Chapter 21

Time Reversal Symmetry

In this chapter we consider the properties of the time reversal operator for the case of no spin and when the spin-orbit interaction is included. The effect of time reversal symmetry on the energy dispersion relations is then considered, first for the case of no spin and then including the spin-orbit interaction.

In high energy physics, arguments regarding time inversion were essential in providing guidance for the development of a theory for the fundamental particles. The CPT invariance in particle physics deals with charge conjugation (C) which is the reversal of the sign of the electrical charge, parity (P) which is spatial inversion, and time inversion (T).

21.1 The Time Reversal Operator

Knowledge of the state of a system at any instant of time t and the deterministic laws of physics are sufficient to determine the state of the system both into the future and into the past. If $\psi(\vec{r}, t)$ specifies the time evolution of state $\psi(\vec{r}, 0)$, then $\psi(\vec{r}, -t)$ is called the **time-reversed conjugate** of $\psi(\vec{r}, t)$. The time-reversed conjugate state is achieved by running the system backwards in time or reversing all the velocities (or momenta) of the system.

The time evolution of a state is governed by Schrödinger's equation

(one of the deterministic laws of physics)

$$i\hbar\frac{\partial\psi}{\partial t} = \mathcal{H}\psi \tag{21.1}$$

which is satisfied by a time-dependent wave function of the form

$$\psi(\vec{r},t) = e^{\frac{-i\mathcal{H}t}{\hbar}}\psi(\vec{r},0) \tag{21.2}$$

where $\tilde{T} \equiv \exp\left[-i\mathcal{H}t/\hbar\right]$ is the time evolution operator. Under time reversal $t \to -t$ we note that $\psi \to \psi^*$ so that

$$\hat{T}\psi(\vec{r},t) = \psi(\vec{r},-t) = \psi^*(\vec{r},t). \tag{21.3}$$

In the following section, we derive some of the important properties of $\hat{T}$.

21.2 Properties of the Time Reversal Operator

The important properties of the time reversal operator include:

1. commutation: $[\hat{T},\mathcal{H}] = 0$
   Because of **energy conservation**, the time reversal operator $\hat{T}$ commutes with the Hamiltonian $\hat{T}\mathcal{H} = \mathcal{H}\hat{T}$. Since $\hat{T}$ commutes with the Hamiltonian, eigenstates of the time reversal operator are also eigenstates of the Hamiltonian.

2. anti-linear: $\hat{T}i = -i\hat{T}$
   From Schrödinger's equation (Eq. 21.1), it is seen that the reversal of time corresponds to a change of $i \to -i$, which implies that $\hat{T}i = -i\hat{T}$. We call an operator **anti-linear** if its operation on a complex number yields the complex conjugate of the number rather than the number itself $\hat{T}a = a^*\hat{T}$.

3. action on wave functions: $\hat{T}\psi = \psi^*\hat{T}$
   Since $\hat{T}\psi = \psi^*\hat{T}$, the action of $\hat{T}$ on a scalar product is

$$\hat{T}(\psi,\phi) = \int \phi^*(\vec{r})\psi(\vec{r})d^3r\ \hat{T} = (\psi,\phi)^*\hat{T} \tag{21.4}$$

4. In the case of no spin $\hat{T} = \hat{K}$ where $\hat{K}$ is the complex conjugation operator. With spin, we show below that $\hat{T} = \hat{K}\sigma_y$ where σ_y is the Pauli spin operator,

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

We will see below that both $\hat{T}$ and $\hat{K}$ are anti-unitary operators. From Schrödinger's equation (no spin), the effect of $\hat{T}$ on $\vec{p}$ is to reverse $\vec{p}$ (time goes backward) and $\hat{T}$ leaves $V(\vec{r})$ invariant, so that indeed $\mathcal{H}$ is invariant under $\hat{T}$; and furthermore $\hat{T} = \hat{K}$ for the case of no spin. When spin is included, however, the Hamiltonian $\mathcal{H}$ must still be invariant under $\hat{T}$. We note that $\hat{T}\vec{p} = -\vec{p}$ and $\hat{T}\vec{L} = -\vec{L}$ (orbital angular momentum). We likewise require that $\hat{T}\vec{S} = -\vec{S}$ where $\vec{S}$ = spin angular momentum. If these requirements are imposed, we show below that the $\mathcal{H}$ is still invariant under $\hat{T}$ (i.e., $\mathcal{H}$ commutes with $\hat{T}$) when the spin-orbit interaction is included:

$$\mathcal{H} = \frac{p^2}{2m} + V(\vec{r}) + \frac{\hbar}{4m^2c^2}\vec{\sigma} \cdot (\vec{\nabla}V \times \vec{p}). \tag{21.5}$$

We note that $\hat{K}[\sigma_x, \sigma_y, \sigma_z] = [\sigma_x, -\sigma_y, \sigma_z]$ when the spin components are written in terms of the Pauli matrices

$$\begin{aligned} \sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned} \tag{21.6}$$

since only the Pauli matrix σ_y contains i. Thus $\hat{K}$ by itself is not sufficient to describe the time reversal operation on the Hamiltonian $\mathcal{H}$ (Eq. 21.5) when the spin-orbit interaction is included. We will see below that the product $\hat{K}\sigma_y$ can describe time reversal of $\mathcal{H}$.

