15

Application of Double Groups to Energy Bands with Spin

In this chapter we apply the group theoretical background for the electron spin and the *spin–orbit* interaction (which is discussed in Chap. 14) to the treatment of electronic energy band models for solids (which is discussed in Chaps. 12 and 13 for the case when the electron spin is neglected). By including the spin–orbit interaction we can also discuss the effective g-factor, which together with the effective mass tensor, characterize the properties of a *semiconductor* in a magnetic field. We also review the *Slater–Koster* method for determination of the electronic energy band structure of crystalline solids by interpolation and extrapolation of energy eigenvalues and eigenfunctions that are accurately known at a few high symmetry points in the Brillouin zone either from *ab initio* calculations or from experiments.

15.1 Introduction

The one-electron Hamiltonian including spin–orbit interaction is written as

$$\mathcal{H} = \frac{p^2}{2m} + V(\boldsymbol{r}) + \frac{\hbar}{4m^2c^2}(\boldsymbol{\nabla}V \times \boldsymbol{p}) \cdot \boldsymbol{\sigma}\,, \tag{15.1}$$

where $\boldsymbol{\sigma}$ is the dimensionless spin operator $[\boldsymbol{S} = (\hbar/2)\boldsymbol{\sigma}]$. The first two terms of (15.1) denote the kinetic energy and periodic potential of the one-electron Hamiltonian in a simple periodic potential $V(\boldsymbol{r})$ that reflects the crystal symmetry, and the third term denotes the spin–orbit interaction $\mathcal{H}'_{\mathrm{SO}}$

$$\mathcal{H}'_{\mathrm{SO}} = \frac{\hbar}{4m^2c^2}(\boldsymbol{\nabla}V \times \boldsymbol{p}) \cdot \boldsymbol{\sigma}\,, \tag{15.2}$$

where $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'_{\mathrm{SO}}$. The Hamiltonian (15.1) is appropriate when the spin–orbit splittings are significant compared with typical energy gaps. The presence of the spin operator $\boldsymbol{\sigma}$ in the spin–orbit term $\mathcal{H}'_{\mathrm{SO}}$ requires the use of *spin-dependent* wave functions with double group symmetry designations

for the energy bands. Since the magnitude of the spin–orbit interaction is comparable to energy band gaps for many important electronic materials, it is important in these cases to consider the spin–orbit interaction explicitly when carrying out energy band calculations.

Thus explicit band calculations of $E(\boldsymbol{k})$ with spin–orbit interaction have been carried out using all the standard techniques for energy band calculations. Quite independent of the particular calculational technique that is used, group theoretical techniques are introduced to classify the states and to bring the secular equation into block diagonal form. To illustrate these points we consider explicitly the use of group theory (i.e., double groups as discussed in Chap. 14) to treat the electronic energy bands for several situations, including the empty lattice, the nearly free electron approximation, for $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory and the Slater–Koster method. These examples are also designed to provide some experience with the handling of double groups.

15.2 $E(\boldsymbol{k})$ for the Empty Lattice Including Spin–Orbit Interaction

In this section the calculation of the empty lattice electronic energy dispersion relations is considered in the presence of spin–orbit interaction following the discussion in Chap. 12 for the case where the electron spin is neglected.

Referring to (15.2) we see that both $V(\boldsymbol{r})$ and $\boldsymbol{\nabla} V(\boldsymbol{r})$ vanish for the empty lattice, and therefore it is only the change in irreducible representations from single group to double group representations that needs to be considered. Thus when considering the plane waves *labeled* by the reciprocal lattice vectors $\{\boldsymbol{K}_{n_i}\}$ in Table 12.2, we should now use double group irreducible representations, which are found by taking the direct product of each single group irreducible representation Γ_i with the spinor $D_{1/2}$. Here the spinor is demonstrated for the cubic O group where $D_{1/2}$ transforms as Γ_6 and the pertinent direct products are easily obtained from Table 14.7. As an example of the effect of spin on the empty lattice, consider the $E(\boldsymbol{k})$ diagram in Fig. 12.1 for the FCC empty lattice. The ground state label would now become Γ_6, and for the next excited state we would have

$$\Gamma_6 \otimes \Gamma_1 + \Gamma_6 \otimes \Gamma_{2'} + \Gamma_6 \otimes \Gamma_{15} + \Gamma_6 \otimes \Gamma_{25'} = 2(\Gamma_6 + \Gamma_7 + \Gamma_8),$$

but the eigenstates now could be also labeled more completely by using also the single group irreducible representations to which they relate:

$$[\Gamma_6(\Gamma_1) + \Gamma_6(\Gamma_{15})] + [\Gamma_7(\Gamma_{2'}) + \Gamma_7(\Gamma_{25'})] + [\Gamma_8(\Gamma_{15}) + \Gamma_8(\Gamma_{25'})] \,.$$

A similar procedure could then be applied to all the labels in Fig. 12.1 using the appropriate character tables for the various symmetry points in the Brillouin zone. The curves in Fig. 12.1 would not change because both $V(\boldsymbol{r}) = 0$ and

$\boldsymbol{\nabla}V(\boldsymbol{r}) = 0$, and because the Kramers degeneracy applies. Introduction of spin into the nearly free electron approximation requires the use of double groups.

15.3 The $\boldsymbol{k} \cdot \boldsymbol{p}$ Perturbation with Spin–Orbit Interaction

Schrödinger's equation including the spin–orbit interaction can be written as

$$\left[\frac{p^2}{2m} + V(\boldsymbol{r}) + \frac{\hbar}{4m^2c^2}(\boldsymbol{\nabla}V \times \boldsymbol{p}) \cdot \boldsymbol{\sigma} \right] \psi_{n\boldsymbol{k}}(\boldsymbol{r}) = E_n(\boldsymbol{k})\psi_{n\boldsymbol{k}}(\boldsymbol{r}) , \qquad (15.3)$$

in which the Bloch functions $\psi_{n\boldsymbol{k}}(\boldsymbol{r})$ for $\mathcal{H}'_{\mathrm{SO}}$ include spinors $\psi_{n\boldsymbol{k}\uparrow}(\boldsymbol{r})$ and $\psi_{n\boldsymbol{k}\downarrow}(\boldsymbol{r})$ rather than the simple wave functions considered in Chap. 13. These spinor basis functions can be written in more expanded notation as

$$\psi_{n\boldsymbol{k}\uparrow}(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}\uparrow}(\boldsymbol{r})$$
$$\psi_{n\boldsymbol{k}\downarrow}(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}\downarrow}(\boldsymbol{r}) , \qquad (15.4)$$

where the arrow in the subscript of $\psi_{n\boldsymbol{k}\uparrow}(\boldsymbol{r})$ means that the state is generally spin up or the expectation value of σ_z in this state is positive, and the down arrow gives a negative expectation value for σ_z so that

$$\langle \psi_{n\boldsymbol{k}\uparrow} | \sigma_z | \psi_{n\boldsymbol{k}\uparrow} \rangle > 0$$
$$\langle \psi_{n\boldsymbol{k}\downarrow} | \sigma_z | \psi_{n\boldsymbol{k}\downarrow} \rangle < 0 . \qquad (15.5)$$

The Bloch states are only pure spin up or spin down states when the spin–orbit interaction is neglected ($\mathcal{H}'_{\mathrm{SO}} \equiv 0$). The spin–orbit interaction mixes the spin-up and spin-down partners, and, as was discussed in Chap. 14 for the atomic case, the $|j, \ell, s, m_j\rangle$ representation becomes the appropriate irreducible representation for the spin–orbit coupled system rather than the $|\ell, s, m_\ell, m_s\rangle$ representation.

Let us focus our attention on one of the periodic spinor $u_{n\boldsymbol{k}}(\boldsymbol{r})$ functions (either of the components $\uparrow$ or $\downarrow$ in (15.4) which diagonalize the Schrödinger equation (15.3)). Using $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory, the corresponding differential equation for $u_{n\boldsymbol{k}}(\boldsymbol{r})$ is

$$\left[\frac{p^2}{2m} + V(\boldsymbol{r}) + \frac{\hbar}{4m^2c^2}(\boldsymbol{\nabla}V \times \boldsymbol{p}) \cdot \boldsymbol{\sigma} \right] u_{n\boldsymbol{k}}(\boldsymbol{r})$$

$$+ \frac{\hbar\boldsymbol{k}}{m} \cdot \left(\boldsymbol{p} + \frac{\hbar}{4mc^2}\boldsymbol{\sigma} \times \boldsymbol{\nabla}V \right) u_{n\boldsymbol{k}}(\boldsymbol{r}) \qquad (15.6)$$

$$= \left[E_n(\boldsymbol{k}) - \frac{\hbar^2 k^2}{2m} \right] u_{n\boldsymbol{k}}(\boldsymbol{r})$$

in which we have made use of the vector identities:

$$(\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C} = (\mathbf{B} \times \mathbf{C}) \cdot \mathbf{A} = (\mathbf{C} \times \mathbf{A}) \cdot \mathbf{B}, \qquad (15.7)$$

or more explicitly

$$(\mathbf{\nabla} V \times \mathbf{p}) \cdot \boldsymbol{\sigma} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = (\boldsymbol{\sigma} \times \mathbf{\nabla} V) \cdot \mathbf{p} \, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \qquad (15.8)$$

and

$$\mathbf{p} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \left[\hbar \mathbf{k} u_{n\mathbf{k}}(\mathbf{r}) + \mathbf{p} u_{n\mathbf{k}}(\mathbf{r}) \right]. \qquad (15.9)$$

If we identify terms in (15.6) with an unperturbed Hamiltonian $\mathcal{H}_0$ and a perturbation Hamiltonian $\mathcal{H}'_{\mathbf{k}\cdot\mathbf{p}}$ we obtain

$$\mathcal{H}_0 = \frac{p^2}{2m} + V(r) + \frac{\hbar}{4m^2c^2}(\mathbf{\nabla} V \times \mathbf{p}) \cdot \boldsymbol{\sigma}, \qquad (15.10)$$

and

$$\mathcal{H}'_{\mathbf{k}\cdot\mathbf{p}} = \frac{\hbar \mathbf{k}}{m} \cdot \left(\mathbf{p} + \frac{\hbar}{4mc^2} \boldsymbol{\sigma} \times \mathbf{\nabla} V \right), \qquad (15.11)$$

so that Rayleigh–Schrödinger perturbation theory for energy bands near $k = 0$ yields the following expression for the nondegenerate state Γ_i [see (13.4) and (13.9)]

$$E_n^{\Gamma_i}(\mathbf{k}) = E_n^{\Gamma_i}(0) + (u_{n,0}^{\Gamma_i}|\mathcal{H}'|u_{n,0}^{\Gamma_i}) + \sum_{n' \neq n} \frac{(u_{n,0}^{\Gamma_i}|\mathcal{H}'|u_{n',0}^{\Gamma_j})(u_{n',0}^{\Gamma_j}|\mathcal{H}'|u_{n,0}^{\Gamma_i})}{E_n^{\Gamma_i}(0) - E_{n'}^{\Gamma_j}(0)},$$

$$(15.12)$$

in which the unperturbed functions $u_{n,0}^{\Gamma_i}$ are evaluated at $\mathbf{k} = 0$ (the expansion point for the $\mathbf{k} \cdot \mathbf{p}$ perturbation) and Γ_j labels the irreducible representations for bands n'. The sum in (15.12) is over states Γ_j that couple to state Γ_i through the $\mathbf{k} \cdot \mathbf{p}$ perturbation Hamiltonian given by (15.11). We note that (15.12) has the same form as the corresponding expression without spin–orbit interaction (13.9) *except* that in (15.12):

(a) The unperturbed Hamiltonian yielding the energy eigenvalues at $\mathbf{k} = 0$ explicitly contains a spin–orbit term.
(b) The $\mathbf{k} \cdot \mathbf{p}$ perturbation Hamiltonian explicitly contains the spin operator and a spin–orbit term.
(c) The irreducible representations Γ_i and Γ_j are both double group representations.

In treating $\mathbf{k}{\cdot}\mathbf{p}$ perturbation theory without explicitly considering the electron spin (see Chap. 13), we have three possibilities: nondegenerate levels, degenerate (or nearly degenerate) levels that are treated in first-order degenerate perturbation theory, and degenerate levels that are treated in second-order degenerate perturbation theory. In all three of these cases, we use group theory

to determine which are the nonvanishing matrix elements of a vector operator taken between double group states, and which of the nonvanishing matrix elements are equal to each other. More explicitly, for the case of a crystal with O_h symmetry, all the Γ_i and Γ_j representations have either $\Gamma_6^{\pm}, \Gamma_7^{\pm}$ and $\Gamma_8^{\pm}$ symmetry at $k = 0$ since the spatial part of the wavefunctions transform according to one of the five ordinary irreducible representations and the direct product of an ordinary irreducible representation with the spinor D_6^+ yields one of the double group representations. By inspection, we find that for the O_h group all the irreducible representations Γ_i are at least twofold degenerate. But this degeneracy is maintained for all $\boldsymbol{k}$ values and is lifted only by the application of an external (or internal) magnetic field. This twofold degeneracy, know as the *Kramers degeneracy* is generally found in the absence of a magnetic field. We therefore look for this degeneracy when working practical problems, because it greatly reduces the *labor* in dealing with problems involving spin. Because of this Kramers degeneracy, we can effectively use *nondegenerate perturbation theory* to deal with twofold levels such as the $\Gamma_6^{\pm}$ and $\Gamma_7^{\pm}$ levels occurring in many applications.

