

Molecular Systems

Electronic States of Molecules and Directed Valence

This chapter considers the electronic states of molecules, the formation of molecular bonds and the simplifications that are introduced through the use of group theory. We organize our discussion in this chapter in terms of a general discussion of molecular energy levels; the general concept of equivalence; the concept of directed valence bonding; the application of the directed valence bond concept to various molecules, including bond strengths in directed valence bonds; and finally σ and π bonding.

7.1 Introduction

The energy levels of molecules are basically more complicated than those of atoms because there are several centers of positive charge which serve to attract a given electron, and because these centers are themselves in relative motion. Since the nuclei are very massive relative to the electrons, we can utilize the Born–Oppenheimer approximation which separates out the electronic motion from the nuclear or ionic motion. In this approximation, the electrons move in a potential generated by the equilibrium positions of the nuclei. We are thus left with three kinds of molecular motion, the electronic motion which is most energetic, the vibrational motion which is less energetic, and the rotational motion which is least energetic. If these motions are independent they can be decoupled (but this is not always the case). In this chapter we consider the electronic energy levels of some typical molecules considering the Born–Oppenheimer approximation, and in Chap. 8 we consider the vibrational and rotational levels of molecules.

The effective one-electron potential $V(\mathbf{r})$ for an electron in a molecule must be invariant under all symmetry operations which leave the molecule invariant. If we did not exploit the symmetry explicitly through group theory, we would then solve the Schrödinger equation to find the energy eigenvalues

and the corresponding eigenfunctions of the molecule taking into account all the valence electrons for all the atoms in the molecule. This would require solution of a large secular equation of the form:

$$|\langle \psi_i | \mathcal{H} | \psi_j \rangle - E \delta_{ij}| = 0. \quad (7.1)$$

Utilization of symmetry (as for example using group theoretical methods) allows us to choose our basis functions wisely, so that many of the matrix elements in the secular equation vanish through symmetry arguments and the secular equation breaks up into block diagonal form. Thus by using symmetry, we have to solve much smaller secular equations, and only those states which transform according to the same irreducible representations will couple to each other according to group theory arguments. Group theory is used in yet another way for solving the electronic problem. Many molecules contain more than one *equivalent* atom. Symmetry is used to simplify the secular equation by forming linear combinations of atomic orbitals that transform according to the irreducible representations of the group of Schrödinger's equation. Using such linear combinations of atomic orbitals, the secular equation can more readily be brought into block diagonal form. In this chapter we show how to form linear combinations of atomic orbitals that transform as irreducible representations of the appropriate symmetry group, and we will show how the *equivalence* concept is used in forming these linear combinations.

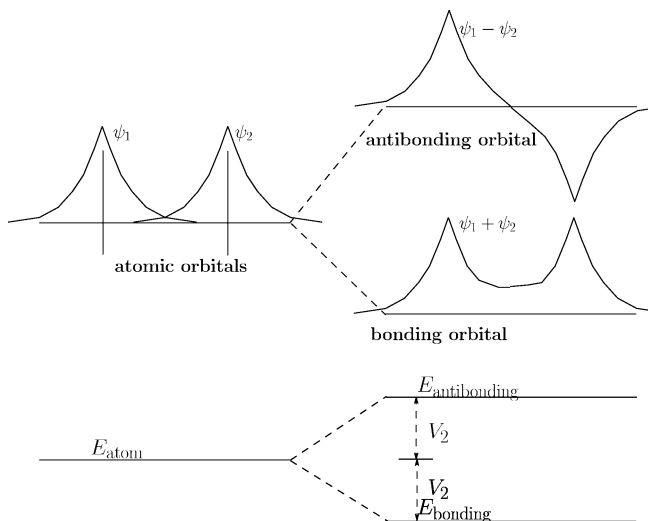


Fig. 7.1. Electronic wave functions for a diatomic molecule. On the *left* the free atomic orbitals are shown for two similar atoms on different sites. On the *right*, the formation of bonding and antibonding states is indicated. To find the energy splitting between the bonding and antibonding states (indicated schematically), the solution of Schrödinger's equation is necessary

In the free atom, the electronic orbitals display the symmetry of a $(1/r)$ potential, and therefore the free-atom orbitals are eigenfunctions which transform according to irreducible representations of the *full rotation group*. In a molecule or in a solid, the electrons tend to spend more time between the ion cores in the bonding state and the increased probability of finding the electron between two nuclei (see Fig. 7.1) is called a chemical bond. These bonds display the known symmetry of the molecule (or the solid). For this reason, the wavefunctions for the electrons in the molecule (or the solid) transform as irreducible representations of the appropriate symmetry group, which in general will be of lower symmetry than the full rotation group. From elementary considerations, we know that molecular bonds arise from the *exchange interaction* whose magnitude depends on the extent of the overlap of the charge clouds between neighboring atoms. Because these orbitals concentrate the charge along preferred directions, the bonding is called *directed valence bonding*, and these directed valence bonds exhibit the symmetry of the molecule (or of the solid). We use the directed valence bonding concepts to identify the kinds of symmetries needed to make the desired orbitals.

Symmetry enters the electronic problem of molecules in yet another way, namely through the Pauli principle and the effect of the permutation of the electrons on the electron wavefunctions. This topic is discussed in Chap. 17 for many-electron states.

7.2 General Concept of Equivalence

Equivalent bonding orbitals for a molecule are required to transform into one another under all the symmetry operations of the point group with no more change than a possible change of phase. The equivalence transformation, which takes one *equivalent function* into another, generates a representation for the point group called the equivalence representation. The equivalence representation will in general be reducible. We denote the representation that generates the transformation between equivalent atom sites by $\Gamma^{\text{a.s.}}$ and its characters by $\chi^{\text{a.s.}}$, where a.s. \equiv atomic sites. In this section we present the equivalence concept, show how to find the irreducible representations contained in the equivalence representation and then give a few examples.

The matrices $D^{\text{a.s.}}(R)_{ji}$ for the equivalence representation $\Gamma^{\text{a.s.}}$ are found from the general definition in (4.1)

$$\hat{P}_R \psi_i = \sum_j D^{\text{a.s.}}(R)_{ji} \psi_j \quad (7.2)$$

or written in matrix form from (4.5)

$$D^{\text{a.s.}}(R)_{ji} = \langle \psi_j | \hat{P}_R | \psi_i \rangle. \quad (7.3)$$

Explicitly, the $D^{\text{a.s.}}(R)_{ji}$ matrices are found by entering unity into the j, i position in the matrix if $\hat{P}(R)$ takes site i into an equivalent site j and zero

otherwise. From this argument we readily see that the characters for the equivalence representation can be found by counting the number of points which are left unaffected by the symmetry operation, because it is only those points that will give a contribution to the matrix on diagonal positions and will thus contribute to the character for that symmetry operator. To obtain the characters for the equivalence representation $\chi^{\text{a.s.}}$, we take a representative member of each class and consider the number of points that are left unchanged under action of the representative symmetry operator.

The representation $\Gamma^{\text{a.s.}}$ is in general reducible. The pertinent symmetry types for the problem are then found by decomposing $\Gamma^{\text{a.s.}}$ into its irreducible representations. To illustrate this concept, consider the example of three identical atoms at the corners of an equilateral triangle as for example the three hydrogen atoms in the NH_3 molecule. The symmetry group is C_{3v} , and the character table for group C_{3v} is given in Table A.10. Referring to Fig. 4.2, where the three equivalent sites are labeled by (a, b, c) we obtain $D^{\text{a.s.}}(R)$ for some typical symmetry operators:

$$D^{\text{(a.s.)}}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (7.4)$$

$$D^{\text{(a.s.)}}(C_3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad (7.5)$$

$$D^{\text{(a.s.)}}(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad (7.6)$$

in which the rows and columns correspond to the sequence of atoms (a, b, c) and the symmetry operations selected are E , D , and A following Fig. 4.2. From these matrices we can compute the characters for each of the classes for the $\Gamma^{\text{a.s.}}$ representation in group $C_{3v}(3m)$. The character $\chi^{\text{a.s.}}(R)$ is always the number of sites that are left unchanged by the operation \hat{P}_R so that for each of the three classes $\chi^{\text{a.s.}}(E) = 3$, $\chi^{\text{a.s.}}(C_3) = 0$, and $\chi^{\text{a.s.}}(\sigma_v) = 1$. These results are summarized in Table 7.1. From Table A.10 we see immediately that $\chi^{\text{a.s.}} = \chi^{\Gamma_1} + \chi^{\Gamma_2}$ for every class, since $\Gamma^{\text{a.s.}} = \Gamma_1 + \Gamma_2$, in agreement with results obtained in Sect. 4.6. The orbitals on the nitrogen atom are then chosen so that they bond to the atomic orbitals of the three hydrogen atoms, as discussed in Sect. 7.5.1.

Table 7.1. $\chi^{\text{a.s.}}$ for the group C_{3v}

	E	$2C_3$	$3\sigma_v$	
$\chi^{\text{a.s.}}$	3	0	1	$\Rightarrow \Gamma_1 + \Gamma_2 = A_1 + E$

7.3 Directed Valence Bonding

For diatomic molecules we know immediately, without recourse to group theory, how to make a bonding orbital out of the free atomic orbitals. In this case, we need simply to take the symmetrical combination $(\psi_a + \psi_b)$ to pile up charge in the directed valence bond (see Fig. 7.1).

For the case of the homopolar diatomic molecule, we thus form an occupied bonding state $(\psi_a + \psi_b)$ and an unoccupied antibonding state of higher energy $(\psi_a - \psi_b)$. Suppose that this diatomic molecule only has two symmetry operations, the identity E and the mirror plane reflections σ_h or m . These are the two symmetry elements of the group C_{1h} (see Table 7.2). (In Sect. 7.4 we will consider the semi-infinite groups $D_{\infty h}$ and $C_{\infty v}$ which give the full symmetry of typical homogeneous and heterogeneous diatomic molecules.) Taking ψ_a as an arbitrary function, and noting that $\hat{P}_m\psi_a = \psi_b$, for the mirror plane operations, the projection operator for one-dimensional irreducible representations (see (4.38)) can be written as

$$\hat{P}^{(\Gamma_n)} = \frac{\ell_n}{h} \sum_R \chi^{(\Gamma_n)}(R)^* \hat{P}_R. \quad (7.7)$$

The basic formula (7.7) for finding linear combinations of atomic orbitals when acting on the wave function ψ_a yields (see Table 7.2):

$$\begin{aligned} \hat{P}^{(\Gamma_1)}\psi_a &= \frac{1}{2}[(1)\hat{P}_E\psi_a + (1)\hat{P}_m\psi_a] = \frac{1}{2}[\psi_a + \psi_b] \quad \text{bonding} \\ \hat{P}^{(\Gamma'_1)}\psi_a &= \frac{1}{2}[(1)\hat{P}_E\psi_a + (-1)\hat{P}_m\psi_a] = \frac{1}{2}[\psi_a - \psi_b] \quad \text{antibonding} \end{aligned} \quad (7.8)$$

for the bonding and antibonding states, so that the bonding orbitals will have Γ_1 symmetry and the antibonding orbitals will have Γ'_1 symmetry. Since there are only two initial wave functions ψ_a and ψ_b , the combinations in (7.8) are all the independent linear combinations that can be formed, and except for a normalization factor of $\sqrt{2}$, these functions are proper bonding and antibonding orbitals.

