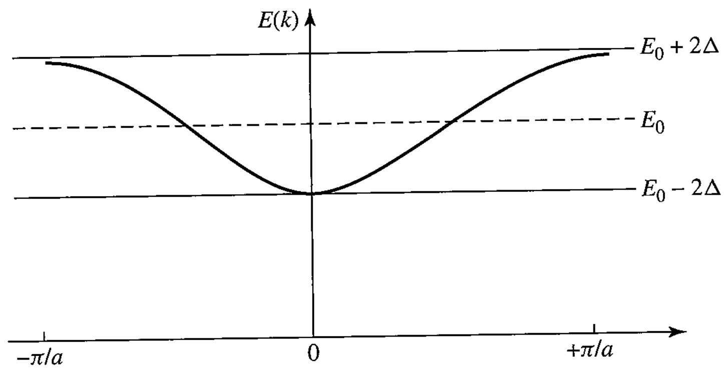

FIGURE 4.9 Dispersion curve for $E(k)$ versus k in the Brillouin zone $|k| \leq \pi/a$.

energy eigenvalue E now depends on k as follows:

$$E(k) = E_0 - 2\Delta \cos ka. \qquad (4.3.19)$$

Notice that this energy eigenvalue equation is independent of the detailed shape of the potential as long as the tight-binding approximation is valid. Note also that there is a cutoff in the wave vector k of the Bloch wave function (4.3.17) given by $|k| = \pi/a$. Equation (4.3.19) defines a dispersion curve, as shown in Figure 4.9. As a result of tunneling, the denumerably infinitefold degeneracy is now completely lifted, and the allowed energy values form a continuous band between $E_0 - 2\Delta$ and $E_0 + 2\Delta$, known as the **Brillouin zone**.

So far we have considered only one particle moving in a periodic potential. In a more realistic situation we must look at many electrons moving in such a potential. Actually, the electrons satisfy the Pauli exclusion principle, as we will discuss more systematically in Chapter 7, and they start filling the band. In this way, the main qualitative features of metals, semiconductors, and the like can be understood as a consequence of translation invariance supplemented by the exclusion principle.

The reader may have noted the similarity between the symmetrical double-well problem of Section 4.2 and the periodic potential of this section. Comparing Figures 4.3 and 4.7, we note that they can be regarded as opposite extremes (two versus infinite) of potentials with a finite number of troughs.

4.4 ■ THE TIME-REVERSAL DISCRETE SYMMETRY

In this section we study another discrete symmetry operator, called **time reversal**. This is a difficult topic for the novice, partly because the term *time reversal* is a misnomer; it reminds us of science fiction. What we do in this section can be more appropriately characterized by the term *reversal of motion*. Indeed, that is the phrase used by E. Wigner, who formulated time reversal in a very fundamental paper written in 1932.

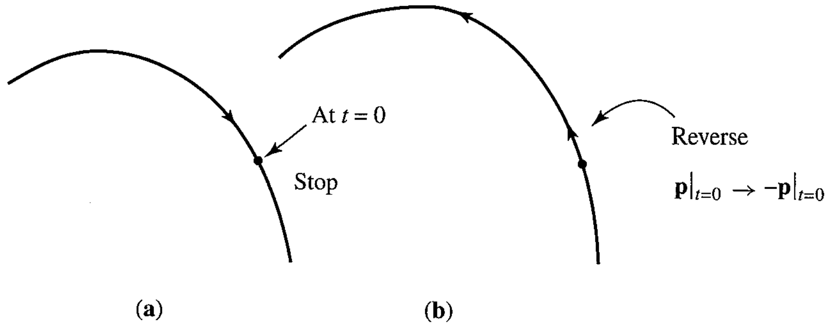

FIGURE 4.10 (a) Classical trajectory that stops at $t = 0$ and (b) reverses its motion $\mathbf{p}|_{t=0} \to -\mathbf{p}|_{t=0}$.

For orientation purposes, let us look at classical mechanics. Suppose there is a trajectory of a particle subject to a certain force field; see Figure 4.10. At $t = 0$, let the particle stop and reverse its motion: $\mathbf{p}|_{t=0} \to -\mathbf{p}|_{t=0}$. The particle traverses backward along the same trajectory. If you run the motion picture of trajectory (a) backward as in (b), you may have a hard time telling whether this is the correct sequence.

More formally, if $\mathbf{x}(t)$ is a solution to

$$m\ddot{\mathbf{x}} = -\nabla V(\mathbf{x}), \tag{4.4.1}$$

then $\mathbf{x}(-t)$ is also a possible solution in the same force field derivable from V. It is, of course, important to note that we do not have a dissipative force here. A block sliding on a table decelerates (because of friction) and eventually stops. But have you ever seen a block on a table spontaneously start to move and accelerate?

With a magnetic field you may be able to tell the difference. Imagine that you are taking the motion picture of a spiraling electron trajectory in a magnetic field. You may be able to tell whether the motion picture is run forward or backward by comparing the sense of rotation with the magnetic pole labeling N and S. However, from a microscopic point of view, $\mathbf{B}$ is produced by moving charges via an electric current; if you could reverse the current that causes $\mathbf{B}$, then the situation would be quite symmetrical. In terms of the picture shown in Figure 4.11, you may have figured out that N and S are mislabeled! Another, more formal way of saying all this is that the Maxwell equations, for example,

$$\nabla \cdot \mathbf{E} = 4\pi\rho, \quad \nabla \times \mathbf{B} - \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi \mathbf{j}}{c}, \quad \nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}, \tag{4.4.2}$$

and the Lorentz force equation $\mathbf{F} = e[\mathbf{E} + (1/c)(\mathbf{v} \times \mathbf{B})]$ are invariant under $t \to -t$, provided that we also let

$$\mathbf{E} \to \mathbf{E}, \quad \mathbf{B} \to -\mathbf{B}, \quad \rho \to \rho, \quad \mathbf{j} \to -\mathbf{j}, \quad \mathbf{v} \to -\mathbf{v}. \tag{4.4.3}$$

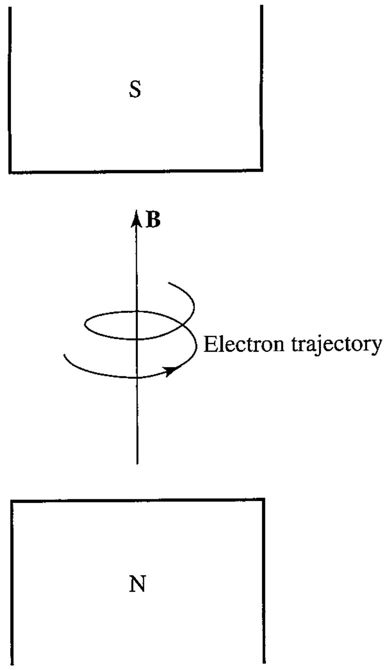

FIGURE 4.11 Electron trajectory between the north and south poles of a magnet.