Group theory can be used to greatly simplify the $\boldsymbol{k} \cdot \boldsymbol{p}$ expansion for one of the $\Gamma_6^{\pm}$ or $\Gamma_7^{\pm}$ levels. For example, take $\Gamma_i = \Gamma_6^+$ and note that the generalized momentum operator $\boldsymbol{P}$ including the spin–orbit interaction explicitly

$$\boldsymbol{P} = \boldsymbol{p} + \frac{\hbar}{4mc^2} \boldsymbol{\sigma} \times \boldsymbol{\nabla} V \tag{15.13}$$

transforms like the Γ_{15}^- irreducible representation. The *generalized* momentum operator $\boldsymbol{P}$ transforms as Γ_{15}^- whether or not the spin–orbit interaction is included, since $\boldsymbol{p}$ is a vector and so is $(\boldsymbol{\sigma} \times \boldsymbol{\nabla} V)$, both being radial vectors. Since $\Gamma_6^+ \otimes \Gamma_{15}^- = \Gamma_6^- + \Gamma_8^-$ and since Γ_6^+ is orthogonal to Γ_6^- and Γ_8^-, we have no linear $\boldsymbol{k}$ term in the $\boldsymbol{k} \cdot \boldsymbol{p}$ expansion of (15.12). In the quadratic term we can only have intermediate states with Γ_6^- and Γ_8^- symmetry. For example, if the spin–orbit interaction is neglected for a crystal with O_h symmetry, then a nondegenerate Γ_1^+ state is coupled by the $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation Hamiltonian only to a Γ_{15}^- intermediate state (see Sect. 13.3). When the spin–orbit interaction is included, the Γ_1^+ and Γ_{15}^- states become the following double group states (see Table 14.7):

$$\Gamma_1^+ \rightarrow \Gamma_6^+$$
$$\Gamma_{15}^- \rightarrow \Gamma_6^- + \Gamma_8^- \, , \tag{15.14}$$

so that, with the spin–orbit interaction, a Γ_6^+ band will couple to bands with Γ_6^- and Γ_8^- symmetries. We note that bands with Γ_8^- symmetry can arise from single-group bands with $\Gamma_{12}^-, \Gamma_{15}^-$ and Γ_{25}^- symmetries. In this sense the spin–orbit interaction gives more possibilities for immediate states.

Again we can use group theory to show relations between the various nonvanishing matrix elements of $\boldsymbol{P}$, and as before, only a very small number

of matrix elements are independent. To study these matrix elements we use the basis functions for the double group irreducible representations discussed in Sects. 14.5–14.7.

15.4 $E(k)$ for a Nondegenerate Band Including Spin–Orbit Interaction

In this section we discuss the form of $E(\boldsymbol{k})$ for a nondegenerate band including spin–orbit interaction while in Sect. 15.5 the corresponding discussion is given for degenerate energy bands, which is followed by a discussion of the effective g-factor in Sect. 15.6, which is a topic that arises because of the presence of spin.

The form of $E(\boldsymbol{k})$ for a nondegenerate band is developed in Sect. 15.3 through nondegenerate $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory see (15.12) by considering the form of the $\boldsymbol{k} \cdot \boldsymbol{p}$ matrix elements implied by group theory. Since $\boldsymbol{p}$ and $\boldsymbol{P}$ both transform as Γ_{15}^-, the group theory is not changed and it is only in the numerical evaluation of the specific terms that we need distinguish between $\boldsymbol{p}$ and $\boldsymbol{P}$. In this section, we illustrate the theory by an example, the nondegenerate Γ_6^+ band for a cubic crystal with O_h symmetry for the group of the wave vector at $k = 0$. From Sect. 14.5, we take as basis functions for the Γ_6^+ state:

$$\Gamma_6^+ : \quad \begin{cases} 1 \uparrow \\ 1 \downarrow \, . \end{cases} \tag{15.15}$$

Within the framework of $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory, the Γ_6^+ state couples only to Γ_6^- and Γ_8^- since $\Gamma_6^+ \otimes \Gamma_{15}^- = \Gamma_6^- + \Gamma_8^-$. For the Γ_6^- and Γ_8^- states, we use the basis functions derived from (14.41) and (14.46), together with the extension $L_x, L_y, L_z \to x, y, z$ discussed in Sect. 14.7 so that for $\Gamma_6^- (\Gamma_{15}^-)$ we write

$|j, m_j\rangle$ State	Basis Function	
$\left\lvert \frac{1}{2}, \frac{1}{2} \right\rangle$	$\left(\frac{1}{\sqrt{3}}\right) [(x + iy) \downarrow -z \uparrow]$	(15.16)
$\left\lvert \frac{1}{2}, -\frac{1}{2} \right\rangle$	$\left(\frac{1}{\sqrt{3}}\right) [-(x - iy) \uparrow +z \downarrow]$,	

and for $\Gamma_8^- (\Gamma_{15}^-)$ we write

$|j, m_j\rangle$ State	Basis Function	
$\left\lvert \frac{3}{2}, \frac{3}{2} \right\rangle$	$\left(\frac{1}{\sqrt{2}}\right) (x + iy) \uparrow$	
$\left\lvert \frac{3}{2}, \frac{1}{2} \right\rangle$	$\left(\frac{1}{\sqrt{6}}\right) [(x + iy) \downarrow +2z \uparrow]$	(15.17)
$\left\lvert \frac{3}{2}, -\frac{1}{2} \right\rangle$	$\left(\frac{1}{\sqrt{6}}\right) [(x - iy) \uparrow +2z \downarrow]$	
$\left\lvert \frac{3}{2}, -\frac{3}{2} \right\rangle$	$\left(\frac{1}{\sqrt{2}}\right) (x - iy) \downarrow \, .$	

We can read off the basis functions relating the $|j, m_j\rangle$ representation and the $|\ell s m_\ell m_s\rangle$ representation for the Γ_6^- $(j = 1/2)$ and Γ_8^- $(j = 3/2)$ states that are derived from the Γ_{15}^- level directly from (15.16) and (15.17). The x, y and z in (15.16) and (15.17) refer to the three partners of the Γ_{15}^- state. For this case there are no nonvanishing matrix elements in (15.12) in first-order perturbation theory. In second-order, the nonvanishing terms are

$$\left(1\uparrow |P_x| \left(\frac{1}{\sqrt{2}}\right)(x + iy)\uparrow\right) = \left(\frac{1}{\sqrt{2}}\right)(1|P_x|x)$$

$$\left(1\uparrow |P_y| \left(\frac{1}{\sqrt{2}}\right)(x + iy)\uparrow\right) = \left(\frac{i}{\sqrt{2}}\right)(1|P_y|y)$$

$$\left(1\uparrow |P_z| \left(\frac{1}{\sqrt{6}}\right)\{(x + iy)\downarrow +2z\uparrow\}\right) = \left(\frac{2}{\sqrt{6}}\right)(1|P_z|z)$$

$$\left(1\uparrow |P_x| \left(\frac{1}{\sqrt{6}}\right)\{(x - iy)\uparrow +2z\downarrow\}\right) = \left(\frac{1}{\sqrt{6}}\right)(1|P_x|x)$$

$$\left(1\uparrow |P_y| \left(\frac{1}{\sqrt{6}}\right)\{(x - iy)\uparrow +2z\downarrow\}\right) = -\left(\frac{i}{\sqrt{6}}\right)(1|P_y|y)$$

$$\left(1\uparrow |P_z| \left(\frac{1}{\sqrt{3}}\right)\{(x + iy)\downarrow -z\uparrow\}\right) = -\left(\frac{1}{\sqrt{3}}\right)(1|P_z|z)$$

$$\left(1\uparrow |P_x| \left(\frac{1}{\sqrt{3}}\right)\{(-x + iy)\uparrow +z\downarrow\}\right) = -\left(\frac{1}{\sqrt{3}}\right)(1|P_x|x)$$

$$\left(1\uparrow |P_y| \left(\frac{1}{\sqrt{3}}\right)\{(-x + iy)\uparrow +z\downarrow\}\right) = \left(\frac{i}{\sqrt{3}}\right)(1|P_y|y). \qquad (15.18)$$

Summing up the second-order terms and *utilizing* the equality

$$(1|P_x|x) = (1|P_y|y) = (1|P_z|z), \qquad (15.19)$$

we obtain

$$E^{\Gamma_6^+}(\boldsymbol{k}) = E^{\Gamma_6^+}(0) + \frac{\hbar^2 |(1|P_x|x)|^2}{m^2 E_g}\left\{\frac{1}{3}k_x^2 + \frac{1}{3}k_y^2 + \frac{1}{3}k_z^2\right\}$$

$$+ \frac{\hbar^2 |(1|P_x|x)|^2}{m^2(E_g + \Delta)}\left\{\frac{1}{2}k_x^2 + \frac{1}{2}k_y^2 + \frac{2}{3}k_z^2 + \frac{1}{6}k_x^2 + \frac{1}{6}k_y^2\right\}$$

$$= E^{\Gamma_6^+}(0) + \frac{\hbar^2 k^2}{m^2}|(1|P_x|x)|^2\left\{\frac{1}{3E_g} + \frac{2}{3(E_g + \Delta)}\right\}, \qquad (15.20)$$

where E_g and $E_g + \Delta$ are defined in Fig. 15.1. One can note that the energy bands in (15.12) have subscripts n and n' to denote their band index identification. The $E^{\Gamma_6^+}(\boldsymbol{k})$ in (15.20) denotes the s-band lying low in the
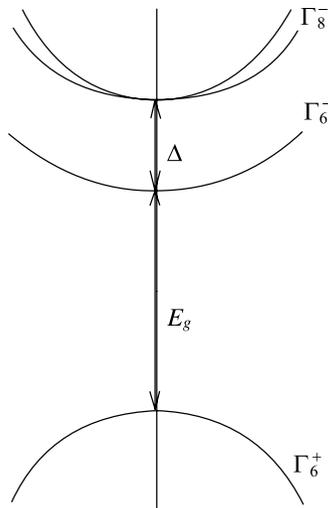
Fig. 15.1. Energy *versus* k at the Γ point showing the effect of the spin–orbit interaction in splitting the p-level. The relevant bands are labeled by the double group representations for a cubic group near $k = 0$ with O_h symmetry

valence band which through $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory is shown to couple to the conduction band levels with Γ_6^- and Γ_8^- symmetries arising from the conduction p bands (see Fig. 15.1).

15.5 $E(k)$ for Degenerate Bands Including Spin–Orbit Interaction

In dealing with $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory for degenerate states we again use basis functions such as are given by (14.41) and (14.46) to classify the degenerate states. For example, instead of the (3×3) secular equation for p-bands (Γ_{15}^- symmetry) without spin–orbit coupling that was discussed in Sect. 13.5, inclusion of the spin–orbit interaction leads to solution of a (6×6) secular equation. This (6×6) equation assumes block diagonal form containing a (4×4) block with Γ_8^- symmetry and a (2×2) block with Γ_6^- symmetry, because the spin functions transform as $D_{1/2}$ or Γ_6^+ and because

$$\Gamma_6^+ \otimes \Gamma_{15}^- = \Gamma_6^- + \Gamma_8^- , \qquad (15.21)$$

where Γ_6^- corresponds to a $j = 1/2$ state and Γ_8^- to a $j = 3/2$ state (see Fig. 15.1). Thus the Γ_{15}^- conduction band for the case of no spin becomes Γ_6^- and Γ_8^- when spin–orbit interaction is included (see Fig. 15.1).

An important application of degenerate $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory including the effects of spin–orbit interaction is to the valence band of the group IV

and III–V compound semiconductors. A description of $E(\boldsymbol{k})$ for the valence band is needed to construct the constant energy surfaces for holes in these semiconductors. The $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory method is useful for analysis of cyclotron resonance measurements on holes in group IV and III–V semiconductors, which were studied in the 1950s and 1960s for 3D crystals and 40–50 years later these measurements are being used to study low-dimensional nanostructured systems.