Our discussion of the use of projection operators (see Sects. 4.5 and 4.6) illustrates how linear combinations of atomic orbitals could be found such that the resulting orbitals transform according to irreducible representations of the

Table 7.2. Character table for the group C_{1h}

$C_{1h}(m)$		E	σ_h
x^2, y^2, z^2, xy	R_z, x, y	A' (Γ_1)	1 1
xz, yz	R_x, R_y, z	A'' (Γ'_1)	1 -1
		$\chi^{\text{a.s.}}$	2 $0 \Rightarrow \Gamma_1 + \Gamma'_1 \equiv A' + A''$

point group. Here we used the C_{1h} group that has only two one-dimensional irreducible representations, and we found the two related electronic states. However, most of the symmetry groups have many irreducible representations with different dimensionalities. To find the right symmetries for the electronic states, one would have to apply the projectors to all of them. This process is largely simplified by using the *directed valence representation* $\Gamma_{D.V.}$, which introduces two kinds of simplifications:

- (a) $\Gamma_{D.V.}$ gives all the *irreducible representations* for the molecular orbitals before the molecular orbitals are found explicitly. This saves time because the projection operator $\hat{P}^{(\Gamma_n)}$ need not then be applied to irrelevant representations, but only to those irreducible representations contained in $\Gamma_{D.V.}$.
- (b) If we are only interested in finding the number of distinct eigenvalues and their degeneracies, this follows directly from the characters $\chi_{D.V.}$ of the representation $\Gamma_{D.V.}$. To obtain this kind of information, it is not necessary to solve Schrödinger's equation or even to find the linear combination of molecular orbitals as in Sect. 4.6.

The directed valence representation $\Gamma_{D.V.}$ uses the equivalence transformation to determine the characters of $\Gamma^{a.s.}$. In Sect. 7.4 we discuss the directed valence representation for diatomic molecules and in Sect. 7.5, we extend the concept to multiatomic molecules with more complicated symmetries.

7.4 Diatomic Molecules

In this section we introduce the semi-infinite groups $D_{\infty h}$ and $C_{\infty v}$ and we illustrate the use of the equivalence transformation to form symmetrized linear combinations of atomic orbitals. We then develop the directed valence representation for the simplest case of diatomic molecules. Both homonuclear molecules (like H_2) and heteronuclear molecules (like CO) are considered.

7.4.1 Homonuclear Diatomic Molecules

The simplest molecules are the homonuclear diatomic molecules. For homonuclear molecules (such as H_2) the appropriate symmetry group is $D_{\infty h}$ and the character table for $D_{\infty h}$ is shown in Table 7.3 (see also Table A.34). We now summarize the main points about this character table. C_ϕ denotes an arbitrary rotation about the linear molecular axis (z -axis) and C'_2 is a twofold axis \perp to C_ϕ . In the group $D_{\infty h}$, each of the operations E , C_ϕ , and C'_2 is also combined with inversion. We further note that σ_v is a mirror plane through the molecular axis, so that $\sigma_v = iC'_2$. The subscripts g and u refer to the evenness and oddness of functions under the inversion operation, while the superscripts $+$ and $-$ refer to the evenness and oddness of functions under reflection in a mirror plane. The characters for σ_v in the $D_{\infty h}$ group are found

Table 7.3. Character table for the semi-infinite group $D_{\infty h} (\infty/mn)$

$D_{\infty h} (\infty/mn)$			E	$2C_\phi$	C'_2	i	$2iC_\phi$	iC'_2
$x^2 + y^2, z^2$		$A_{1g}(\Sigma_g^+)$	1	1	1	1	1	1
		$A_{1u}(\Sigma_u^-)$	1	1	1	-1	-1	-1
	R_z	$A_{2g}(\Sigma_g^-)$	1	1	-1	1	1	-1
		$A_{2u}(\Sigma_u^+)$	1	1	-1	-1	-1	1
(xz, yz)	(R_x, R_y)	$E_{1g}(\Pi_g)$	2	$2 \cos \phi$	0	2	$2 \cos \phi$	0
		$E_{1u}(\Pi_u)$	2	$2 \cos \phi$	0	-2	$-2 \cos \phi$	0
$(x^2 - y^2, xy)$	(x, y)	$E_{2g}(\Delta_g)$	2	$2 \cos 2\phi$	0	2	$2 \cos 2\phi$	0
		$E_{2u}(\Delta_u)$	2	$2 \cos 2\phi$	0	-2	$-2 \cos 2\phi$	0
		\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots

Table 7.4. $\chi^{\text{a.s.}}$ for the group $D_{\infty h}$

	E	$2C_\phi$	$C'_2 = i\sigma_v$	i	$2iC_\phi$	$iC'_2 = \sigma_v$	
$\chi^{\text{a.s.}}$	2	2	0	0	0	2	$\Rightarrow A_{1g} + A_{2u}$ $\Rightarrow \Sigma_g^+ + \Sigma_u^+$

most conveniently by considering the effect of the operation σ_v on the basis functions which correspond to a given irreducible representation. For example, the symmetry operation σ_v changes (x, y) into $(-x, y)$ yielding a transformation matrix

$$D(\sigma_v) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad (7.9)$$

and the corresponding character for σ_v is $\chi(\sigma_v) = 0$ which from the character table is associated with the E_{1u} irreducible representation.

For a homogeneous diatomic molecule (such as H_2) use of the equivalence transformation on the two sites of the homogeneous diatomic molecule, as shown in Table 7.4 yields the characters for the equivalence transformation. When forming a linear combination of atomic orbitals (LCAOs) from s functions on the two equivalent atomic sites (see Sect. 7.3), the normalized bonding orbital $\psi_S = (\psi_a + \psi_b)/\sqrt{2}$ is symmetric and has Σ_g^+ or A_{1g} symmetry and the normalized antibonding orbital $\psi_A = (\psi_a - \psi_b)/\sqrt{2}$ is antisymmetric and has Σ_u^+ or A_{2u} symmetry. These two LCAOs correspond to directed valence orbitals because they result in a rearrangement of the charge on the individual atomic sites. The bonding LCAO is a directed valence orbital corresponding to a pile up of charge between the two atoms to produce a lower energy state. By using the equivalence concept in Sect. 7.2, we have constructed a linear combination of atomic orbitals which transform as irreducible representations of the group of Schrödinger's equation. Thus ψ_S and ψ_A form such basis functions and the Hamiltonian for the homogeneous diatomic molecule will not couple states ψ_S and ψ_A to each other. This follows from the argument that the product $(\mathcal{H}\psi_S)$ transforms as A_{1g} , since \mathcal{H} transforms as A_{1g} and so does

ψ_S . Also ψ_A transforms as A_{2u} . The selection rules thus tell us that the matrix element $(\psi_A|\mathcal{H}|\psi_S)$ must vanish. Thus to bring the secular equation into block diagonal form, we have to make a unitary transformation on the atomic basis functions (ψ_a, ψ_b) to bring them into the form (ψ_S, ψ_A) :

$$\begin{pmatrix} \psi_S \\ \psi_A \end{pmatrix} = \underbrace{U}_{\text{unitary matrix}} \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}. \quad (7.10)$$

Applying the unitary transformation $U\mathcal{H}U^\dagger$ to the original matrix (written in terms of the original ψ_a and ψ_b) will bring the secular matrix into block diagonal form. Bringing the secular equation into block diagonal form greatly simplifies the solution of the secular equation. In this simple case, the equivalence transformation and group theoretical arguments took a coupled (2×2) secular equation and decomposed it into two decoupled (1×1) secular equations. The bonding or directed valence state will be the state of lowest energy.

As an example of homonuclear diatomic molecule we discuss the hydrogen molecule H_2 . In this case we can put each electron in a $(\sigma_g 1s)$ orbital and construct bonding and antibonding orbitals. For H_2 , the bonding orbital σ_g is occupied with electrons having opposite spin states and the antibonding σ_u orbital is unoccupied. The $(\sigma_g 1s)$ state is symmetric under both inversion i and reflection σ_v . Hence the symmetry for each of the separated atoms is Σ_g^+ so that the symmetry for the molecule is $\Sigma_g^+ \otimes \Sigma_g^+ = \Sigma_g^+$. We write this state as $^1\Sigma_g^+$ where the superscript 1 denotes a singlet ($s = 0$) with a total spin degeneracy of $(2s + 1) = 1$. By making spatial bonding orbitals that are symmetric under exchange of the electrons, the Pauli principle tells us that the spin state for the directed valence bonding orbital must be antisymmetric:

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)], \quad (7.11)$$

where (α, β) give the spin state (up, down), and 1,2 number the electrons (group theory aspects for spin are treated in Chaps. 14 and 15). In Problem 7.1 we extend the concepts of Sect. 7.4.1 to the hypothetical He_2 molecule and the H_2^- ion.