Let us now look at wave mechanics, where the basic equation of the Schrödinger wave equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi. \tag{4.4.4}$$

Suppose $\psi(\mathbf{x},t)$ is a solution. We can easily verify that $\psi(\mathbf{x},-t)$ is not a solution, because of the appearance of the first-order time derivative. However, $\psi^*(\mathbf{x},-t)$ is a solution, as you may verify by complex conjugation of (4.4.4). It is instructive to convince ourselves of this point for an energy eigenstate—that is, by substituting

$$\psi(\mathbf{x},t) = u_n(\mathbf{x})e^{-iE_nt/\hbar}, \quad \psi^*(\mathbf{x},-t) = u_n^*(\mathbf{x})e^{-iE_nt/\hbar} \tag{4.4.5}$$

into the Schrödinger equation (4.4.4). Thus we conjecture that time reversal must have something to do with complex conjugation. If at $t = 0$ the wave function is given by

$$\psi = \langle\mathbf{x}|\alpha\rangle, \tag{4.4.6}$$

then the wave function for the corresponding time-reversed state is given by $\langle\mathbf{x}|\alpha\rangle^*$. We will later show that this is indeed the case for the wave function of a spinless system. As an example, you may easily check this point for the wave function of a plane wave; see Problem 4.8 of this chapter.

Digression on Symmetry Operations

Before we begin a systematic treatment of the time-reversal operator, some general remarks on symmetry operations are in order. Consider a symmetry operation

$$|\alpha\rangle \rightarrow |\tilde{\alpha}\rangle, \quad |\beta\rangle \rightarrow |\tilde{\beta}\rangle. \tag{4.4.7}$$

One may argue that it is natural to require the inner product $\langle\beta|\alpha\rangle$ to be preserved—that is,

$$\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\beta|\alpha\rangle. \tag{4.4.8}$$

Indeed, for symmetry operations such as rotations, translations, and even parity, this is indeed the case. If $|\alpha\rangle$ is rotated and $|\beta\rangle$ is also rotated in the same manner, $\langle\beta|\alpha\rangle$ is unchanged. Formally, this arises from the fact that for the symmetry operations considered in the previous sections, the corresponding symmetry operator is unitary, so

$$\langle\beta|\alpha\rangle \rightarrow \langle\beta|U^\dagger U|\alpha\rangle = \langle\beta|\alpha\rangle. \tag{4.4.9}$$

However, in discussing time reversal, we see that requirement (4.4.8) turns out to be too restrictive. Instead, we merely impose the weaker requirement that

$$|\langle\tilde{\beta}|\tilde{\alpha}\rangle| = |\langle\beta|\alpha\rangle|. \tag{4.4.10}$$

Requirement (4.4.8) obviously satisfies (4.4.10). But this is not the only way;

$$\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\beta|\alpha\rangle^* = \langle\alpha|\beta\rangle \tag{4.4.11}$$

works equally well. We pursue the latter possibility in this section because, from our earlier discussion based on the Schrödinger equation, we inferred that time reversal has something to do with complex conjugation.

Definition The transformation

$$|\alpha\rangle \rightarrow |\tilde{\alpha}\rangle = \theta|\alpha\rangle, \quad |\beta\rangle \rightarrow |\tilde{\beta}\rangle = \theta|\beta\rangle \tag{4.4.12}$$

is said to be ***antiunitary*** if

$$\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\beta|\alpha\rangle^*, \tag{4.4.13a}$$

$$\theta(c_1|\alpha\rangle + c_2|\beta\rangle) = c_1^*\theta|\alpha\rangle + c_2^*\theta|\beta\rangle. \tag{4.4.13b}$$

In such a case the operator θ is an antiunitary operator. Relation (4.4.13b) alone defines an **antilinear** operator.

We now claim that an antiunitary operator can be written as

$$\theta = UK, \tag{4.4.14}$$

where U is a unitary operator and K is the complex-conjugate operator that forms the complex conjugate of any coefficient that multiplies a ket (and stands on the right of K). Before checking (4.4.13), let us examine the property of the K operator. Suppose we have a ket multiplied by a complex number c. We then have

$$Kc|\alpha\rangle = c^* K|\alpha\rangle. \tag{4.4.15}$$

One may further ask, what happens if $|\alpha\rangle$ is expanded in terms of base kets $\{|a'\rangle\}$? Under the action K, we have

$$\begin{aligned} |\alpha\rangle = \sum_{a'} |a'\rangle\langle a'|\alpha\rangle \xrightarrow{K} |\tilde{\alpha}\rangle &= \sum_{a'} \langle a'|\alpha\rangle^* K|a'\rangle \\ &= \sum_{a'} \langle a'|\alpha\rangle^* |a'\rangle. \end{aligned} \tag{4.4.16}$$

Notice that K acting on the base ket does not change the base ket. The explicit representation of $|a'\rangle$ is

$$|a'\rangle = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \tag{4.4.17}$$

and there is nothing to be changed by K. The reader may wonder, for instance, whether the S_y eigenkets for a spin $\frac{1}{2}$ system change under K. The answer is that if the S_z eigenkets are used as base kets, we must change the S_y eigenkets because the S_y eigenkets (1.1.14) undergo, under the action of K,

$$K\left(\frac{1}{\sqrt{2}}|+\rangle \pm \frac{i}{\sqrt{2}}|-\rangle\right) \rightarrow \frac{1}{\sqrt{2}}|+\rangle \mp \frac{i}{\sqrt{2}}|-\rangle. \tag{4.4.18}$$

On the other hand, if the S_y eigenkets themselves are used as the base kets, we do not change the S_y eigenkets under the action of K. Thus the effect of K changes with the basis. As a result, the form of U in (4.4.14) also depends on the particular representation (that is, on the choice of base kets) used.

