of the atom is a linear combination of the two states and the cat being alive, then the state of the system is (including the link between the atom and the cat as part of the cat for simplicity)

$$|\Psi(t=0)\rangle = |\psi\rangle|\text{live}\rangle, \tag{6.5.1}$$

where the atomic state is

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|g\rangle + |e\rangle), \tag{6.5.2}$$

$|e\rangle$ being at a higher energy than $|g\rangle$. We expect that, if the link of the parts to the cat is unbiased, at some time t later the reduced density matrix of the atom and the cat in the basis set of $(|g\rangle|\text{live}\rangle, |e\rangle|\text{dead}\rangle)$ would have diagonal elements of 1/2 each. The question is whether there is a finite off-diagonal density matrix element.

If there is no dissipative or dephasing process of the system of the atom and the cat, then their interaction would lead to the ideal state of the system being entangled:

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}}(|g\rangle|\text{live}\rangle + |e\rangle|\text{dead}\rangle), \tag{6.5.3}$$

Our experimental experience leads us to expect that the cat is either dead or alive and that there could be no interference effect between the two states. Consider the coefficient, $(\langle C|\otimes\langle E_k|)|C, E\rangle$, of the state of the cat and the atom plus the environment (or reservoir) in the expansion in terms of the basis states of the environment, $\{|E_k\rangle\}$, with the state of the atom and the cat denoted by $C =$(e, dead) or (g, live). It is plausible that the cat is a system of so many degrees of freedom interacting with the environment that the two components, $(\langle C|\otimes\langle E_k|)|C, E\rangle$ with $C =$(e, dead) and (g, live) have very different phase dependence on k. Then to obtain the reduced density matrix element between the dead and the live state of the cat the sum over the environmental states must be negligible because of the destructive interference of the phase variation over k.

The rapid disappearance of the phase coherence between two states of a macroscopic system (or equivalently, any interference effect between two macroscopic states) is called

decoherence. Clearly, the statement cannot be absolute. If the number of degrees of freedom of the system is increased from 2 to A, the dephasing time can decrease rapidly but may still have to go through intermediate stages. Such an experiment will be discussed in the next subsection. There are also notable exceptions to the rule of rapid decoherence. The interference of classical light beams is explained by the fact that the photons have very weak mutual interaction. The macroscopic interference effects of a superconducting state, a superfluid, or a Bose-Einstein condensate of atoms are explained by the existence of a cooperative phenomenon leading to a macroscopic order parameter signifying macroscopic coherence.

In the literature, especially on quantum computing, it is a fairly common practice to call the dephasing in a microscopic system decoherence. I have chosen to follow the practice of distinguishing the dephasing in a microscopic system from the decoherence when the number of degrees of freedom in the system is macroscopic. This can be made precise by the notation of negligible error in the statement of "instantaneous decoherence" in a macroscopic system, analogous to the "thermodynamics limit". The active study of the mesoscopic systems blurs the demarcation line. Hence, it is a useful distinction but not an indispensable one.

The problem of Schrödinger's cat is a problem in the understanding of the measurement theory at the microscopic level. One only needs to substitute a macroscopic measuring "meter" for the cat. The coupling between the two-state atom and the meter leads to a linear combination of two entangled states of the system of the atom and the meter. The decoherence effect leads the meter pointing to one of two positions indicating one of the two atomic states. This is then in accord with the von Neumann postulate that after measurement the density matrix of the atom reduces to one of the pure state (Section 2.7.1). An explicit theoretical proof and an experimental demonstration of the decoherence effect are, therefore, of fundamental importance.

6.5.2 A demonstration of decoherence

While the dephasing time of a microscopic system has been measured, the decoherence effect of a macroscopic system is nearly impossible since the decoherence time is expected to be extremely short. One possibility is to make a series of mesoscopic systems bridging

the gap between the microscopic and the macroscopic and to observe the change of the dephasing time. The group of Brune *et al.* in Ecole Normale Supèrieure, Paris has observed the progressive decoherence of the measurement "meter" coupled to the atom as the meter is increased in scale from microscopic to mesoscopic. The decoherence effect of the macroscopic meter is then inferred.