7.4.2 Heterogeneous Diatomic Molecules

We next illustrate the case of a linear heterogeneous diatomic molecule with the CO molecule. Since the electronic wave functions on each site are not equivalent (see Fig. 7.2), there is no inversion symmetry. The appropriate symmetry group for CO is $C_{\infty v}$ which has the Character Table 7.5 (see also Table A.33). The symmetry operations of $C_{\infty v}$ have already been covered when discussing the symmetry operations of $D_{\infty h}$ (see Sect. 7.4.1). Using the equivalence operation on the carbon and oxygen atoms in CO, we have the result $\Gamma^{a.s.} = 2A_1$ (see also $\chi^{a.s.}(E, 2C_\phi, \sigma_v)$ for H_2 with $D_{\infty h}$ symmetry in

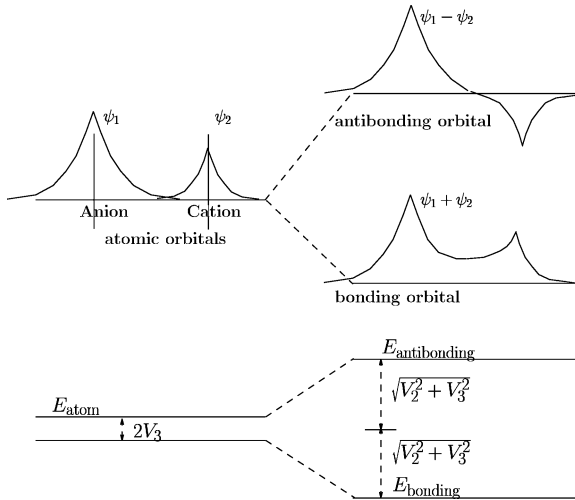


Fig. 7.2. The wave functions for a heteropolar diatomic molecule and their formation of bonding and antibonding states. If $2V_3$ is the energy separation between the anion and cation for large interatomic distance, the splitting resulting from an interaction energy $2V_2$ is shown

Table 7.5. Character Table for Group $C_{\infty v}$

$C_{\infty v} (\infty m)$			E	$2C_\phi$	σ_v
$(x^2 + y^2, z^2)$	z	$A_1(\Sigma^+)$	1	1	1
	R_z	$A_2(\Sigma^-)$	1	1	-1
(xz, yz)	$\left. \begin{matrix} (x, y) \\ (R_x, R_y) \end{matrix} \right\}$	$E_1(\Pi)$	2	$2 \cos \phi$	0
		$E_2(\Delta)$	2	$2 \cos 2\phi$	0
$(x^2 - y^2, xy)$		\vdots	\vdots	\vdots	\vdots

Sect. 7.4.1). Now the C atom in CO has the electronic configuration $2s^2 2p^2$ while O has the configuration $2s^2 2p^4$. We will then make bonding and antibonding molecular orbitals from $2s, 2p_z,$ and $2p_{x,y}$ atomic orbitals. From the basis functions given in the character table for group $C_{\infty v}$ we see that the irreducible representations for these atomic orbitals are

$$\begin{aligned} 2s &\rightarrow A_1 \\ 2p_z &\rightarrow A_1 \\ 2p_{x,y} &\rightarrow E_1 . \end{aligned}$$

To find the direct products using the character table for $C_{\infty v}$ we note that

$$\cos^2 \phi = \left(\frac{1}{2}\right) (1 + \cos 2\phi),$$

which allows us to evaluate the direct product $E_1 \otimes E_1$ to obtain

$$E_1 \otimes E_1 = A_1 + A_2 + E_2 .$$

state is symmetric, the spin state is antisymmetric by the Pauli principle (a singlet spin configuration). However, an antisymmetric spatial state (such as the A_2 state) is accompanied by a symmetric spin state (a triplet spin configuration) and therefore would have a molecular orbital notation ${}^3\Sigma^-$ (see character table for $D_{\infty h}$ in Sect. 7.4.1). The secular equation implied by the interactions in Fig. 7.2 (see caption) is

$$\begin{vmatrix} V_3 - E & V_2 \\ V_2 & -V_3 - E \end{vmatrix} = 0, \quad (7.12)$$

whose solution gives the splitting between the bonding and antibonding states of heteropolar diatomic molecules

$$E = \pm \sqrt{V_2^2 + V_3^2} \quad (7.13)$$

as shown in Fig. 7.2.

Referring to Fig. 7.3 the number of electrons which form bonds in CO are four from carbon and six from oxygen to give a total of ten electrons. We note from Fig. 7.3 that the occupied levels include the 2s A_1 bonding

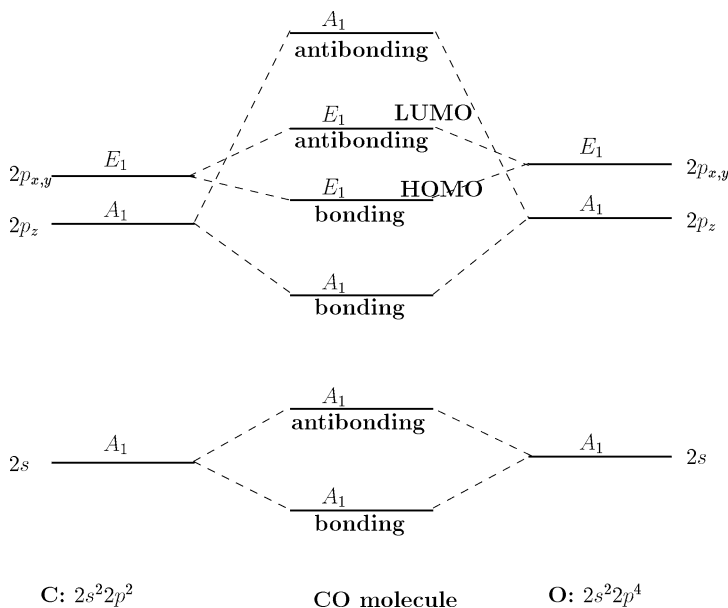


Fig. 7.3. Bonding and antibonding molecular levels for the CO molecule

and antibonding orbitals and the 2p A_1 and E_1 bonding orbitals. The 2p A_1 and E_1 antibonding orbitals will remain unoccupied. Since the p_z orbitals are directed along the molecular axis, the bonding–antibonding interaction (and level splitting) will be largest for the p_z orbitals, as shown in Fig. 7.3.

The symmetry of the s-function orbitals for a diatomic molecule are found directly from the transformation properties of $\chi^{\text{a.s.}}$. However, since p electrons have angular momentum $l = 1$, they transform like the vector (basis functions x, y, z), so that for p-function orbitals we must take the direct product of the transformation of the equivalent sites with the transformation properties of a vector at each site written as $\chi^{\text{a.s.}} \otimes \chi^{\text{vector}}$. For the case of the heterogeneous CO molecule with $C_{\infty v}$ symmetry $\chi^{\text{a.s.}} = 2A_1 = 2\Sigma^+$ and $\chi^{\text{vector}} = A_1 + E_1 = \Sigma^+ + \Pi$. With regard to the p_z orbital, both the bonding and antibonding orbitals (see Fig. 7.3) have A_1 or Σ^+ symmetry. For the bonding p_z orbital, there is a maximum of the charge accumulation between the C and O atoms which results in the large separation in energy between the bonding and antibonding orbitals. For the (p_x, p_y) orbitals, the bonding and antibonding levels both have E_1 or Π symmetry. The character table for group $C_{\infty v}$ (Table 7.5) relates the notation for the irreducible representations

$\mathcal{H}_{A_1, A_1}^{C, C}(ss)$	$\mathcal{H}_{A_1, A_1}^{C, C}(sz)$	\mathcal{O}	$\mathcal{H}_{A_1, A_1}^{C, O}(ss)$	$\mathcal{H}_{A_1, A_1}^{C, O}(sz)$	\mathcal{O}
$\mathcal{H}_{A_1, A_1}^{C, C}(zs)$	$\mathcal{H}_{A_1, A_1}^{C, C}(zz)$	\mathcal{O}	$\mathcal{H}_{A_1, A_1}^{C, O}(zs)$	$\mathcal{H}_{A_1, A_1}^{C, O}(zz)$	\mathcal{O}
\mathcal{O}	\mathcal{O}	$\mathcal{H}_{E_1, E_1}^{C, C}(xy, xy)$	\mathcal{O}	\mathcal{O}	$\mathcal{H}_{E_1, E_1}^{C, O}(xy, xy)$
$\mathcal{H}_{A_1, A_1}^{C, O}(ss)$	$\mathcal{H}_{A_1, A_1}^{C, O}(sz)$	\mathcal{O}	$\mathcal{H}_{A_1, A_1}^{O, O}(ss)$	$\mathcal{H}_{A_1, A_1}^{O, O}(sz)$	\mathcal{O}
$\mathcal{H}_{A_1, A_1}^{C, O}(zs)$	$\mathcal{H}_{A_1, A_1}^{C, O}(zz)$	\mathcal{O}	$\mathcal{H}_{A_1, A_1}^{O, O}(zs)$	$\mathcal{H}_{A_1, A_1}^{O, O}(zz)$	\mathcal{O}
\mathcal{O}	\mathcal{O}	$\mathcal{H}_{E_1, E_1}^{C, O}(xy, xy)$	\mathcal{O}	\mathcal{O}	$\mathcal{H}_{E_1, E_1}^{O, O}(xy, xy)$

Fig. 7.4. Schematic diagram of the block structure of the matrix Hamiltonian for molecular orbitals for the CO molecule arising from the symmetry of the orbitals

with angular momenta states. The directed valence bonding is along the z -axis and involves only bonding levels.

The symmetry types of each of the molecular orbitals determines the form of the secular equation, as shown in Fig. 7.4. The minimum basis for describing the bonding states is eight, including the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals for each atom, since the $1s$ level is too low in energy to be of importance. The terms on the diagonals represent the self energy of the electronic orbitals, and the terms in the off-diagonal positions are the coupling terms. Only electronic states belonging to the same irreducible representation can couple, and the block structure of the matrix Hamiltonian of the secular equation then assumes the form shown in Fig. 7.4.

7.5 Electronic Orbitals for Multiatomic Molecules

In this section, we consider the electronic levels for several multiatomic molecules, each selected for particular pedagogic purposes.