Let us now consider the effect of $\hat{K}\sigma_y$ on the spin matrices $\hat{K}\sigma_y[\sigma_x, \sigma_y, \sigma_z]$. We note that

$$\begin{array}{lcl} \sigma_y\sigma_x = -\sigma_x\sigma_y & \text{so that} & \hat{K}\sigma_y\sigma_x = -\hat{K}\sigma_x\sigma_y = -\sigma_x\hat{K}\sigma_y \\ \sigma_y\sigma_z = -\sigma_z\sigma_y & \text{so that} & \hat{K}\sigma_y\sigma_z = -\hat{K}\sigma_z\sigma_y = -\sigma_z\hat{K}\sigma_y \\ \hat{K}\sigma_y\sigma_y = -\sigma_y\hat{K}\sigma_y & \text{since, from above} & \hat{K}\sigma_y = -\sigma_y\hat{K}. \end{array}$$

Thus we obtain

$$\hat{K}\sigma_y\vec{\sigma} = -\vec{\sigma}\hat{K}\sigma_y$$

so that the operator $\hat{K}\sigma_y$ transforms $\vec{\sigma}$ (or $\vec{S}$) into $-\vec{\sigma}$ (or $-\vec{S}$). Clearly σ_y does not act on any of the other terms in the Hamiltonian. We note that $\hat{K}$ cannot be written in matrix form.

Since $\hat{K}\hat{K} = \hat{K}^2 = 1$, we can write the important relation $\hat{T} = \hat{K}\sigma_y$ which implies $\hat{K}\hat{T} = \sigma_y =$ **unitary operator**. Thus $\sigma_y^\dagger\sigma_y^{-1} = 1$ and since $\sigma_y^2 = \sigma_y\sigma_y = 1$ we have $\sigma_y^\dagger = \sigma_y$ and $\sigma_y^{\dagger 2} = 1$, where the symbol † is used to denote the adjoint of an operator.

5. In the case of no spin $\hat{T}^2 = 1$, since $\hat{K}^2 = 1$ and $\hat{T} = \hat{K}$. With spin we will now show that $\hat{T}^2 = -1$. Since $\hat{T} = \hat{K}\sigma_y$ when the effect of the electron spin is included,

$$\hat{T}^2 = (\hat{K}\sigma_y)(\hat{K}\sigma_y) = -(\sigma_y\hat{K})(\hat{K}\sigma_y) = -\sigma_y\hat{K}^2\sigma_y = -\sigma_y\sigma_y = -1.$$

More generally if we write $\hat{K}\hat{T} = U =$ unitary operator (not necessarily σ_y), we can then show that $\hat{T}^2 = \pm 1$. Since two consecutive operations by $\hat{T}$ on a state ψ must produce the same physical state ψ, we have $\hat{T}^2 = C1$ where C is a phase factor $e^{i\phi}$ of unit magnitude. Since $\hat{K}^2 = 1$, we can write

$$\hat{K}^2\hat{T} = \hat{T} = \hat{K}U = U^*\hat{K} \tag{21.7}$$

$$\hat{T}^2 = \hat{K}U\hat{K}U = U^*\hat{K}^2U = U^*U = C1 \tag{21.8}$$

We show below that $C = \pm 1$. Making use of the unitary property $U^\dagger U = UU^\dagger = 1$, we obtain by writing $U^* = U^*UU^\dagger = CU^\dagger$,

$$U^* = CU^\dagger = C\tilde{U}^* \tag{21.9}$$

Taking the transpose of both sides of Eq. 21.9 yields

$$\tilde{U^*} = U^\dagger = CU^* = C(C\tilde{U^*}) = C^2 U^\dagger \text{ or } C^2 = 1 \text{ and } C = \pm 1. \tag{21.10}$$

We thus obtain either $\hat{T}^2 = +1$ or $\hat{T}^2 = -1$.

6. Operators $H, \vec{r}, V(\vec{r})$ are even under time reversal $\hat{T}$; operators $\vec{p}, \vec{L}, \vec{\sigma}$ are odd under $\hat{T}$. Operators are either even or odd under time reversal. We can think of spin angular momentum classically as due to a current loop in a plane $\perp$ to the z-axis. Time reversal causes the current to flow in the opposite direction.

7. $\hat{T}$ and $\hat{K}$ are anti-unitary operators, as shown below.

In this subsection we show that $\hat{T}\hat{T}^\dagger = -1$ and $\hat{K}\hat{K}^\dagger = -1$, which is valid whether or not the spin is considered explicitly. The properties of the inverse of $\hat{T}$ and $\hat{K}$ are readily found. Since $\hat{K}^2 = 1$, then $\hat{K}\hat{K} = 1$ and $\hat{K}^{-1} = \hat{K}$. If for the case where the spin is treated explicitly $\hat{T}^2 = -1$, then $\hat{T}\hat{T} = -1$ and $\hat{T}^{-1} = -\hat{T}$; $\hat{T} = \hat{K}\sigma_y$ for the case of spin. For the spinless case, $\hat{T}^2 = 1$ and $\hat{T}^{-1} = \hat{T}$.

