6

s–p bonding—a case study in silicon

s–p bonding

In this chapter we shall enlarge the basis set that we assume for each atom to include p electrons. It is necessary to do this in order to understand the cohesion of many elements of the periodic table and their compounds. In Chapter 9 we shall consider bonding caused by interactions between d states. By surveying the elements of the periodic table we see that s–p bonding occurs among the valence electrons of the elements of groups I–VII. The elements of the first three groups have densely packed metallic structures, i.e. f.c.c., h.c.p., and b.c.c. As we go down the elements of group IV from C to Si, Ge, Sn, and Pb, the stable crystal structures change from three-fold coordination in graphite, to four-fold coordination in the diamond cubic structure in Si and Ge, to 12-fold coordination in f.c.c. Pb. In group V (apart from N which forms diatomic molecules) the pnictides take structures based on the stacking of three-fold coordinated buckled layers of atoms. In group VI the chalcogenides take structures based on two-fold coordinated helical chains. The group VII halogens crystallize as diatomic molecules (and thus with a coordination number of 1) which are held together by weak van der Waals interactions. Thus, s–p bonding in the elements gives rise to a wide variety of crystal structures and coordination numbers. Using an atomic basis set of s and p states Cressoni and Pettifor (1991) have shown that it is possible to understand these trends by looking at the third and fourth moments of the local densities of states and the number of electrons per atom. For example, the stability of the metals of the first three groups in close-packed crystal structures follows from the fact that the third moment of the local density of states in these structures is large and negative, which in turn follows from the large number of three-membered rings. Therefore, the local density of states is skewed with a long tail below the centre of gravity (see Problem 19). The electronic energy is thus relatively low when the band is less than half full, i.e. less than four electrons per atom.

In this chapter we shall consider crystalline Si in detail. The reason for choosing Si is that it is very important in semiconductor technology and an understanding of its electronic structure will help to understand its many varied applications in devices. We shall start by looking at interactions

between s and p states on adjacent atoms. These are slightly more compli-cated than interactions between just s states, with the important new ingredient that the interactions are directional. This directionality is the origin of directional bonding, and it may be present in metals as well as insulators. We shall then consider a range of approximations for the band structure of Si in which we consider hybrids of s and p states as the basis states rather than the s and p states themselves. Since hybrids are just linear combinations of the atomic states and the eigenstates of the crystal are just linear combinations of the atomic states why do we bother to go through the intermediate step of constructing hybrids? The answer is that the hybrids give us physical and chemical insight which suggests a range of simplifying approximations. These insights are particularly useful when we come to consider amorphous silicon in Chapter 12. But if we want the band structure of crystalline Si without making these simplifying approximations we do not bother with the hybrids and give the job to a computer. We shall show band structures for silicon computed in this way. We conclude with a discussion of bonding in silicon based on calculations of bond orders and occupancies of atomic states.

s–p bonding between two silicon atoms

The electron configuration in a free silicon atom is $1s^2 2s^2 2p^6 3s^2 3p^2$ and thus there are four valence electrons in the outer shell, two of them occupying an s state and two of them occupying p states. The 3d states are empty, and although they are necessary for a good description of the higher energy antibonding states (in the 'conduction band') we shall not include them in the basis set. Our basis set consists of the 3s state and the three 3p states, $3p_x$, $3p_y$, and $3p_z$, and we shall omit the principal quantum number '3' in our labelling of them and call them $|s\rangle$, $|x\rangle$, $|y\rangle$, and $|z\rangle$, respectively. These states form an orthonormal set. This basis set is the smallest set of atomic states we can use to describe the bonding states of silicon. It is called a 'minimal basis set'.