7.5.1 The NH_3 Molecule

To bond to the H atoms, the N atom must make orbitals directed to the three hydrogens (see Fig. 7.5). We refer to this as the directed valence bonds of the nitrogen atoms. The directed valence bonds $\Gamma_{\text{D.V.}}$ for the nitrogen must therefore exhibit the same symmetry as does the LCAO (linear combination of atomic orbitals) for the hydrogens which transform as $\Gamma^{\text{a.s.}}$. We have already seen in Sect. 4.6 how to construct LCAOs for the three equivalent atoms at the

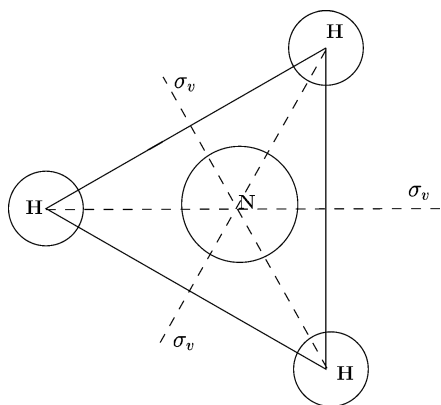


Fig. 7.5. Schematic diagram of the symmetry operations for an NH_3 molecule (group C_{3v}) where the three hydrogen atoms are at the corners of an equilateral triangle and the N atom is along the normal through the midpoint of this triangle but not coplanar with the hydrogens

corners of an equilateral triangle (e.g., the hydrogen atoms in NH_3). In this case we use group C_{3v} (see Fig. 7.5) and obtain the irreducible representations $A_1 + E$ for the linear combination of atomic orbitals for the three hydrogen atoms discussed in Sects. 4.6 and 7.2. To bond to the nitrogen atom, it is necessary for the directed valence representation $\Gamma_{\text{D.V.}}$ for the nitrogen atom to have the same symmetries as $\Gamma^{\text{a.s.}}$, so that $\Gamma_{\text{D.V.}} = \Gamma_1 + \Gamma_2 = A_1 + E$.

We now explore the orbitals that can be made at the nitrogen site. Nitrogen has the electronic configuration $1s^2 2s^2 2p^3$. The $1s$ and $2s$ electrons will lie low in energy, and bonding orbitals to the hydrogens will be made with the three $2p$ electrons [40]. The p electrons transform like the vectors (x, y, z) and the character table for C_{3v} shows that the p_x and p_y functions will transform as $E(\Gamma_2)$ and the p_z as $A_1(\Gamma_1)$. The nitrogen atom thus bonds to the linear combination of atomic orbitals of the three hydrogen atoms with the same symmetries $A_1 + E$ that comes from $\Gamma^{\text{a.s.}}$. Thus the nitrogen has three p electrons for bonding and the H_3 likewise has three electrons for bonding. The A_1 bonding states will hold two electrons and the E bonding state will hold four electrons. These bonding states can then accommodate all six valence electrons, with three coming from the hydrogen atoms and three from the nitrogen atom. All the antibonding states will be unoccupied. See reference [40] for a detailed analysis of the molecular orbitals of NH_3 and other molecules discussed in this chapter from a group theory standpoint.

7.5.2 The CH_4 Molecule

In this example we consider generally how carbon atoms can form tetrahedral bonds. One example of such tetrahedral bonds for carbon is in the diamond structure. The tetrahedral carbon bonds in diamond have the same point group symmetry as the directed valence bond of carbon in the CH_4 methane molecule. The methane molecule forms a regular tetrahedron (see Fig. 3.3), where the carbon atom is at the center of the tetrahedron, and the four H atoms are at the tetrahedral vertices; this structure has T_d point symmetry (see Table A.32).

The bonding of the CH_4 molecule is produced by a directed valence bond from the carbon atom to the four hydrogen atoms at the corners of a tetrahedron. The ground state of the carbon atom is $1s^2 2s^2 2p^2$. We will see below that the carbon atom must be promoted to a $1s^2 2s^1 2p^3$ configuration to make the directed valence bonds. The four equivalent hydrogen atoms form LCAOs to make the bonds from the four points labeled a, b, c, d in Fig. 3.3 (where the four hydrogens are located) to the center of the tetrahedron where the carbon atom is located.

Let us start with the symmetry of the linear combination of atomic orbitals of the four hydrogen atoms at the corner of a regular tetrahedron which has T_d symmetry (see Table A.32 and Table 7.6). The 24 symmetry operations of T_d are described in Sect. 3.11 and in Fig. 3.3. If we now consider each of the symmetry operations the group T_d acting on the points a, b, c, d (see Fig. 3.3)

Table 7.6. Character Table for group $T_d(43m)$

$T_d(43m)$		E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	
(R_x, R_y, R_z) (x, y, z)	A_1	1	1	1	1	1	
	A_2	1	1	1	-1	-1	
	E	2	-1	2	0	0	
	T_1	3	0	-1	-1	1	
	T_2	3	0	-1	1	-1	
$\Gamma^{\text{a.s.}}$		4	1	0	2	0	$\Rightarrow A_1 + T_2$

where the four hydrogens are located, we obtain the equivalence representation for the hydrogen orbitals $\Gamma^{\text{a.s.}}$. Some typical matrices for the symmetry operations of T_d in the equivalence representation $\Gamma^{\text{a.s.}}$ for the four hydrogen atoms are

$$D^{\text{a.s.}}(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (7.14)$$

$$D^{\text{a.s.}}(C_3) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad (7.15)$$

etc., where the rows and columns relate to the array $(a \ b \ c \ d)$ of Fig. 3.3. To find the characters for each class we use the equivalence transformation principle to find how many sites go into themselves under the symmetry operations of each class of T_d . The results for the characters of the equivalence representation $\Gamma^{\text{a.s.}}$ formed from transforming the atom sites (a.s.) according to the symmetry operations of group T_d are summarized just under the character table for T_d (see Table 7.6). Using the decomposition theorem (3.20) we then find the irreducible representations of T_d that are contained in $\Gamma^{\text{a.s.}}$ (see Table 7.6). Thus $\Gamma^{\text{a.s.}}$ gives the symmetries for the LCAOs for the equivalence transformation showing that these orbitals are made of an s-function transforming as A_1 and a p-function transforming as T_2 .

The linear combination of the atomic orbitals of the four hydrogen atoms transforming as A_1 is clearly the symmetric sum of the atomic orbitals.

$$\psi(A_1) = \frac{1}{2}(\psi_a + \psi_b + \psi_c + \psi_d) \quad (7.16)$$

and the three degenerate partners of the T_2 representation are

Table 7.7. Characters and symmetries for the angular momentum states in T_d symmetry

	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$		
$\chi_{\ell=0}$	1	1	1	1	1	A_1	$A_1 \rightarrow s$ state
$\chi_{\ell=1}$	3	0	-1	1	-1	T_2	$T_2 \rightarrow p$ state
$\chi_{\ell=2}$	5	-1	1	1	-1	$E + T_2$	

$$\begin{aligned}\psi_1(T_2) &= \frac{1}{2}(\psi_a + \psi_b - \psi_c - \psi_d) \\ \psi_2(T_2) &= \frac{1}{2}(\psi_a - \psi_b + \psi_c - \psi_d) \\ \psi_3(T_2) &= \frac{1}{2}(\psi_a - \psi_b - \psi_c + \psi_d).\end{aligned}\tag{7.17}$$

The T_2 orbitals must be orthogonal to the A_1 orbitals and to each other and must transform as irreducible representation T_2 under symmetry operations of the group (see Problem 7.6).

The symmetries for the directed valence orbitals for the carbon atom can be related conveniently to angular momentum states using the full rotation group and the characters for rotations and inversions (see (5.11) and (5.13)). To make a directed valence bond from the central carbon atom to the four hydrogen atoms at locations a, b, c, d in Fig. 3.3, the carbon atom must have wave functions with the same symmetries for its four valence electrons as the four LCAOs for the hydrogen atoms (see (7.16) and (7.17)). This tells us that the electronic states for the carbon directed valence state must have a $2s^1 2p^3$ configuration and $A_1 + T_2$ symmetries for the carbon valence electrons. The symmetries for the angular momentum states are found from

$$\begin{aligned}\chi(\alpha) &= \frac{\sin[(\ell + \frac{1}{2})\alpha]}{\sin(\alpha/2)} \quad \text{for pure rotations} \\ \chi(i\alpha) &= (-1)^\ell \frac{\sin[(\ell + \frac{1}{2})\alpha]}{\sin(\alpha/2)} \quad \text{for improper rotations.}\end{aligned}$$

We thus obtain the characters for the angular momentum states in the T_d group and list them in Table 7.7, where we have made use of the fact that

$$\begin{cases} \sigma_d = iC'_2 \\ S_4 = iC_4, \end{cases}$$

in which the C'_2 is a (110) twofold axis. We note that the C'_2 operation together with the inversion operation take one of the a, b, c, d vertices in Fig. 3.3 into a vertex occupied by a hydrogen atom. The joint operation $iC_4 = S_4$ transforms the a, b, c, d vertices another themselves.

Table 7.8. Relation between angular momentum states and basis functions for group T_d

		basis functions
$\ell = 0$	s -state	1
$\ell = 1$	p -state	(x, y, z)
$\ell = 2$	d -state	$\underbrace{(xy, yz, zx)}_{T_2}, \underbrace{(x^2 - y^2, 3z^2 - r^2)}_E$

The results in Table 7.7 could equally well have been obtained by looking at the character table for group T_d (see Table A.32) and making the identifications as displayed in Table 7.8, and by associating the various basis functions of the angular momentum states with the appropriate irreducible representations for the T_d group.

If we now apply this discussion to the CH_4 molecule we see that the directed valence orbitals for the carbon contain one $2s$ (A_1) state and three $2p$ (T_2) states to bond to the four hydrogen atoms. These A_1 and T_2 states can accommodate all eight valence electrons for the CH_4 molecule. A linear combination of s and p_x, p_y, p_z functions which transforms at A_1 and T_2 for the directed valence orbitals of the carbon atom along the four diagonal directions of the cube (see Fig. 3.3) is

$$\begin{aligned}
 \Psi(1, 1, 1) &= \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}) \\
 \Psi(1, -1, -1) &= \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) \\
 \Psi(-1, 1, -1) &= \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z}) \\
 \Psi(-1, -1, 1) &= \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}). \quad (7.18)
 \end{aligned}$$

The linear combination with all “+” signs $\Psi(1, 1, 1)$ transforms as the A_1 irreducible representation. The other three functions with two “+” and two “-” signs transform as the three partners of the T_2 irreducible representation as can be seen by applying the symmetry operations of group T_d to these directed valence wave functions. Thus (7.18) gives a set of orthonormal wave functions for the four electrons of the carbon atom.

Bonding states are made between the A_1 carbon orbital and the A_1 orbital of the four hydrogens and between the corresponding T_2 carbon and hydrogen orbitals following the same type of block diagonal form as is shown in Fig. 7.4 for the CO molecule. Although the carbon electrons must be promoted to the excited sp^3 configuration to satisfy the bonding orbitals in the molecule, the attractive bonding energy due to the CH_4 bonds more than

compensates for the electronic excitation to form the sp^3 excited state for the carbon atom. It is of interest that the orbitals in (7.18) also represent normalized functions for tetrahedral bonding orbitals in common semiconductors.