One way to solve for the energy levels of the valence band of a group IV semiconductor about the valence band maximum $\boldsymbol{k} = 0$ (Γ_{25}^{+} single group level) is to start with the (6×6) matrix labeled by the double group basis functions. The secular equation is constructed by considering

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'_{\boldsymbol{k}\cdot\boldsymbol{p}}, \tag{15.22}$$

in which the matrix elements for $\mathcal{H}'_{\boldsymbol{k}\cdot\boldsymbol{p}}$ vanish in first-order. Therefore in degenerate second-order perturbation theory we must replace each matrix element $\langle i|\mathcal{H}'|j\rangle$ by

$$\langle i|\mathcal{H}'|j\rangle + \sum_{\alpha} \frac{\langle i|\mathcal{H}'|\alpha\rangle\langle\alpha|\mathcal{H}'|j\rangle}{E_i - E_\alpha}, \tag{15.23}$$

in which $\mathcal{H}'$ denotes the $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation Hamiltonian (see Sect. 13.5), and i, j, α all denote double group irreducible representations. In this case we obtain the appropriate basis functions for the Γ_7^{+} and Γ_8^{+} states from the combination that we previously derived using the raising operator $J_+ = L_+ + S_+$ see (14.41) and (14.46) and making the transcription $L_x, L_y, L_z \rightarrow \varepsilon_x, \varepsilon_y, \varepsilon_z$ discussed in Sect. 14.7. Thus for the $\Gamma_7^{+}(\Gamma_{25}^{+})$ states, the basis functions are

$|j, m_j\rangle$ State	Basis Function	
$\left|\frac{1}{2}, \frac{1}{2}\right\rangle$	$\mu_1 = \frac{1}{\sqrt{3}}[(\varepsilon_x + i\varepsilon_y) \downarrow -\varepsilon_z \uparrow]$	(15.24)
$\left|\frac{1}{2}, \frac{1}{2}\right\rangle$	$\mu_2 = \frac{1}{\sqrt{3}}[-(\varepsilon_x - i\varepsilon_y) \uparrow +\varepsilon_z \downarrow]$,	

and for the $\Gamma_8^{+}(\Gamma_{25}^{+})$ states, the basis functions are

$|j, m_j\rangle$ State	Basis Function	
$\left|\frac{3}{2}, \frac{3}{2}\right\rangle$	$\nu_1 = \frac{1}{\sqrt{2}}(\varepsilon_x + i\varepsilon_y) \uparrow$	
$\left|\frac{3}{2}, \frac{1}{2}\right\rangle$	$\nu_2 = \frac{1}{\sqrt{6}}[(\varepsilon_x + i\varepsilon_y) \downarrow +2\varepsilon_z \uparrow]$	(15.25)
$\left|\frac{3}{2}, -\frac{1}{2}\right\rangle$	$\nu_3 = \frac{1}{\sqrt{6}}[(\varepsilon_x - i\varepsilon_y) \uparrow +2\varepsilon_z \downarrow]$	
$\left|\frac{3}{2}, -\frac{3}{2}\right\rangle$	$\nu_4 = \frac{1}{\sqrt{2}}(\varepsilon_x - i\varepsilon_y) \downarrow$,	

in which the states Γ_7^{+} and Γ_8^{+} are labeled by $|j, m_j\rangle$ and the components of the function ε_i relate to x, y, z partners according to

$$\varepsilon_x = yz$$

$$\varepsilon_y = zx$$

$$\varepsilon_z = xy. \tag{15.26}$$

In solving for $E(\boldsymbol{k})$ for the valence band of a semiconductor, such as germanium, we use the unperturbed and perturbed Hamiltonians given by (15.10) and (15.11), respectively. The states used to solve the eigenvalue problem are labeled by the wave functions that diagonalize the "unperturbed" Hamiltonian $\mathcal{H}_0$ of (15.10). Since $\mathcal{H}'_{\boldsymbol{k}\cdot\boldsymbol{p}}$ transforms as Γ_{15}^- and since $\Gamma_{15}^- \otimes \Gamma_7^+ = \Gamma_7^- + \Gamma_8^-$, we conclude that $\mathcal{H}'_{\boldsymbol{k}\cdot\boldsymbol{p}}$ does not couple band Γ_7^+ to band Γ_7^+. This same result follows more easily just from parity arguments (i.e., the evenness and oddness of states for systems exhibiting inversion symmetry).

A solution to the resulting (6×6) secular equation involves explicit computation of matrix elements as was done for the spinless case in Sect. 13.5. For brevity, we will not include a detailed evaluation of all the matrix elements, but we will instead just *summarize* the results. For the $\Gamma_7^+(\Gamma_{25}^+)$ level, the dispersion relation (see Fig. 14.1) $E(\boldsymbol{k})$ assumes the form

$$E(\Gamma_7^+) = k^2 \left(\frac{\hbar^2}{2m} + 4C_1 + \frac{4}{3}C_2 + C_3 \right), \tag{15.27}$$

where

$$C_1 = \frac{\hbar^2}{m^2} \left\{ \sum_{\Gamma_8^-(\Gamma_{12}^-)} \frac{|\langle \Gamma_7^+ | P_x | \Gamma_8^- \rangle|^2}{E_0 - E_\ell} + \sum_{\Gamma_8^-(\Gamma_{25}^-)} \frac{|\langle \Gamma_7^+ | P_x | \Gamma_8^- \rangle|^2}{E_0 - E_\ell} \right\}$$

$$C_2 = \frac{\hbar^2}{m^2} \sum_{\Gamma_8^-(\Gamma_{15}^-)} \frac{|\langle \Gamma_7^+ | P_x | \Gamma_8^- \rangle|^2}{E_0 - E_\ell}$$

$$C_3 = \frac{\hbar^2}{m^2} \sum_{\Gamma_7^-(\Gamma_2^-)} \frac{|\langle \Gamma_7^+ | P_z | \Gamma_7^- \rangle|^2}{E_0 - E_\ell}, \tag{15.28}$$

in which

$$\boldsymbol{P} = \boldsymbol{p} + \frac{\hbar}{4m^2c^2}(\boldsymbol{\sigma} \times \boldsymbol{\nabla}V), \tag{15.29}$$

and E_ℓ is an intermediate state with the indicated symmetries. Since bands with Γ_{12}^- and Γ_{25}^- symmetries do not lie close to the valence band Γ_{25}^+ in a typical cubic semiconductor, we would expect C_1 to be much smaller than C_2 or C_3.

The solution for the Γ_8^+ level in the valence band is a good deal more complicated than that for the Γ_7^+ level, and yields the result

$$E[\Gamma_8^+(\Gamma_{25}^+)] = A\,k^2 \pm \sqrt{B^2 k^4 + C^2(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)}, \tag{15.30}$$

where

$$A = \tfrac{\hbar^2}{2m} + \tfrac{2}{3}E_1 + 2E_2 + E_3 + 5E_4 + \tfrac{1}{2}E_5$$

$$B^2 = \tfrac{4}{9}E_1^2 + 4E_2^2 + 16E_4^2 + \tfrac{1}{4}E_5^2 - \tfrac{8}{3}E_1E_2 + \tfrac{16}{3}E_1E_4$$

$$\qquad - \tfrac{2}{3}E_1E_5 - 16E_2E_4 + 2E_2E_5 - 4E_4E_5$$

$$C^2 = -\tfrac{9}{16}E_5^2 + 16E_1E_2 - 32E_1E_4 + E_1E_5 - 9E_2E_5 + 18E_4E_5 \,, (15.31)$$

and where

$$E_1 = \frac{\hbar^2}{m^2} \sum_{\Gamma_6^-(\Gamma_{15}^-)} \frac{|\langle \Gamma_8^+ | P_x | \Gamma_6^- \rangle|^2}{E_0 - E_\ell}$$

$$E_2 = \frac{\hbar^2}{m^2} \sum_{\Gamma_7^-(\Gamma_2^-)} \frac{|\langle \Gamma_8^+ | P_x | \Gamma_7^- \rangle|^2}{E_0 - E_\ell}$$

$$E_3 = \frac{\hbar^2}{m^2} \sum_{\Gamma_8^-(\Gamma_{15}^-)} \frac{|\langle \Gamma_8^+(\Gamma_{25}^+)| P_z | \Gamma_8^-(\Gamma_{15}^-)\rangle|^2}{E_0 - E_\ell}$$

$$E_4 = \frac{\hbar^2}{m^2} \sum_{\Gamma_8^-(\Gamma_{25}^-)} \frac{|\langle \Gamma_8^+(\Gamma_{25}^+)| P_z | \Gamma_8^-(\Gamma_{25}^-)\rangle|^2}{E_0 - E_\ell}$$

$$E_5 = \frac{\hbar^2}{m^2} \sum_{\Gamma_8^-(\Gamma_{12}^-)} \frac{|\langle \Gamma_8^+(\Gamma_{25}^+)| P_z | \Gamma_8^-(\Gamma_{12}^-)\rangle|^2}{E_0 - E_\ell} \,. \qquad (15.32)$$

In (15.32), E_4 and E_5 are expected to be small using arguments similar to those given in (15.28) for the $E[\Gamma_7^+(\Gamma_{25}^+)]$ band dispersion. Because of the $E_0 - E_\ell$ denominator that enters second-order degenerate perturbation theory, the most important contributions to $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory come from bands lying close in energy to the E_0 level, which in this case refers to the Γ-point valence band energy extrema. For germanium the levels lying relatively close to the Fermi level have $\Gamma_{25}^+, \Gamma_1^+, \Gamma_2^-$ and Γ_{15}^- symmetries (see Fig. 14.1) so that only the double group states derived from these states will contribute significantly to the sums in (15.32). The far-lying levels only contribute small correction terms. See Problem 15.2 for more details on the solutions to $E[\Gamma_8^+(\Gamma_{25}^+)]$ and $E[\Gamma_7^+(\Gamma_{25}^+)]$. To construct $E(\boldsymbol{k})$ throughout the Brillouin zone as in Fig. 14.1, we use compatibility relations to move away from $k = 0$, and then we use different compatibility relations to get to the BZ boundary.

Although the spin–orbit perturbation term contained in $\mathcal{H}_0$ in (15.10) does not depend on $\boldsymbol{k}$, the resulting energy bands show a $\boldsymbol{k}$-dependent spin–orbit splitting. For example, in Fig. 14.1 we note that the spin–orbit splitting of the Γ_8^+ (Γ_{25}^+) level is $\Delta = 0.29\,\mathrm{eV}$ at the Γ point in

Ge while along the Λ axis, the splitting is only about 2/3 this value and remains constant over most of the Λ axis. For the corresponding levels along the Δ or (100) direction, the spin–orbit splitting is very much smaller (see Fig. 14.1). When the spin–orbit interaction is weak, it is convenient to deal with this interaction in perturbation theory. We note that the spin–orbit interaction can be written in a diagonal form using the $|j, m_j\rangle$ representation. Therefore instead of writing the wavefunctions for the unperturbed problem in the $|\ell, s, m_\ell, m_s\rangle$ representation, as we did here, it is convenient to use the $|j, m_j\rangle$ representation for the whole perturbation theory problem. A classic work on spin–orbit interaction in solids [33] has been applied to $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory [31].

15.6 Effective g-Factor

One of the important applications of double groups in *solid-state physics* is to the treatment of the effective g-factor which directly relates to the electron spin. In calculating the effective g-factor (g_{eff}), we employ $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory with spin, and show that in a magnetic field B, new terms arise in the one-electron Hamiltonian. Some of these new terms have the symmetry of an axial vector (e.g., the magnetic moment μ_{eff}), giving rise to an interaction $\boldsymbol{\mu}_{\text{eff}} \cdot \boldsymbol{B}$. We review first the origin of the effective g-factor in solid state physics and show the important role of group theory in the evaluation of the pertinent matrix elements. In this problem we consider three perturbations:

(a) Spin–orbit interaction,
(b) $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation,
(c) Perturbation by a magnetic field.

We will see that the effective one-electron Hamiltonian for an electron in a solid in an applied magnetic field can be written as

$$\mathcal{H}_{\text{eff}} = \frac{1}{2m^*_{\alpha\beta}} \left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A} \right)^2 - g_{\text{eff}}\mu_B m_s B \,, \tag{15.33}$$

which implies that in effective mass theory, the periodic potential is replaced by both an effective mass tensor and an effective g-factor. Just as the effective mass of an electron can differ greatly from the free electron value, so can the effective g-factor differ greatly from the free electron value of 2. To see how this comes about, let us consider energy bands about a band extrema in a crystal with O_h symmetry. The discussion given here follows closely that given for $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory in Chap. 13, and as expanded in this chapter by including the spin–orbit interaction.