Consider two Si atoms separated by a distance d. Let the basis states on the first atom be $|s_1\rangle$, $|x_1\rangle$, $|y_1\rangle$, and $|z_1\rangle$ and on the second atom be $|s_2\rangle$, $|x_2\rangle$, $|y_2\rangle$, and $|z_2\rangle$. The overlap between these states in normal crystalline Si is actually quite large, about 0.5. However, using a theory called 'chemical pseudopotential theory' (see Heine (1980) for details) it is possible to transform the basis set into an orthonormal basis set with the overlap now appearing in the on-site Hamiltonian matrix elements $\varepsilon_s = \langle s_1|H|s_1\rangle = \langle s_2|H|s_2\rangle$ and $\varepsilon_p = \langle x_1|H|x_1\rangle = \langle y_1|H|y_1\rangle = \langle z_1|H|z_1\rangle = \langle x_2|H|x_2\rangle = \langle y_2|H|y_2\rangle = \langle z_2|H|z_2\rangle$. Although this has the drawback that ε_s and ε_p vary with the atomic environment it enables us to treat the basis states as an orthonormal set. Furthermore the transformation does not affect the angular character of the basis states so that, for example,
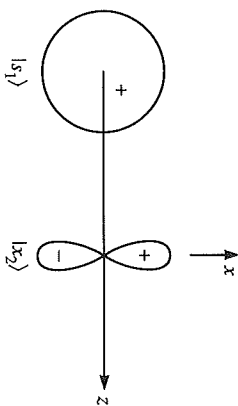
Fig. 6.1 The hopping integral between the s orbital on atom 1 and the p_x orbital on atom 2 is zero by symmetry.

we may continue to treat the $|x_1\rangle$ states as a p_x state. We choose the z-axis to be along the bond.

Many of the hopping integrals between the two atoms are zero. For example, consider the hopping integral $\langle s_1|H|x_2\rangle$, as shown in Fig. 6.1. This is zero because the contribution from the positive lobe of the p orbital is cancelled by an equal and opposite contribution from the negative lobe. The rule for a nonvanishing hopping integral is that the two atomic states at either end of the bond share the same angular momentum component about the bond axis. (See p. 15 if you need reminding of how to find the angular momentum of an orbital about a particular axis.) There are just four nonzero hopping integrals, as shown in Fig. 6.2. Hopping integrals between states with no angular momentum about the bond axis are labelled with a σ (greek 's') and hopping integrals with angular momentum $m = \pm 1$ about the bond axis are labelled with a π (greek 'p'). We now consider these four hopping integrals in turn
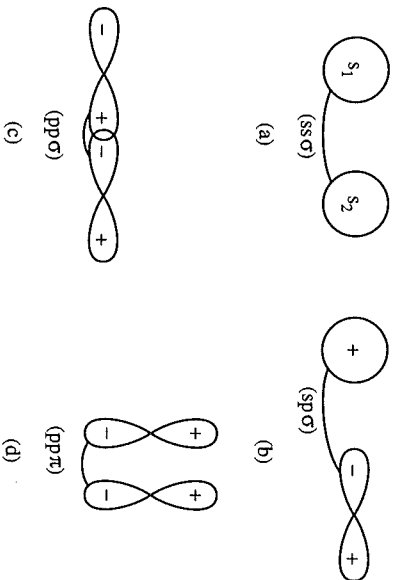

Fig. 6.2 The four fundamental hopping integrals between s and p orbitals: (a) (ssσ), (b) (spσ), (c) (ppσ), and (d) (ppπ).

a. $\langle s_1|H|s_2\rangle$ is the hopping integral we have worked with in earlier chapters. It is called (ssσ), and is shown in Fig. 6.2(a). As we have noted before (ssσ) is a negative quantity because the s orbitals have the same sign.

b. $\langle s_1|H|z_2\rangle$ is called (spσ), and is shown in Fig. 6.2(b). The p_z orbital has zero angular momentum about the z-axis. Note that $\langle z_1|H|s_2\rangle = -(spσ)$. The hopping integral (spσ) is positive because the negative lobe of the $|z_2\rangle$ orbital is nearer to the (positive) $|s_1\rangle$ orbital than the positive lobe.

c. $\langle z_1|H|z_2\rangle$ is called (ppσ), and is shown in Fig. 6.2(c). This hopping integral is a positive quantity because it is dominated by the contribution from the positive lobe of the $|z_1\rangle$ orbital overlapping with the negative lobe of the $|z_2\rangle$ orbital.

d. $\langle x_1|H|x_2\rangle$ is called (ppπ), and is shown in Fig. 6.2(d). It is the same as $\langle y_1|H|y_2\rangle$. The p_x and p_y orbitals have angular momentum ± 1 about the z-axis. The hopping integral (ppπ) is a negative quantity because it is dominated by the overlap between the two positive lobes and the overlap between the two negative lobes.