Returning to $\theta = UK$ and (4.4.13), let us first check property (4.4.13b). We have

$$\begin{aligned} \theta(c_1|\alpha\rangle + c_2|\beta\rangle) &= UK(c_1|\alpha\rangle + c_2|\beta\rangle) \\ &= c_1^* UK|\alpha\rangle + c_2^* UK|\beta\rangle \\ &= c_1^* \theta|\alpha\rangle + c_2^* \theta|\beta\rangle, \end{aligned} \tag{4.4.19}$$

so (4.4.13b) indeed holds. Before checking (4.4.13a), we assert that it is always safer to work with the action of θ on kets only. We can figure out how the bras change just by looking at the corresponding kets. In particular, it is not necessary to consider θ acting on bras from the right, nor is it necessary to define $\theta^\dagger$. We have

$$\begin{aligned}|\alpha\rangle \overset{\theta}{\rightarrow} |\tilde{\alpha}\rangle &= \sum_{a'} \langle a'|\alpha\rangle^* UK|a'\rangle \\ &= \sum_{a'} \langle a'|\alpha\rangle^* U|a'\rangle \\ &= \sum_{a'} \langle \alpha|a'\rangle U|a'\rangle. \end{aligned} \tag{4.4.20}$$

As for $|\beta\rangle$, we have

$$\begin{aligned}|\tilde{\beta}\rangle &= \sum_{a'} \langle a'|\beta\rangle^* U|a'\rangle \overset{\text{DC}}{\leftrightarrow} \langle\tilde{\beta}| = \sum_{a'} \langle a'|\beta\rangle\langle a'|U^\dagger \\ \langle\tilde{\beta}|\tilde{\alpha}\rangle &= \sum_{a''}\sum_{a'} \langle a''|\beta\rangle\langle a''|U^\dagger U|a'\rangle\langle\alpha|a'\rangle \\ &= \sum_{a'} \langle\alpha|a'\rangle\langle a'|\beta\rangle = \langle\alpha|\beta\rangle \\ &= \langle\beta|\alpha\rangle^*, \end{aligned} \tag{4.4.21}$$

so this checks. (Recall the notion of "dual correspondence," or DC, from Section 1.2.)

In order for (4.4.10) to be satisfied, it is of physical interest to consider just two types of transformations—unitary and antiunitary. Other possibilities are related to either of the preceding via trivial phase changes. The proof of this assertion is actually very difficult and will not be discussed further here. See, however, Gottfried and Yan (2003), Section 7.1.

Time-Reversal Operator

We are finally in a position to present a formal theory of time reversal. Let us denote the time-reversal operator by Θ, to be distinguished from θ, a general antiunitary operator. Consider

$$|\alpha\rangle \rightarrow \Theta|\alpha\rangle, \tag{4.4.22}$$

where $\Theta|\alpha\rangle$ is the time-reversed state. More appropriately, $\Theta|\alpha\rangle$ should be called the motion-reversed state. If $|\alpha\rangle$ is a momentum eigenstate $|\mathbf{p}'\rangle$, we expect $\Theta|\alpha\rangle$ to be $|-\mathbf{p}'\rangle$ up to a possible phase. Likewise, $\mathbf{J}$ is to be reversed under time reversal.

We now deduce the fundamental property of the time-reversal operator by looking at the time evolution of the time-reversed state. Consider a physical system represented by a ket $|\alpha\rangle$, say at $t = 0$. Then, at a slightly later time $t = \delta t$, the

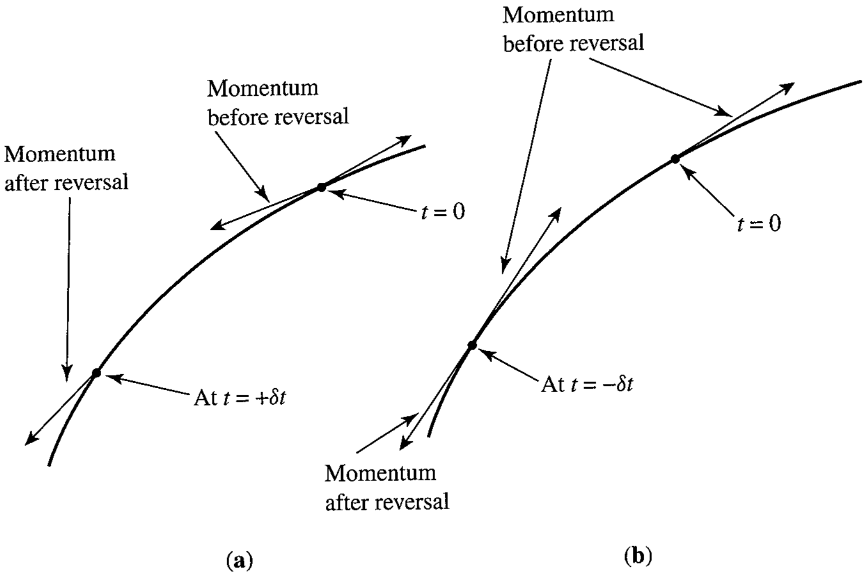

FIGURE 4.12 Momentum before and after time reversal at time $t = 0$ and $t = \pm\delta t$.

system is found in

$$|\alpha, t_0 = 0; t = \delta t\rangle = \left(1 - \frac{iH}{\hbar}\delta t\right)|\alpha\rangle, \tag{4.4.23}$$

where H is the Hamiltonian that characterizes the time evolution. Instead of the preceding equation, suppose we first apply Θ, say at $t = 0$, and then let the system evolve under the influence of the Hamiltonian H. We then have, at δt,

$$\left(1 - \frac{iH\delta t}{\hbar}\right)\Theta|\alpha\rangle. \tag{4.4.24a}$$

If motion obeys symmetry under time reversal, we expect the preceding state ket to be the same as

$$\Theta|\alpha, t_0 = 0; t = -\delta t\rangle. \tag{4.4.24b}$$

That is, first consider a state ket at *earlier time* $t = -\delta t$, and then reverse **p** and **J**; see Figure 4.12. Mathematically,

$$\left(1 - \frac{iH}{\hbar}\delta t\right)\Theta|\alpha\rangle = \Theta\left(1 - \frac{iH}{\hbar}(-\delta t)\right)|\alpha\rangle. \tag{4.4.25}$$

If the preceding relation is to be true for any ket, we must have

$$-iH\Theta|\,\rangle = \Theta iH|\,\rangle, \tag{4.4.26}$$

where the blank ket $|\,\rangle$ emphasizes that (4.4.26) is to be true for any ket.