The atom used in the experiment is rubidium with the chosen states $(n, \ell, m) = (50, 49, 49)$ and $(51, 50, 50)$. The meter is a coherent state of a harmonic oscillator (Problem 3.7) from a resonant mode of the electromagnetic wave in a cavity:

$$|\lambda\rangle = e^{\left\{-\frac{1}{2}(N+i\alpha)\right\}} e^{\lambda c^\dagger} |0\rangle \tag{6.5.4}$$

where $|0\rangle$ is the ground state, $c^\dagger$ the creation operator and

$$\lambda = \sqrt{N}\, e^{-i\alpha}. \tag{6.5.5}$$

An ideal measurement would lead to the entangled state,

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|g\rangle|\lambda\rangle + |e\rangle|\lambda^*\rangle). \tag{6.5.6}$$

The "distance" between the two meter states is $D = 2\sqrt{N}\sin\alpha$. Decoherence was observed when N is increased from 0 to 5 or when α is increased with $N = 3.3$.

The result can be understood on the basis that the decoherence time is proportional to T_p/D^2 where T_p is the dissipative time of the harmonic oscillator via the photon leakage through the cavity and D defined above is a measure of the macroscopic nature of the meter. We deduce the T_p/N dependence of the decoherence time from the physics of pure dephasing due to the field fluctuation in Section 5.6.3 adapted to the electric field excitation between two atomic levels (Problem 5.9). The pure dephasing rate Γ^* is the coefficient in the Markovian form of the correlation function,

$$C(t) = 2\Gamma^*\delta(t), \tag{6.5.7}$$

and the correlation function is defined as

$$C(t) = \mu^2\langle\lambda|\mathcal{E}(t)\mathcal{E}^*(0)|\lambda\rangle, \tag{6.5.8}$$

where μ is the transition dipole moment and $\mathcal{E}$ is the oscillating electric field at the atom in the center of the resonant cavity. The electric field of the cavity mode of frequency

ω_c is in the quantized form related to the harmonic oscillator (in the rotating wave approximation),

$$\mathcal{E} = \mathcal{E}_0 c, \tag{6.5.9}$$

where c is the annihilation operator and

$$\mathcal{E}_0 = \sqrt{\frac{\hbar\omega_c}{2\epsilon_0 V}}, \tag{6.5.10}$$

V being the cavity volume. The form of $\mathcal{E}_0$ comes the consideration of the energy of the electromagnetic field or from the quantization of the electric field in Chapter 14. If the damping of the harmonic oscillator is taken as

$$c(t) = ce^{-i\omega_c t - \Gamma_c t}, \tag{6.5.11}$$

the solution of Problem 11 yields,

$$\Gamma^* \propto \frac{\mu^2 \varepsilon^2 N}{\hbar^2 \Gamma_c} \sim N \frac{a^3}{V} \frac{\omega_c}{\Gamma_c} \frac{R}{\hbar}, \tag{6.5.12}$$

using $\mu \sim ea$, a being the atomic radius. This expression shows the physical origin of the decoherence rate. It is proportional to N which is a measure of the size of the meter. The ratio of the atomic volume to the cavity volume is a measure of the coupling strength of the atom to the meter. The ratio ω_c/Γ_c is the quality factor of the cavity. It is inversely proportional to the leakage of the cavity mode. $R \sim e^2/\epsilon_0 a$ is the Ryberg energy of the atomic state.

6.6 Problems

1. **Another Bell Inequality** [29]

   In the notation of Sec. 6.2.3 for the singlet state, show that from the Einstein locality

   $$P_\phi(+a,-b) \leq P_\phi(+a,-c) + P_\phi(+c,-b). \tag{6.6.1}$$

   Find a case where this is contradicted by the quantum prediction.

2. **An experimental test of Bell's inequalities** In an experiment by Aspect *et al.*, an entangled pair of photons of opposite linear polarizations are measured by two separate polarizers.

   (a) Prove the Bell inequality used. [2].

   (b) Write a short account of the experiment or give a 15-minute talk on the experiment.