Every entry in the secular equation for the $\boldsymbol{k} \cdot \boldsymbol{p}$ Hamiltonian is of the following form since there are no entries in *first-order* that couple the degenerate states:

$$\frac{\hbar^2 k^2}{2m} \delta_{n,n'} + \sum_{n''} \frac{\langle n|\mathcal{H}'|n''\rangle \langle n''|\mathcal{H}'|n'\rangle}{E_n - E_{n''}} , \qquad (15.34)$$

where $\sum_{n''}$ denotes the sum over states outside the nearly degenerate set (NDS, see Sect. 13.5) and where we are assuming that every member in the NDS is of approximately the same energy, like the situation for degenerate p-bands or of strongly coupled s and p bands. The $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation Hamiltonian is either $\mathcal{H}' = (\hbar/m)\boldsymbol{k} \cdot \boldsymbol{p}$ for the spinless problem or it is $\mathcal{H}' = (\hbar/m)\boldsymbol{k} \cdot \boldsymbol{P}$ for the problem with spin, where $\boldsymbol{P} = \boldsymbol{p} + (\hbar/4mc^2)\boldsymbol{\sigma} \times \boldsymbol{\nabla}V$. With this identification of $\mathcal{H}'$ we can rewrite the entries to the secular equation (15.34) as

$$\sum_{\alpha\beta} D_{nn'\alpha\beta} k_\alpha k_\beta = \sum_{\alpha\beta} k_\alpha k_\beta \left\{ \frac{\hbar^2}{2m} \delta_{nn'} \delta_{\alpha\beta} + \frac{\hbar^2}{m^2} \sum_{n''} \frac{\langle n|P_\alpha|n''\rangle \langle n''|P_\beta|n'\rangle}{E_n^{(0)} - E_{n''}^{(0)}} \right\} , \qquad (15.35)$$

where $\sum_{\alpha\beta}$ denotes a sum on components of the $\boldsymbol{k}$ vectors, and $\sum_{n''}$ denotes a sum over members outside the NDS, and where $D_{nn'\alpha\beta}$ denotes the term in curly brackets, and depends on the band indices n, n'. The eigenvalues are found by solving the secular equation

$$\sum_{n'} \left[\sum_{\alpha\beta} D_{nn'\alpha\beta} k_\alpha k_\beta - E\delta_{nn'} \right] f_{n'} = 0 . \qquad (15.36)$$

Equation (15.36) is the eigenvalue problem in zero magnetic field. The same form for the secular equation also applies when $B \neq 0$. This equation symbolically represents the problem with spin if the $f_{n'}$ functions are taken to transform as irreducible representations of the crystal double group and the $\boldsymbol{P}$ vectors are chosen so that they include the spin–orbit interaction $\boldsymbol{P} = \boldsymbol{p} + (\hbar/4mc^2)(\boldsymbol{\sigma} \times \boldsymbol{\nabla}V)$.

In an external magnetic field we replace the operator $\boldsymbol{p} \to \boldsymbol{p} - (e/c)\boldsymbol{A}$ (where $\boldsymbol{A}$ is the vector potential, and the magnetic field $\boldsymbol{B}$ is related to $\boldsymbol{A}$ by $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$), in the Hamiltonian and from this it follows generally that in (15.36) we must make the transcription

$$\hbar\boldsymbol{k} \to \frac{\hbar}{i}\boldsymbol{\nabla} - \frac{e}{c}\boldsymbol{A} , \qquad (15.37)$$

when a magnetic field is applied. The relation (15.37) is called the Kohn–Luttinger transcription and is widely used in the solution of magnetic field problems in semiconductor physics. As a result of (15.37), $\boldsymbol{k}$ in a magnetic field becomes a noncommuting operator, rather than just a simple commuting

operator in zero magnetic field. Let us, for example, select a gauge for the vector potential

$$A_x = -By \tag{15.38}$$

$$A_y = 0 \tag{15.39}$$

$$A_z = 0, \tag{15.40}$$

so that $\boldsymbol{B} = B\hat{z}$, and from (15.37), $\hbar k_z$ becomes

$$\hbar k_x = \frac{\hbar}{i}\frac{\partial}{\partial x} + \frac{e}{c}By, \tag{15.41}$$

$$\hbar k_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \tag{15.42}$$

so that k_x and k_y no longer commute and we obtain the commutation relation

$$[k_x, k_y] = \frac{ieB}{\hbar c}. \tag{15.43}$$

The commutation relation (15.43) tells us that the amount by which the operators k_x and k_y fail to commute is proportional to B. We note that all other pairs of wave vector components, such as $[k_x, k_z]$, etc. still commute. Since the order of operators is important in a magnetic field, we will need to rewrite the secular equation (15.36) when $B \neq 0$ in terms of a symmetric and an antisymmetric part:

$$D_{nn'\alpha\beta}k_\alpha k_\beta = \frac{1}{2}D^S_{nn'\alpha\beta}\underbrace{\{k_\alpha, k_\beta\}}_{\text{anticommutator}} + \frac{1}{2}D^A_{nn'\alpha\beta}\underbrace{[k_\alpha, k_\beta]}_{\text{commutator}}, \tag{15.44}$$

where the symmetric part is

$$D^S_{nn'\alpha\beta} = \frac{1}{2}\left[D_{nn'\alpha\beta} + D_{nn'\beta\alpha}\right], \tag{15.45}$$

and the antisymmetric part is

$$D^A_{nn'\alpha\beta} = \frac{1}{2}\left[D_{nn'\alpha\beta} - D_{nn'\beta\alpha}\right], \tag{15.46}$$

in which the commutator is $[k_\alpha, k_\beta] = k_\alpha k_\beta - k_\beta k_\alpha$ and the anticommutator is $\{k_\alpha, k_\beta\} = k_\alpha k_\beta + k_\beta k_\alpha$. Thus the symmetric part $D^S_{nn'\alpha\beta}$ can be written explicitly as

$$D^S_{nn'\alpha\beta} = \frac{\hbar^2}{2m}\delta_{nn'}\delta_{\alpha\beta} + \frac{\hbar^2}{2m^2}\sum_{n''}\frac{\langle n|P_\alpha|n''\rangle\langle n''|P_\beta|n'\rangle + \langle n|P_\beta|n''\rangle\langle n''|P_\alpha|n'\rangle}{E_n(0) - E_{n''}(0)}$$

$$\tag{15.47}$$

and gives the effective mass tensor through the relation

$$\frac{1}{m^*_{\alpha\beta}} = \frac{\partial^2 E_n}{\hbar^2 \partial k_\alpha \partial k_\beta} . \qquad (15.48)$$

Since the electron spin is now included, the states in (15.47) are labeled by irreducible representations of the double groups and $\boldsymbol{P}$ is a function of $\boldsymbol{\sigma}$, as seen in (15.11).

The antisymmetric part $D^A_{nn'\alpha\beta}$ is from the above definition:

$$D^A_{nn'\alpha\beta} = \frac{\hbar^2}{2m^2} \sum_{n''} \frac{\langle n|P_\alpha|n''\rangle\langle n''|P_\beta|n'\rangle - \langle n|P_\beta|n''\rangle\langle n''|P_\alpha|n'\rangle}{E_n(0) - E_{n''}(0)} . \qquad (15.49)$$

In the case of a spinless electron in a cubic crystal, $D^A_{nn'\alpha\beta}$ would vanish identically because there is only one independent momentum matrix element in cubic O_h symmetry in the absence of a magnetic field. If now we also include the electron spin and the double group representations, these arguments do not apply and we will find that $D^A_{nn'\alpha\beta}$ does not generally vanish and in fact contributes strongly to the effective g-factor. By way of comparison, the zero magnetic field eigenvalue problem is

$$\sum_{n'}\left[\sum_{\alpha\beta} D_{nn'\alpha\beta} k_\alpha k_\beta - E\delta_{nn'}\right] f_{n'} = 0, \qquad (15.50)$$

and the magnetic field eigenvalue problem then becomes

$$\sum_{n'}\left\{\sum_{\alpha\beta} \frac{1}{2}\left[D^S_{nn'\alpha\beta}\{k_\alpha, k_\beta\} + D^A_{nn'\alpha\beta}[k_\alpha, k_\beta]\right] - \mu_B\boldsymbol{\sigma}\cdot\boldsymbol{B} - E\delta_{nn'}\right\} f_{n'} = 0, \qquad (15.51)$$

where μ_B is the Bohr magneton

$$\mu_B = -\frac{|e|\hbar}{2mc},$$

and $\boldsymbol{\sigma} = 2\boldsymbol{S}/\hbar$. The term $D^S_{nn'\alpha\beta}$ gives rise to a replacement of the periodic potential by an effective mass tensor. In computing $m^*_{\alpha\beta}$ we ordinarily neglect the difference between $\boldsymbol{p}$ and $\boldsymbol{P}$.

In the presence of a magnetic field, the wavevectors $\boldsymbol{k}$ are operators which act on the effective mass wave functions $f_{n'}$. From (15.43) we see that the components of the wave vector operator do not commute, so that

$$[k_\alpha, k_\beta] = \frac{ieB_\gamma}{\hbar c}, \qquad (15.52)$$

and the commutator in (15.52) vanishes in zero magnetic field, as it should. Here the α, β, γ directions form a right-handed coordinate system. The term

$D^A_{nn'\alpha\beta}$ vanishes if there is no spin. The commutator $[k_\alpha, k_\beta]$ transforms as an axial vector. Because of the form of $D^A_{nn'\alpha\beta}$ given in (15.49), we see that $D^A_{nn'\alpha\beta}$ also transforms as an axial vector. Therefore the term $D^A_{nn'\alpha\beta}$ has the same symmetry properties as $-\mu_B\boldsymbol{\sigma}$ and gives rise to an effective magnetic moment different from the free electron value of the Bohr magneton μ_B. If we now write

$$[k_x, k_y] = \frac{ieB_z}{\hbar c} = iB_z\left(\frac{e\hbar}{2mc}\right)\left(\frac{2m}{\hbar^2}\right) = i\mu_B B_z\frac{2m}{\hbar^2}, \tag{15.53}$$

then

$$D^A_{N's}[k_x, k_y] = \frac{iB_z}{m}\mu_B\sum_{n''}\frac{\langle n|P_x|n''\rangle\langle n''|P_y|n'\rangle - \langle n|P_y|n''\rangle\langle n''|P_x|n'\rangle}{E_n(0) - E_{n''}(0)}, \tag{15.54}$$

so that the effective magnetic moment of an electron in a crystal is

$$\mu^*_{\alpha\beta} = |\mu_B|\left[\delta_{\alpha\beta} + \frac{i}{m}\sum_{n''}\frac{\langle n|P_\alpha|n''\rangle\langle n''|P_\beta|n\rangle - \langle n|P_\beta|n''\rangle\langle n''|P_\alpha|n\rangle}{E_n(0) - E_{n''}(0)}\right], \tag{15.55}$$

where the effective g-factor is related to $\mu^*_{\alpha\beta}$ by

$$g_{\text{eff}\,\alpha\beta} = 2\mu^*_{\alpha\beta}/\mu_B. \tag{15.56}$$

We recall that the energy levels of a free electron in a magnetic field are

$$E_{m_s} = g\mu_B m_s B, \tag{15.57}$$

so that for spin 1/2, the spin splitting of the levels is $2\mu_B B$. In a crystalline solid, the spin splitting becomes $2\mu^* B$.

For comparison we include the corresponding formula for the effective mass tensor component

$$\frac{1}{m^*_{\alpha\beta}} = \frac{\delta_{\alpha\beta}}{m} + \frac{1}{m^2}\sum_{n''}\frac{\langle n|P_\alpha|n''\rangle\langle n''|P_\beta|n\rangle + \langle n|P_\beta|n''\rangle\langle n''|P_\alpha|n\rangle}{E_n(0) - E_{n''}(0)}, \tag{15.58}$$

in which

$$\boldsymbol{P} = \boldsymbol{p} + \frac{\hbar}{4mc^2}\boldsymbol{\sigma}\times\boldsymbol{\nabla}V. \tag{15.59}$$

Thus an electron in a magnetic field and in a periodic potential acts as if the periodic potential can be replaced by letting $m \to m^*_{\alpha\beta}$ and $\mu_B \to \mu^*_{\alpha\beta}$. Thus, symbolically we would write an effective Hamiltonian as

$$H_{\text{eff}} = \frac{1}{2m^*}\left(p - \frac{e}{c}A\right)^2 - \mu^*\boldsymbol{\sigma}\cdot\boldsymbol{B}, \tag{15.60}$$

where

$$\mu^* = \mu_B g_{\text{eff}}/2 \,. \tag{15.61}$$

In deriving the formula for the effective g-factor above, we did not pay much attention to whether $\boldsymbol{P}$ was merely the momentum operator $\boldsymbol{p}$ or the more complete quantity including the spin–orbit interaction

$$\boldsymbol{p} + \frac{\hbar}{4mc^2}(\boldsymbol{\sigma} \times \boldsymbol{\nabla}V) \,.$$

It turns out that it is not very important whether we distinguish between matrix elements of $\boldsymbol{p}$ and of $\boldsymbol{P}$ since the matrix element of

$$\frac{\hbar}{4mc^2}(\boldsymbol{\sigma} \times \boldsymbol{\nabla}V)$$

is generally quite small. However, what is important, and even crucial, is that we consider the states n, n', n'' in the above expressions as states characterized by the irreducible representations of the crystal double groups.

