Chapter 3  SCHRÖDINGER TIME EVOLUTION

This chapter marks our final step in developing the mathematical basis of a quantum theory. In Chapter 1, we learned how to use kets to describe quantum states and how to predict the probabilities of results of measurements. In Chapter 2, we learned how to use operators to represent physical observables and how to determine the possible measurement results. The key missing aspect is the ability to predict the future. Physics theories are judged on their predictive power. Classical mechanics relies on Newton's second law $F = ma$ to predict the future of a particle's motion. The ability to predict the quantum future started with Erwin Schrödinger and bears his name.

3.1 Schrödinger Equation

The 6th postulate of quantum mechanics says that the time evolution of a quantum system is governed by the differential equation

$$i\hbar \frac{d}{dt} \psi(t) = H(t) \psi(t),$$

(3.1)

where the operator $H$ corresponds to the total energy of the system and is called the Hamiltonian operator of the system because it is derived from the classical Hamiltonian. This equation is known as the Schrödinger equation.

Postulate 6

The time evolution of a quantum system is determined by the Hamiltonian or total energy operator $H(t)$ through the Schrödinger equation

$$i\hbar \frac{d}{dt} \psi(t) = H(t) \psi(t).$$

The Hamiltonian is a new operator, but we can use the same ideas we developed in Chap. 2 to understand its basic properties. The Hamiltonian $H$ is an observable, so it is an Hermitian operator. The eigenvalues of the Hamiltonian are the allowed energies of the quantum system and the eigenstates of $H$ are the energy eigenstates of the system. If we label the allowed energies as $E_n$, then the energy eigenvalue equation is

$$H |E_n\rangle = E_n |E_n\rangle.$$

(3.2)

If we have the Hamiltonian $H$ in a matrix representation, then we diagonalize the matrix to find the eigenvalues $E_n$ and the eigenvectors $|E_n\rangle$ just as we did with the spin operators in Chap. 2. For the moment, let's assume that we have already diagonalized the Hamiltonian (i.e., solved Eqn. (3.2)) so that know the eigenvalues $E_n$ and the
eigenvectors $|E_n\rangle$, and let's see what we can learn about quantum time evolution in general by solving the Schrödinger equation.

The eigenvectors of the Hamiltonian form a complete basis because the Hamiltonian is an observable, and therefore an Hermitian operator. Because $H$ is the only operator appearing in the Schrödinger equation, it would seem reasonable (and will prove invaluable) to consider the energy eigenstates as the basis of choice for expanding general state vectors:

$$|\psi(t)\rangle = \sum_n c_n(t)|E_n\rangle. \quad (3.3)$$

The basis of eigenvectors of the Hamiltonian is also orthonormal, so

$$\langle E_k|E_n\rangle = \delta_{kn}. \quad (3.4)$$

We refer to this basis as the **energy basis**.

For now, we assume that the Hamiltonian is time independent (we will do the time-dependent case $H(t)$ in section 3.4). The eigenvectors of a time-independent Hamiltonian come from the diagonalization procedure we used in Chap. 2, so there is no reason to expect the eigenvectors themselves to carry any time dependence. Thus if a general state $|\psi\rangle$ is to be time dependent, as the Schrödinger equation implies, then the time dependence must reside in the expansion coefficients $c_n(t)$, as expressed in Eqn. (3.3). Substitute this general state into the Schrödinger equation (3.1)

$$i\hbar \frac{d}{dt} \sum_n c_n(t)|E_n\rangle = H \sum_n c_n(t)|E_n\rangle \quad (3.5)$$

and use the energy eigenvalue equation (3.2) to obtain

$$i\hbar \sum_n \frac{dc_n(t)}{dt}|E_n\rangle = \sum_n c_n(t)E_n|E_n\rangle. \quad (3.6)$$

Each side of this equation is a sum over all the energy states of the system. To simplify this equation, we isolate single terms in these two sums by taking the inner product of the ket on each side with one particular ket $|E_k\rangle$ (this ket can have any label $k$, but must not have the label $n$ that is already used in the summation). The orthonormality condition $\langle E_k|E_n\rangle = \delta_{kn}$ then collapses the sums:

$$\langle E_k|i\hbar \sum_n \frac{dc_n(t)}{dt}|E_n\rangle = \langle E_k|\sum_n c_n(t)E_n|E_n\rangle$$

$$i\hbar \sum_n \frac{dc_n(t)}{dt}\langle E_k|E_n\rangle = \sum_n c_n(t)E_n\langle E_k|E_n\rangle$$

$$i\hbar \sum_n \frac{dc_n(t)}{dt}\delta_{kn} = \sum_n c_n(t)E_n\delta_{kn}$$

$$i\hbar \frac{dc_k(t)}{dt} = c_k(t)E_k. \quad (3.7)$$
We are left with a single differential equation for each of the possible energy states of the systems \( k = 1, 2, 3, \ldots \). This first-order differential equation can be rewritten as

\[
\frac{dc_k(t)}{dt} = -i \frac{E_k}{\hbar} c_k(t) \tag{3.8}
\]