Since complex conjugation changes $i \rightarrow -i$, we can write $\hat{K}^\dagger = -\hat{K}$ so that $\hat{K}$ is anti-unitary.

We now use this result to show that both $\hat{T}$ and $\hat{K}$ are **anti-unitary**. This is the most important property of $\hat{T}$ from the point of view of group theory. Since $\hat{K} = \hat{T}$ in the absence of spin, and since $\hat{K}$ is anti-unitary, it follows that $\hat{T}$ is anti-unitary in this case. However, when spin is included, $\hat{T} = \hat{K}\sigma_y$ and

$$\begin{aligned} \sigma_y &= \hat{K}\hat{T} \\ \sigma_y^\dagger &= \hat{T}^\dagger \hat{K}^\dagger. \end{aligned} \tag{21.11}$$

Since σ_y is a unitary operator, thus $\hat{T}^\dagger\hat{K}^\dagger\hat{K}\hat{T} = 1$ but since $\hat{K}^\dagger\hat{K} = -1$ it follows that $\hat{T}^\dagger\hat{T} = -1$, showing that $\hat{T}$ is also **anti-unitary**.

Furthermore $\hat{K}$ and $\hat{T}$ behave differently from all the operators that we have thus far encountered in group theory, such as the point group operations (rotations, improper rotations, mirror planes, inversion and $\mathcal{R}$= rotation of 2π for spin problems). Thus in considering symmetry operations in group theory, we treat all the unitary operators separately by use of character tables and all the associated apparatus, and then we treat **time reversal symmetry** as an **additional symmetry constraint**. We will see in Chapter 22 how time reversal symmetry enters directly as a symmetry element for magnetic point groups.

We discuss first in §21.3 and §21.4 the general effect of $\hat{T}$ on the form of $E(\vec{k})$ for the case of electronic bands (a) neglecting spin and (b) including spin. After that, we will consider the question of degeneracies imposed on energy levels by time reversal symmetry (the Herring Rules).

21.3 The Effect of $\hat{T}$ on $E(\vec{k})$, Neglecting Spin

If for the moment we neglect spin, then the time reversal operation acting on a solution of Schrödinger's equation yields

$$\hat{T}\psi(\vec{r}) = \psi^*(\vec{r}). \tag{21.12}$$

Since the Hamiltonian commutes with $\hat{T}$, then both $\psi(\vec{r})$ and $\psi^*(\vec{r})$ satisfy Schrödinger's equation for the same energy eigenvalue, so that a two-fold degeneracy occurs. We will now show that time reversal symmetry leads to two symmetry properties for the energy eigenvalues for Bloch states: the evenness of the energy eigenvalues $E(\vec{k}) = E(-\vec{k})$, and the zero slope of $E_n(\vec{k})$ at the Brillouin zone boundaries.

The effect of the translation operation on a Bloch state is

$$\psi_k(\vec{r} + \vec{R}_n) = e^{i\vec{k}\cdot\vec{R}_n}\psi_k(\vec{r}) \tag{21.13}$$

and the effect of time reversal is

$$\hat{T}\psi_k(\vec{r}) = \psi_k^*(\vec{r}). \tag{21.14}$$

We can write the following relation for the complex conjugate of Bloch's theorem

$$\psi_k^*(\vec{r} + \vec{R}_n) = e^{-i\vec{k}\cdot\vec{R}_n}\psi_k^*(\vec{r}) \tag{21.15}$$

and we can also rewrite Eq. 21.15 in terms of $\vec{k} \to -\vec{k}$ as

$$\psi^*_{-k}(\vec{r} + \vec{R}_n) = e^{i\vec{k}\cdot\vec{R}_n}\psi^*_{-k}(\vec{r}) \tag{21.16}$$

which upon comparing Eqs. 21.13, 21.15 and 21.16 implies that for non-degenerate levels the time reversal operator transforms $\vec{k} \to -\vec{k}$

$$\hat{T}\psi_k(\vec{r}) = \psi_{-k}(\vec{r}) = \psi^*_k(\vec{r}). \tag{21.17}$$

If the level is doubly degenerate and $\psi_k(\vec{r})$ and $\phi_k(\vec{r})$ are the corresponding eigenstates, then if $\hat{T}\psi_k(\vec{r}) = \phi_k(\vec{r}) = \psi_{-k}(\vec{r})$, no additional degeneracy is required by time reversal symmetry. Time reversal symmetry thus implies that for a spinless system

$$E_n(\vec{k}) = E_n(-\vec{k}) \tag{21.18}$$

and the energy is an even function of wave vector $\vec{k}$ whether or not there is inversion symmetry.

Using this result (Eq. 21.18) and the $E(\vec{k}) = E(\vec{k} + \vec{K})$ periodicity in $\vec{k}$ space, we obtain:

$$E\left(\frac{\vec{K}}{2} - \delta\vec{k}\right) = E\left(-\frac{\vec{K}}{2} + \delta\vec{k}\right) = E\left(\frac{\vec{K}}{2} + \delta\vec{k}\right) \tag{21.19}$$

where $\delta\vec{k}$ is an infinitesimal distance to the Brillouin zone boundary. Thus referring to Fig. 21.1, $E(\vec{k})$ comes into the zone boundary with **zero slope** for both the lower and upper branches of the solutions in Fig. 21.1. For the case where there is degeneracy at the zone boundary, the upper and lower bands will have **equal and opposite slopes**.