We now argue that Θ *cannot* be unitary if the motion of time reversal is to make sense. Suppose Θ were unitary. It would then be legitimate to cancel the i's in (4.4.26), and we would have the operator equation

$$-H\Theta = \Theta H. \tag{4.4.27}$$

Consider an energy eigenket $|n\rangle$ with energy eigenvalue E_n. The corresponding time-reversed state would be $\Theta|n\rangle$, and we would have, because of (4.4.27),

$$H\Theta|n\rangle = -\Theta H|n\rangle = (-E_n)\Theta|n\rangle. \tag{4.4.28}$$

This equation says that $\Theta|n\rangle$ is an eigenket of the Hamiltonian with energy eigenvalues $-E_n$. But this is nonsensical even in the very elementary case of a free particle. We know that the energy spectrum of the free particle is positive semidefinite—from 0 to $+\infty$. There is no state lower than a particle at rest (momentum eigenstate with momentum eigenvalue zero); the energy spectrum ranging from $-\infty$ to 0 would be completely unacceptable. We can also see this by looking at the structure of the free-particle Hamiltonian. We expect $\mathbf{p}$ to change sign but not $\mathbf{p}^2$; yet (4.4.27) would imply that

$$\Theta^{-1}\frac{\mathbf{p}^2}{2m}\Theta = \frac{-\mathbf{p}^2}{2m}. \tag{4.4.29}$$

All these arguments strongly suggest that if time reversal is to be a useful symmetry at all, we are not allowed to cancel the i's in (4.4.26); hence, Θ had better be antiunitary. In this case the right-hand side of (4.4.26) becomes

$$\Theta i H|\,\rangle = -i\Theta H|\,\rangle \tag{4.4.30}$$

by antilinear property (4.4.13b). Now at last we can cancel the i's in (4.4.26). This leads finally, via (4.4.30), to

$$\Theta H = H\Theta. \tag{4.4.31}$$

Equation (4.4.31) expresses the fundamental property of the Hamiltonian under time reversal. With this equation the difficulties mentioned earlier [see (4.4.27) to (4.4.29)] are absent, and we obtain physically sensible results. From now on, we will always take Θ to be antiunitary.

We mentioned earlier that it is best to avoid an antiunitary operator acting on bras from the right. Nevertheless, we may use

$$\langle\beta|\Theta|\alpha\rangle, \tag{4.4.32}$$

which is to be understood always as

$$(\langle\beta|)\cdot(\Theta|\alpha\rangle) \tag{4.4.33}$$

and never as

$$(\langle\beta|\Theta)\cdot|\alpha\rangle. \tag{4.4.34}$$

In fact, we do not even attempt to define $\langle\beta|\Theta$. This is one place where the Dirac bra-ket notation is a little confusing. After all, that notation was invented to handle linear operators, not antilinear operators.

With this cautionary remark, we are in a position to discuss the behavior of operators under time reversal. We continue to take the point of view that the Θ operator is to act on kets

$$|\tilde{\alpha}\rangle = \Theta|\alpha\rangle, \quad |\tilde{\beta}\rangle = \Theta|\beta\rangle, \tag{4.4.35}$$

yet it is often convenient to talk about operators—in particular, observables—which are odd or even under time reversal. We start with an important identity:

$$\langle\beta|\otimes|\alpha\rangle = \langle\tilde{\alpha}|\Theta\otimes^{\dagger}\Theta^{-1}|\tilde{\beta}\rangle, \tag{4.4.36}$$

where $\otimes$ is a linear operator. This identity follows solely from the antiunitary nature of Θ. To prove this let us define

$$|\gamma\rangle \equiv \otimes^{\dagger}|\beta\rangle. \tag{4.4.37}$$

By dual correspondence we have

$$|\gamma\rangle \overset{\text{DC}}{\leftrightarrow} \langle\beta|\otimes = \langle\gamma|. \tag{4.4.38}$$

Hence,

$$\begin{aligned}\langle\beta|\otimes|\alpha\rangle &= \langle\gamma|\alpha\rangle = \langle\tilde{\alpha}|\tilde{\gamma}\rangle \\ &= \langle\tilde{\alpha}|\Theta\otimes^{\dagger}|\beta\rangle = \langle\tilde{\alpha}|\Theta\otimes^{\dagger}\Theta^{-1}\Theta|\beta\rangle \\ &= \langle\tilde{\alpha}|\Theta\otimes^{\dagger}\Theta^{-1}|\tilde{\beta}\rangle,\end{aligned} \tag{4.4.39}$$

which proves the identity. In particular, for *Hermitian* observables A, we get

$$\langle\beta|A|\alpha\rangle = \langle\tilde{\alpha}|\Theta A\Theta^{-1}|\tilde{\beta}\rangle. \tag{4.4.40}$$

We say that observables are even or odd under time reversal according to whether we have the upper or lower sign in

$$\Theta A\Theta^{-1} = \pm A. \tag{4.4.41}$$

Note that this equation, together with (4.4.40), gives a phase restriction on the matrix elements of A taken with respect to time-reversed states as follows:

$$\langle\beta|A|\alpha\rangle = \pm\langle\tilde{\beta}|A|\tilde{\alpha}\rangle^{*}. \tag{4.4.42}$$

If $|\beta\rangle$ is identical to $|\alpha\rangle$, so that we are talking about expectation values, we have

$$\langle\alpha|A|\alpha\rangle = \pm\langle\tilde{\alpha}|A|\tilde{\alpha}\rangle, \tag{4.4.43}$$

where $\langle\tilde{\alpha}|A|\tilde{\alpha}\rangle$ is the expectation value taken with respect to the time-reversed state.