Finally we consider the bond strengths along a directed valence orbital to show that the bond strength is a maximum along the directed valence orbital. To illustrate bond strengths, consider the $(1, 1, 1)$ directed valence bond $\frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z})$ with A_1 symmetry for CH_4 (see (7.18)). We express each of the terms of this equation in terms of spherical harmonics, using polar coordinates. For angular momentum $\ell = 0$ and $\ell = 1$ the spherical harmonics yield

$$\begin{aligned}\psi_s &= 1, & \psi_{p_y} &= \sqrt{3} \sin \theta \sin \phi, \\ \psi_{p_x} &= \sqrt{3} \sin \theta \cos \phi, & \psi_{p_z} &= \sqrt{3} \cos \theta.\end{aligned}\quad (7.19)$$

We can thus write the angular dependence of the directed valence bond along (111) as

$$\Psi(1, 1, 1)|_{(\theta, \phi)} = \frac{f(r)}{2} \left[1 + \sqrt{3} \sin \theta (\cos \phi + \sin \phi) + \sqrt{3} \cos \theta \right]. \quad (7.20)$$

Differentiation with respect to θ and ϕ determines the values of θ and ϕ which give a maximum bond strength. It is found that this wavefunction is a maximum along the (111) direction, but not along another one of the diagonal axes (see Problem 7.6).

7.5.3 The Hypothetical SH_6 Molecule

As another illustrative example, consider a hypothetical molecule SH_6 where the six identical H atoms are arranged on a regular hexagon (e.g., the benzene ring has this basic symmetry) and the sulfur is at the center. For the hydrogens, we have six distinct atomic orbitals. To simplify the secular equation we use group theory to make appropriate linear combinations of atomic orbitals:

$$\begin{pmatrix} \psi_a \\ \psi_b \\ \psi_c \\ \psi_d \\ \psi_e \\ \psi_f \end{pmatrix}, \quad (7.21)$$

so that the transformed linear combinations are proper basis functions for irreducible representations of the point symmetry group D_{6h} which applies to this problem. We see that the largest dimension for an irreducible representation in D_{6h} is $n = 2$. We show below that the use of symmetry will result in

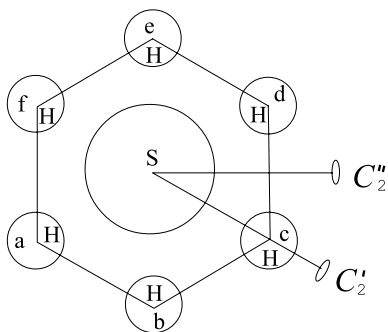


Fig. 7.6. Geometry of the hypothetical SH_6 planar molecule with six hydrogens at the corners of a hexagon and the sulfur atom at the center (D_{6h} symmetry)

a secular equation with block diagonal form, having blocks with dimensions no greater than (2×2) .

To find the proper linear combination of atomic orbitals, we find the characters for the equivalence transformation $\Gamma^{\text{a.s.}}(R)$ for the six hydrogen atoms in D_{6h} symmetry (see Fig. 7.6) by considering how many atom sites go into each other under the various symmetry operations of the group. The results for $\Gamma^{\text{a.s.}}$ for each class are given at the bottom of the Character Table 7.9 for D_6 where $D_{6h} = D_6 \otimes i$. We now set up the appropriate linear combinations of atomic orbitals for the six hydrogen atoms. This can be done most easily by utilizing the correspondence of this problem with the sixth roots of unity. We will denote the sixth roots of unity by $1, \Omega, \omega, -1, \omega^2, \Omega^5$, where $\omega = e^{2\pi i/3}$ and $\Omega = e^{2\pi i/6}$. For simplicity we will denote the atomic orbitals at a site α by ψ_α and use the abbreviated notation α . In terms of the site notation (a, b, c, d, e, f), the sixth orthogonal linear combinations formed by taking the sixth roots of unity are

$$\begin{aligned}
 \psi_1 & a + b + c + d + e + f \quad \text{transforms as } \Gamma_1, \\
 \psi_2 & a + \Omega b + \omega c - d + \omega^2 e + \Omega^5 f, \\
 \psi_3 & a + \omega b + \omega^2 c + d + \omega e + \omega^2 f, \\
 \psi_4 & a - b + c - d + e - f \quad \text{transforms as } \Gamma_3, \\
 \psi_5 & a + \omega^2 b + \omega c + d + \omega^2 e + \omega f, \\
 \psi_6 & a + \Omega^5 b + \omega^2 c - d + \omega e + \Omega f.
 \end{aligned}$$

To obtain the symmetries of the functions ψ_1, \dots, ψ_6 we examine $\hat{P}_R \psi_i$ where \hat{P}_R is a symmetry operation in group D_6 . Clearly ψ_2 and ψ_6 are partners since $\psi_2^* = \psi_6$, and similarly ψ_3 and ψ_5 are partners since $\psi_3^* = \psi_5$, so these provide good candidates for representing the Γ_5 and Γ_6 irreducible

Table 7.9. Character table for point group D_6

D_6		E	C_2	$2C_3$	$2C_6$	$3C'_2$	$3C''_2$	
$x^2 + y^2, z^2$	$\Gamma_1(A_1)$	1	1	1	1	1	1	
z	$\Gamma_2(A_2)$	1	1	1	1	-1	-1	
	$\Gamma_3(B_1)$	1	-1	1	-1	1	-1	
	$\Gamma_4(B_2)$	1	-1	1	-1	-1	1	
$(x^2 - y^2, xy)$	$\Gamma_5(E_2)$	2	2	-1	-1	0	0	
$(xz, yz), (x, y)$	$\Gamma_6(E_1)$	2	-2	-1	1	0	0	
	$\Gamma^{\text{a.s.}}$	6	0	0	0	2	0	$\Rightarrow \Gamma_1 + \Gamma_3 + \Gamma_5 + \Gamma_6$

$\mathcal{H}_{\Gamma_1, \Gamma_1}$	\mathcal{O}	\mathcal{O}	\mathcal{O}
\mathcal{O}	$\mathcal{H}_{\Gamma_3, \Gamma_3}$	\mathcal{O}	\mathcal{O}
\mathcal{O}	\mathcal{O}	$\mathcal{H}_{\Gamma_5, \Gamma_5}$	\mathcal{O}
\mathcal{O}	\mathcal{O}	\mathcal{O}	$\mathcal{H}_{\Gamma_6, \Gamma_6}$

Fig. 7.7. Schematic of the secular equation for six hydrogen orbitals at the corners of a regular hexagon. Outside of the block structure, all entries are zeros. The Γ_1 and Γ_3 are one-dimensional representations and the Γ_5 and Γ_6 are two-dimensional representations

representations. By inspection, ψ_1 is invariant under all the symmetry operations of the group and thus ψ_1 transforms as Γ_1 . As for ψ_4 , application of $C_6(\psi_4) = -\psi_4$, and $C_3\psi_4 = \psi_4$, etc. verifies that ψ_4 transforms as Γ_3 . Inspection of the character table shows differences between Γ_5 and Γ_6 under the operations in classes C_2 and $2C_6$. It is clear that the basis formed by ψ_2 and ψ_6 transforms under C_6 as

$$C_6(\psi_2, \psi_6) = \begin{pmatrix} \Omega^5 & 0 \\ 0 & \Omega \end{pmatrix} \begin{pmatrix} \psi_2 \\ \psi_6 \end{pmatrix} \quad (7.22)$$

since $a \rightarrow b, b \rightarrow c, c \rightarrow d$, etc. Thus the trace of the matrix is

$$\Omega + \Omega^5 = e^{2\pi i/6} + e^{-2\pi i/6} = 2 \cos \frac{2\pi}{6} = 1, \quad (7.23)$$

which is the proper character for Γ_6 . As a check, we see that $C_2(\psi_2, \psi_6)$ results in a trace $= \Omega^3 + \Omega^{15} = \Omega^3 + \Omega^3 = 2 \cos \pi = -2$, and this also checks. Similarly we see that the transformation matrix for

$$C_6(\psi_3, \psi_5) = D^{\Gamma_5}(C_6) \begin{pmatrix} \psi_3 \\ \psi_5 \end{pmatrix}$$

again sends $a \rightarrow b, b \rightarrow c, c \rightarrow d$, etc. and yields a trace of $\omega + \omega^2 = -1$ while $C_2(\psi_3, \psi_5)$ yields a trace of $\omega^3 + \omega^6 = 2$. The unitary transformation U which takes the original basis a, b, c, d, e, f into a basis that exhibits D_6 symmetry

$$U \begin{pmatrix} a \\ b \\ c \\ d \\ e \\ f \end{pmatrix} = \begin{pmatrix} \psi_1 \\ \psi_4 \\ \psi_2 \\ \psi_6 \\ \psi_3 \\ \psi_5 \end{pmatrix} \quad (7.24)$$

brings the one-electron molecular secular matrix into the block diagonal form shown in Fig. 7.7, and zeros in all the off-diagonal positions coupling these blocks.

Just as we used some intuition to write down the appropriate basis functions, we can use physical arguments to suggest the ordering of the energy levels. The fully symmetric state yields a maximum charge density *between* the atom sites and therefore results in maximum bonding. On the other hand, the totally antisymmetric state yields a minimum bonding and therefore should be the highest energy state. The doubly degenerate levels have an intermediate amount of wave function overlap.

The six symmetric orbitals that we make can be populated by 12 electrons. But we only have six electrons at our disposal and these will go into the lowest energy states. Figure 7.8 shows a schematic view of the pile up of charge for

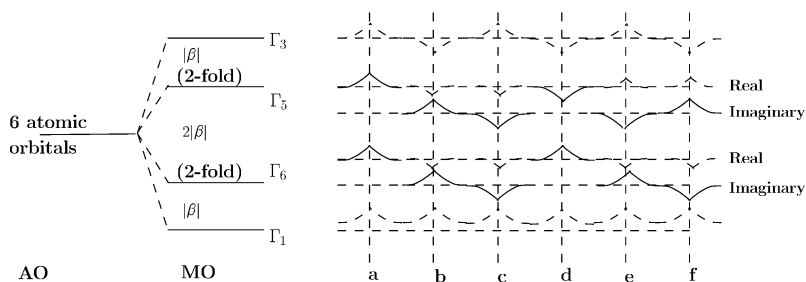


Fig. 7.8. Energies of the LCAOs formed by six hydrogen atoms at the corners of a hexagon. Also shown is a schematic summary of the wave functions for the various orbitals

the states of various symmetry. The Γ_1 state has the strongest bonding and the Γ_6 state has the next strongest binding, and therefore we can expect the six electrons to populate these states preferentially. For this reason, the molecular bonding produces a lower energy state than the free atoms.