We have been using the symmetry properties in Eqs. 21.18 and 21.19 throughout our solid state physics courses. In the most familiar cases, $E(\vec{k})$ depends on k^2. Figure 21.1 taken from Kittel illustrates the symmetry properties of Eqs. 21.18 and 21.19 for a simple parabolic band at $\vec{k} = 0$.

Let us now consider the consequences of these ideas from a group theoretical point of view, and enumerate Herring's rules. If $\psi(\vec{r})$ belongs to the irreducible representation D, then $\hat{T}\psi(\vec{r}) = \psi^*(r)$ will transform

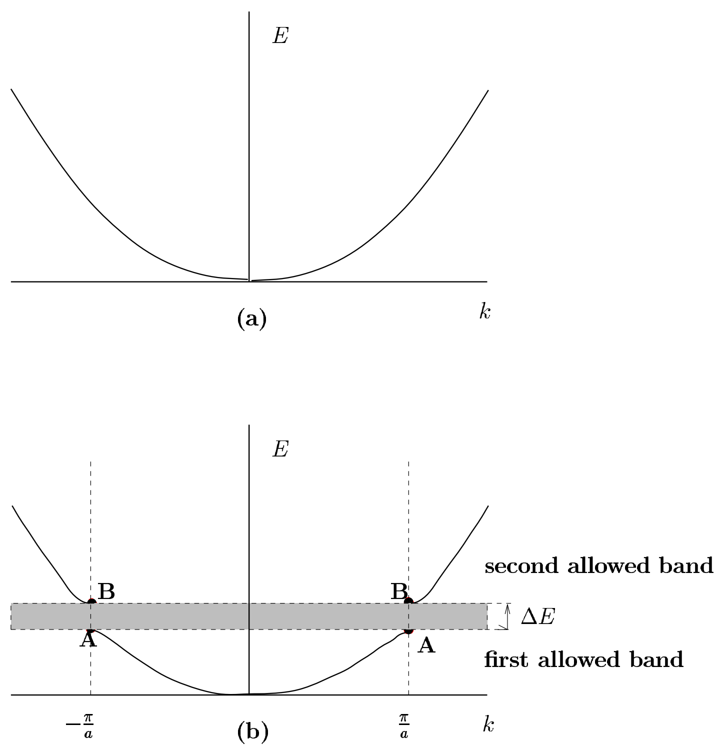


Figure 21.1: Simple $E(\vec{k})$ diagram from Kittel for a spinless electron illustrating both $E(\vec{k}) = E(-\vec{k})$ and the zero slope of $E(\vec{k})$ at the Brillouin zone boundary.

Table 21.1: Character table for point group C_4.

C_4 (4)			E	C_2	C_4	C_4^3	Time reversal
x^2+y^2, z^2	R_z, z	A	1	1	1	1	(a)
x^2-y^2, xy		B	1	1	-1	-1	(a)
(xz, yz)	(x,y)	E	1	-1	i	$-i$	(b)
	(R_x, R_y)		1	-1	$-i$	i	(b)

according to D^* which consists of the complex conjugate of all the matrices in D.

We can distinguish three different possibilities in the case of **no spin**:

(a) All of the matrices in the representation D can be written as real matrices. In this case, the time reversal operator leaves the representation D invariant and no additional degeneracies in $E(\vec{k})$ result.

(b) If the representations D and D^* cannot be brought into equivalence by a unitary transformation, there is a doubling of the degeneracy of such levels due to time reversal symmetry. Then the representations D and D^* are said to form a **time reversal symmetry pair** and these levels will stick together.

(c) If the representations D and D^* can be made equivalent under a suitable unitary transformation, but the matrices in this representation cannot be made real, then the time reversal symmetry also requires a doubling of the degeneracy of D and the bands will stick together.

To illustrate these possibilities, consider the point group C_4 (see Table 21.1). Here irreducible representations A and B are of type (a) above and each of these representations correspond to non-degenerate energy levels. However, the two representations labeled E are complex conjugates of each other and are of type (b) since there is no unitary transformation that can bring them into equivalence. Thus because of the time reversal symmetry requirement, representation E corresponds to a doubly degenerate level. This is an example where time reversal symmetry gives rise to an additional degeneracy.

The time reversal partners are treated as different representations when applying the following rules on character:

1. The number of irreducible representations is equal to the number of classes.

2. $\sum_i \ell_i^2 = h$.