The solution to Eqn. (3.8) is a complex exponential

\[
c_k(t) = c_k(0)e^{-iE_k t/\hbar}. \tag{3.9}
\]

In Eqn. (3.9), we have denoted the initial condition as \( c_k(0) \), but we denote it simply as \( c_k \) hereafter. Each coefficient in the energy basis expansion of the state obeys the same form of the time dependence in Eqn. (3.9), but with a different factor due to the different energies. The time dependent solution for the full state vector is summarized by saying that if the initial state of the system at time \( t = 0 \) is

\[
|\psi(0)\rangle = \sum_n c_n |E_n\rangle, \tag{3.10}
\]

then the time evolution of this state under the action of the time-independent Hamiltonian \( H \) is

\[
|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar} |E_n\rangle. \tag{3.11}
\]

So the time dependence of the original state vector is found by multiplying each energy eigenstate coefficient by its own phase factor \( e^{-iE_n t/\hbar} \) that depends on the energy of that eigenstate. Note that the factor \( E/\hbar \) is an angular frequency, so that the time dependence is of the form \( e^{-i\omega t} \), a form commonly found in many areas of physics. It is important to remember that one must use the energy eigenstates for the expansion in Eqn. (3.10) in order to use the simple phase factor multiplication in Eqn. (3.11) to account for the Schrödinger time evolution of the state. This key role of the energy basis accounts for the importance of the Hamiltonian operator and for the common practice of finding the energy eigenstates to use as the preferred basis.

A few examples help to illustrate some of the important consequences of this time evolution of the quantum mechanical state vector. First consider the simplest possible situation where the system is initially in one particular energy eigenstate:

\[
|\psi(0)\rangle = |E_i\rangle, \tag{3.12}
\]

for example. The prescription for time evolution tells us that after some time \( t \) the system is in the state

\[
|\psi(t)\rangle = e^{-iE_i t/\hbar} |E_i\rangle. \tag{3.13}
\]

But this state differs from the original state only by an overall phase factor, which we have said before does not affect any measurements (problem 1.3). For example, if we measure an observable \( A \), then the probability of measuring an eigenvalue \( a_j \) is given by
This probability is time-independent and is equal to the probability at the initial time. Thus we conclude that there is no measurable time evolution for this state. Hence the energy eigenstates are called stationary states. If a system begins in an energy eigenstate, then it remains in that state.

Now consider an initial state that is a superposition of two energy eigenstates:

\[ |\psi(0)\rangle = c_1 |E_1\rangle + c_2 |E_2\rangle. \]  

(3.15)

In this case, time evolution takes the initial state to the later state

\[ |\psi(t)\rangle = c_1 e^{-iE_1 t/\hbar} |E_1\rangle + c_2 e^{-iE_2 t/\hbar} |E_2\rangle. \]  

(3.16)

A measurement of the system energy at the time \( t \) would yield the value \( E_1 \) with a probability

\[ P_{E_1} = |\langle E_1 |\psi(t)\rangle|^2 \]
\[ = |\langle E_1 |[c_1 e^{-iE_1 t/\hbar} |E_1\rangle + c_2 e^{-iE_2 t/\hbar} |E_2\rangle]|^2, \]  

(3.17)

which is independent of time. The same is true for the probability of measuring the energy \( E_2 \). Thus the probabilities of measuring the energies are stationary, as they were in the first example.

However, now consider what happens if another observable is measured on this system in this superposition state. There are two distinct situations: (1) If the other observable \( A \) commutes with the Hamiltonian \( H \), then \( A \) and \( H \) have common eigenstates. In this case, measuring \( A \) is equivalent to measuring \( H \) because the inner products used to calculate the probabilities use the same eigenstates. Hence the probability of measuring any particular eigenvalue of \( A \) is time independent as in Eqn. (3.17). (2) If \( A \) and \( H \) do not commute, then they do not share common eigenstates. In this case, the eigenstates of \( A \) in general consist of superpositions of energy eigenstates. For example, suppose that the eigenstate of \( A \) corresponding to the eigenvalue \( a_1 \) were

\[ |a_1\rangle = \alpha_1 |E_1\rangle + \alpha_2 |E_2\rangle. \]  

(3.18)

Then the probability of measuring the eigenvalue \( a_1 \) would be
\[ \mathcal{P}_{a_n} = |\langle a_n | \psi(t) \rangle|^2 \]

\[
= | \alpha_1^* \langle E_1 | + \alpha_2^* \langle E_2 | [c_1 e^{-iE_1t/\hbar} | E_1 \rangle + c_2 e^{-iE_2t/\hbar} | E_2 \rangle ]^2 \\
= | \alpha_1^* c_1 e^{-iE_1t/\hbar} + \alpha_2^* c_2 e^{-iE_2t/\hbar} |^2 \\
\] (3.19)