Let us now consider making directed valence orbitals from the S atom at the center of the hexagon to the six hydrogens. An isolated S atom is in a $1s^2 2s^2 2p^6 3s^2 3p^4$ configuration. Thus to bond to the hydrogen atoms in the six LCAOs, given by ψ_1, \dots, ψ_6 , would require all the bonding states and all the antibonding states to be occupied. This implies that the sulfur atom would have to be promoted to a high energy state to bond in a planar configuration (see Problem 7.3). The sulfur atom in the ground state configuration would only bond to the Γ_1 and Γ_6 blocks of the secular equation for SH_6 in Fig. 7.7.

7.5.4 The Octahedral SF_6 Molecule

We next give an example of SF_6 with a molecular configuration that involves octahedral bonding (see Fig. 7.9). The octahedral configuration is very common in solid state physics.

If we now use the symmetry operations of O_h (Table A.30) we get the characters for the equivalence representation $\Gamma^{\text{a.s.}}$ for the six atoms which sit at the corners of the octahedron (see Fig. 7.9 and Table 7.10). The decomposition of the reducible representation $\Gamma^{\text{a.s.}}$ for the six equivalent fluorine atoms gives

$$\Gamma^{\text{a.s.}} = A_{1g} + E_g + T_{1u}. \quad (7.25)$$

If we (hypothetically) were to put s-functions on each of the six fluorine sites, then $\Gamma^{\text{a.s.}}$ given by (7.25) would be appropriate to make the linear combination of atomic orbitals for the six fluorine atoms. However, if we put

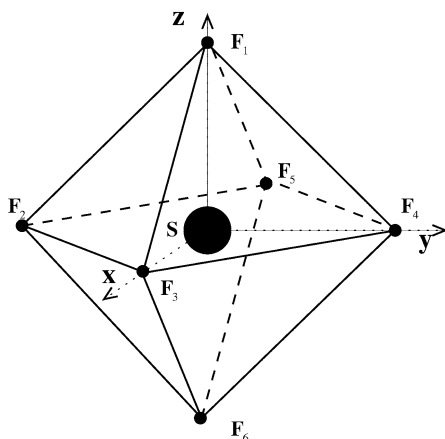


Fig. 7.9. Schematic diagram of the SF_6 molecule which exhibits octahedral bonding

p-functions on each fluorine site then the appropriate equivalence transformation for p-electrons would be $\Gamma^{\text{a.s.}} \otimes \Gamma^{(T_{1u})}$, where we note that for O_h symmetry the vector transforms as T_{1u} . This general concept of taking the direct product of the transformation of the atom sites with the symmetry of the orbital on each site is frequently used in applications of the equivalence principle.

Let us now look at the orbitals for electrons on the sulfur site to make the directed valence bonds as shown in Fig. 7.9. Bonding orbitals are found by setting the directed valence representation equal to the symmetries found from the equivalence transformation for the fluorine electrons bonding to the sulfur. For simplicity let us assume that $\Gamma^{\text{a.s.}} = \Gamma_{\text{D.V.}}$ to fully exploit the bonding of the cation and anions. We then need to identify the irreducible representations contained in $\chi_{\text{D.V.}}$ with angular momentum states. The characters for the angular momentum states in O_h symmetry are then found from

$$\chi(\alpha) = \frac{\sin(\ell + \frac{1}{2})\alpha}{\sin(\alpha/2)} \quad (7.26)$$

and using the character table for O_h (see Table A.30). The results for the angular momentum states are tabulated in Table 7.11. As an example, let us suppose for simplicity that we have s functions on each of the six fluorine sites. Then to produce $\Gamma_{\text{D.V.}} = A_{1g} + E_g + T_{1u}$ as in (7.25) we can use an s state $\ell = 0$ for the A_{1g} symmetry, a p state ($\ell = 1$) for the T_{1u} symmetry, and a d state ($\ell = 2$) for the E_g symmetry in (7.25). Thus sp^3d^2 orbitals are required for the directed valence of the sulfur ion, which ordinarily has an atomic ground state configuration $3s^23p^4$. Thus to make the necessary bonding, we must promote the S atom to an excited state, namely to a $3s^13p^33d^2$ state. This type of excitation is called *configuration mixing*. In Problem 7.2, a more realistic version of the octahedral SF_6 molecule is considered, with p -function wave functions for each of the six fluorine sites.

7.6 σ - and π -Bonds

We now discuss the difference between σ - and π -bonds which are defined in the diagram in Fig. 7.10. The situation which we have considered until now is bonding by s -functions or by p -functions in the direction of the bond and this is denoted by σ -bonding, as shown in Fig. 7.10. Because of their asymmetry, the

Table 7.10. Characters for the 6 atoms sitting at the corners of an octahedron, e.g., for the F sites of the SF_6 molecule

	E	$8C_3$	$3C_2$	$6C'_2$	$6C_4$	i	$8iC_3$	$3iC_2$	$6iC'_2$	$6iC_4$
$\Gamma^{\text{a.s.}}$	6	0	2	0	2	0	0	4	2	0

Table 7.11. Characters for angular momentum states and their irreducible representations in O_h symmetry

	E	$8C_3$	$3C_2$	$6C'_2$	$6C_4$	i	$8iC_3$	$3iC_2$	$6iC'_2$	$6iC_4$	
$\ell = 0$	1	1	1	1	1	1	1	1	1	1	$\Rightarrow A_{1g}$
$\ell = 1$	3	0	-1	-1	1	-3	0	1	1	-1	$\Rightarrow T_{1u}$
$\ell = 2$	5	-1	1	1	-1	5	-1	1	1	-1	$\Rightarrow E_g + T_{2g}$
$\ell = 3$	7	1	-1	-1	-1	-7	-1	1	1	1	$\Rightarrow A_{2u} + T_{1u} + T_{2u}$
$\ell = 4$	9	0	1	1	1	-9	0	-1	-1	-1	$\Rightarrow A_{1g} + E_g + T_{1g} + T_{2g}$

σ bonds with p -functions ($V_{pp\sigma}$ in Fig. 7.10) play an important role in making directed valence bonding orbitals. We can also obtain some degree of bonding by directing our p -functions \perp to the bond direction, as also shown in Fig. 7.10, and this is called π -bonding. We note that there are two equivalent mutually perpendicular directions that are involved in π -bonding. From considerations of overlapping wavefunctions, we would expect π -bonding to be much weaker than σ -bonding.

Just as group theory tells us which LCAOs are needed to form σ -bonds, group theory also provides the corresponding information about the linear combination of atomic orbitals that form π -bonds. We now describe in this section a procedure for finding the symmetry for both σ -bonds and π -bonds.

Let us first review the situation for the σ -bonds. To find a σ -bond, we consider the atomic wave function at each equivalent site to be degenerate with the corresponding wave functions on the other sites and we find the transformation matrices that transform equivalent sites into one another according to the symmetry operations of the group. To find out if an entry in this matrix is 1 or 0 we ask the question whether or not a site goes into itself under a particular symmetry operation. If it goes into itself we produce a 1 on the diagonal, otherwise a 0. Therefore by asking how many sites go into themselves, we obtain the character for each symmetry operation. This is the procedure we have used throughout the chapter to find $\Gamma^{\text{a.s.}}$ which denotes the equivalence transformation. This gives the symmetry designations for $V_{ss\sigma}$ bonds.

To find the characters for a π -bond, we have to consider how many vectors normal to the bond direction remain invariant under the symmetry operations of the group. The simplest way to obtain the characters for the σ -bonds and π -bonds is to consider the transformation as the product of two operations: the transformation of one equivalent site into another, followed by the transformation of the vector on a site. Thus we write

$$\begin{aligned} \Gamma^{\text{(a.s.)}} \otimes \Gamma_{\text{general vector}} &= \Gamma^{\text{(a.s.)}} \otimes \Gamma_{\text{vector} \perp \text{ to } \sigma\text{-bonds}} \\ &+ \Gamma^{\text{(a.s.)}} \otimes \Gamma_{\text{vector} \parallel \text{ to } \sigma\text{-bonds}}. \end{aligned} \quad (7.27)$$

But

$$\Gamma_{\text{D.V. } \sigma\text{-bonds}} \equiv \Gamma^{\text{(a.s.)}} \otimes \Gamma_{\text{(vector } \parallel \text{ to } \sigma\text{-bonds)}}.$$

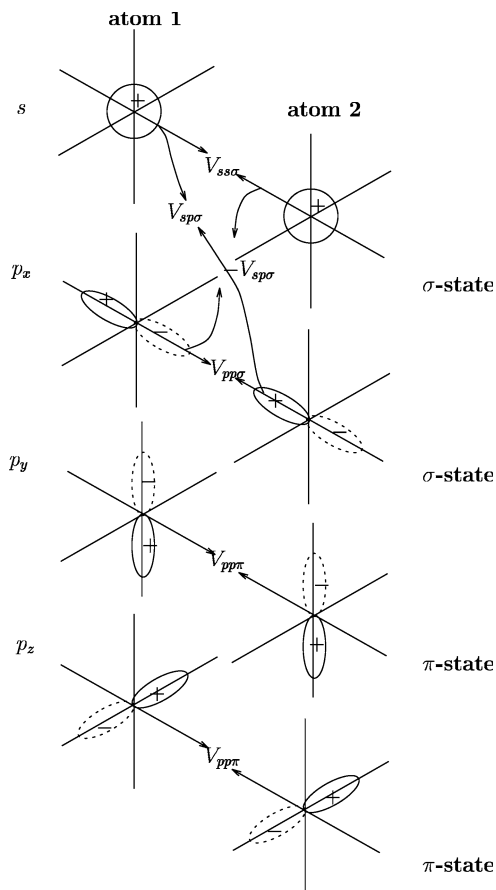


Fig. 7.10. Schematic diagram of: σ -bonding ($V_{ss\sigma}$) by s -functions and ($V_{pp\sigma}$) by longitudinally oriented p -functions. Directed valence $V_{sp\sigma}$ are also indicated. π -bonding ($V_{pp\pi}$) with transverse p -functions shown for two orientations

Thus

$$\Gamma_{D.V. \pi\text{-bonds}} = \Gamma^{(a.s.)} \otimes \Gamma_{\text{general vector}} - \Gamma_{D.V. \sigma\text{-bonds}}, \quad (7.28)$$

and we thus obtain the desired result

$$\Gamma_{D.V. \pi\text{-bonds}} = \Gamma^{(a.s.)} \otimes \Gamma_{\text{vector } \perp \text{ to } \sigma\text{-bonds}}. \quad (7.29)$$