To summarize, the signs of the hopping integrals are as follows

$$(ssσ) < 0; \quad (spσ) > 0; \quad (ppσ) > 0; \quad (ppπ) < 0. \quad (6.1)$$

We emphasize that the (ppσ) interaction is positive. This means that if we had a linear chain along z with one p_z state on each atom the band structure would be $E(k) = \varepsilon_p + 2(ppσ) \cos ka$, as shown in Fig. 6.3. Because (ppσ) is positive the energy $E(k)$ decreases from $k = 0$ to the Brillouin zone boundaries at $k = \pm \pi/a$. The eigenstate at $k = \pm \pi/a$ is sketched in Fig. 6.4 and it is seen that adjacent lobes on neighbouring atoms now have the same sign so that the energy is lowest.

For a given separation, d, the magnitudes of the four hopping integrals depend on the extent to which the relevant orbitals overlap. For example,
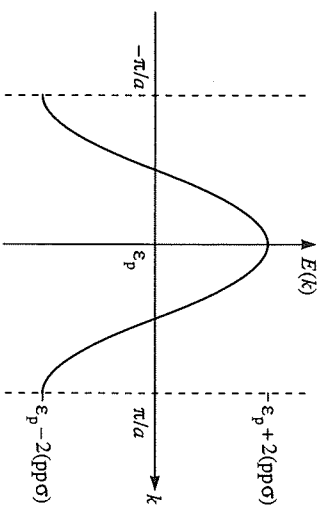

Fig. 6.3 A one-dimensional energy band arising from (ppσ) interactions. Note that the energy is a maximum at $k = 0$ and a minimum at the Brillouin zone boundaries, in contrast to energy bands arising from (ssσ) interactions.
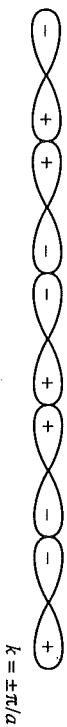
Fig. 6.4 The arrangement of p_z orbitals at $k = \pm \pi/a$, corresponding to the energy minimum in Fig. 6.3.

$$k = \pm \pi/a$$

the two p_z orbitals in the (ppσ) interaction in Fig. 6.2(c) point towards each other and the overlap is very large. Thus we expect $|(\text{pp}\sigma)|$ to be larger than the other three hopping integrals. On the other hand the extent of the overlap in the (ppπ) integral, Fig. 6.2(d), is considerably smaller and therefore we expect $|(\text{pp}\pi)|$ to be correspondingly smaller. For a given separation, d, Harrison (1980) expresses the ratios of the hopping integrals as follows

$$(\text{ss}\sigma):(\text{sp}\sigma):(\text{pp}\sigma):(\text{pp}\pi) = -1.40:1.84:3.24:-0.81. \qquad (6.2)$$

Angular dependence of s–p and p–p hopping integrals

When we assign p states to an atom we must choose a coordinate system to define the directions along which the p_x, p_y, and p_z orbitals lie. As we rotate one atom around another atom, whose centre is the origin of the coordinate system, the (ssσ) hopping integral is obviously invariant, see Fig. 6.5(a). However, the s–p and p–p hopping integrals change.

In Fig. 6.5(b) we show an interaction between an s state at the origin and a p_z orbital on an atom where the bond axis is at an angle θ to the z-axis. We may express the p_z orbital as a linear combination of p orbitals in the rotated coordinate system. Let the rotated coordinate system be denoted by primes (') and let z' be along the rotated bond axis and x' be normal to both the rotated bond axis and the axis of rotation, as shown in Fig. 6.5(b). The p_z can be expressed as a linear combination of orbitals p'_x and p'_z: $p'_z \cos\theta + p'_x \sin\theta$, as shown in Fig. 6.5(c). The s orbital at the origin is the same in the rotated and unrotated coordinate systems. Now the Hamiltonian matrix element between the s orbital at the origin and the p'_z orbital is (spσ), while that between the s orbital and the p'_x orbital is zero. In effect what we have done here is resolve the p_z orbital into components parallel and perpendicular to the bond axis.