Using the character table for the group of the wave vector, we can distinguish which of the 3 cases apply for a given irreducible representation using the Herring test (ref. C. Herring, Phys. Rev. 52, 361 (1937)). Let Q_0 be an element in the space group which transforms $\vec{k}$ into $-\vec{k}$. Then Q_0^2 is an element in the group of the wave vector $\vec{k}$ and all elements in the group of the wave vector are elements of Q_0^2. If the inversion operator i is contained in the group of the wave vector $\vec{k}$, then all the elements Q_0 are in the group of the wave vector $\vec{k}$. If i is not an element of the group of the wave vector $\vec{k}$, then the elements Q_0 may or may not be an element in the group of the wave vector. Let h equal the number of elements Q_0. The Herring space group test is then

$$\begin{array}{lll} \sum_{Q_0} \chi(Q_0^2) & = h & \text{case (a)} \\ & = 0 & \text{case (b)} \\ & = -h & \text{case (c)} \end{array}$$

where χ is the character for a representation of the group of the wave vector $\vec{k}$. These tests can be used to decide whether or not time reversal symmetry introduces any additional degeneracies to this representation. Information on the Herring test is contained for every one of the 32 point groups in the character tables in Koster's book.

To apply the Herring test to the point group C_4, and consider the group of the wave vector for $\vec{k} = 0$. Then all four symmetry operations take $\vec{k} \to -\vec{k}$ since $\vec{k} = 0$. Furthermore, $E^2 = E, C_2^2 = E, C_4^2 = C_2$ and $(C_4^3)^2 = C_2$ so that for representations A and B

$$\sum_{Q_0} \chi(Q_0^2) = 1 + 1 + 1 + 1 = 4 \qquad (21.20)$$

from which we conclude that A and B correspond to case (a), in agreement with Koster's tables.

On the other hand, for each representation under E,

$$\sum_{Q_0} \chi(Q_0^2) = 1 + 1 + (-1) + (-1) = 0 \tag{21.21}$$

from which we conclude that representations E correspond to case (b). Therefore the two irreducible representations under E correspond to the same energy and the corresponding $E(\vec{k})$ will stick together. The two representations under E are called **time reversal conjugate representations**.

21.4 The Effect of $\hat{T}$ on $E(\vec{k})$, Including the Spin-Orbit Interaction

When the **spin-orbit interaction is included**, then the Bloch functions transform as irreducible representations of the double group. The degeneracy of the energy levels is different from the spinless situation, and in particular every level is at least doubly degenerate.

When the spin-orbit interaction is included, $\hat{T} = \hat{K}\sigma_y$ and not only do we have $\vec{k} \to -\vec{k}$, but we also have $\vec{\sigma} \to -\vec{\sigma}$ under time reversal symmetry. This is written schematically as:

$$\hat{T}\psi_{n,k\uparrow}(\vec{r}) = \psi_{n,-k\downarrow}(\vec{r}) \tag{21.22}$$

so that the time reversal conjugate states are

$$E_{n\uparrow}(\vec{k}) = E_{n\downarrow}(-\vec{k}) \tag{21.23}$$

and

$$E_{n\downarrow}(\vec{k}) = E_{n\uparrow}(-\vec{k}). \tag{21.24}$$

If inversion symmetry exists as well,

$$E_n(\vec{k}) = E_n(-\vec{k}) \tag{21.25}$$

then

$$E_{n\uparrow}(\vec{k}) = E_{n\uparrow}(-\vec{k}) \text{ and } E_{n\downarrow}(\vec{k}) = E_{n\downarrow}(-\vec{k}) \tag{21.26}$$

making $E_{n\uparrow}(\vec{k})$ and $E_{n\downarrow}(\vec{k})$ degenerate. In more detail, since $\hat{T} = \hat{K}\sigma_y$ and since

$$\begin{aligned} \sigma_y \uparrow &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = i \begin{pmatrix} 0 \\ 1 \end{pmatrix} = i \downarrow \\ \sigma_y \downarrow &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -i \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -i \uparrow \end{aligned}$$

we obtain

$$\hat{T}\psi_{n,k\uparrow}(\vec{r}) = \hat{T} e^{i\vec{k}\cdot\vec{r}} \left[u_{n,k\uparrow} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right] = e^{-i\vec{k}\cdot\vec{r}} \left[i u^*_{n,k\uparrow} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] = e^{-i\vec{k}\cdot\vec{r}} u_{n,-k\downarrow} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{21.27}$$

which is a Bloch state for wave vector $-\vec{k}$ and spin $\downarrow$. Likewise

$$\hat{T}\psi_{n,k\downarrow}(\vec{r}) = \hat{T} e^{i\vec{k}\cdot\vec{r}} \left[u_{n,k\downarrow} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] = e^{-i\vec{k}\cdot\vec{r}} \left[-i u^*_{n,k\downarrow} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right] = e^{-i\vec{k}\cdot\vec{r}} u_{n,-k\uparrow} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{21.28}$$

which is a Bloch state for wave vector $-\vec{k}$ and spin $\uparrow$ in which we have written

$$i u^*_{n,k\uparrow} = u_{n,-k\downarrow}$$

and

$$-i u^*_{n,k\downarrow} = u_{n,-k\uparrow}.$$

For a general point in the Brillouin zone, and in the absence of spin-orbit coupling but including the spin on the electron, the energy levels have a **necessary 2-fold spin degeneracy** and also exhibit the property $E(\vec{k}) = E(-\vec{k})$, whether or not there is inversion symmetry. This is illustrated in Fig. 21.2(a). When the spin-orbit interaction is turned on and there **is** inversion symmetry then we get the situation illustrated in Fig. 21.2(b) where the 2-fold degeneracy remains. However, if there is no inversion symmetry, then the only relationships that remain are those of Eqs. 21.23 and 21.24 shown in Fig. 21.2(c), and the Kramers degeneracy results in $E_\uparrow(\vec{k}) = E_\downarrow(-\vec{k})$ and $E_\downarrow(\vec{k}) = E_\uparrow(-\vec{k})$.