Let us illustrate how we would proceed to calculate an effective g-factor for a typical semiconductor. Let us consider the effective g-factor for germanium at the Γ point ($\boldsymbol{k} = 0$). In Fig. 15.2 we let E_g denote the energy gap between the conduction band and the uppermost valence band, and we let Δ denote the spin–orbit splitting of the valence band. In germanium $E_g \sim 0.8$ eV and $\Delta \sim 0.3$ eV. We will assume in this simple example that these are the only bands to be included in carrying out the sum on n''. Since the band extrema occur at $k = 0$, the effect of the translations $\boldsymbol{\tau} = (a/4)(1,1,1)$ are not important for Ge in this limit and can be neglected.

To evaluate μ^* and m^* in (15.55) and (15.58) we use the basis functions discussed in Sects. 14.6 and 14.7 to find the nonvanishing matrix elements of $\hbar\boldsymbol{k} \cdot \boldsymbol{p}/m$. We write the basis functions for $\Gamma_8^+(\Gamma_{25}^+)$ and $\Gamma_7^+(\Gamma_{25}^+)$ in a symbolic form from (15.24) and (15.25) so that we can make use of all the group theory ideas that were discussed in Sect. 13.5 in connection with the corresponding problem without spin. This approximation is valid if $\Delta \ll E_g$ and each double group level can be clearly identified with the single group level from which it originates. Otherwise the Γ_8^+ levels mix appreciably with one another and all matrix elements must be evaluated in the double group representation directly, so that the numerical estimates obtained here would have to be revised.

Now let us evaluate the matrix elements that go into (15.55) for μ^*. One set of matrix elements have the form:

$$\left\langle \gamma^- \uparrow |p_x| \frac{3}{2}, \frac{3}{2} \right\rangle = \left\langle \gamma^- \uparrow |p_x| \frac{1}{\sqrt{2}}(\varepsilon_x + i\varepsilon_y) \uparrow \right\rangle \,. \tag{15.62}$$
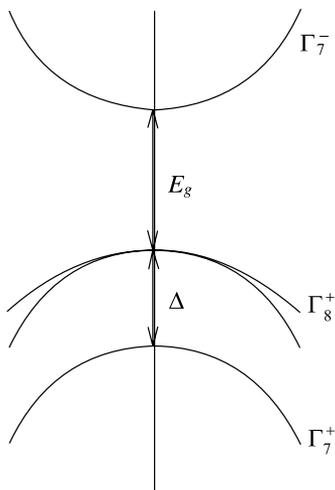
Fig. 15.2. Level ordering at the Γ point in Ge for the energy bands near the Fermi level

For the Γ_7^- state we take the basis functions to be $(\gamma^- \uparrow, \gamma^- \downarrow)$ where γ^- is a basis function for the Γ_2^- representation. For the basis functions for Γ_8^+ (Γ_{25}^+) we use

$$
\begin{array}{ll}
|j, m_j\rangle \text{ State} & \text{Basis Function} \\
\left|\frac{3}{2}, \frac{3}{2}\right\rangle & \nu_1 = \frac{1}{\sqrt{2}}(\varepsilon_x + i\varepsilon_y) \uparrow \\
\left|\frac{3}{2}, \frac{1}{2}\right\rangle & \nu_2 = \frac{1}{\sqrt{6}}[(\varepsilon_x + i\varepsilon_y) \downarrow +2\varepsilon_z \uparrow] \\
\left|\frac{3}{2}, -\frac{1}{2}\right\rangle & \nu_3 = \frac{1}{\sqrt{6}}[(\varepsilon_x - i\varepsilon_y) \uparrow +2\varepsilon_z \downarrow] \\
\left|\frac{3}{2}, -\frac{3}{2}\right\rangle & \nu_4 = \frac{1}{\sqrt{2}}(\varepsilon_x - i\varepsilon_y) \downarrow \;.
\end{array} \qquad (15.63)
$$

From Sect. 13.5 we have $(\Gamma_2^\pm|\mathcal{H}'|\Gamma_{25,\alpha}^\mp) = A_2\hbar k_\alpha/m$, where $A_2 = (\Gamma_2^\pm|p_x|\Gamma_{25,x}^\mp)$ is the only independent matrix element connecting these symmetry types, where we note that the basis function for Γ_2^- symmetry is xyz. Using the basis functions for $\Gamma_8^+(\Gamma_{25}^+)$ given by (15.63) we obtain

$$
\left\langle \gamma^- \uparrow \left| p_x \right| \frac{3}{2}, \frac{3}{2} \right\rangle = \frac{1}{\sqrt{2}} A_2
$$

$$
\left\langle \gamma^- \uparrow \left| p_x \right| \frac{3}{2}, \frac{1}{2} \right\rangle = 0
$$

$$
\left\langle \gamma^- \uparrow \left| p_x \right| \frac{3}{2}, -\frac{1}{2} \right\rangle = \frac{1}{\sqrt{6}} A_2
$$

$$
\left\langle \gamma^- \uparrow \left| p_x \right| \frac{3}{2}, -\frac{3}{2} \right\rangle = 0 \,,
$$

where we consider the *ortho-normality* of both the spin and orbital states. For the p_y matrix, the same procedure gives

$$\langle \gamma^- \uparrow | p_y \left| \frac{3}{2}, \frac{3}{2} \right\rangle = \frac{i}{\sqrt{2}} A_2$$

$$\langle \gamma^- \uparrow | p_y \left| \frac{3}{2}, \frac{1}{2} \right\rangle = 0$$

$$\langle \gamma^- \uparrow | p_y \left| \frac{3}{2}, -\frac{1}{2} \right\rangle = -\frac{i}{\sqrt{6}} A_2$$

$$\langle \gamma^- \uparrow | p_y \left| \frac{3}{2}, -\frac{3}{2} \right\rangle = 0 \,.$$

To find the contribution to μ^*/μ_B, we sum (15.55) over the four Γ_8^+ levels to obtain

$$\sum_i \frac{[\langle \gamma^- \uparrow | p_x | \nu_i \rangle \langle \nu_i | p_y | \gamma^- \uparrow \rangle - \langle \gamma^- \uparrow | p_y | \nu_i \rangle \langle \nu_i | p_x | \gamma^- \uparrow \rangle]}{E_g}$$

$$= \frac{1}{E_g} \left[\left\{ \frac{A_2}{\sqrt{2}} \right\} \left\{ -\frac{iA_2^*}{\sqrt{2}} \right\} + \left\{ \frac{A_2}{\sqrt{6}} \right\} \left\{ \frac{iA_2^*}{\sqrt{6}} \right\} \right.$$

$$\left. - \left\{ \frac{iA_2}{\sqrt{2}} \right\} \left\{ \frac{A_2^*}{\sqrt{2}} \right\} - \left\{ -\frac{iA_2}{\sqrt{6}} \right\} \left\{ \frac{A_2^*}{\sqrt{6}} \right\} \right]$$

$$= \frac{|A_2|^2}{E_g} \left[-\frac{2i}{3} \right] \,. \tag{15.64}$$

We thus obtain for the contribution from the $\Gamma_8^+(\Gamma_{25}^+)$ levels to (μ^*/μ_B) a value of

$$\frac{i}{m} \left(-\frac{2i}{3} \right) \frac{|A_2|^2}{E_g} = \frac{2|A_2|^2}{3mE_g} \,. \tag{15.65}$$

Let us now find the contribution to μ^*/μ_B from the spin–orbit split-off bands. Here we use the basis functions for $\Gamma_7^+(\Gamma_{25}^+)$

$|j, m_j\rangle$ State	Basis Function	
$\left| \frac{1}{2}, \frac{1}{2} \right\rangle$	$\mu_1 = \frac{1}{\sqrt{3}}[(\varepsilon_x + i\varepsilon_y)\downarrow -\varepsilon_z \uparrow]$	(15.66)
$\left| \frac{1}{2}, -\frac{1}{2} \right\rangle$	$\mu_2 = \frac{1}{\sqrt{3}}[-(\varepsilon_x - i\varepsilon_y)\uparrow +\varepsilon_z \downarrow]$,	

so that the matrix elements for p_x and p_y become

$$\langle \gamma^- \uparrow | p_x \left| \frac{1}{2}, \frac{1}{2} \right\rangle = 0$$

$$\langle \gamma^- \uparrow | p_x \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = -\frac{1}{\sqrt{3}} A_2$$

$$\left\langle \gamma^- \uparrow \middle| p_y \middle| \frac{1}{2}, \frac{1}{2} \right\rangle = 0$$

$$\left\langle \gamma^- \uparrow \middle| p_y \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle = \frac{i}{\sqrt{3}} A_2 .$$

We thus obtain the contribution of

$$\frac{i}{m(E_g + \Delta)} \left[\frac{2i}{3} |A_2|^2 \right] = -\frac{2}{3} \frac{|A_2|^2}{m(E_g + \Delta)} \tag{15.67}$$

to μ^*/μ_B in (15.55) from the $\Gamma_7^+ (\Gamma_{25}^+)$ levels. Adding up the two contributions from (15.65) and (15.67) we finally obtain

$$\left(\frac{\mu^*}{\mu_B} \right)_{\text{orbital}} = -\frac{2|A_2|^2}{3m} \left[\frac{1}{E_g + \Delta} - \frac{1}{E_g} \right] + 1 , \tag{15.68}$$

where $+1$ in (15.68) is the free electron contribution.

We can now evaluate $|A_2|^2$ in terms of the conduction band effective mass using the symmetric contribution $D_{nn'\alpha\beta}^S$ and for this term we can use the relation

$$\frac{m}{m^*} = 1 + \frac{2}{m} \sum_n \frac{|\langle \gamma^- \uparrow |p_x|n \rangle|^2}{E_{\Gamma_{2'}}(0) - E_n(0)} . \tag{15.69}$$

Evaluating the matrix elements in (15.69), we thus obtain

$$\frac{m}{m^*} = 1 + \frac{2}{m} \left[\frac{|A_2|^2}{2E_g} + \frac{|A_2|^2}{6E_g} + \frac{|A_2|^2}{3(E_g + \Delta)} \right] \approx \frac{2}{3m} |A_2|^2 \left[\frac{2}{E_g} + \frac{1}{E_g + \Delta} \right] , \tag{15.70}$$

where the free electron term of unity is usually small compared to other terms in the sum in (15.70) and can be neglected in many cases. Neglecting this term, we now substitute for $|A_2|^2$ in terms of m^* to obtain

$$g_{\text{eff}} = \frac{2\mu^*}{\mu_B} = 2 - \frac{2m}{m^*} \left(\frac{\Delta}{3E_g + 2\Delta} \right) . \tag{15.71}$$

In the limit, $\Delta \to 0$, then $g \to 2$ in agreement with the results for the free electron g-factor. In the limit $\Delta \gg E_g$

$$g_{\text{eff}} \to 2 - \frac{m}{m^*} , \tag{15.72}$$

which implies $g_{\text{eff}} \to -m/m^*$ for carriers with very light masses.

For germanium, for which $m^*/m \sim 0.12$, $\Delta \sim 0.3\,\text{eV}$, and $E_g \sim 0.8\,\text{eV}$, the effective g-factor mostly cancels the free electron contribution:

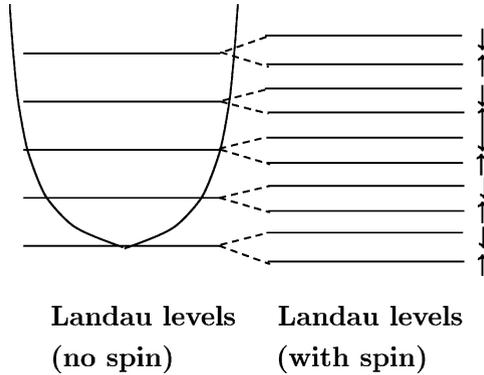Landau levels   Landau levels
(no spin)   (with spin)

Fig. 15.3. Landau levels in InSb showing the spin splitting resulting from the large negative effective g-factor

$$g_{\text{eff}} = 2 \left[1 - \left(\frac{1}{0.12} \right) \frac{0.3}{3(0.8) + 2(0.3)} \right] = 2 \left[1 - \frac{1}{1.2} \right] \simeq \frac{1}{3} . \qquad (15.73)$$

For InSb the spin–orbit splitting is large compared with the direct band gap $m^*/m \sim 0.013$, $\Delta \sim 0.9\,\text{eV}$, and $E_g \sim 0.2\,\text{eV}$

$$g_{\text{eff}} \sim 2 \left[1 - \left(\frac{1}{0.013} \right) \frac{0.9}{3(0.2) + 2(0.9)} \right] \sim 2(1 - 28) \simeq -54 \qquad (15.74)$$

leading to the picture for InSb shown in Fig. 15.3. In InSb, the spin splitting is almost as large as the Landau level separation. However, the g_{eff} has the opposite sign as compared with the free electron spin g-value, where we note that because of the negative sign of the charge on the electron and on the Bohr magneton, the free electron spin state of lowest energy is aligned antiparallel to the applied field. Sometimes it is convenient to define the spin effective mass by the relation

$$\frac{\mu^*}{\mu_{\text{B}}} = \frac{m}{m_{\text{s}}^*} , \qquad (15.75)$$

where m_{s}^* denotes spin effective mass, so that $g_{\text{eff}} = 2m/m_{\text{s}}^*$ [19, 52, 62, 74, 77].