Factoring out the common phase gives

\[
\mathcal{P}_{a_n} = |e^{-iE_1t/\hbar}|^2 | \alpha_1^* c_1 + \alpha_2^* c_2 e^{-i(E_2-E_1)t/\hbar} |^2 \\
= |\alpha_1^*| |c_1|^2 + |\alpha_2^*| |c_2|^2 + 2 \text{Re} (\alpha_1^* c_1^* \alpha_2^* c_2 e^{-i(E_2-E_1)t/\hbar}) \\
\] (3.20)

The different time-evolution phases of the two components of \(|\psi(t)\rangle\) lead to a time dependence in the probability. The overall phase in Eqn. (3.20) drops out, and only the relative phase remains in the probability calculation. Hence the time dependence is determined by the difference of the energies of the two states involved in the superposition. The corresponding angular frequency of the time evolution

\[
\omega_{21} = \frac{E_2 - E_1}{\hbar} \\
\] (3.21)

is called the Bohr frequency.

To summarize, we list below a recipe for solving a standard time-dependent quantum mechanics problem with a time-independent Hamiltonian.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Diagonalize ( H ) (find the eigenvalues ( E_n ) and eigenvectors (</td>
</tr>
<tr>
<td>2.</td>
<td>Write (</td>
</tr>
<tr>
<td>3.</td>
<td>Multiply each eigenstate coefficient by ( e^{-\frac{E_n t}{\hbar}} ) to get (</td>
</tr>
<tr>
<td>4.</td>
<td>Calculate the probability ( \mathcal{P}_{a_n} =</td>
</tr>
</tbody>
</table>

### 3.2 Spin Precession

Now apply this new concept of Schrödinger time evolution to the case of a spin-1/2 system. The Hamiltonian operator represents the total energy of the system, but because only energy differences are important in time dependent solutions (and because we can define the zero of potential energy as we wish), we need consider only energy terms that differentiate between the two possible spin states in the system. Our experience with the Stern-Gerlach apparatus tells us that the magnetic potential energy of the magnetic dipole differs for the two possible spin component states. So to begin, we consider the potential energy of a single magnetic dipole (e.g., in a silver atom) in a
uniform magnetic field as the sole term in the Hamiltonian. Recalling that the magnetic dipole is given by
\[ \mu = g \frac{q}{2m_e} \mathbf{S}, \]  
(3.22)
the Hamiltonian is
\[ H = -\mu \cdot \mathbf{B} = -g \frac{q}{2m_e} \mathbf{S} \cdot \mathbf{B}, \]  
(3.23)
\[ = e \frac{m_e}{m_e} \mathbf{S} \cdot \mathbf{B} \]
where \( q = -e \) and \( g = 2 \) have been used in the last line. The gyromagnetic ratio, \( g \), is slightly different from 2, but we ignore that detail.

### 3.2.1 Magnetic Field in z-direction

For our first example, we assume that the magnetic field is uniform and directed along the \( z \)-axis. Writing the magnetic field as
\[ \mathbf{B} = B_0 \hat{\mathbf{z}}, \]  
(3.24)
allows the Hamiltonian to be simplified to
\[ H = eB_0 S_z = \omega_0 S_z, \]  
(3.25)
where we have introduced the definition
\[ \omega_0 \equiv \frac{eB_0}{m_e}. \]  
(3.26)
This definition of an angular frequency simplifies the notation now and will have an obvious interpretation at the end of the problem.

The Hamiltonian in Eqn. (3.25) is proportional to the \( S_z \) operator, so \( H \) and \( S_z \) commute and therefore share common eigenstates. This is clear if we write the Hamiltonian as a matrix in the \( S_z \) representation:
\[ H \equiv \frac{\hbar \omega_0}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]  
(3.27)
Because \( H \) is diagonal, we have already completed step 1 of the Schrödinger time evolution recipe. The eigenstates of \( H \) are the basis states of the representation, while the eigenvalues are the diagonal elements of the matrix in Eqn. (3.27). The eigenvalue equations for the Hamiltonian are thus
with eigenvalues and eigenvectors given by

\[ E_+ = \frac{\hbar \omega_0}{2}, \quad E_- = -\frac{\hbar \omega_0}{2} \]

\[ |E_+\rangle = |+\rangle, \quad |E_-\rangle = |-\rangle \]  

The information regarding the energy eigenvalues and eigenvectors is commonly presented in a graphical diagram, which is shown in Fig. 3.1 for this case. The two energy states are separated by the energy difference \( E_+ - E_- = \hbar \omega_0 \), so the angular frequency \( \omega_0 \) characterizes the energy scale of this system. The spin up state \(|+\rangle\) has a higher energy because the magnetic moment is aligned against the field in that state; the negative charge in Eqn. (3.22) causes the spin and magnetic moment to be anti-parallel.