As an example of σ -bonds and π -bonds let us consider the problem of *trigonal bonding* of a hypothetical C_4 cluster, where one carbon atom is at the center of an equilateral triangle and the other three carbon atoms are at the corners of the triangle, as shown in Fig. 7.11. The pertinent character table is D_{3h} which is given in Table 7.12. For this group σ_h denotes an x - y reflection plane and σ_v denotes a reflection plane containing the threefold axis and one

of the twofold axes. Consider the linear combination of atomic orbitals made out of the three carbon atoms at the corners of the equilateral triangle. From the equivalence transformation for these three carbons, we obtain $\Gamma^{(a.s.)}$ (see Table 7.13). Clearly if each of the orbitals at the corners of the equilateral triangle were s -functions, then the appropriate linear combination of atomic orbitals would transform as $A'_1 + E'$

$$A'_1 : \psi_1 + \psi_2 + \psi_3, \quad (7.30)$$

$$E' : \begin{cases} \psi_1 + \omega\psi_2 + \omega^2\psi_3 \\ \psi_1 + \omega^2\psi_2 + \omega\psi_3 \end{cases}, \quad (7.31)$$

where

$$\omega = \exp\left(\frac{2\pi i}{3}\right). \quad (7.32)$$

In transforming wavefunctions corresponding to higher angular momentum states, we must include the transformation of a tensor (vector) on each of the equivalent sites. This is done formally by considering the direct product of $\Gamma^{(a.s.)}$ with Γ_{tensor} , where Γ_{tensor} gives the transformation properties of the orbital: a scalar for s -functions, a vector for p -functions, a tensor for d -functions, etc.

We now illustrate the construction of LCAOs from s - and p -functions, noting that from the character table for the group D_{3h} , s -functions transform

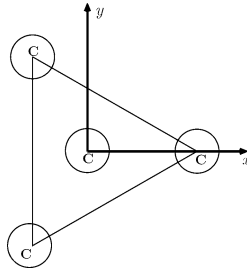


Fig. 7.11. Schematic diagram of a carbon atom forming bonds to three other carbon atoms at the corners of an equilateral triangle

Table 7.12. Character Table for Group $D_{3h}(6m2)$

$D_{3h}(6m2) \equiv D_3 \otimes \sigma_h$		E	σ_h	$2C_3$	$2S_3$	$3C'_2$	$3\sigma_v$	
$x^2 + y^2, z^2$	R_z	A'_1	1	1	1	1	1	
		A'_2	1	1	1	1	-1	-1
		A''_1	1	-1	1	-1	1	-1
$(x^2 - y^2, xy)$	(x, y)	A''_2	1	-1	1	-1	-1	1
		E'	2	2	-1	-1	0	0
(xz, yz)	(R_x, R_y)	E''	2	-2	-1	1	0	0

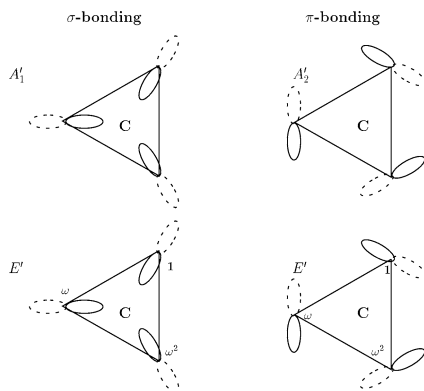


Fig. 7.12. Schematic diagram for the σ -bonds and the in-plane π -bonds for carbon atoms at the corners of a triangle to a carbon atom at the center of the triangle

as A'_1 , p_z functions as A''_2 and (p_x, p_y) functions as E' . We thus obtain for the transformation properties of the three s -functions at the corners of an equilateral triangle as

$$\Gamma^{\text{a.s.}} \otimes \Gamma_s = (A'_1 + E') \otimes A'_1 = A'_1 + E'. \quad (7.33)$$

For the p_z functions which transform as A''_2 we have for the direct product:

$$\Gamma^{\text{a.s.}} \otimes \Gamma_{p_z} = (A'_1 + E') \otimes A''_2 = A''_2 + E''. \quad (7.34)$$

Finally for the $p_{x,y}$ functions which transform as E' we obtain

$$\Gamma^{\text{a.s.}} \otimes \Gamma_{p_{x,y}} = (A'_1 + E') \otimes E' = A'_1 + A'_2 + 2E'. \quad (7.35)$$

We will see below that the $A'_1 + E'$ symmetries correspond to σ -bonds and the remaining $(A'_2 + E') + (A''_2 + E'')$ correspond to π -bonds, as shown in Fig. 7.12.

For the carbon atom at the center of the equilateral triangle (see Fig. 7.11) we make directed valence orbitals to the carbon atoms at sites (1), (2), and (3) from states with A'_1 and E' symmetry (see Sect. 7.5.1), which in accordance with the character table for D_{3h} , transform as the ψ_s and ψ_{p_x}, ψ_{p_y} wave functions. The directed orbitals from the central carbon atom are thus

Table 7.13. Characters for the $\Gamma^{\text{a.s.}}$ representation of three carbon atoms sitting at the corners of an equilateral triangle (D_{3h} symmetry)

	E	σ_h	$2C_3$	$2S_3$	$3C'_2$	$3\sigma_v$	
$\Gamma^{\text{(a.s.)}}$	3	3	0	0	1	1	$\Rightarrow A'_1 + E'$

$$\begin{aligned}
 \psi_1 &= \alpha\psi_s + \beta\psi_{p_x} \\
 \psi_2 &= \alpha\psi_s + \beta \left[-\frac{1}{2}\psi_{p_x} + \frac{\sqrt{3}}{2}\psi_{p_y} \right] \\
 \psi_3 &= \alpha\psi_s + \beta \left[-\frac{1}{2}\psi_{p_x} - \frac{\sqrt{3}}{2}\psi_{p_y} \right].
 \end{aligned} \tag{7.36}$$

The orthonormality condition on the three waves functions in (7.36), gives

$$\alpha^2 + \beta^2 = 1, \quad \beta^2 = 2\alpha^2, \tag{7.37}$$

or

$$\alpha = \frac{1}{\sqrt{3}}, \quad \beta = \sqrt{\frac{2}{3}}, \tag{7.38}$$

so that

$$\begin{aligned}
 \psi_1 &= \sqrt{\frac{1}{3}}\psi_s + \sqrt{\frac{2}{3}}\psi_{p_x} \\
 \psi_2 &= \sqrt{\frac{1}{3}}\psi_s - \sqrt{\frac{1}{6}}\psi_{p_x} + \sqrt{\frac{1}{2}}\psi_{p_y} \\
 \psi_3 &= \sqrt{\frac{1}{3}}\psi_s - \sqrt{\frac{1}{6}}\psi_{p_x} - \sqrt{\frac{1}{2}}\psi_{p_y}.
 \end{aligned} \tag{7.39}$$

Using the basis functions in the character table for D_{3h} and the classification of angular momentum states in Table 7.14, we can make σ -bonding orbitals with the following orbitals for the central carbon atom, neglecting for the moment the energetic constraints on the problem:

$$\begin{aligned}
 2s2p^2 & \quad s + (p_x, p_y) \\
 2s3d^2 & \quad s + (d_{xy}, d_{x^2-y^2}) \\
 3d2p^2 & \quad d_{3z^2-r^2} + (p_x, p_y) \\
 3d^3 & \quad d_{3z^2-r^2} + (d_{xy}, d_{x^2-y^2}).
 \end{aligned}$$

It is clear from Table 7.14 that the lowest energy σ -bond is made with the $2s2p^2$ configuration. The carbon atom has four valence electrons, three of which make the in-plane trigonal σ -bonds. The fourth electron is free to bond in the z -direction. This electron is involved in π -bonds, frequently discussed in organic chemistry.

To obtain π -bonds from the central carbon atom to the atoms at the corners of the triangle, we look at the character table to see how the vector (x, y, z) transforms:

$$\Gamma_{\text{vector}} = E' + A_2'' \tag{7.40}$$

Table 7.14. Characters for the angular momentum states and their irreducible representations for the group D_{3h} ^(a)

	E	σ_h	$2C_3$	$2S_3$	$3C'_2$	$3\sigma_v$	
$\ell = 0$	1	1	1	1	1	1	A'_1
$\ell = 1$	3	1	0	-2	-1	1	$A''_2 + E'$
$\ell = 2$	5	1	-1	1	1	1	$A'_1 + E' + E''$
$\ell = 3$	7	1	1	1	-1	1	$A'_1 + A'_2 + A''_2 + E' + E''$

^(a)In this character table, the characters for the various entries are found using the relations $\sigma_h = iC_2$, $2S_3 = 2iC_6$ and $3\sigma_v = 3iC_2$

We then take the direct product:

$$\begin{aligned}
 \Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vector}} &= \overbrace{(A'_1 + E')}^{\Gamma^{\text{a.s.}}} \otimes \underbrace{(E' + A''_2)}_{\chi_{\text{vector}}} \\
 &= (A'_1 \otimes E') + (A'_1 \otimes A''_2) + (E' \otimes E') + (E' \otimes A''_2) \\
 &= (E') + (A''_2) + (E' + A'_1 + A'_2) + (E'') \\
 &= (A'_1 + E') + (E' + A''_2 + A'_2 + E''). \tag{7.41}
 \end{aligned}$$

Since the irreducible representations for the σ -bonds are A'_1 and E' , we have the desired result that the irreducible representations for the π -bonds are

$$E' + A''_2 + A'_2 + E''.$$

We can now go one step further by considering the polarization of the π -bonds in terms of the irreducible representations that are even and odd under the horizontal mirror plane operation σ_h :

$$\chi_{\text{D.V. } \pi\text{-bonds}} = \overbrace{A'_2 + E'}^{\text{Even under } \sigma_h} + \underbrace{A''_2 + E''}_{\text{Odd under } \sigma_h}. \tag{7.42}$$

This polarization analysis identifies the bonds in (7.33)–(7.35).