The role of inversion symmetry is also important for the $E(\vec{k})$ relations for degenerate bands. This is illustrated in Fig. 21.3 for degenerate bands near $\vec{k} = 0$. We take as examples: (a) diamond for which the

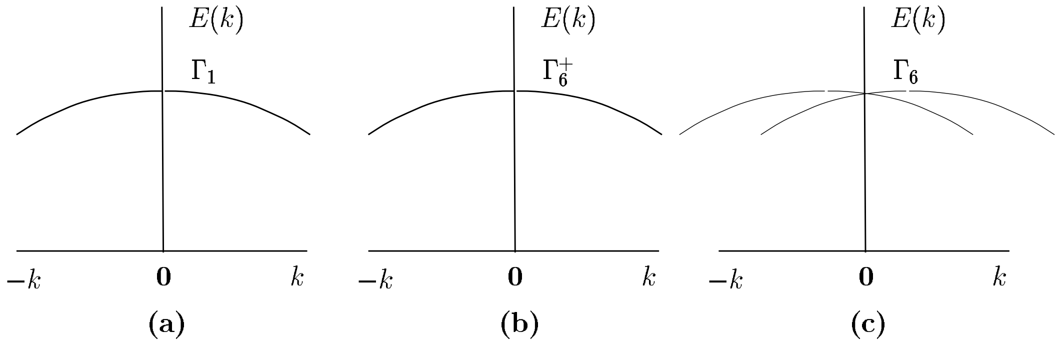


Figure 21.2: Schematic example of Kramers degeneracy in a crystal in the case of: (a) no spin-orbit interaction where each level is doubly degenerate $(\uparrow, \downarrow)$, (b) both spin-orbit interaction and inversion symmetry are present and the levels are doubly degenerate, (c) spin-orbit interaction and no spatial inversion symmetry where the relations 21.23 and 21.24 apply.

spin-orbit interaction can be neglected and all levels are doubly degenerate at a general point in the Brillouin zone, (c) InSb or GaAs which have T_d symmetry (lacking inversion) so that relations 21.23 and 21.24 apply and the two-fold Kramers degeneracy is lifted, (b) Ge or Si which have O_h symmetry (including inversion) and the two-fold Kramers degeneracy is retained at a general point in the Brillouin zone.

We give in Table 21.2 the Herring rules (see §21.3) whether or not the spin-orbit interaction is included. When the spin-orbit interaction

Table 21.2: Summary of rules regarding degeneracies and time reversal.

Case	**Relation between D and D^***	**Frobenius-Schur test**	**Spinless electron**	**Half-integral spin electron**
Case (a)	D and D^* are equivalent to the same real irreducible representation	$\sum_R \chi(Q_0^2) = h$	No extra degeneracy	Doubled degeneracy
Case (b)	D and D^* are inequivalent	$\sum_R \chi(Q_0^2) = 0$	Doubled degeneracy	Doubled degeneracy
Case (c)	D and D^* are equivalent to each other but not to a real representation	$\sum \chi(Q_0^2) = -h$	Double degeneracy	No extra degeneracy

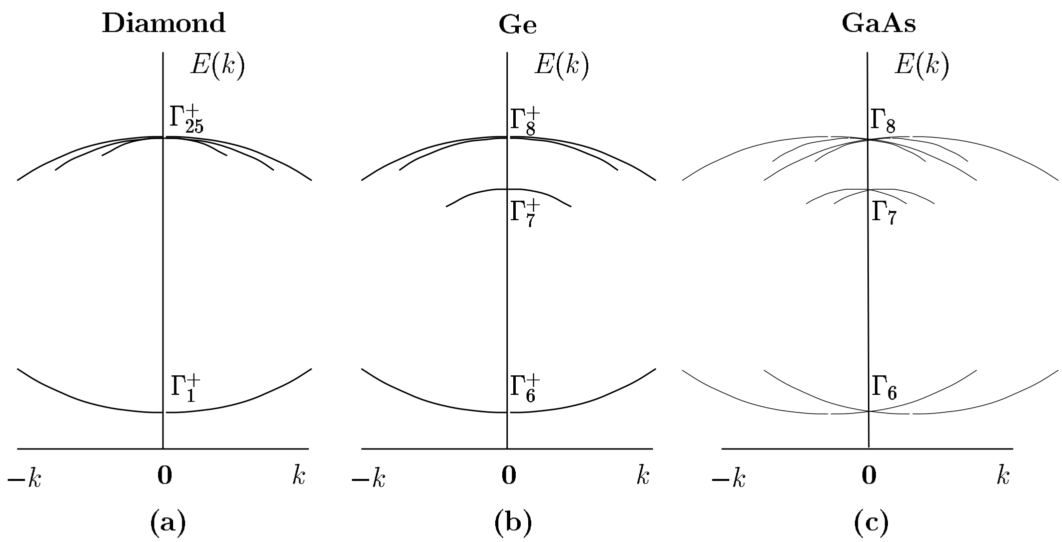


Figure 21.3: Schematic examples of energy bands $E(\vec{k})$ in diamond, Ge and GaAs near $\vec{k} = 0$. (a) Without spin-orbit coupling, each band in diamond has a two-fold spin degeneracy. (b) Splitting by spin-orbit coupling in Ge, with each band remaining doubly degenerate. (c) Splitting of the valence bands by the spin-orbit coupling in GaAs. The magnitudes of the splittings are not to scale.