Now we look at a few examples to illustrate the key features of the behavior of a spin 1/2 system in a uniform magnetic field. First consider the case where the initial state is spin up along \( z \)-axis:

\[ |\psi(0)\rangle = |+\rangle. \]  

(3.30)

This initial state is already expressed in the energy basis (step 2 of Schrödinger recipe), so the Schrödinger equation time evolution takes this initial state to the state

\[ |\psi(t)\rangle = e^{-iE_+t/\hbar} |+\rangle = e^{-i\omega_0 t/2} |+\rangle. \]  

(3.31)

Figure 3.1 Energy level diagram of a spin-1/2 particle in a uniform magnetic field.
according to step 3 of the Schrödinger recipe. As we saw before (Eqn. (3.13)), because the initial state is an energy eigenstate, the time evolved state acquires an overall phase factor, which does not represent a physical change of the state. The probability for measuring the spin to be up along the $z$-axis is (step 4 of Schrödinger recipe),

$$\mathcal{P}_+ = \left| \langle + | \psi(t) \rangle \right|^2 = \left| \langle + | e^{-i\omega t/2} | + \rangle \right|^2 = 1. \quad (3.32)$$

As expected, this probability is not time dependent, and we therefore refer to $|+\rangle$ as a stationary state for this system. A schematic diagram of this experiment is shown in Fig. 3.2, where we have introduced a new element to represent the applied field. This new depiction is the same as the depictions in the SPINS software, where the number in the applied magnetic field box (42 in Figure 3.2) is a measure of the magnetic field strength. In this experiment, the results shown are independent of the applied field strength, as indicated by Eqn. (3.32), and as you can verify with the software.

Next consider the most general initial state, which we saw in Chap. 2 corresponds to spin up along an arbitrary direction defined by the polar angle $\theta$ and the azimuthal angle $\phi$. The initial state is

$$|\psi(0)\rangle = |+\rangle_\theta = \cos \frac{\theta}{2} |+\rangle + \sin \frac{\theta}{2} e^{i\phi} |-\rangle \quad (3.33)$$

or using matrix notation:

$$|\psi(0)\rangle \equiv \begin{pmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{pmatrix}. \quad (3.34)$$

Schrödinger time evolution introduces a time dependent phase term for each component, giving

**Figure 3.2** Schematic diagram of a Stern-Gerlach measurement with an applied uniform magnetic field represented by the box in the middle, with the number 42 representing the strength of the magnetic field.
\[ |\psi(t)\rangle = \begin{pmatrix}
  e^{-iE_it/2} \cos(\theta/2) \\
  e^{-iE_it/2} e^{i\phi} \sin(\theta/2)
\end{pmatrix}
\]
\[ = \begin{pmatrix}
  e^{-i\omega_0t/2} \cos(\theta/2) \\
  e^{i\omega_0t/2} e^{i\phi} \sin(\theta/2)
\end{pmatrix}.
\] (3.35)

Note again that an overall phase does not have a measurable effect, so the evolved state is a spin up eigenstate along a direction that has the same polar angle \(\theta\) as the initial state and a new azimuthal angle \(\phi + \omega_0t\). The state appears to have simply rotated around the \(z\)-axis, the axis of the magnetic field, by the angle \(\omega_0t\). Of course, we have to limit our discussion to results of measurements, so let's first calculate the probability for measuring the spin component along the \(z\)-axis:

\[ P_+ = \left|\langle + |\psi(t)\rangle\right|^2 \]
\[ = \left| \begin{pmatrix} 1 & 0 \end{pmatrix} e^{-i\omega_0t/2} \begin{pmatrix} \cos(\theta/2) \\ e^{i(\phi+\omega_0t)} \sin(\theta/2) \end{pmatrix} \right|^2.
\] (3.36)
\[ = \left| e^{-i\omega_0t/2} \cos(\theta/2) \right|^2 \]
\[ = \cos^2(\theta/2) \]

This probability is time independent because the \(S_z\) eigenstates are also energy eigenstates for this problem, \(i.e., H\) and \(S_z\) commute. The probability in Eqn. (3.36) is consistent with the interpretation that the angle \(\theta\) that the spin vector makes with the \(z\)-axis does not change.