3. **Bell's Theorem without Inequalities** [19]

   Consider a composite made of three spin-1/2 particles, labeled a, b, c. In a spin-conserving separation, they fly off in the same plane in three directions z_a, z_b, z_c. The normal to the common plane is given by the unit vector x. The spin components along the Cartesian directions x, y_j, z_j for particle j are given by the Pauli matrices, $\sigma_x^j, \sigma_y^j, \sigma_z^j$, (times $\hbar/2$ which will be understood), where $j = a, b, c$. Imagine that each Stern-Gerlach apparatus is set up along one particle path to measure either σ_x^j or σ_y^j when the three particles are far enough apart to have no interaction with one another. We shall consider in order the predictions (1) of the quantum theory and (2) of a theory using the Einstein locality for the measurements of the four observables:

   $$\begin{aligned} K_a &= \sigma_x^a \sigma_y^b \sigma_y^c, \\ K_b &= \sigma_y^a \sigma_x^b \sigma_y^c, \\ K_c &= \sigma_y^a \sigma_y^b \sigma_x^c, \end{aligned}$$

$$B = \sigma_x^a \sigma_x^b \sigma_x^c. \tag{6.6.2}$$

(a) Show that $K_j, j = a, b, c$ form a complete set of three commuting Hermitian operators and that $K_j^2 = 1$. Hence, find the eigenvalues of K_j. For the state

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left(|+z_a, +z_b, +z_c\rangle - |-z_a, -z_b, -z_c\rangle \right), \tag{6.6.3}$$

where $\pm z_j$ denote the spin-up and down states along the z_j direction for particle j, show that it is an eigenstate of each K_j with the eigenvalue $+1$.

(b) Show that $B = -K_a K_b K_c$ and, hence, that it commutes with each K_j and that the state Ψ given by Eq. (6.6.3) is also an eigenstate of B but with eigenvalue -1. Note the minus sign.

(c) Deduce what the quantum theory prediction is for K_j in state Ψ with a simultaneous measurement of the x-component of spin for particle j and the y-components for the other two particles. Deduce also what the prediction is for B with a simultaneous measurement of the x-components of all three particles in the state Ψ.

(d) Now construct a theory including the Einstein reality and spin conservation. This means that when the particles are apart, the spin values of $m_x^j = \pm 1$, $m_y^j = \pm 1$ of each particle in the two directions must be measurable. Make sure that this theory yields the same predictions for the simultaneous measurement of the x-component of spin for particle j and the y-components for the other two particles as the quantum theory for K_j in state Ψ. Deduce what the prediction is for the product $m_x^a m_x^b m_x^c$ for the simultaneous measurement of the x-components of all three particles separately according to the locality theory.

(e) Discuss the contradictions with quantum theory of the two locality results (1) the values m_x^j and m_y^j are known for particle j and (2) the value of $m_x^a m_x^b m_x^c$ for state Ψ.

4. **Security of transmission**

For the example of quantum cryptography described in Sec. 6.3.1, devise a method to provide spot checks whether the messages have been intercepted.

5. **How to entangle uncorrelated states**

   (a) Show that a Hadamard transform on the first qubit followed by the controlled-NOT operation with the first qubit as source and the second qubit as target can change the two-qubit product states into the four Bell states.

   (b) A friend told you that she took one product state, followed the above procedure and got the Φ_- Bell state. What product state did she start with?

   (c) If she had used a $\pi/2$ rotation about the y-axis followed by a controlled π rotation as defined in the text, which of the four product states would be her starting state to reach the Φ_- Bell state? Did you or she leave out any information in this answer? Is it important?

6. **Local operations on the Bell states**

   The phase-shift operation on the Bell states is σ_z^ϕ acting only on the first particle, ϕ. The flipping operator is σ_x^χ acting only on the second particle χ. Find (in either order) the transformation matrices and the resultant states of the four operations: identity, phase-shift, bit-flip, and the combination of phase-shift and bit-flip.

7. **Quantum no-cloning theorem**

   (a) Show that if one starts out with the quantum equivalent of a sheet of black and white dots and a blank (white) sheet, there is a quantum transformation to copy the first sheet onto the second.

   (b) Consider a close-system with the state space made up of three subspaces named the "original" and the "copy" with equal number of qubits and the "machine". Show that there is no single process that can made copies of all possible originals.