Similarly, when we consider the interaction between two p orbitals on neighbouring atoms we resolve both p orbitals parallel and perpendicular to the bond axis. In Fig. 6.5(d) we show the interaction between a p orbital along the unit vector a_1 on one atom and a p orbital along the unit vector a_2 on an adjacent atom. The bond axis is along the unit vector d. The components $(a_1 \cdot d)$ and $(a_2 \cdot d)$ parallel to the bond axis give a contribution $(a_1 \cdot d)(a_2 \cdot d)(\text{pp}\sigma)$ while the components $a_1 - (a_1 \cdot d)d$ and $a_2 - (a_2 \cdot d)d$ normal to the bond axis give a contribution $(a_1 - (a_1 \cdot d)d) \cdot (a_2 - (a_2 \cdot d)d)(\text{pp}\pi)$
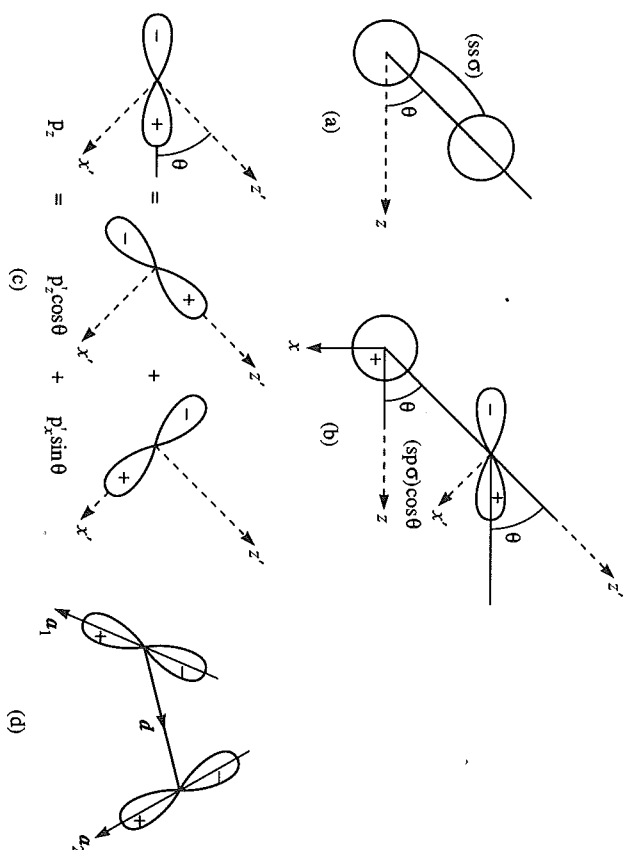
$$\langle a_1 | H | a_2 \rangle = (a_1 \cdot d)(a_2 \cdot d)(\text{pp}\sigma) + (a_1 - (a_1 \cdot d)d) \cdot (a_2 - (a_2 \cdot d)d)(\text{pp}\pi) \qquad (6.3)$$

Fig. 6.5 (a) The interaction (ssσ) is independent of θ. (b) The interaction between an s orbital at the origin and a p_z orbital is (spσ) $\cos\theta$ where θ is the angle between the bond axis and the z-axis. (c) The orbital p_z may be expressed as a linear combination of p'_z and p'_x orbitals in the rotated coordinate system. (d) The interaction between p orbitals pointing along the unit vectors a_1 and a_2 separated by the unit bond vector d.

It is the angular dependence of the s–p and p–p hopping integrals that is the origin of directional bonding in sp-bonded materials.