In general, the spin and orbital effective masses will not be the same. If they are (see Fig. 15.4), the Landau level spacing is equal to the spacing between spin levels. The physical reason why these masses are not expected to be equal is that the orbital mass is determined by a momentum matrix element (which transforms as a radial vector). Since the spin mass depends on the coupling between electronic energy bands through an operator which transforms as an axial vector, different energy bands with different symmetries are coupled for the two cases.

In treating cyclotron resonance transitions, the transitions are spin conserving and the g-factors usually cancel out. They are, however, important for
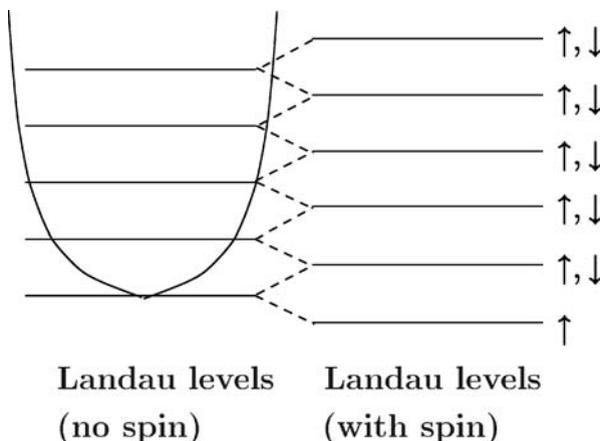
Fig. 15.4. Strict two-band model where the Landau level separation is equal to the spin splitting, as occurs for the case of a free electron gas. This limit applies quite well to the L-point Landau levels for the conduction band in bismuth

interband Landau level transitions even though the transitions are spin conserving, since the g-factors in the valence and conduction bands can be different. Thus spin up and spin down transitions can occur at different energies. The effective g-factors are directly observed in spin resonance experiments which occur between the same Landau level but involve a spin flip.

Of interest also is the case where the spin effective mass and the orbital effective mass are equal to one another. In a strict two-band model this must be the case. For bismuth, the strongly coupled two-band model is approximately valid and $m_s^* \simeq m^*$ (see Fig. 15.4). Landau level separations equal to the spin splitting also occur for the free electron magnetic energy levels. However, for band electrons, the Landau level separations are proportional to the inverse cyclotron effective mass rather than the inverse free electron mass.

For high mobility (low effective mass) materials with a small spin–orbit interaction, the Landau level separation is large compared with the spin splitting (see Fig. 15.3). On the other hand, some high mobility narrow gap semiconductors with a large spin–orbit interaction can have spin splittings larger than the Landau level separations; such a situation gives rise to interesting phenomena at high magnetic fields.

Summarizing, the effective mass Hamiltonian was considered in the presence of a magnetic field, taking into account the spin on the electron. In this case, we form the following symmetrized combinations of wave vectors:

$$\Gamma_1^+ \to k_x^2 + k_y^2 + k_z^2$$
$$\Gamma_{12}^+ \to k_x^2 + \omega k_y^2 + \omega^2 k_z^2, k_x^2 + \omega^2 k_y^2 + \omega k_z^2 ,$$
$$\Gamma_{25}^+ \to (\{k_y, k_z\}, \{k_z, k_x\}, \{k_x, k_y\})$$
$$\Gamma_{15}^+ \to ([k_y, k_z], [k_z, k_x], [k_x, k_y]) \tag{15.76}$$

in which the wave vector is taken as an operator. These symmetrized forms of the wave vector are used in connection with the effective g-factor for an electron in a periodic solid to which a magnetic field is applied [19,52,62,74,77].

We will return to the g-factor in semiconductors in Chap. 16 where we discuss time reversal symmetry. Since a magnetic field breaks time reversal symmetry, the form of $E(\mathbf{k})$ is sensitive to spin and time reversal symmetry. These considerations are very important to the field of spintronics.

15.7 Fourier Expansion of Energy Bands: Slater–Koster Method

The Slater–Koster technique uses group theory to provide the most general form for the energy bands throughout the Brillouin zone which is consistent with the crystal symmetry. The method is used when experiments or theory provide information relevant to $E(\mathbf{k})$ at different points in the Brillouin zone. The method provides the best fit to the form of $E(\mathbf{k})$ consistent with the experimental or theoretical constraints. Like the $\mathbf{k}\cdot\mathbf{p}$ method, it is an approach whereby the energy bands can be determined from experimental data without recourse to a definite energy band model or to a specific crystal potential. In contrast to $\mathbf{k}\cdot\mathbf{p}$ perturbation theory which makes use of the group of the wavevector for an expansion of $E(\mathbf{k})$ about a specific point in the Brillouin zone such as $k = 0$, the Slater–Koster method considers the entire Brillouin zone and makes use of the full space group symmetry to form $E(\mathbf{k})$ on an equal basis. The original work done by Slater and Koster provided an interpolation formula for calculating energy bands at high symmetry points in the Brillouin zone [66], and the method was later applied to silicon and germanium [29]. We will illustrate the method here for a simple cubic lattice [27].

Because of the periodicity of the lattice, the energy bands $E_n(\mathbf{k})$ are periodic in the extended Brillouin zone

$$E_n(\mathbf{k} + \mathbf{K}_{n_i}) = E_n(\mathbf{k}), \tag{15.77}$$

where $\mathbf{K}_{n_i}$ is a reciprocal lattice vector so that $\mathbf{K}_{n_i} \cdot \mathbf{R_m} = 2\pi p$, with p an integer. The energy bands $E_n(\mathbf{k})$ are furthermore continuous across a zone boundary and they approach this boundary with zero slope (giving the electrons zero velocity at a zone boundary). We make use of this periodicity as follows. Suppose that we have a function $V(\mathbf{r})$ which is periodic in the three-dimensional lattice. This function reflects the full symmetry of the crystal and symmetry operations of the space group. The function $V(\mathbf{r})$ can be Fourier expanded in the reciprocal lattice

$$V(\mathbf{r}) = \sum_{\mathbf{K}_{n_i}} v(\mathbf{K}_{n_i})e^{i\mathbf{K}_{n_i}\cdot\mathbf{r}} \tag{15.78}$$

in which the summation is over all reciprocal lattice vectors. In the extended zone scheme, the *energy $E_n(\mathbf{k})$ is periodic* in a three-dimensional space defined

by the reciprocal lattice vectors. Therefore it is possible to Fourier expand $E_n(\mathbf{k})$ in a space "reciprocal" to the reciprocal lattice, i.e., in the direct lattice, to obtain:

$$E_n(\mathbf{k}) = \sum_{\mathbf{d}} \varepsilon_n(\mathbf{d})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{d}}, \qquad (15.79)$$

where $\mathbf{d} = \mathbf{R_m}$ are Bravais lattice vectors and $\varepsilon_n(\mathbf{d})$ can be interpreted as an overlap integral in the tight binding approximation. What is important here is that the tight binding wave functions reflect the symmetry operations of the space group. Crystal symmetry restricts the number of independent expansion coefficients $\varepsilon_n(\mathbf{d})$ following the principles that govern the determination of the number of independent nonvanishing matrix elements (see Sect. 6.6). Provided that the Fourier series of (15.79) is rapidly convergent, it is possible to describe $E_n(\mathbf{k})$ in terms of a small number of expansion parameters $\varepsilon_n(\mathbf{d})$. The number of $\varepsilon_n(\mathbf{d})$ is determined by group theory and their values, in principle, can be determined by experiment.

For example, let us consider a nondegenerate, isolated s-band in a simple cubic crystal. Such a band has Γ_1^+ symmetry and is invariant under the point group operations of the cubic group. The Fourier expansion would then take the form of the tight binding functions and relate to linear combinations of plane waves (see Sect. 12.2):

$$
\begin{aligned}
E_n(\mathbf{k}) = {} & \varepsilon_n(0) + \varepsilon_n(1)\left[\cos ak_x + \cos ak_y + \cos ak_z\right] \\
& + \varepsilon_n(2)\left[\cos a(k_y + k_z) + \cos a(k_y - k_z) + \cos a(k_z + k_x)\right. \\
& \left. + \cos a(k_z - k_x) + \cos a(k_x + k_y) + \cos a(k_x - k_y)\right] \\
& + \varepsilon_n(3)\left[\cos a(k_x + k_y + k_z) + \cos a(k_x - k_y - k_z)\right. \\
& \left. + \cos a(-k_x + k_y - k_z) + \cos a(-k_x - k_y + k_z)\right] + \cdots \quad (15.80)
\end{aligned}
$$

where | $d = 0$ | is the zeroth *neighbor* at $a(0,0,0)$
| $d = 1$ | is the nearest neighbor at $a(1,0,0)$
| $d = 2$ | is the next nearest neighbor at $a(1,1,0)$
| $d = 3$ | is the next–next nearest neighbor at $a(1,1,1)$, etc.

In the tight binding approximation, the expansion coefficients appear as overlap integrals and transfer integrals of various kinds. Thus, the tight binding form is written to satisfy the symmetry of the space group and is of the Slater–Koster form. Now suppose that *ab initio* calculations provide the energy levels and wave functions with high accuracy at a few points in the Brillouin zone. The Slater–Koster method allows all these solutions to be brought together to give $E(\mathbf{k})$ throughout the Brillouin zone, consistent with space group symmetry. For example in Ge, we could have experimental data relevant to the Γ point from measurements of the hole

constant energy surfaces at the Γ point, and electron constant energy surfaces about the L points in the Brillouin zone [29] and optical transitions at both the Γ point and the L point. The Slater–Koster method provides a framework that allows use of each of these experiments to aid in the determination of the electronic energy band structure throughout the Brillouin zone [27].

Now for energy bands of practical interest, we will not have isolated nondegenerate bands, but rather coupled bands of some sort. We can express the eigenvalue problem for n coupled bands in terms of an $(n \times n)$ secular equation of the form

$$|\langle i|\mathcal{H}|j\rangle - E_n(\boldsymbol{k})\delta_{ij}| = 0 \,. \tag{15.81}$$

In (15.81) the indices i and j denote Bloch wave functions which diagonalize the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + V(\boldsymbol{r}) \,, \tag{15.82}$$

and are labeled by the wave vector $\boldsymbol{k}$. The matrix elements $\langle i|\mathcal{H}|j\rangle$ thus constitute a $\boldsymbol{k}$-dependent matrix. But at each $\boldsymbol{k}$ point, these matrix elements are invariant under the symmetry operations of the group of the wave vector at $\boldsymbol{k}$. The Hamiltonian at $\boldsymbol{k} = 0$ has Γ_1^+ symmetry just like its eigenvalues $E_n(\boldsymbol{k})$. This matrix is also periodic in the reciprocal lattice in the extended zone scheme and therefore can be Fourier expanded.

The expansion is carried out in terms of a complete set of basis matrices which are taken as angular momentum matrices in the spirit of Sect. 14.6. For example, a (2×2) Hamiltonian including the electron spin (i.e., the double group representations $\Gamma_6^\pm$ or $\Gamma_7^\pm$ in Chap. 14) would be expanded in terms of four basis matrices 1, S_x, S_y and S_z, representing the angular momentum matrices for spin 1/2. A (3×3) Hamiltonian, such as would be used to describe the valence bands of many common semiconductors, is expanded in terms of the nine linearly independent basis matrices which span this space, namely, $\hat{1}$, S_x, S_y, S_z, S_x^2, S_y^2, $\{S_z, S_y\}$, $\{S_z, S_x\}$ and $\{S_x, S_y\}$, in which $\hat{1}$ is a (3×3) unit matrix, S_x, S_y, S_z are angular momentum matrices for spin 1, and $\{S_i, S_j\}$ denotes the anticommutator for matrices S_i and S_j. Under the point group operations of the group of the wave vector, the angular momentum matrices S_i transform as an axial vector – i.e., at $\boldsymbol{k} = 0$, S_i transforms as Γ_{15}^+, while the matrix Hamiltonian still is required to be invariant. Therefore, it is necessary to take products of symmetrized combinations of the n basis matrices with appropriate symmetrized combinations of the Fourier expansion functions so that an invariant matrix Hamiltonian results.