The probability for measuring spin up along the \(x\)-axis is

\[ P_{+x} = \left| \langle + |\psi(t)\rangle \right|^2 \]
\[ = \frac{1}{2} \left| \begin{pmatrix} 1 & 1 \end{pmatrix} e^{-i\omega_0t/2} \begin{pmatrix} \cos(\theta/2) \\ e^{i(\phi+\omega_0t)} \sin(\theta/2) \end{pmatrix} \right|^2 \]
\[ = \frac{1}{2} \left[ \cos(\theta/2) + e^{i(\phi+\omega_0t)} \sin(\theta/2) \right]^2.
\] (3.37)
\[ = \frac{1}{2} \left[ \cos^2(\theta/2) + \cos(\theta/2) \sin(\theta/2) \left( e^{i(\phi+\omega_0t)} + e^{-i(\phi+\omega_0t)} \right) + \sin^2(\theta/2) \right]
\[ = \frac{1}{2} \left[ 1 + \sin \theta \cos(\phi + \omega_0t) \right] \]
This probability is time dependent because the $S_x$ eigenstates are not stationary states, i.e., $H$ and $S_x$ do not commute. The time dependence in Eqn. (3.37) is consistent with the spin precessing around the z-axis.

To illustrate this spin precession further, it is useful to calculate the expectation values for each of the spin components. For $S_z$, we have

$$
\langle S_z \rangle = \langle \psi(t) | S_z | \psi(t) \rangle
= e^{i\omega_0 t/2} \left( \cos \left( \frac{\theta}{2} \right) e^{-i(\phi+\omega_0 t)} \sin \left( \frac{\theta}{2} \right) \right) \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} e^{-i\omega_0 t/2} \begin{pmatrix} \cos(\theta/2) \\ e^{i(\phi+\omega_0 t)} \sin(\theta/2) \end{pmatrix}
= \frac{\hbar}{2} \left[ \cos^2 \left( \frac{\theta}{2} \right) - \sin^2 \left( \frac{\theta}{2} \right) \right]
= \frac{\hbar}{2} \cos \theta
$$

while the other components are

$$
\langle S_y \rangle = \langle \psi(t) | S_y | \psi(t) \rangle
= e^{i\omega_0 t/2} \left( \cos \left( \frac{\theta}{2} \right) e^{-i(\phi+\omega_0 t)} \sin \left( \frac{\theta}{2} \right) \right) \frac{\hbar}{2} \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix} e^{-i\omega_0 t/2} \begin{pmatrix} \cos(\theta/2) \\ e^{i(\phi+\omega_0 t)} \sin(\theta/2) \end{pmatrix}
= \frac{\hbar}{2} \sin \theta \sin (\phi + \omega_0 t)
$$

and

$$
\langle S_x \rangle = \langle \psi(t) | S_x | \psi(t) \rangle
= \frac{\hbar}{2} \sin \theta \cos (\phi + \omega_0 t).
$$

The expectation value of the total spin vector $\langle S \rangle$ is shown in Fig 3.3, where it is seen to precess around the magnetic field direction with an angular frequency $\omega_0$. The precession of the spin vector is known as Larmor precession and the frequency of precession is known as the Larmor frequency.

The quantum mechanical Larmor precession is analogous to the classical behavior of a magnetic moment in a uniform magnetic field. A classical magnetic moment $\mu$ experiences a torque $\mu \times B$ when placed in a magnetic field. If the magnetic moment is associated with an angular momentum $L$, then we can write

$$
\mu = \frac{q}{2m} L,
$$

where $q$ and $m$ are the charge and mass, respectively, of the system. The equation of motion for the angular momentum

$$
\frac{dL}{dt} = \hbar \gamma (S_x B - S_y B).
$$
Figure 3.3 The expectation value of the spin vector precesses in a uniform magnetic field.

\[ \frac{dL}{dt} = \mu \times B \]  

(3.42)

then results in

\[ \frac{d\mu}{dt} = \frac{q}{2m} \mu \times B, \]  

(3.43)

Because the torque \( \mu \times B \) is perpendicular to the angular momentum \( L = 2m\mu/q \), it causes the magnetic moment to precess about the field with the classical Larmor frequency \( \omega_{cl} = qB/2m \).

In the quantum mechanical example we are considering, the charge \( q \) is negative (meaning the spin and magnetic moment are anti-parallel), so the precession is counterclockwise around the field. A positive charge would result in clockwise precession. This precession of the spin vector makes it clear that the system has angular momentum, as opposed to simply having a magnetic dipole moment. The equivalence of the classical Larmor precession and the expectation value of the quantum mechanical spin vector is one example of Ehrenfest's theorem, which states that quantum mechanical expectation values obey classical laws.

Precession experiments like the one discussed here are of great practical value. For example, if we measure the magnetic field strength and the precession frequency, then the gyromagnetic ratio can be determined. This spin precession problem is also of considerable theoretical utility because it is mathematically equivalent to many other quantum systems that can be modeled as two-state systems. This utility is broader than you might guess at first glance because many multi-state quantum systems can be reduced to two-state systems if the experiment is designed to interact only with two of the many levels of the system.
Example 3.1

A spin-1/2 particle with a magnetic moment is prepared in the state $|\downarrow\rangle_z$ and is subject to a uniform applied magnetic field $\mathbf{B} = B_0 \hat{z}$. Find the probability of measuring spin up in the $x$-direction after a time $t$. This experiment is depicted in Fig. 3.4.