As an example, let us look at the expectation value of $\mathbf{p}$. It is reasonable to assume that the expectation value of $\mathbf{p}$ taken with respect to the time-reversed state will be of opposite sign. Thus

$$\langle\alpha|\mathbf{p}|\alpha\rangle = -\langle\tilde{\alpha}|\mathbf{p}|\tilde{\alpha}\rangle, \tag{4.4.44}$$

so we take $\mathbf{p}$ to be an odd operator, namely

$$\Theta\mathbf{p}\Theta^{-1} = -\mathbf{p}. \tag{4.4.45}$$

This implies that

$$\begin{aligned} \mathbf{p}\Theta|\mathbf{p}'\rangle &= -\Theta\mathbf{p}\Theta^{-1}\Theta|\mathbf{p}'\rangle \\ &= (-\mathbf{p}')\Theta|\mathbf{p}'\rangle. \end{aligned} \tag{4.4.46}$$

Equation (4.4.46) agrees with our earlier assertion that $\Theta|\mathbf{p}'\rangle$ is a momentum eigenket with eigenvalue $-\mathbf{p}'$. It can be identified with $|-\mathbf{p}'\rangle$ itself with a suitable choice of phase. Likewise, we obtain

$$\begin{aligned} \Theta\mathbf{x}\Theta^{-1} &= \mathbf{x} \\ \Theta|\mathbf{x}'\rangle &= |\mathbf{x}'\rangle \qquad \text{(up to a phase)} \end{aligned} \tag{4.4.47}$$

from the (eminently reasonable) requirement

$$\langle\alpha|\mathbf{x}|\alpha\rangle = \langle\tilde{\alpha}|\mathbf{x}|\tilde{\alpha}\rangle. \tag{4.4.48}$$

We can now check the invariance of the fundamental commutation relation

$$[x_i, p_j]|\ \rangle = i\hbar\delta_{ij}|\ \rangle, \tag{4.4.49}$$

where the blank ket $|\ \rangle$ stands for any ket. Applying Θ to both sides of (4.4.49), we have

$$\Theta\,[x_i, p_j]\Theta^{-1}\Theta|\ \rangle = \Theta i\hbar\delta_{ij}|\ \rangle, \tag{4.4.50}$$

which leads, after passing Θ through $i\hbar$, to

$$[x_i, (-p_j)]\Theta|\ \rangle = -i\hbar\delta_{ij}\Theta|\ \rangle. \tag{4.4.51}$$

Note that the fundamental commutation relation $[x_i, p_j] = i\hbar\delta_{ij}$ is preserved by virtue of the fact that Θ is antiunitary. This can be given as yet another reason for taking Θ to be antiunitary; otherwise, we would be forced to abandon either (4.4.45) or (4.4.47)! Similarly, to preserve

$$[J_i, J_j] = i\hbar\varepsilon_{ijk}J_k, \tag{4.4.52}$$

the angular-momentum operator must be odd under time reversal; that is,

$$\Theta\mathbf{J}\Theta^{-1} = -\mathbf{J}. \tag{4.4.53}$$

This is consistent for a spinless system where $\mathbf{J}$ is just $\mathbf{x}\times\mathbf{p}$. Alternatively, we could have deduced this relation by noting that the rotational operator and the time-reversal operator commute (note the extra i!).

Wave Function

Suppose at some given time, say at $t=0$, a spinless single-particle system is found in a state represented by $|\alpha\rangle$. Its wave function $\langle \mathbf{x}'|\alpha\rangle$ appears as the expansion coefficient in the position representation

$$|\alpha\rangle = \int d^3x' |\mathbf{x}'\rangle\langle \mathbf{x}'|\alpha\rangle. \tag{4.4.54}$$

Applying the time-reversal operator yields

$$\begin{aligned}\Theta|\alpha\rangle &= \int d^3x' \Theta|\mathbf{x}'\rangle\langle \mathbf{x}'|\alpha\rangle^* \\ &= \int d^3x' |\mathbf{x}'\rangle\langle \mathbf{x}'|\alpha\rangle^*,\end{aligned} \tag{4.4.55}$$

where we have chosen the phase convention so that $\Theta|\mathbf{x}'\rangle$ is $|\mathbf{x}'\rangle$ itself. We then recover the rule

$$\psi(\mathbf{x}') \rightarrow \psi^*(\mathbf{x}') \tag{4.4.56}$$

inferred earlier by looking at the Schrödinger wave equation [see (4.4.5)]. The angular part of the wave function is given by a spherical harmonic Y_l^m. With the usual phase convention, we have

$$Y_l^m(\theta,\phi) \rightarrow Y_l^{m*}(\theta,\phi) = (-1)^m Y_l^{-m}(\theta,\phi). \tag{4.4.57}$$

Now $Y_l^m(\theta,\phi)$ is the wave function for $|l,m\rangle$ [see (3.6.23)]; therefore, from (4.4.56) we deduce

$$\Theta|l,m\rangle = (-1)^m|l,-m\rangle. \tag{4.4.58}$$

If we study the probability current density (2.4.16) for a wave function of type (3.6.22) going like $R(r)Y_l^m$, we shall conclude that for $m>0$ the current flows in the counterclockwise direction, as seen from the positive z-axis. The wave function for the corresponding time-reversed state has its probability current flowing in the opposite direction because the sign of m is reversed. All this is very reasonable.

As a nontrivial consequence of time-reversal invariance, we state an important theorem on the reality of the energy eigenfunction of a spinless particle.

Theorem 4.2. Suppose the Hamiltonian is invariant under time reversal and the energy eigenket $|n\rangle$ is nondegenerate; then the corresponding energy eigenfunction is real (or, more generally, a real function times a phase factor independent of $\mathbf{x}$).

Proof. To prove this, first note that

$$H\Theta|n\rangle = \Theta H|n\rangle = E_n\Theta|n\rangle, \tag{4.4.59}$$

so $|n\rangle$ and $\Theta|n\rangle$ have the same energy. The nondegeneracy assumption prompts us to conclude that $|n\rangle$ and $\Theta|n\rangle$ must represent the *same* state; otherwise, there would be two different states with the same energy E_n, an obvious contradiction! Let us recall that the wave functions for $|n\rangle$ and $\Theta|n\rangle$ are $\langle \mathbf{x}'|n\rangle$ and $\langle \mathbf{x}'|n\rangle^*$, respectively. They must be the same—that is,

$$\langle \mathbf{x}'|n\rangle = \langle \mathbf{x}'|n\rangle^* \tag{4.4.60}$$

for all practical purposes—or, more precisely, they can differ at most by a phase factor independent of $\mathbf{x}$.