   (c) Show that if the initial state of the original is known (in binary form), then it is possible to design a special process to make a copy.

8. **Teleportation**

(a) Design the circuit for teleportation of a spin-1/2 state starting with, instead of the singlet state as in the text, the Bell state

$$|\Phi_+\rangle = \frac{1}{\sqrt{2}}(|+,+\rangle + |-,-\rangle). \tag{6.6.4}$$

Show that your scheme works.

(b) **Teleportation without message?** Can you design an all-quantum algorithm for three qubits so that any state in the first qubit can be transferred to the third qubit in a distant location?

9. **Deutsch's Problem**

(a) Verify the solution of the Deutsch problem in Sec. 6.4. In particular, evaluate the matrix elements $\langle +x, -x|U_f|+x, -x\rangle$ and $\langle -x, -x|U_f|+x, -x\rangle$.

(b) Design an algorithm to solve the two-qubit Deutsch problem using only rotations and controlled rotations about the x or y axis [8].

10. **Quantum Fourier Transform.** Design an algorithm for the quantum Fourier Transform [24, 8] for a two-qubit system using only proper rotations (determinant = 1):

$$Q\sum_{j=0}^{3}|j\rangle x_j = \sum_{k=0}^{3}|k\rangle y_k, \tag{6.6.5}$$

where

$$y_k = \frac{1}{4}\sum_{j=0}^{3} e^{\pi ijk/2}x_j. \tag{6.6.6}$$

11. **Correlation function of a harmonic oscillator**

(a) Show that the Fourier transform $C(\omega)$ of the correlation function $C(t) = \langle\lambda|c(t)c^\dagger(0)|\lambda\rangle$ with respect to a coherent state [Eq. (6.5.4)] of a simple harmonic oscillator of frequency ω_c and a damping constant $\Gamma_c/2$ for the annihilation operator $c(t)$ is given by

$$C(\omega) = \frac{i}{\omega - \omega_c + i\Gamma_c}. \tag{6.6.7}$$

(b) Recover the Markovian form $C(t) = \gamma\delta(t)$ and determine γ.

6.7 Source Material and Further Reading

General Omnès' book [25] gives an easily understandable account of the interpretation aspects of quantum theory which takes into account the advances made in the last two decades and which uses a language close to the every-day usage by practising physicists. It is also a most accessible source for several topics in this chapter, especially the EPR paradox and decoherence. Another readable account of the measurement theory is a book by an experimentalist and a theory [6].

Section 6.2 The classic paper [15] by Einstein, Podolsky, and Rosen is interesting to read for its formulation of the philosophy of physical reality. Our account of the EPR paradox follows Bohm's use of the entangled state of two spin1/2 particles ([5], p. 614). The Bell inequalities [3] enable the experiment [1] to decide on the quantum version of the reality over the EPR formulation of the reality. Exchanges among Einstein, Bohr, and Schrödinger are found in the book [28]. Landauer [22] had emphasized the physical basis of information.

Section 6.3 A good account for non-specialists of the modern approach to quantum information and computation is given by a special issue of Physics World [26]. I am indebted to the pioneering course notes by Preskill [27]. A marvelous textbook on the subject is the book by Nielsen and Chuang [24]. An elementary account of information theory from the physicist's viewpoint is given by Gershenfeld [17].

Section 6.4 Richard Feynman's [16] vision of the analog quantum computer is worth reading for its educational value. The idea for a digital quantum computer was given by [4]. The original papers on the implementation of the Deutsch-Jozsa algorithm [11, 12] by nuclear magnetic resonance are [9, 21]. The five requirements for a quantum computer, which have been much quoted, follow an account by DiVincenzo [14]. The proof of the universal computation by the one qubit operations and CNOT is due to DiVincenzo [13]. The development of algorithms for quantum computing are key stimulus to the recent rapid development of physical implementation. The important algorithms include the factorization [30] and the search [20] .

Section 6.5 Omnès' book [25] is a must-read for any neophyte seeking to understand decoherence. For the experiment by Brune et al., see the original paper [7] and an alternate description in Omnès' book. For macroscopic quantum tunneling see Leggett's suggestion using a superconducting junction [23] and a report of the experiments [10].

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