We solve this problem using the 4 steps of the Schrödinger time evolution recipe from Sec. 3.1. The initial state is

$$|\psi(0)\rangle = |\downarrow\rangle_z$$

The applied magnetic field is in the $z$-direction, so the Hamiltonian is $H = \omega_0 S_z$ and the energy eigenstates are $|\pm\rangle$ with energies $E_{\pm} = \pm \hbar \omega_0 / 2$ (step 1). The Larmor precession frequency is $\omega_0 = eB_0/m_e$. We must express the initial state in the energy basis (step 2):

$$|\psi(0)\rangle = |\downarrow\rangle_z = \frac{1}{\sqrt{2}} |+\rangle - \frac{1}{\sqrt{2}} |-\rangle$$

The time evolved state is obtained by multiplying each energy eigenstate coefficient by the appropriate phase factor (step 3):

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{-iE_{+} t / \hbar} |+\rangle - \frac{1}{\sqrt{2}} e^{-iE_{-} t / \hbar} |-\rangle$$

$$= \frac{1}{\sqrt{2}} e^{-i\omega_0 t / 2} |+\rangle - \frac{1}{\sqrt{2}} e^{i\omega_0 t / 2} |-\rangle$$

The measurement probability is found by projecting $|\psi(t)\rangle$ onto the measured state and complex squaring (step 4):

Figure 3.4 Spin precession experiment.
\[ \mathcal{P}_{+x} = \left| \langle + | \psi(t) \rangle \right|^2 \]

\[ = \left| \langle + | \left( \frac{1}{\sqrt{2}} e^{-i \omega_0 t/2} |+\rangle - \frac{1}{\sqrt{2}} e^{i \omega_0 t/2} |-\rangle \right) \right|^2 \]

\[ = \left( \frac{1}{\sqrt{2}} \langle + | + \frac{1}{\sqrt{2}} \langle - | \left( \frac{1}{\sqrt{2}} e^{-i \omega_0 t/2} |+\rangle - \frac{1}{\sqrt{2}} e^{i \omega_0 t/2} |-\rangle \right) \right)^2 \]

\[ = \frac{1}{4} \left( e^{-i \omega_0 t/2} - e^{i \omega_0 t/2} \right)^2 \]

\[ = \sin^2 \left( \frac{\omega_0 t}{2} \right) \]

The probability that the system has spin up in the \( x \)-direction oscillates between zero and unity as time evolves, as shown in Fig. 3.5(a), which is consistent with the model of the spin vector precessing around the applied field, as shown in Fig. 3.5(b).

**Figure 3.5** (a) Probability of a spin component measurement and (b) the corresponding precession of the expectation value of the spin.

### 3.2.2 Magnetic field in a general direction

For our second example, consider a more general direction for the magnetic field by adding a magnetic field component along the \( x \)-axis to the already existing field along the \( z \)-axis. The simplest approach to solving this new problem would be to redefine the coordinate system so the \( z \)-axis pointed along the direction of the new total magnetic field. Then the solution would be the same as was obtained above, with a new value for the magnitude of the magnetic field being the only change. This approach would be considered astute in many circumstances, but we will not take it because we want to get practice solving this new type of problem and because we want to address some issues
that are best posed in the original coordinate system. Thus we define a new magnetic field as

\[ B = B_0 \hat{z} + B_1 \hat{x}. \] (3.48)

This field is oriented in the \(xz\)-plane at an angle \(\theta\) with respect to the \(z\)-axis, as shown in Fig. 3.6. In light of the solution above, it is useful to define Larmor frequencies associated with each of the field components:

\[ \omega_0 \equiv \frac{eB_0}{m_e}, \quad \omega_1 \equiv \frac{eB_1}{m_e}. \] (3.49)

Using these definitions, the Hamiltonian becomes

\[ H = -\mathbf{\mu} \cdot \mathbf{B} = \omega_0 S_z + \omega_1 S_x, \] (3.50)

or in matrix representation

\[ H = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 \\ \omega_1 & -\omega_0 \end{pmatrix}. \] (3.51)

This Hamiltonian is not diagonal, so its eigenstates are not the same as the eigenstates of \(S_z\). Rather we must use the diagonalization procedure to find the new eigenvalues and eigenvectors. The characteristic equation determining the energy eigenvalues is

\[
\begin{vmatrix}
\frac{\hbar}{2} \omega_0 - \lambda & \frac{\hbar}{2} \omega_1 \\
\frac{\hbar}{2} \omega_1 & -\hbar \omega_0 - \lambda
\end{vmatrix} = 0,
\]

\[
-\left(\frac{\hbar}{2} \omega_0\right)^2 + \lambda^2 - \left(\frac{\hbar}{2} \omega_1\right)^2 = 0
\]

with solutions

\[ \lambda = \pm \frac{\hbar}{2} \sqrt{\omega_0^2 + \omega_1^2}. \] (3.53)