To find the irreducible representations contained in the directed valence π -bonds, we have to go to rather high angular momentum states: $\ell = 2$ for an E'' state and $\ell = 3$ for an A'_2 state. Such high angular momentum states correspond to much higher energy. Therefore π -bonding will be much weaker than σ -bonding. The irreducible representations $A''_2 + E''$ correspond to π -bonding in the z -direction while the $A'_2 + E'$ representations correspond to π -bonding in the plane of the triangle, but \perp to the σ -bonding directions. We further note that the symmetries $A''_2 + E''$ correspond to p_z and d_{xz}, d_{yz} orbitals for angular momentum 1 and 2, respectively. On the other hand, the

symmetries $A'_2 + E'$ require $\ell = 3$ states, and therefore correspond to higher energies than the $A''_2 + E''$ orbitals. A diagram showing the orbitals for the σ -bonds and π -bonds for the various carbon atoms is given in Fig. 7.12.

7.7 Jahn–Teller Effect

The Jahn–Teller (JT) effect was discovered in 1937 [42] and it represents one of the earliest applications of group theory to solid-state physics [9]. The Jahn–Teller Theorem states that “any nonlinear molecular system in a degenerate electronic state will be unstable and will undergo a distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy.” The spontaneous geometrical distortion in an electronically excited state results in a lowering of the symmetry and a splitting of energy levels.

Both static and dynamic JT effects must be considered. In the static JT effect, a structural distortion lowers the symmetry of the system and lifts the degeneracy of the state. For a partially filled band, such a distortion thus leads to a lowering of the total energy of the system as the lower energy states of the multiplet are occupied and the higher-lying states remain empty.

The dynamic JT effect [44] can occur when there is more than one possible distortion that could lead to a lowering of the symmetry (and consequently also the lowering of the energy) of the system. If the potential minima of the adiabatic potential are degenerate for some symmetry-lowered states of a molecule, the electrons will jump from one potential minimum to another, utilizing their vibrational energy, and if this hopping occurs on the same time scale as atomic or molecular vibrations, then no static distortion will be observed by most experimental probes. Those vibrational modes which induce the dynamic JT effect contribute strongly to the electron–phonon coupling.

The Jahn–Teller effect applies to some simple polyatomic molecules, such as H_3 , and to complex organic molecules including carbon nanotubes as well as defect centers. The effect has also been discussed for different symmetry structures, such as cubic, tetrahedral, tetragonal, trigonal [60], and even icosahedral systems, such as C_{60} [32].

For nonlinear molecules in a geometry described by a point symmetry group possessing degenerate irreducible representations there always exists at least one nontotally symmetric vibration that makes such electronically degenerate states unstable. Under this symmetry-lowering vibration, the nuclei are displaced to new equilibrium positions of lower symmetry causing a splitting of the originally degenerate state. The Jahn–Teller effect describes the geometrical distortion of the electron cloud in the nonlinear molecule under certain situations. Consider a molecule that is in a degenerate state $\Psi_\mu^{T_i}$, belonging to the irreducible representation T_i , with partners μ . Then the complex conjugate wave function $K\Psi_\nu^{T_i}$ is necessarily a state with the same energy

where K is the complex conjugation operator (see Chapter 16). If the nuclear coordinates are displaced from the high-symmetry configuration by a normal mode vibration $Q_r^{\Gamma_j}$, the electronic potential deviates from its equilibrium situation. The electronic potential can, therefore, be expanded in terms of the vibrational symmetry coordinates:

$$V(\mathbf{r}, Q) = V_0 + \sum_{\Gamma_j, r} V_r^{\Gamma_j} Q_r^{\Gamma_j} + \sum_{\Gamma_j k, r, s} V_{rs}^{\Gamma_j \Gamma_k} Q_r^{\Gamma_j} Q_s^{\Gamma_k} + \dots \quad (7.43)$$

For small displacements only the first sum can be considered, and we have the “linear” Jahn–Teller effect. A first-order perturbation approach to the electronic levels involves the matrix elements:

$$M = \langle \Psi_\mu^{\Gamma_i} | V(\mathbf{r}, Q) | \Psi_\nu^{\Gamma_i} \rangle. \quad (7.44)$$

The argument of Jahn and Teller is that, since M reverses its sign if Q is replaced by $-Q$, each perturbation ΔE of an electronic energy level should also reverse its sign. Consequently, if $M \neq 0$ due to any term related to a Q^{Γ_i} belonging to $\Gamma_i \neq \Gamma_1$, i.e., the lattice mode vibration does not belong to the totally symmetric representation, the symmetry of the unperturbed molecular configuration also becomes unstable.

An interesting and instructive example of the Jahn–Teller effect occurs in the C_{60} molecule which has 60 carbon atoms at the 60 vertices of a truncated regular icosahedron. Although each carbon atom is in an equivalent site to every other carbon atom on the icosahedron, two of the nearest neighbor C–C bonds are single bonds while one is a double bond to satisfy the valence requirements of the carbon atom which is in column IV of the periodic table. Since the length of the double bond (0.140 nm) is shorter than that of the single bond (0.146 nm), the icosahedron becomes slightly distorted. This distortion does not affect the energy of the neutral atom in the ground state (HOMO), but does affect the filling of the excited states as charge is added to the fullerene [32]. The Jahn–Teller effect often involves spins and time reversal symmetry (see Chap. 16), as illustrated in Fig. 16.5 and the associated text.

We also comment on the Renner–Teller effect, that is a splitting on the vibrational levels of molecules due to even terms in the vibronic perturbation expansion (7.43). This effect is usually smaller than the linear Jahn–Teller effect, which is due to the odd terms in the expansion in (7.43), but it becomes important for linear diatomic molecules where the Jahn–Teller effect is absent. More details about the Jahn–Teller effect can be found in the literature, for example in [60].

Selected Problems

7.1. This problem is on diatomic molecules and considers the helium molecule He_2 and the hydrogen molecular ion with an extra electron H_2^- .

- (a) Suppose that we could make a bound diatomic molecule containing four electrons out of two helium atoms. What would you expect the ground state electronic configuration to be, what would its symmetry state be, and what would be its total electronic spin? Since the He_2 molecule is not formed under ordinary circumstances we know that the antibonding state lies too high in energy to form a bound state.
- (b) H_2^- however involves occupation of an antibonding state and does indeed form a bound state. What is the symmetry configuration of the three electrons in H_2^- ? Why is it possible for H_2^- to form a stable bound state but not for He_2 ? Group Theory gives us the symmetry designation for each molecular electronic state, but does not by itself give definitive information as to whether or not a bound state is formed.

7.2. Consider a hypothetical SF_6 molecule with octahedral symmetry (see Sect. 7.5.4 and Fig. 7.9).

- (a) Using $\Gamma^{\text{a.s.}}$, construct the linear combination of atomic orbitals for the six holes on the six fluorine atoms which transform according to the three irreducible representations $A_{1g} + E_g + T_{1u}$ contained in $\Gamma^{\text{a.s.}}$, assuming that wave functions with p symmetry ($\ell = 1$) are used to describe the valence states for the fluorine wave functions. Note that it is easier to consider a single hole rather than all the electrons in the nearly filled shell of the fluorine atom.
- (b) What are the angular momentum states required to bond the sulfur to the six fluorine atoms in p states.
- (c) What are the irreducible representations corresponding to σ -bonds and π -bonds for the central sulfur atom to the six fluorine atoms? Sketch the orientation of these bonding orbitals.

7.3. Why would the octahedral configuration of Fig. 7.9 be more stable for a hypothetical SH_6 molecule than the planar configuration in Fig. 7.6? Consider the angular momentum states required for the S atom to make the appropriate directed valence bonds to the six hydrogens in the planar SH_6 hypothetical molecule.

7.4. C_2H_4 (ethylene) is a planar molecule which has the configuration shown in Fig. 7.13.

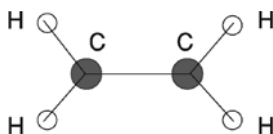


Fig. 7.13. Symmetry of the ethylene C_2H_4 molecule

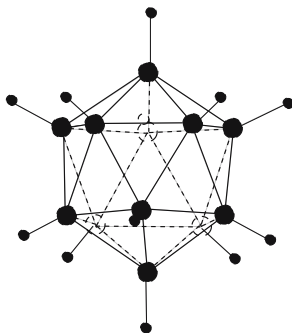


Fig. 7.14. Symmetry of the $B_{12}H_{12}$ icosahedral molecule

- Identify the appropriate point group for C_2H_4 .
- Find the equivalence representation $\Gamma^{a.s.}$ for the two carbon atoms and for the four hydrogen atoms in the C_2H_4 molecule.
- Considering the directed valence orbitals, how do the carbon atoms satisfy their bonding requirements? Which angular momentum states are needed to form bonding orbitals from each carbon atom?
- Give the block diagonal structure for the secular equation for the electronic energy levels of ethylene.

7.5. Consider the $B_{12}H_{12}$ molecule shown in Fig. 7.14 where the 12 hydrogen atoms (small balls) and the 12 boron atoms (large balls) are at vertices of a regular icosahedron.

- What are the symmetry operations associated with the ten classes of the full icosahedral group I_h (see Table A.28).
- What are the symmetries and degeneracies of the 12 linear combinations of atomic orbitals (LCAOs) associated with the 12 equivalent hydrogen atoms?
- Write the linear combinations of the 12 atomic orbitals (LCAOs) for the 12 hydrogen atoms in $B_{12}H_{12}$ in I_h symmetry.
- What are the angular momentum states involved with each of the directed valence σ orbitals from a boron atom to a hydrogen atom?

7.6. This problem further develops the symmetry properties of the CH_4 molecule introduced in Sect. 7.5.2.

- Using one symmetry operation from each class of the point group T_d , show that the linear combination of atomic orbitals $\psi_1(T_2)$ in (7.17) transforms as one of the partners of the irreducible representation T_2 .
- Using the symmetrized linear combination of atomic orbitals for the four hydrogen atoms in (7.16) and (7.17) and the wave functions for the four valence electrons for the carbon atom, construct the matrix Hamiltonian for the secular equation for the CH_4 molecule in block form showing the

nonzero entries and their symmetries, analogous to the corresponding matrix Hamiltonian for finding the electronic states for the CO molecule in Fig. 7.4.

- (c) Show that the directed valence bond wave function for CH_4 given by (7.20) has its maximum value along the (111) direction. What is the value of this bond along a $(\bar{1}\bar{1}\bar{1})$ direction? Along what direction does this bond have its minimum value?
- (d) What are the symmetries for the two lowest energy antibonding levels for the four hydrogen atoms and the four electrons on the carbon atom yielding the antibonding excited states of the CH_4 molecule? Why do you expect these excited states to have higher energies than the bonding states discussed in Sect. 7.5.2?