Sp hybrids

The concept of hybridization was introduced on p. 103 as the construction of new states from linear combinations of atomic states on the same atom. In this section we shall discuss the construction of hybrid states as linear combinations of s and p states on the same atom. The reason for considering such sp hybrids is that they often allow much greater insight into the band structure and stability of a particular crystal structure than working with the atomic states directly. The construction of sp hybrids is based on two principles:

1. Bonding is maximized when the extent to which orbitals on adjacent sites overlap spatially is maximized. In eqn (6.2) we saw that the hopping integral (ppσ) is greater in magnitude than the other hopping integrals because the lobes of the p orbitals point towards each other and thus the

overlap is maximized. The larger the hopping integral the greater the bond energy because the band width is correspondingly larger, and therefore the difference in energy between the most bonding and most antibonding states is greater. It follows that if we construct hybrids which lead to a maximum overlap between the hybrids on neighbouring sites we shall account for most of the bonding energy of the system by considering the interactions between these hybrids and discarding other interactions where the overlap is much smaller. This is called the *principle of maximum overlap*.

2. The hybrid orbitals at a given atomic centre should be orthogonal. This is the *principle of orthogonality*. This principle is not a physical requirement but it exists to ensure a physically transparent breakdown of the *total valence electronic charge* of the molecule or solid into separable contributions, one from each hybrid. This is already the case for the atomic basis states on each atom. The total charge is the integral of the charge density taken over the molecule or solid. If $h_i(r)$ and $h_j(r)$ are two hybrid orbitals on the same atomic state then the total charge associated with $\Psi(r) = c_i h_i(r) + c_j h_j(r)$ is given by

$$\int \Psi^*(r)\Psi(r)\, dr = |c_i|^2 \int h_i(r)^* h_i(r)\, dr + |c_j|^2 \int h_j(r)^* h_j(r)\, dr$$
$$+ c_i^* c_j \int h_i(r)^* h_j(r)\, dr + c_j^* c_i \int h_j(r)^* h_i(r)\, dr. \quad (6.4)$$

If $h_i(r)$ and $h_j(r)$ are orthonormal then the last two integrals are zero and the first two integrals are equal to 1. The total charge is then separated into contributions, $|c_i|^2$ and $|c_j|^2$, from the individual hybrids with no overlap terms to complicate the picture.

We can construct a p orbital on a given atom with any required orientation simply as a normalized linear combination of the available p_x, p_y, and p_z orbitals. For example, suppose we want a p orbital in the plane $z = 0$ at an angle θ to the x-axis, as shown in Fig. 6.6. This is just $p_x \cos \theta + p_y \sin \theta$. Now suppose we have two equivalent hybrid orbitals on the same atom (i.e. they differ only in their orientation)

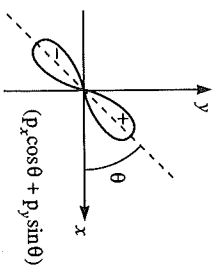$$h_1 = N(s + \lambda p_1), \qquad h_2 = N(s + \lambda p_2) \quad (6.5)$$

Fig. 6.6 A normalized p orbital in the plane $z = 0$ at an angle θ to the x-axis. This is $p_x \cos \theta + p_y \sin \theta$.

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where N is the normalization constant $(1 + \lambda^2)^{-1/2}$ and p_1 and p_2 are normalized p orbitals with arbitrary orientations. The mixing ratio of p orbitals to s orbital in the hybrids h_1 and h_2 is λ^2. The overlap $\langle h_1|h_2 \rangle$ is given by

$$\langle h_1|h_2 \rangle = N^2(1 + \lambda\langle p_1|s \rangle + \lambda\langle s|p_2 \rangle + \lambda^2\langle p_1|p_2 \rangle), \quad (6.6)$$

which we want to be zero to satisfy the principle of orthogonality. The integrals $\langle p_1|s \rangle$ and $\langle s|p_2 \rangle$ are zero by symmetry. To evaluate $\langle p_1|p_2 \rangle$ we may arbitrarily let the orbital p_1 point along the x-axis, and resolve the orbital p_2 into parallel, $p_x \cos \theta_{12}$, and perpendicular, $p_y \sin \theta_{12}$, components. Then

$$\langle p_1|p_2 \rangle = \cos \theta_{12}. \quad (6.7)$$

Inserting this value in eqn (6.6) and requiring that $\langle h_1|h_2 \rangle = 0$ leads to the result that

$$\lambda^2 = -1/\cos \theta_{12}. \quad (6.8)$$

Since λ^2 is positive the angle between the hybrids, θ_{12}, must be greater than 90°. The angle between the hybrids varies with the amount of s–p mixing. With this preparation we can now discuss the three principal types of s–p hybridization involving equivalent hybrids on the same atom.