is included, there are also three cases which can be distinguished. When the time reversal operator $\hat{T}$ acts on a spin dependent wavefunction ψ which transforms according to an irreducible representation D, then we have three possibilities:

(a) If the representation D is real, or can be transformed by a unitary transformation into a set of real matrices, then the action of $\hat{T}$ on these matrices will yield the same set of matrices. To achieve the required additional degeneracy, we must have D occur twice.

(b) If representations D and D^* cannot be brought into equivalence by a unitary transformation, then the corresponding levels must stick together in pairs to satisfy the time reversal degeneracy requirement.

(c) If representations D and D^* can be brought into equivalence but neither can be made all real, then no additional degeneracy need be introduced and both make up the time reversal degenerate pair.

These results are summarized in Table 21.2 for both the case of no spin and when spin-orbit interaction is included. We now illustrate these rules with two cases:

1. the double group representations of the point group C_4 (symmorphic)

2. the double group representation at the L point in Ge (or Si) where the levels are degenerate by time reversal symmetry (nonsymmorphic)

For the first illustration, we give the character table for the double group C_4 taken from Koster et al. in Table 21.3. We note that the Koster table contains an entry for time inversion, which summarizes the results discussed in §21.1 for the spinless bands. Inspection of this character table shows that the double group representations involve the 4^{th} roots of unity (as shown below) and obey the relation $\chi(A_i) = -\chi(\bar{A}_i)$ for each of the pairs of symmetry operations A_i and $\bar{A}_i$. Note that the character table originally given in Koster has some misprints with

Table 21.3: Character table for C_4

C_4	E	$\bar{E}$	C_4	$\bar{C}_4$	C_2	$\bar{C}_2$	C_4^{-1}	$\bar{C}_4^{-1}$	Time Inv.	Bases for C_4
Γ_1	1	1	1	1	1	1	1	1	a	z or S_z
Γ_2	1	1	-1	-1	1	1	-1	-1	a	xy
Γ_3	1	1	i	i	-1	-1	$-i$	$-i$	b	$-i(x+iy)$ or $-(S_x+iS_y)$
Γ_4	1	1	$-i$	$-i$	-1	-1	i	i	b	$i(x-iy)$ or (S_x-iS_y)
Γ_5	1	-1	ω	$-\omega$	i	$-i$	$-\omega^3$	ω^3	b	$\phi(1/2,1/2)$
Γ_6	1	-1	$-\omega^3$	ω^3	$-i$	i	ω	$-\omega$	b	$\phi(1/2,-1/2)$
Γ_7	1	-1	$-\omega$	ω	i	$-i$	ω^3	$-\omega^3$	b	$\phi(3/2,-3/2)$
Γ_8	1	-1	ω^3	$-\omega^3$	$-i$	i	$-\omega$	ω	b	$\phi(3/2,3/2)$

regard to $\chi(C_4^{-1}) = -\chi(\bar{C}_4^{-1})$, which are corrected in Table 21.3. This character table shows that the characters for the Γ_5 and Γ_6 irreducible representations are time reversal degenerate pairs, and likewise for the Γ_7 and Γ_8 irreducible representations:

	E	$\bar{E}$	C_4	$\bar{C}_4$	C_2	$\bar{C}_2$	C_4^{-1}	$\bar{C}_4^{-1}$
Γ_5:	ω^0	ω^4	ω	ω^5	ω^2	ω^6	ω^7	ω^3
Γ_6:	ω^0	ω^4	ω^7	ω^3	ω^6	ω^2	ω	ω^5
Γ_7	ω^0	ω^4	ω^5	ω	ω^2	ω^6	ω^3	ω^7
Γ_8:	ω^0	ω^4	ω^3	ω^7	ω^6	ω^2	ω^5	ω

Application of the Frobenius–Schur test for Γ_5 yields:

$$\begin{aligned}\sum \chi(Q_0^2) &= (1)(-1) + (1)(-1) - \omega^2 - \omega^2 + 1 + 1 - \omega^6 - \omega^6 \\ &= -1 - 1 - i - i + 1 + 1 + i + i = 0\end{aligned} \tag{21.29}$$

where we note that for the double group representations we consider the character $\chi(Q_0\bar{Q}_0)$ in the Frobenius–Schur test. We thus find that the representations Γ_6, Γ_7 and Γ_8 are also of the b type with respect to time reversal symmetry and this information is also given in Table 21.3.