Thus if we have, for instance, a nondegenerate bound state, its wave function is always real. On the other hand, in the hydrogen atom with $l \neq 0$, $m \neq 0$, the energy eigenfunction characterized by definite (n,l,m) quantum numbers is complex because Y_l^m is complex; this does not contradict the theorem because $|n,l,m\rangle$ and $|n,l,-m\rangle$ are degenerate. Similarly, the wave function of a plane wave $e^{i\mathbf{p}\cdot\mathbf{x}/\hbar}$ is complex, but it is degenerate with $e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar}$.

We see that for a spinless system, the wave function for the time-reversed state, say at $t=0$, is simply obtained by complex conjugation. In terms of ket $|\alpha\rangle$ written as in (4.4.16) or in (4.4.54), the Θ operator is the complex-conjugate operator K itself because K and Θ have the same effect when acting on the base ket $|a'\rangle$ (or $|\mathbf{x}'\rangle$). We may note, however, that the situation is quite different when the ket $|\alpha\rangle$ is expanded in terms of the momentum eigenket, because Θ must change $|\mathbf{p}'\rangle$ into $|-\mathbf{p}'\rangle$ as follows:

$$\Theta|\alpha\rangle = \int d^3p'|-\mathbf{p}'\rangle\langle\mathbf{p}'|\alpha\rangle^* = \int d^3p'|\mathbf{p}'\rangle\langle-\mathbf{p}'|\alpha\rangle^*. \tag{4.4.61}$$

It is apparent that the momentum-space wave function of the time-reversed state is not just the complex conjugate of the original momentum-space wave function; rather, we must identify $\phi^*(-\mathbf{p}')$ as the momentum-space wave function for the time-reversed state. This situation once again illustrates the basic point that the particular form of Θ depends on the particular representation used.

Time Reversal for a Spin $\frac{1}{2}$ System

The situation is even more interesting for a particle with spin—spin $\frac{1}{2}$, in particular. We recall from Section 3.2 that the eigenket of $\mathbf{S}\cdot\hat{\mathbf{n}}$ with eigenvalue $\hbar/2$ can be written as

$$|\hat{\mathbf{n}};+\rangle = e^{-iS_z\alpha/\hbar}e^{-iS_y\beta/\hbar}|+\rangle, \tag{4.4.62}$$

where $\hat{\mathbf{n}}$ is characterized by the polar and azimuthal angles β and α, respectively. Noting (4.4.53), we have

$$\Theta|\hat{\mathbf{n}};+\rangle = e^{-iS_z\alpha/\hbar}e^{-iS_y\beta/\hbar}\Theta|+\rangle = \eta|\hat{\mathbf{n}};-\rangle. \tag{4.4.63}$$

On the other hand, we can easily verify that

$$|\hat{\mathbf{n}};-\rangle = e^{-i\alpha S_z/\hbar}e^{-i(\pi+\beta)S_y/\hbar}|+\rangle. \tag{4.4.64}$$

In general, we saw earlier that the product UK is an antiunitary operator. Comparing (4.4.63) and (4.4.64) with Θ set equal to UK, and noting that K acting on the base ket $|+\rangle$ gives just $|+\rangle$, we see that

$$\Theta = \eta e^{-i\pi S_y/\hbar}K = -i\eta\left(\frac{2S_y}{\hbar}\right)K, \tag{4.4.65}$$

where η stands for an arbitrary phase (a complex number of modulus unity). Another way to be convinced of (4.4.65) is to verify that if $\chi(\hat{\mathbf{n}};+)$ is the two-component eigenspinor corresponding to $|\hat{\mathbf{n}};+\rangle$ [in the sense that $\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\chi(\hat{\mathbf{n}};+) = \chi(\hat{\mathbf{n}};+)$], then

$$-i\sigma_y\chi^*(\hat{\mathbf{n}};+) \tag{4.4.66}$$

(note the complex conjugation!) is the eigenspinor corresponding to $|\hat{\mathbf{n}};-\rangle$, again up to an arbitrary phase, see Problem 4.7 of this chapter. The appearance of S_y or σ_y can be traced to the fact that we are using the representation in which S_z is diagonal and the nonvanishing matrix elements of S_y are purely imaginary.

Let us now note

$$e^{-i\pi S_y/\hbar}|+\rangle = +|-\rangle, \quad e^{-i\pi S_y/\hbar}|-\rangle = -|+\rangle. \tag{4.4.67}$$

Using (4.4.67), we are in a position to work out the effect of Θ, written as (4.4.65), on the most general spin $\frac{1}{2}$ ket:

$$\Theta(c_+|+\rangle + c_-|-\rangle) = +\eta c_+^*|-\rangle - \eta c_-^*|+\rangle. \tag{4.4.68}$$

Let us apply Θ once again:

$$\begin{aligned}\Theta^2(c_+|+\rangle + c_-|-\rangle) &= -|\eta|^2 c_+|+\rangle - |\eta|^2 c_-|-\rangle \\ &= -(c_+|+\rangle + c_-|-\rangle)\end{aligned} \tag{4.4.69}$$

or

$$\Theta^2 = -1, \tag{4.4.70}$$

(where -1 is to be understood as -1 times the identity operator) for *any* spin orientation. This is an extraordinary result. It is crucial to note here that our conclusion is completely independent of the choice of phase; (4.4.70) holds no matter what phase convention we may use for η. In contrast, we may note that two successive applications of Θ to a spinless state give

$$\Theta^2 = +1, \tag{4.4.71}$$

as is evident from, say, (4.4.58).