1. *sp hybrids.* We mix an s orbital with *one* p orbital, leaving the other two p orbitals unchanged, and form *two* equivalent hybrids

$$\left.\begin{aligned} h_1 &= \frac{1}{2^{1/2}}(s + p_x) \\ h_2 &= \frac{1}{2^{1/2}}(s - p_x). \end{aligned}\right\} \quad (6.9)$$

In the case of the hybrid h_1 the positive lobe of the p_x orbital adds to the positive s orbital to produce an enlarged positive lobe along $+x$ and, similarly, a smaller negative lobe along $-x$ results from the partial cancellation between the negative lobe of the p_x orbital and the s orbital. The opposite holds for h_2. See Fig. 6.7(a). The s orbital content of these hybrids is 1/2.

2. *sp² hybrids.* We mix an s orbital with *two* p orbitals, leaving the third p orbital unchanged, and form *three* equivalent hybrids. The s content of each hybrid is 1/3. Therefore $1/(1 + \lambda^2) = 1/3$ and hence $\lambda = 2^{1/2}$. From eqn (6.8) we have $\cos \theta = -1/\lambda^2 = -1/2$ and therefore the three hybrids are at 120° to each other in a plane. If the hybrids lie in the x-y plane then

$$\left.\begin{aligned} h_1 &= (s + 2^{1/2} p_x)/3^{1/2} \\ h_2 &= \left(s - \frac{p_x}{2^{1/2}} + \frac{3^{1/2}}{2^{1/2}} p_y\right)/3^{1/2} \\ h_3 &= \left(s - \frac{p_x}{2^{1/2}} - \frac{3^{1/2}}{2^{1/2}} p_y\right)/3^{1/2}. \end{aligned}\right\} \quad (6.10)$$
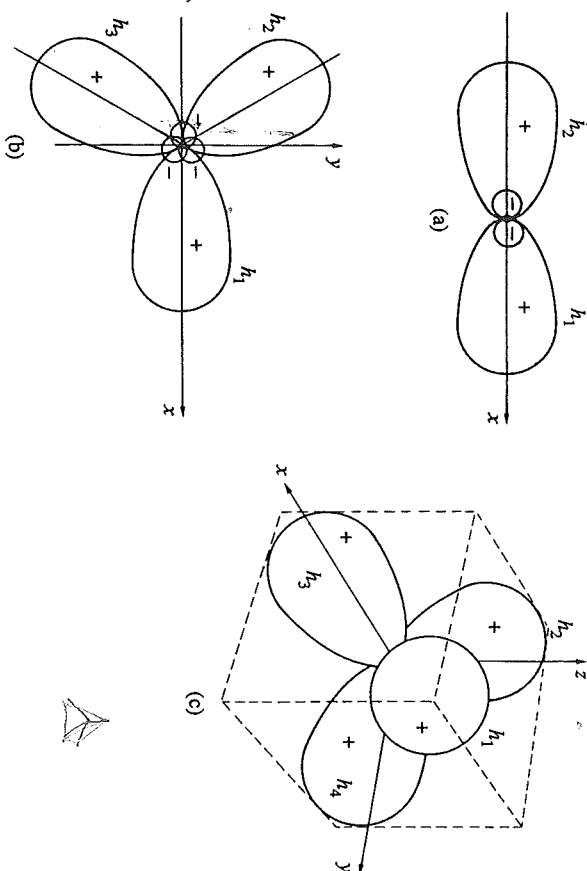
(a)

(b)

(c)

Fig. 6.7 Principal types of s–p hybridization: (a) sp hybrids pointing in opposite directions along the same axis, (b) sp² hybrids at 120° to each other in a plane, (c) sp³ hybrids at cos(−1/3) ≈ 109° to each other, pointing towards the corners of a tetrahedron. From McWeeny (1979).