Table 21.4: Character Table and Basis Functions for the Group D_{3d}

	D_{3d}	E	$\bar{E}$	$2C_3$	$2\bar{C}_2$	$3C_2'$	$3\bar{C}_2'$	I	$\bar{I}$	$2S_6$	$2\bar{S}_6$	$3\sigma_d$	$3\bar{\sigma}_d$	Time Inv.	Bases
L_1^+	Γ_1^+	1	1	1	1	1	1	1	1	1	1	1	1	a	R
L_2^+	Γ_2^+	1	1	1	1	−1	−1	1	1	1	1	−1	−1	a	S_x
Ł$_3^+$	Γ_3^+	2	2	−1	−1	0	0	2	2	−1	−1	0	0	a	$(S_x - iS_y)$, $-(S_x + iS_y)$
L_1^-	Γ_1^-	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	a	zS_z
L_2^-	Γ_2^-	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	a	z
L_3^-	Γ_3^-	2	2	−1	−1	0	0	−2	−2	1	1	0	0	a	$(x - iy)$, $-(x + iy)$
L_6^+	Γ_4^+	2	−2	1	−1	0	0	2	−2	1	−1	0	0	c	$\phi(1/2, -1/2)$
L_4^+	Γ_5^+	1	−1	−1	1	i	$-i$	1	−1	−1	1	i	$-i$	b	$\phi(3/2, -3/2)$ $-i\phi(3/2, 3/2)$
L_5^+	Γ_6^+	1	−1	−1	1	$-i$	i	1	−1	−1	1	$-i$	i	b	$-(\phi(3/2, 3/2)$ $-i\phi(3/2, -3/2))$
L_6^-	Γ_4^-	2	−2	1	−1	0	0	−2	2	−1	1	0	0	c	$\Gamma_4^+ \times \Gamma_1^-$
L_4^-	Γ_5^-	1	−1	−1	1	i	$-i$	−1	1	1	−1	$-i$	i	b	$\Gamma_5^+ \times \Gamma_1^-$
L_5^-	Γ_6^-	1	−1	−1	1	$-i$	i	−1	1	1	−1	i	$-i$	b	$\Gamma_6^+ \times \Gamma_1^-$

For the L-point levels in Ge, see the $E(\vec{k})$ diagram in Fig. 19.2b for the case where the spin-orbit interaction is included. The character table appropriate to the L-point is given in Table 21.4. The designation for the L-point representations have been added on the left column of Koster's table.

For a Λ point, the operations $E, 2C_3$ and $3C_2$ take $\vec{k} \to -\vec{k}$. For the L-point, all operations are of the Q_0 type, so that for the representations L_1, L_2 and L_3, we have $\Sigma\chi(Q_0^2) = 12$, yielding representations of type a, in agreement with the character table for D_{3d} (Table 21.4).

For the double group representation L_6^+ we obtain

$$L_6^+ = \Sigma\chi(Q_0^2) = -4 - 2 + 0 - 4 - 2 + 0 = -12 \quad \text{type (c)} \qquad (21.30)$$

where again we write $Q_0\bar{Q}_0$ for Q_0^2. For the double group representation L_4^+ the Frobenius–Schur test yields:

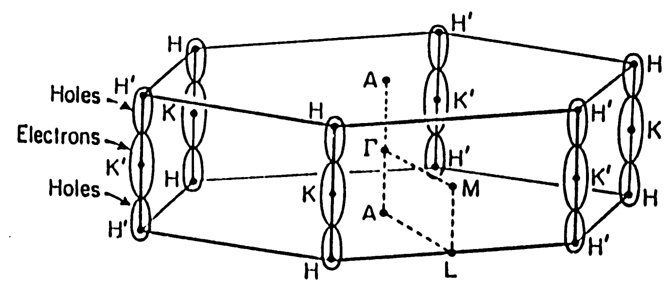
$$L_4^+ : \Sigma\chi(Q_0^2) = -1 - 2 + 3 - 1 - 2 + 3 = 0 \quad \text{type (b)} \qquad (21.31)$$

Likewise L_5^+ is of type b. Since L_4^+ and L_5^+ are complex conjugate representations, L_4^+ and L_5^+ form time reversal degenerate pairs. Similarly, L_4^- and L_5^- are type b representations and form time reversal degenerate pairs (see Fig. 19.2b).

With this discussion of time reversal symmetry, we have explained all the entries to the character tables, and have explained why because of time reversal symmetry certain bands stick together on the $E(\vec{k})$ diagrams. In the following Chapter we see how the time reversal operator becomes a symmetry element in magnetic point groups.

21.5 Selected Problems

1. Consider the space group D_{6h}^4 (#194) which we discussed in connection with the lattice modes for graphite. We will now concern ourselves with the electronic structure. Since the Fermi surfaces are located close to the HK axes in the Brillouin Zone it is important to work with the group of the wave vector at points H, K and P (see diagram).



   (a) Using Miller and Love, and Koster et al., give the character table including double groups for the group of the wave vector at point K. Classify each of the irreducible representations according to whether they behave as a, b or c under time reversal symmetry.

   (b) Find the compatibility relations as we move away from K toward H.