More generally, we now prove

$$\Theta^2|j \text{ half-integer}\rangle = -|j \text{ half-integer}\rangle \tag{4.4.72a}$$

$$\Theta^2|j \text{ integer}\rangle = +|j \text{ integer}\rangle. \tag{4.4.72b}$$

Thus the eigenvalue of Θ^2 is given by $(-1)^{2j}$. We first note that (4.4.65) generalizes for arbitrary j to

$$\Theta = \eta e^{-i\pi J_y/\hbar} K. \tag{4.4.73}$$

For a ket $|\alpha\rangle$ expanded in terms of $|j,m\rangle$ base eigenkets, we have

$$\begin{aligned}\Theta\left(\Theta \sum |jm\rangle\langle jm|\alpha\rangle\right) &= \Theta\left(\eta \sum e^{-i\pi J_y/\hbar}|jm\rangle\langle jm|\alpha\rangle^*\right) \\ &= |\eta|^2 e^{-2i\pi J_y/\hbar} \sum |jm\rangle\langle jm|\alpha\rangle.\end{aligned} \tag{4.4.74}$$

But

$$e^{-2i\pi J_y/\hbar}|jm\rangle = (-1)^{2j}|jm\rangle, \tag{4.4.75}$$

as is evident from the properties of angular-momentum eigenstates under rotation by 2π.

In (4.4.72b), $|j \text{ integer}\rangle$ may stand for the spin state

$$\frac{1}{\sqrt{2}}(|+-\rangle \pm |-+\rangle) \tag{4.4.76}$$

of a two-electron system or the orbital state $|l,m\rangle$ of a spinless particle. It is important only that j is an integer. Likewise, $|j \text{ half-integer}\rangle$ may stand, for example, for a three-electron system in any configuration. Actually, for a system made up exclusively of electrons, any system with an odd (even) number of electrons—regardless of their spatial orientation (for example, relative orbital angular momentum)—is odd (even) under Θ^2; they need not even be $\mathbf{J}^2$ eigenstates!

We make a parenthetical remark on the phase convention. In our earlier discussion based on the position representation, we saw that with the usual convention for spherical harmonics, it is natural to choose the arbitrary phase for $|l,m\rangle$ under time reversal so that

$$\Theta|l,m\rangle = (-1)^m|l,-m\rangle. \tag{4.4.77}$$

Some authors find it attractive to generalize this to obtain

$$\Theta|j,m\rangle = (-1)^m|j,-m\rangle \quad (j \text{ an integer}), \tag{4.4.78}$$

regardless of whether j refers to l or s (for an integer spin system). We may naturally ask, is this compatible with (4.4.72a) for a spin $\frac{1}{2}$ system when we visualize $|j,m\rangle$ as being built up of "primitive" spin $\frac{1}{2}$ objects according to Wigner and Schwinger? It is easy to see that (4.4.72a) is indeed consistent, provided that we choose η in (4.4.73) to be $+i$. In fact, in general, we can take

$$\Theta|j,m\rangle = i^{2m}|j,-m\rangle \tag{4.4.79}$$

for any j—either a half-integer j or an integer j; see Problem 4.10 of this chapter. The reader should be warned, however, that this is not the only convention found in the literature. See, for instance, Frauenfelder and Henley (1974). For some physical applications, it is more convenient to use other choices; for instance, the phase convention that makes the $\mathbf{J}_\pm$ operator matrix elements simple is *not* the phase convention that makes the time-reversal operator properties simple. We emphasize once again that (4.4.70) is completely independent of phase convention.

Having worked out the behavior of angular-momentum eigenstates under time reversal, we are in a position to study once again the expectation values of a Hermitian operator. Recalling (4.4.43), we obtain, under time reversal (canceling the i^{2m} factors),

$$\langle\alpha,j,m|A|\alpha,j,m\rangle = \pm\langle\alpha,j,-m|A|\alpha,j,-m\rangle. \tag{4.4.80}$$

Now suppose A is a component of a spherical tensor $T_q^{(k)}$. Because of the Wigner-Eckart theorem, it is sufficient to examine just the matrix element of the $q=0$ component. In general, $T^{(k)}$ (assumed to be Hermitian) is said to be even or odd under time reversal, depending on how its $q=0$ component satisfies the upper or lower sign in

$$\Theta T_{q=0}^{(k)}\Theta^{-1} = \pm T_{q=0}^{(k)}. \tag{4.4.81}$$

Equation (4.4.80) for $A = T_0^{(k)}$ becomes

$$\langle\alpha,j,m|T_0^{(k)}|\alpha,j,m\rangle = \pm\langle\alpha,j,-m|T_0^{(k)}|\alpha,j,-m\rangle. \tag{4.4.82}$$

Relying on (3.6.46)–(3.6.49), we expect $|\alpha,j,-m\rangle = \mathcal{D}(0,\pi,0)|\alpha,j,m\rangle$ up to a phase. We next use (3.11.22) for $T_0^{(k)}$, which leads to

$$\mathcal{D}^\dagger(0,\pi,0)T_0^{(k)}\mathcal{D}(0,\pi,0) = (-1)^k T_0^{(k)} + (q\neq 0 \text{ components}), \tag{4.4.83}$$

where we have used $\mathcal{D}_{00}^{(k)}(0,\pi,0) = P_k(\cos\pi) = (-1)^k$, and the $q\neq 0$ components give vanishing contributions when sandwiched between $\langle\alpha,j,m|$ and $|\alpha,j,m\rangle$. The net result is

$$\langle\alpha,j,m|T_0^{(k)}|\alpha,j,m\rangle = \pm(-1)^k\langle\alpha,j,m|T_0^{(k)}|\alpha,j,m\rangle. \tag{4.4.84}$$

As an example, when we take $k=1$, the expectation value $\langle\mathbf{x}\rangle$ taken with respect to eigenstates of j, m vanishes. We may argue that we already know $\langle\mathbf{x}\rangle = 0$ from parity inversion if the expectation value is taken with respect to parity eigenstates [see (4.2.41)]. But note that here, $|\alpha,j,m\rangle$ need not be parity eigenkets! For example, the $|j,m\rangle$ for spin $\frac{1}{2}$ particles could be $c_s|s_{1/2}\rangle + c_p|p_{1/2}\rangle$.