The $(n \times n)$ matrix Hamiltonian which is denoted by $D_{\Gamma_1}(\boldsymbol{k})$ can be Fourier expanded in terms of these basis function matrices in the form

$$D_{\Gamma_1}(\boldsymbol{k}) = \sum_{\boldsymbol{d}} \alpha_{d,\Gamma_j} \mathcal{C}_{\Gamma_j}(\boldsymbol{d}) \cdot \boldsymbol{S}_{\Gamma_j} \,, \tag{15.83}$$

which is a generalization of (15.79). In (15.83), $\mathcal{S}_{\Gamma_j}$ denotes a collection of basis matrices which transforms as Γ_j, and these symmetrized products of angular momentum matrices are given in Table 15.1 for the simple cubic lattice (space group #221). The distance $\boldsymbol{d}$ denotes the order of the expansion in (15.83) and corresponds to the distance of neighbors in the Fourier expansion in the tight binding sense, so that orders $0, 1, 2, \ldots$, etc. correspond to $d = 0$ or $d = 1$ (nearest neighbor terms) or $d = 2$ (next nearest neighbor terms), etc. The angular momentum matrices in Table 15.1 are given by

$$S_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}, \quad S_y = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}, \quad S_z = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{15.84}$$

Products of the dimensionless angular momentum matrices S_i are listed representations of cubic group in Table 15.1, using an abbreviated notation. For example, $\mathcal{S}_{\Gamma_{15}^+}^{(x)}(1)$ denotes the x component of a three component vector S_x, S_y, S_z and all three components would appear in (15.83). Similarly, $\mathcal{S}_{\Gamma_{12}^+}^{(i)}(2)$ is a two component vector with partners

$$S_x^2 + \omega S_y^2 + \omega^2 S_z^2$$

and

$$S_x^2 + \omega^2 S_y^2 + \omega S_z^2 \,,$$

and only one of the partners is listed in Table 15.1, where several other three component matrices are found, such as $\mathcal{S}_{\Gamma_{25}^+}^{(\alpha)}(2)$ for which the x component is the anticommutator $\{S_y, S_z\}$ and the y and z components of $\mathcal{S}_{\Gamma_{25}^+}^{(\alpha)}(2)$ are found by cyclic permutation of the indices x, y, z. It is worth

Table 15.1. Symmetrized products of angular momenta for the cubic group

order	representation	notation	symmetrized products
0	Γ_1^+	$\mathcal{S}_{\Gamma_1^+}(0)$	1
1	Γ_{15}^+	$\mathcal{S}_{\Gamma_{15}^+}^x(1)$	S_x
2	Γ_{12}^+	$\mathcal{S}_{\Gamma_{12}^+}^{(1)}(2)$	$S_x^2 + \omega S_y^2 + \omega^2 S_z^2$
	Γ_{25}^+	$\mathcal{S}_{\Gamma_{25}^+}^{(x)}(2)$	$\{S_y, S_z\}$
3	Γ_2^+	$\mathcal{S}_{\Gamma_2^+}(3)$	$S_x S_y S_z + S_x S_z S_y$
	Γ_{15}^+	$\mathcal{S}_{\Gamma_{15}^+}^{(x)}(3)$	S_x^3
	Γ_{25}^+	$\mathcal{S}_{\Gamma_{15}^+}^{(x)}(3)$	$\{S_x, (S_y^2 - S_z^2)\}$

mentioning that all of the $\mathcal{S}$ matrices in (15.83) are 3×3 matrices which are found explicitly by carrying out the indicated matrix operations. For example:

$$\{S_y, S_z\} = S_y S_z + S_z S_y = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}. \tag{15.85}$$

Also useful for carrying out matrix operations are the definitions:

$$S_x = \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{15.86}$$

so that

$$S_x \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \frac{\hbar}{i} \begin{pmatrix} 0 \\ -z \\ y \end{pmatrix}. \tag{15.87}$$

Another point worth mentioning about Table 15.1 concerns the terms that do *not* appear. For example, in second-order we could have terms like $S_x^2 + S_y^2 + S_z^2$ but this matrix is just the unit matrix which has already been listed in the table. Similarly, the commutators $[S_y, S_z]$ which enter in second-order are matrices that have already appeared in first-order as iS_x.

We give below the nine basis matrices that span the (3×3) matrices for spin 1, where we note that $(\Gamma_{15}^+ \otimes \Gamma_{15}^+) = \Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{15}^+ + \Gamma_{25}^+$:

$$\mathcal{S}_{\Gamma_1^+} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{15.88}$$

$$\mathcal{S}_{\Gamma_{12}^+}^{(1)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 + \omega^2 & 0 \\ 0 & 0 & 1 + \omega \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -\omega & 0 \\ 0 & 0 & -\omega^2 \end{pmatrix}, \tag{15.89}$$

$$\mathcal{S}_{\Gamma_{12}^+}^{(2)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 + \omega & 0 \\ 0 & 0 & 1 + \omega^2 \end{pmatrix}, \tag{15.90}$$

$$\mathcal{S}_{\Gamma_{15}^+}^{(x)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}, \tag{15.91}$$

$$\mathcal{S}_{\Gamma_{15}^+}^{(y)} = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}, \tag{15.92}$$

$$\mathcal{S}^{(z)}_{\Gamma^+_{15}} = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \tag{15.93}$$

$$\mathcal{S}^{(x)}_{\Gamma^+_{25}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} , \tag{15.94}$$

$$\mathcal{S}^{(y)}_{\Gamma^+_{25}} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} , \tag{15.95}$$

$$\mathcal{S}^{(z)}_{\Gamma^+_{25}} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \tag{15.96}$$

Any arbitrary (3×3) matrix can be written as a linear combination of these nine matrices.

Table 15.1 however was constructed to be more general than just to describe interacting p-bands in a 3×3 matrix formulation. The table can equally well be used to form the appropriate 16 basis matrices which are needed to deal with interacting s and p bands, such as would arise in semiconductor physics. Such interacting s and p bands give rise to a 4×4 matrix Hamiltonian and therefore 16 basis matrices are needed to span the space for the secular equation in this case. The symmetries involved for order $0, 1, 2, 3, \ldots$ correspond to the symmetries of the angular momentum matrices in cubic symmetry.

Now let use return to the Fourier expansion of (15.83). For each neighbor distance $|\boldsymbol{d}|$ there are several lattice vectors that enter, just as in the plane wave problem of Chap. 12 where we considered sets of $\boldsymbol{K}_{n_i}$ vectors of equal magnitude. The terms in (15.83) can be labeled by their symmetry types so that the sum on $\boldsymbol{d}$ breaks up into a sum on the magnitude $|\boldsymbol{d}|$ and on the symmetry type Γ_j occurring at distance $\boldsymbol{d}$. The linear combinations of the exponential functions $\exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{d})$ which transform as the pertinent irreducible representations of the cubic group are given in Table 15.2 out through third nearest neighbor distances. Once again, if a representation is one-dimensional, the basis function itself is given. For the two-dimensional representations, only one of the functions is listed, the partner being the complex conjugate of the listed function. For the three-dimensional representations, only the x-component is listed; the partners are easily found by cyclic permutations of the indices.

The combinations of plane waves and basis functions that enter the Fourier expansion of (15.83) are the scalar products of these symmetrized Fourier functions $\boldsymbol{C}_{\Gamma_j}(\boldsymbol{d})$ and the basis functions $\boldsymbol{S}_{\Gamma_j}(\boldsymbol{d})$. This means that for the two-dimensional representations, we write

$$\mathcal{C}^{(1)}_{\Gamma^+_{12}} \left(\mathcal{S}^{(1)}_{\Gamma^+_{12}} \right)^* + \mathcal{C}^{(2)}_{\Gamma^+_{12}} \left(\mathcal{S}^{(2)}_{\Gamma^+_{12}} \right)^* , \tag{15.97}$$

Table 15.2. Symmetrized Fourier functions for a simple cubic lattice

d	repr.	notation	symmetrized Fourier functions
$a(0,0,0)$	Γ_1^+	$\mathcal{C}_{\Gamma_1^+}(000)$	1
$a(1,0,0)$	Γ_1^+	$\mathcal{C}_{\Gamma_1^+}(100)$	$\cos ak_x + \cos ak_y + \cos ak_z$
	Γ_{12}^+	$\mathcal{C}_{\Gamma_{12}^+}^{(1)}(100)$	$\cos ak_x + \omega \cos ak_y + \omega^2 \cos ak_z$
	Γ_{15}^-	$\mathcal{C}_{\Gamma_{15}^-}^{(x)}(100)$	$\sin ak_x$
$a(1,1,0)$	Γ_1^+	$\mathcal{C}_{\Gamma_1^+}(110)$	$\cos a(k_y + k_z) + \cos a(k_y - k_z) + \cos a(k_z + k_x)$
			$+ \cos a(k_z - k_x) + \cos a(k_x + k_y) + \cos a(k_x - k_y)$
	Γ_{12}^+	$\mathcal{C}_{\Gamma_{12}^+}^{(1)}(110)$	$[\cos a(k_y + k_z) + \cos a(k_y - k_z)]$
			$+ \omega[\cos a(k_z + k_x) + \cos a(k_z - k_x)]$
			$+ \omega^2[\cos a(k_x + k_y) + \cos a(k_x - k_y)]$
	Γ_{15}^-	$\mathcal{C}_{\Gamma_{15}^-}^{(x)}(110)$	$\sin a(k_x + k_y) + \sin a(k_x - k_y)$
			$+ \sin a(k_x + k_z) + \sin a(k_x - k_z)$
	Γ_{25}^-	$\mathcal{C}_{\Gamma_{25}^-}^{(x)}(110)$	$\sin a(k_x + k_y) + \sin a(k_x - k_y)$
			$- \sin a(k_x + k_z) - \sin a(k_x - k_z)$
	Γ_{25}^+	$\mathcal{C}_{\Gamma_{25}^+}^{(x)}(110)$	$\cos a(k_y + k_z) - \cos a(k_y - k_z)$
$a(1,1,1)$	Γ_1^+	$\mathcal{C}_{\Gamma_1^+}(111)$	$\cos a(k_x + k_y + k_z) + \cos a(k_x - k_y - k_z)$
			$+ \cos a(-k_x + k_y - k_z) + \cos a(-k_x - k_y + k_z)$
	Γ_2^-	$\mathcal{C}_{\Gamma_2^-}(111)$	$\sin a(k_x + k_y + k_z) + \sin a(k_x - k_y - k_z)$
			$+ \sin a(-k_x + k_y - k_z) + \sin a(-k_x - k_y + k_z)$
	Γ_{15}^-	$\mathcal{C}_{\Gamma_{15}^-}^{(x)}(111)$	$\sin a(k_x + k_y + k_z) + \sin a(k_x - k_y - k_z)$
			$- \sin a(-k_x + k_y - k_z) - \sin a(-k_x - k_y + k_z)$
	Γ_{25}^+	$\mathcal{C}_{\Gamma_{25}^+}^{(x)}(111)$	$\cos a(k_x + k_y + k_z) + \cos a(k_x - k_y - k_z)$
			$- \cos a(-k_x + k_y - k_z) - \cos a(-k_x - k_y + k_z)$

$\omega = \exp(2\pi i/3)$ and a is the lattice constant

where the second term is the complex conjugate of the first so that the sum is real. For the three-dimensional representations we write for the scalar product

$$\mathcal{C}^x \mathcal{S}^x + \mathcal{C}^y \mathcal{S}^y + \mathcal{C}^z \mathcal{S}^z . \tag{15.98}$$

Finally, the Fourier expansion parameters α_{d,Γ_j} are just numbers that give the magnitude of all the terms which enter the Fourier expansion. By taking the C_{Γ_i} and S_{Γ_i} to transform according to the same irreducible representation, the direct product will contain Γ_1 which is invariant under the symmetry operations of the group. These coefficients are often evaluated from experimental data.

Now suppose that we are going to do a Fourier expansion for p-bands. If the spin–orbit interaction is neglected, the p-bands have Γ_{15}^- symmetry. We

ask what symmetry types can we have in the coupling between p-bands – clearly only the symmetries that enter into the direct product

$$\Gamma_{15}^- \otimes \Gamma_{15}^- = \Gamma_1^+ + \Gamma_{12}^+ + \Gamma_{15}^+ + \Gamma_{25}^+. \tag{15.99}$$

We will now indicate the terms which contribute at each neighbor distance to (15.83).