Figure 3.6 A uniform magnetic field in a general direction.
Note that the energy eigenvalues are $\pm (\hbar \omega / 2)$ when $\omega_1 = 0$, which they must be given our previous solution. Rather than solve directly for the eigenvectors, let's make them obvious by rewriting the Hamiltonian. From Fig. 3.6 it is clear that the angle $\theta$ is determined by the equation

$$\tan \theta = \frac{B_1}{B_0} = \frac{\omega_1}{\omega_0}.$$ (3.54)

Using this, the Hamiltonian can be written as

$$H \doteq \frac{\hbar}{2} \sqrt{\omega_0^2 + \omega_1^2} \left( \begin{array}{cc} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{array} \right).$$ (3.55)

If we let $\hat{\mathbf{n}}$ be the unit vector in the direction of the total magnetic field, then the Hamiltonian is proportional to the spin component $S_n$ along the direction $\hat{\mathbf{n}}$

$$H = \sqrt{\omega_0^2 + \omega_1^2} S_n.$$ (3.56)

This is what we expected at the beginning: that the problem could be solved by using the field direction to define a coordinate system. Thus the eigenvalues are as we found in Section 2.2.1 and the eigenstates are the spin up and down states along the direction $\hat{\mathbf{n}}$, which are

$$|+\rangle_n = \cos \frac{\theta}{2} |+\rangle + \sin \frac{\theta}{2} \langle -|$$

$$|-\rangle_n = \sin \frac{\theta}{2} |+\rangle - \cos \frac{\theta}{2} \langle -|$$

(3.57)

for this case because the azimuthal angle $\phi$ is zero. These are the same states you would find by directly solving for the eigenstates of the Hamiltonian. Because we have already done that for the $S_n$ case, we do not repeat it here.

Now consider performing the following experiment: begin with the system in the spin up state along the $z$-axis, and measure the spin component along the $z$-axis after the system has evolved in this magnetic field for some time, as depicted in Fig. 3.7. Let's specifically calculate the probability that the initial $+\rangle$ is later found to have evolved to the $-\rangle$ state. This is commonly known as a spin flip. According to our time evolution prescription, we must first write the initial state in terms of the energy eigenstates of the system. In the previous examples, this was trivial because the energy eigenstates were the $|\pm\rangle$ states that we used to express all general states. But now this new problem is more involved, so we proceed more slowly. The initial state

$$|\psi(0)\rangle = |+\rangle$$

(3.58)

must be written in the $|\pm\rangle_n$ basis. Because the $|\pm\rangle_n$ basis is complete, we can use the closure relation (Eqn. 2.55) to decompose the initial state
Figure 3.7 A spin precession experiment with a uniform magnetic field aligned in a general direction $\hat{n}$.

\[
|\psi(0)\rangle = (|+\rangle_n |+\rangle + |\rangle_n |\rangle)
\]
\[
= |+\rangle_n (|+\rangle + |\rangle_n |\rangle)
\]
\[
= _n (|+\rangle |+\rangle + _n |\rangle).
\]
\[
= \cos \frac{\theta}{2} |+\rangle + \sin \frac{\theta}{2} |\rangle.
\]

Now that the initial state is expressed in the energy basis, the time-evolved state is obtained by multiplying each coefficient by a phase factor dependent on the energy of that eigenstate:

\[
|\psi(t)\rangle = e^{-iE_z t/\hbar} \cos \frac{\theta}{2} |+\rangle + e^{-iE_z t/\hbar} \sin \frac{\theta}{2} |\rangle.
\]

We leave it in this form and substitute the energy eigenvalues

\[
E_\pm = \pm \hbar \sqrt{\omega_0^2 + \omega_1^2}
\]

at the end of the example.

The probability of a spin flip is

\[
P_{\rightarrow -} = |\langle \rightarrow |\psi(t)\rangle|^2
\]
\[
= \left| \cos \frac{\theta}{2} \sin \frac{\theta}{2} e^{i(E_+ - E_-) t} \right|^2
\]
\[
= \cos^2 \frac{\theta}{2} \sin^2 \frac{\theta}{2} \left( 1 - e^{i(E_+ - E_-) t} \right)
\]
\[
= \sin^2 \theta \sin^2 \left( \frac{(E_+ - E_-) t}{2\hbar} \right)
\]
The probability oscillates at the frequency determined by the difference in energies of the eigenstates. This time dependence results because the initial state was a superposition state, as we saw in Eqn. (3.20). In terms of the Larmor frequencies used to define the Hamiltonian in Eqn. (3.51), the probability of a spin flip is

\[ P_+ \rightarrow - = \frac{\omega_1^2}{\omega_0^2 + \omega_1^2} \sin^2 \left( \frac{\sqrt{\omega_0^2 + \omega_1^2} t}{2} \right), \]  

(3.63)

Equation (3.63) is often called Rabi's formula, and it has important applications in many problems as we shall see.