These three hybrids are shown in Fig. 6.7(b). The unaffected p_z orbital remains normal to the x–y plane and is orthogonal to all three hybrids.

3. *sp³ hybrids*. We mix an s orbital with all *three* p orbitals and form *four* equivalent hybrids. The s content of each hybrid is now 1/4. Therefore $1/(1 + \lambda^2) = 1/4$ and hence $\lambda^2 = 3$. It follows from eqn (6.8) that the hybrids are at $\cos^{-1}(-1/3) \approx 109°$ to each other in a tetrahedral arrangement. The hybrids are

$$\left.\begin{aligned}
h_1 &= \tfrac{1}{2}(s + p_x + p_y + p_z)\\
h_2 &= \tfrac{1}{2}(s + p_x - p_y - p_z)\\
h_3 &= \tfrac{1}{2}(s - p_x + p_y - p_z)\\
h_4 &= \tfrac{1}{2}(s - p_x - p_y + p_z)
\end{aligned}\right\} . \qquad (6.11)$$

These four hybrids are sketched in Fig. 6.7(c).

The significance of the angular disposition of the hybrids is that it favours bonding geometries which maximize the overlap of hybrids on neighbouring atoms. For example, sp² hybridization favours planar structures in which each atom is at the vertex of three bonds at 120° to each other forming a

Angular dependence of s–p and p–p hopping integrals

hexagonal network. This is the structure in the basal plane of graphite for example. On the other hand, sp³ hybridization favours tetrahedral bonding, such as we find in the diamond cubic, wurtzite, and sphalerite structures. We shall discuss this point in more detail in Chapter 10, where we shall also consider hybridization involving d states.

It is very important to distinguish between the s and p content of hybrids and the numbers of electrons occupying s and p states at an atomic site. This distinction is often not made and can lead to a great deal of confusion. The s and p content of a hybrid is defined simply by the particular linear combination of s and p orbitals from which the hybrid is constructed. Thus, the s content of sp, sp², and sp³ hybrids is 1/2, 1/3, and 1/4 respectively. However, this *does not* mean that 1/2, 1/3, or 1/4 of the electrons associated with an atom that has formed sp, sp², or sp³ hybrids respectively are occupying an s state. The occupation of s and p states is determined by solving the Schrödinger equation and filling the lowest eigenstates until the required number of electrons per atom is attained. The construction of hybrids does not imply that the Schrödinger equation has been solved—it is merely a linear transformation of the atomic basis.

The energy of a hybrid state

$$|h\rangle = \frac{|s\rangle + \lambda|p\rangle}{(1 + \lambda^2)^{1/2}} \qquad (6.12)$$

is given by

$$\varepsilon_h = \langle h|H|h\rangle = \frac{\varepsilon_s + \lambda^2 \varepsilon_p}{1 + \lambda^2} \qquad (6.13)$$

and is therefore a weighted average of the on-site energies ε_s and ε_p. For example, the energy of an sp³ hybrid is $(\varepsilon_s + 3\varepsilon_p)/4$. If we occupy four sp³ hybrids at a site with one electron each the on-site energy will be $\varepsilon_s + 3\varepsilon_p$. On the other hand in the free atom of Si there are two electrons in the s state and two electrons in p states. The energy associated with that is $2\varepsilon_s + 2\varepsilon_p$. Therefore, in order to populate four sp³ hybrids with one electron each we must provide a *promotion energy* $\varepsilon_p - \varepsilon_s$ to promote an electron from an s state into a p state. The cost of the promotion energy is offset by the energy gain associated with the enhanced bonding energy provided by having electrons occupying strongly overlapping sp³ hybrids. It is the balance between the promotion energy and the bonding energy that determines the occupations of the s and p states at each atomic site. If the promotion energy is very large then the energy penalty of occupying sp³ hybrids is too large and we say that hybridization takes place to only a small extent. On the other hand if the promotion energy is small then there is relatively little cost associated with occupying hybridized orbitals and we say that the orbitals are strongly hybridized. A high degree of hybridization leads to strong, directional bonds.