15.7.1 Contributions at $d = 0$

From Table 15.2 we can have only Γ_1^+ symmetry at $d = 0$ for which the basis matrix is

$$\begin{pmatrix} 1\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{pmatrix}, \tag{15.100}$$

and the symmetrical Fourier function is the number 1, so that the net contribution to (15.83) is

$$\alpha_{0,\Gamma_1^+} \begin{pmatrix} 1\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{pmatrix}. \tag{15.101}$$

15.7.2 Contributions at $d = 1$

For Γ_1^+ symmetry the contribution is in analogy to (15.101)

$$\alpha_{1,\Gamma_1^+}\, \mathcal{C}_{\Gamma_1^+}(100) \begin{pmatrix} 1\ 0\ 0 \\ 0\ 1\ 0 \\ 0\ 0\ 1 \end{pmatrix}, \tag{15.102}$$

while for Γ_{12}^+ symmetry, the contribution is

$$\alpha_{1,\Gamma_{12}^+}\, \mathcal{C}_{\Gamma_{12}^+}^{(1)} \begin{pmatrix} \omega + \omega^2 & 0 & 0 \\ 0 & 1 + \omega^2 & 0 \\ 0 & 0 & 1 + \omega \end{pmatrix} + \alpha_{1,\Gamma_{12}^+} \mathcal{C}_{\Gamma_{12}^+}^{(2)} \begin{pmatrix} \omega + \omega^2 & 0 & 0 \\ 0 & 1 + \omega & 0 \\ 0 & 0 & 1 + \omega^2 \end{pmatrix},$$
$$\tag{15.103}$$

where we have used the relation $S_{\Gamma_{12}}^{(1)} = S_x^2 + \omega S_y^2 + \omega^2 S_z^2$ to obtain the appropriate matrices. We also use the relations $1 + \omega + \omega^2 = 0$ for the cube roots of unity to simplify (15.103). We note that both terms in (15.103) have the same expansion parameter α_{1,Γ_{12}^+}.

These are all the contributions for $d = 1$. The symmetry type Γ_{15}^- does not enter into this sum since there are no basis matrices with symmetries Γ_{15}^- for $\mathbf{d} = 1$ (see Table 15.1). This symmetry would however enter into treating the interaction between s and p bands. Group theory thus tells us that we get no off-diagonal terms until we go to second-neighbor distances. This should not be surprising to us since this is exactly what happens in the $\mathbf{k} \cdot \mathbf{p}$ treatment of p bands. In fact, *the Fourier expansion technique contains in it a $\mathbf{k} \cdot \mathbf{p}$ expansion for every point in the Brillouin zone.*

15.7.3 Contributions at $d = 2$

At the second-neighbor distance Table 15.2 yields contributions from Γ_1^+, Γ_{12}^+ and Γ_{25}^+ symmetries. These contributions at $d = 2$ are:

$$\Gamma_1^+ \text{ symmetry } \alpha_{2,\Gamma_1^+} \, \mathcal{C}_{\Gamma_1^+}(110) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad (15.104)$$

$$\Gamma_{12}^+ \text{ symmetry } \alpha_{2,\Gamma_{12}^+} \left[\mathcal{C}_{\Gamma_{12}^+}^{(1)}(110) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -\omega & 0 \\ 0 & 0 & -\omega^2 \end{pmatrix} + c.c. \right] \quad (15.105)$$

$$\Gamma_{25}^+ \text{ symmetry } \alpha_{2,\Gamma_{25}^+} \begin{pmatrix} 0 & \mathcal{C}_{\Gamma_{25}^+}^{(z)}(110) & \mathcal{C}_{\Gamma_{25}^+}^{(y)}(110) \\ \mathcal{C}_{\Gamma_{25}^+}^{(z)}(110) & 0 & \mathcal{C}_{\Gamma_{25}^+}^{(x)}(110) \\ \mathcal{C}_{\Gamma_{25}^+}^{(y)}(110) & \mathcal{C}_{\Gamma_{25}^+}^{(x)}(110) & 0 \end{pmatrix} \quad (15.106)$$

Terms with Γ_{15}^- and Γ_{25}^- symmetries in Table 15.2 do not enter because there are no basis matrices with these symmetries.

15.7.4 Summing Contributions through $d = 2$

Symmetries Γ_1^+ and Γ_{25}^+ contribute and these are written down as above. To get the matrix Hamiltonian we add up contributions from (15.101)–(15.106). There are six parameters α_{d,Γ_j} that enter into the Fourier expansion through second-neighbor terms ($d = 0, 1, 2$). The Γ_1^+ representation at $d = 0$ contributes to the (1,1) position in the secular equation a term in α_{0,Γ_1^+} and at $d = 1$ contributes a term $\alpha_{1,\Gamma_1^+}(\cos ak_x + \cos ak_y + \cos ak_z)$ in which the two coefficients α_{0,Γ_1^+} and α_{1,Γ_1^+} will have different numerical values. The other entries into the (3×3) matrix are found similarly. The resulting (3×3) matrix Hamiltonian is then diagonalized and the eigenvalues are the $E_n(\boldsymbol{k})$ we are looking for. This $E_n(\boldsymbol{k})$ properly expresses the crystal symmetry at all points in the Brillouin zone.

It is instructive to write out this matrix Hamiltonian in detail along the (100), (110) and (111) directions and to verify that all connectivity relations and symmetry requirements are automatically satisfied. It is directly shown that near $\boldsymbol{k} = 0$, the Hamiltonian of (15.83) is of the $\boldsymbol{k} \cdot \boldsymbol{p}$ form previously derived. As stated above, the Fourier expansion approach contains the $\boldsymbol{k} \cdot \boldsymbol{p}$ form for all expansion points $\boldsymbol{k}_0$ in the Brillouin zone.

15.7.5 Other Degenerate Levels

The Fourier expansion can also be applied to the twofold Γ_{12}^+ levels in cubic symmetry arising from d-bands, or to $\Gamma_{12}^\pm$ levels more generally. Of particular

interest is application of the Slater–Koster method [66] to coupled s and p-bands as has been done for silicon and germanium, both of which crystallize in the diamond structure. In the case of coupled s and p bands, the 3×3 expansion in Sect. 15.7 and the s-band expansion are coupled with the Fourier terms from Table 15.2 having symmetries $\Gamma_i \otimes \Gamma_{15}^-$. We give an outline in this section for setting up the secular equation to solve the Fourier expansion for these two interesting cases.

The four 2×2 matrices that are used as basis matrices for Fourier expanding the $\Gamma_{12}^\pm$ levels are implied by $\Gamma_{12}^\pm \otimes \Gamma_{12}^\pm = \Gamma_1^+ + \Gamma_2^+ + \Gamma_{12}^+$:

$$\text{for } \Gamma_1^+ \text{ symmetry } \mathcal{S}_{\Gamma_1^+} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{15.107}$$

$$\text{for } \Gamma_2^+ \text{ symmetry } \mathcal{S}_{\Gamma_2^+} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{15.108}$$

$$\text{for } \Gamma_{12}^+ \text{ symmetry } \mathcal{S}_{\Gamma_{12,1}^+} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \tag{15.109}$$

where the partner of $\mathcal{S}_{\Gamma_{12,1}^+}$ is the Hermitian transpose

$$\mathcal{S}_{\Gamma_{12,2}^+} = \mathcal{S}_{\Gamma_{12,1}^+}^* = \mathcal{S}_{\Gamma_{12,1}^+}^\dagger = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \tag{15.110}$$

Using these matrices we see that

$$\mathcal{S}_{\Gamma_{12,1}^+} \mathcal{S}_{\Gamma_{12,1}^+}^\dagger + \mathcal{S}_{\Gamma_{12,2}^+} \mathcal{S}_{\Gamma_{12,2}^+}^\dagger = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathcal{S}_{\Gamma_1^+}, \tag{15.111}$$

and

$$\mathcal{S}_{\Gamma_{12,1}^+} \mathcal{S}_{\Gamma_{12,1}^+}^\dagger - \mathcal{S}_{\Gamma_{12,2}^+} \mathcal{S}_{\Gamma_{12,2}^+}^\dagger = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \mathcal{S}_{\Gamma_2^+}. \tag{15.112}$$

The dispersion relation of $E(\boldsymbol{k})$ for a band with Γ_{12}^+ symmetry at $\boldsymbol{k} = 0$ can then be Fourier expanded throughout the Brillouin zone in terms of the basis functions in (15.107)–(15.110) as

$$E_{\Gamma_{12}^\pm}(\boldsymbol{k}) = \sum_{\boldsymbol{d}} \alpha_{d,\Gamma_1^+} \mathcal{C}_{\Gamma_1^+}(\boldsymbol{d}) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \sum_{\boldsymbol{d}} \alpha_{d,\Gamma_2^+} \mathcal{C}_{\Gamma_2^+}(\boldsymbol{d}) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
$$+ \sum_{\boldsymbol{d}} \alpha_{d,\Gamma_{12}^+} \mathcal{C}_{\Gamma_{12}^\pm}^{(1)}(\boldsymbol{d}) \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + \sum_{\boldsymbol{d}} \alpha_{d,\Gamma_{12}^+} \mathcal{C}_{\Gamma_{12}^\pm}^{(2)}(\boldsymbol{d}) \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \tag{15.113}$$

where $\mathcal{C}_{\Gamma_{12}^\pm}^{(2)}(\boldsymbol{d}) = \mathcal{C}_{\Gamma_{12}^\pm}^{(1)*}(\boldsymbol{d})$ and the $\mathcal{C}_{\Gamma_i^\pm}(\boldsymbol{d})$ functions are found in Table 15.2.

For the case of interacting s (Γ_1^+) and p (Γ_{15}^-) bands, the interaction terms have $\Gamma_1^+ \otimes \Gamma_{15}^- = \Gamma_{15}^-$ symmetry so the 4×4 expansion matrices must be supplemented by the matrices

$$\mathcal{S}_{\Gamma_{15}^-}^x = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{15.114}$$

and the two partners

$$\mathcal{S}_{\Gamma_{15}^-}^y = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \qquad \mathcal{S}_{\Gamma_{15}^-}^z = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \tag{15.115}$$

The detailed treatment of the Fourier expansion for the eight coupled s and p bonding and antibonding bands in the nonsymmorphic diamond structure has been presented [29] and was used to describe the Si and Ge bands throughout the Brillouin zone. The nonsymmorphic diamond structure requires certain restrictions on the energy bands, as discussed in Sect. 12.5 and in Appendix C. The same basic treatment without the s bands was used to treat the lattice dynamics for the diamond structure [30].

Selected Problems

15.1. Consider the empty lattice $E(\mathbf{k})$ diagram in Fig. 12.1 for an FCC structure, but now also including the electron spin.

(a) Find the symmetry designations and energy for the lowest nonzero double group energy level which arises from the single group L_1 and $L_{2'}$ levels.
(b) Then find the symmetry designations and energy for the next lowest energy level which is derived from the X_1 and $X_{4'}$ levels.
(c) What are the corresponding basis functions for these levels?
(d) What is the difference between these lowest energy levels for the case of the diamond structure in comparison to the symmorphic FCC space group? The character tables for the group of the wave vector for the diamond structure can be found in Appendix C.

15.2. (a) Give more details to show how group theory leads to the form of $E(\Gamma_7^+)$ given by (15.27).
(b) Similarly, give more details to show how the form of $E(\mathbf{k})$ for the four-fold degenerate valence band of Ge is obtained.

(c) The derivation given in Sect. 15.5 was for a symmorphic cubic group. How-
ever, Ge is described by the space group #227 which is nonsymmorphic.
What is the effect of the screw axis in the diamond structure on the forms
of $E(\Gamma_7^+)$ and $E(\Gamma_8^+)$ discussed in (a) and (b)? When would the sticking
together of bands discussed in Sect. 12.5 become important? You may find
the character tables for the diamond structure in Appendix C useful for
this problem.

15.3. Find the form of $E(\boldsymbol{k})$ including the spin–orbit interaction for a non-
degenerate valence band level in a column IV semiconductor (2 atoms/unit
cell) with a simple symmorphic hexagonal structure (space group #191) at
the Γ point and at the K point in the Brillouin zone using $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation
theory. Assume that at $k = 0$, the energy bands have D_{6h} symmetry and that
the nondegenerate band in this problem is derived from the fully symmetric
single group irreducible representation Γ_1.

15.4. Apply the formalism in Sect. 15.6 to find the effective g-factor for a car-
rier pocket at the Γ point for a nondegenerate valence band for a crystal with
hexagonal symmetry (space group #191) as in Problem 15.3.

15.5. (a) Using the procedure in Sect. 15.7, write down the matrices for S_x,
S_y and S_z for angular momentum 3/2. Products of these matrices and
the (4×4) unit matrix form the 16 matrix basis functions which span the
vector space for the (4×4) Slater–Koster secular equation for coupled s
and p bands for a simple cubic lattice. Find these 16 matrices and indicate
the combination of S_x, S_y and S_z used and indicate the symmetry type
of each.
(b) Returning to the Slater–Koster (3×3) secular determinant for a simple
cubic lattice, write the explicit expression for this matrix along a (100)
direction. Show that by doing a Taylor's expansion of the Slater–Koster
Hamiltonian about the X point, the proper $\boldsymbol{k} \cdot \boldsymbol{p}$ Hamiltonian is obtained
at the X point.

15.6. (a) Using the Slater–Koster technique [66], find the form for $E(\boldsymbol{k})$ for
the lowest two levels for a face centered cubic lattice at the X point, the
L point and the K point (see Table C.6).
(b) Using your results in (a), expand $E(\boldsymbol{k})$ about the L-point in a Taylor
expansion and compare your results with those obtained using $\boldsymbol{k} \cdot \boldsymbol{p}$ per-
turbation theory.