To gain insight into Rabi's formula, consider two simple cases. First, if there is no added field in the \( x \)-direction, then \( \omega_1 = 0 \) and \( P_+ \rightarrow - = 0 \) because the initial state is a stationary state. Second, if there is no field component in the \( z \)-direction, then \( \omega_0 = 0 \) and \( P_+ \rightarrow - \) oscillates between 0 and 1 at the frequency \( \omega_1 \), as shown in Fig. 3.8(a). The second situation corresponds to spin precession around the applied magnetic field in the \( x \)-direction, as shown in Fig. 3.8(b), with a complete spin flip from \( |+\rangle \) to \( |-\rangle \) and back again occurring at the precession frequency \( \omega_1 \). In the general case where both magnetic field components are present, the probability does not reach unity and so there is no time at which the spin is certain to flip over. If the \( x \)-component of the field is small compared to the \( z \)-component, then \( \omega_1 \ll \omega_0 \) and \( P_+ \rightarrow - \) oscillates between 0 and a value much less than one at a frequency approximately equal to \( \omega_0 \), as shown in Fig. 3.9.

Figure 3.8 (a) Spin flip probability for a uniform magnetic field in the \( x \)-direction and (b) the corresponding precession of the expectation value of the spin.
Figure 3.9 (a) Spin flip probability for a uniform magnetic field with x- and z-components and (b) the corresponding precession of the expectation value of the spin.

Example 3.2

A spin-1/2 particle with a magnetic moment is prepared in the state $| - \rangle$ and is subject to a uniform applied magnetic field $B = B_0 \hat{y}$. Find the probability of measuring spin up in the z-direction after a time $t$.

The initial state is

$$| \psi(0) \rangle = | - \rangle $$

(3.64)

The applied magnetic field is in the y-direction, so the Hamiltonian is $H = \omega_0 S_y$ and the energy eigenstates are $| \pm \rangle_y$ with energies $E_{\pm} = \pm \hbar \omega_0 / 2$ (step 1). The Larmor precession frequency is $\omega_0 = eB_0 / m_e$. We must express the initial state in the energy basis (step 2), which in this case is the $S_y$ basis:

$$| \psi(0) \rangle = | - \rangle$$

$$= |+_y \rangle y \langle + | -_y \rangle + | -_y \rangle y \langle - | - \rangle$$

$$= -i \langle -y | + \rangle + i \langle +y | - \rangle$$

(3.65)

The time evolved state is obtained by multiplying each energy eigenstate coefficient by a phase factor (step 3):

$$| \psi(t) \rangle = \frac{-i}{\sqrt{2}} e^{-\frac{E_+ t}{\hbar}} | + \rangle_y + \frac{i}{\sqrt{2}} e^{-\frac{E_- t}{\hbar}} | - \rangle_y$$

$$= \frac{-i}{\sqrt{2}} e^{-\frac{\omega_0 t}{2}} | + \rangle_y + \frac{i}{\sqrt{2}} e^{\frac{\omega_0 t}{2}} | - \rangle_y$$

(3.66)
The measurement probability is found by projecting onto the measured state and squaring (step 4):

\[ P_+ = |\langle + | \psi(t) \rangle|^2 \]

\[ = \left| \langle + \left( -i \frac{\omega_0 t}{\sqrt{2}} |+\rangle + i \frac{\omega_0 t}{\sqrt{2}} |-\rangle \right) \right|^2 \]

\[ = \left| \frac{-i}{\sqrt{2}} e^{-\frac{\omega_0 t}{2}} (|+\rangle + i \frac{\omega_0 t}{\sqrt{2}} |+\rangle) \right|^2 \]

\[ = \frac{1}{4} -i e^{-\frac{\omega_0 t}{2}} + i e^{+\frac{\omega_0 t}{2}} = \frac{1}{4} \left| -2 \sin \left( \frac{\omega_0 t}{2} \right) \right|^2 \]

\[ = \sin^2 \left( \frac{\omega_0 t}{2} \right) \]

The probability oscillates between zero and unity as time evolves, as shown in Fig. 3.10(a), which is consistent with the model of the spin vector precessing around the applied field, as shown in Fig. 3.10(b).

Figure 3.10 (a) Spin measurement probability and (b) the corresponding precession of the expectation value of the spin.

Though we have derived Rabi's formula (Eqn. (3.63)) in the context of a spin-1/2 particle in a uniform magnetic field, its applicability is much more general. If we can express the Hamiltonian of any two-state system in the matrix form of Eqn. (3.51) with the parameters \( \omega_0 \) and \( \omega_1 \), then we can use Rabi's formula to find the probability that the system starts in the "spin-up" state \( |+\rangle \) and is then measured to be in the "spin-down" state \( |-\rangle \) after some time \( t \). In the general case, the \( |+\rangle \) and \( |-\rangle \) states are whatever