Interactions with Electric and Magnetic Fields; Kramers Degeneracy

Consider charged particles in an external electric or magnetic field. If we have only a static electric field interacting with the electric charge, the interaction part of the Hamiltonian is just

$$V(\mathbf{x}) = e\phi(\mathbf{x}), \tag{4.4.85}$$

where $\phi(\mathbf{x})$ is the electrostatic potential. Because $\phi(\mathbf{x})$ is a real function of the time-reversal even operator $\mathbf{x}$, we have

$$[\Theta, H] = 0. \tag{4.4.86}$$

Unlike the parity case, (4.4.86) does not lead to an interesting conservation law. The reason is that

$$\Theta U(t,t_0) \neq U(t,t_0)\Theta \tag{4.4.87}$$

even if (4.4.86) holds, so our discussion following (4.1.9) of Section 4.1 breaks down. As a result, there is no such thing as the "conservation of time-reversal quantum number." As we have already mentioned, requirement (4.4.86) does, however, lead to a nontrivial phase restriction: the reality of a nondegenerate wave function for a spinless system [see (4.4.59) and (4.4.60)].

Another far-reaching consequence of time-reversal invariance is the **Kramers degeneracy**. Suppose H and Θ commute, and let $|n\rangle$ and $\Theta|n\rangle$ be the energy eigenket and its time-reversed state, respectively. It is evident from (4.4.86) that $|n\rangle$ and $\Theta|n\rangle$ belong to the same energy eigenvalue $E_n(H\Theta|n\rangle = \Theta H|n\rangle = E_n\Theta|n\rangle)$. The question is, does $|n\rangle$ represent the same state as $\Theta|n\rangle$? If it does, $|n\rangle$ and $\Theta|n\rangle$ can differ at most by a phase factor. Hence,

$$\Theta|n\rangle = e^{i\delta}|n\rangle. \tag{4.4.88}$$

Applying Θ again to (4.4.88), we have $\Theta^2|n\rangle = \Theta e^{i\delta}|n\rangle = e^{-i\delta}\Theta|n\rangle = e^{-i\delta}e^{+i\delta}|n\rangle$; hence,

$$\Theta^2|n\rangle = +|n\rangle. \tag{4.4.89}$$

But this relation is impossible for half-integer j systems, for which Θ^2 is always -1, so we are led to conclude that $|n\rangle$ and $\Theta|n\rangle$, which have the same energy, must correspond to distinct states—that is, there must be a degeneracy. This means, for instance, that for a system composed of an odd number of electrons in an external electric field $\mathbf{E}$, each energy level must be at least twofold degenerate no matter how complicated $\mathbf{E}$ may be. Considerations along this line have interesting applications to electrons in crystals, where odd-electron and even-electron systems exhibit very different behaviors. Historically, Kramers inferred degeneracy of this kind by looking at explicit solutions of the Schrödinger equation; subsequently, Wigner pointed out that Kramers degeneracy is a consequence of time-reversal invariance.

Let us now turn to interactions with an external magnetic field. The Hamiltonian H may then contain terms like

$$\mathbf{S}\cdot\mathbf{B}, \quad \mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}, \quad (\mathbf{B} = \nabla\times\mathbf{A}), \tag{4.4.90}$$

where the magnetic field is to be regarded as external. The operators $\mathbf{S}$ and $\mathbf{p}$ are odd under time reversal; these interaction terms therefore do lead to

$$\Theta H \neq H\Theta. \tag{4.4.91}$$

As a trivial example, for a spin $\frac{1}{2}$ system the spin-up state $|+\rangle$ and its time-reversed state $|-\rangle$ no longer have the same energy in the presence of an external magnetic field. In general, Kramers degeneracy in a system containing an odd number of electrons can be lifted by applying an external magnetic field.

Notice that when we treat **B** as external, we do not change **B** under time reversal; this is because the atomic electron is viewed as a closed quantum-mechanical system to which we apply the time-reversal operator. This should not be confused with our earlier remarks concerning the invariance of the Maxwell equations (4.4.2) and the Lorentz force equation under $t \to -t$ and (4.4.3). There we were to apply time reversal to the *whole world*, for example, even to the currents in the wire that produces the **B** field!

Problems

4.1 Calculate the *three lowest* energy levels, together with their degeneracies, for the following systems (assume equal-mass *distinguishable* particles).

(a) Three noninteracting spin $\frac{1}{2}$ particles in a box of length L.

(b) Four noninteracting spin $\frac{1}{2}$ particles in a box of length L.

4.2 Let $\mathcal{T}_{\mathbf{d}}$ denote the translation operator (displacement vector $\mathbf{d}$); let $\mathcal{D}(\hat{\mathbf{n}},\phi)$ denote the rotation operator ($\hat{\mathbf{n}}$ and ϕ are the axis and angle of rotation, respectively); and let π denote the parity operator. Which, if any, of the following pairs commute? Why?

(a) $\mathcal{T}_{\mathbf{d}}$ and $\mathcal{T}_{\mathbf{d}'}$ ($\mathbf{d}$ and $\mathbf{d}'$ in different directions).

(b) $\mathcal{D}(\hat{\mathbf{n}},\phi)$ and $\mathcal{D}(\hat{\mathbf{n}}',\phi')$ ($\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}'$ in different directions).

(c) $\mathcal{T}_{\mathbf{d}}$ and π.

(d) $\mathcal{D}(\hat{\mathbf{n}},\phi)$ and π.

4.3 A quantum-mechanical state Ψ is known to be a simultaneous eigenstate of two Hermitian operators A and B that *anticommute*:

$$AB + BA = 0.$$

What can you say about the eigenvalues of A and B for state Ψ? Illustrate your point using the parity operator (which can be chosen to satisfy $\pi = \pi^{-1} = \pi^{\dagger}$) and the momentum operator.

4.4 A spin $\frac{1}{2}$ particle is bound to a fixed center by a spherically symmetrical potential.

(a) Write down the spin-angular function $\mathcal{Y}_{l=0}^{j=1/2,m=1/2}$.

(b) Express $(\sigma\cdot\mathbf{x})\,\mathcal{Y}_{l=0}^{j=1/2,m=1/2}$ in terms of some other $\mathcal{Y}_l^{j,m}$.

(c) Show that your result in (b) is understandable in view of the transformation properties of the operator $\mathbf{S}\cdot\mathbf{x}$ under rotations and under space inversion (parity).

4.5 Because of weak (neutral-current) interactions, there is a parity-violating potential between the atomic electron and the nucleus as follows:

$$V = \lambda[\delta^{(3)}(\mathbf{x})\mathbf{S}\cdot\mathbf{p} + \mathbf{S}\cdot\mathbf{p}\delta^{(3)}(\mathbf{x})],$$