

Chapter 2

Model problems that form important starting points

The model problems discussed in this chapter form the basis for chemists' understanding of the electronic states of atoms, molecules, clusters, and solids as well as the rotational and vibrational motions of molecules.

2.1 Free electron model of polyenes

The particle-in-a-box problem provides an important model for several relevant chemical situations.

The "particle-in-a-box" model for motion in two dimensions discussed earlier can obviously be extended to three dimensions or to one. For two and three dimensions, it provides a crude but useful picture for electronic states on surfaces or in metallic crystals, respectively. I say metallic crystals because it is in such systems that the outermost valence electrons are reasonably well treated as moving freely. Free motion within a spherical volume gives rise to eigenfunctions that are used in nuclear physics to describe the motions of neutrons and protons in nuclei. In the so-called shell model of nuclei, the neutrons and protons fill separate s, p, d, etc. orbitals with each type of nucleon forced to obey the Pauli principle (i.e., to have no more than two nucleons in each orbital because protons and neutrons are fermions). To remind you, I display in Fig. 2.1 the angular shapes that characterize s, p, and d orbitals.

This same spherical box model has also been used to describe the orbitals of valence electrons in clusters of metal atoms such as Cs_n , Cu_n , Na_n and their positive and negative ions. Because of the metallic nature of these species, their valence electrons are essentially free to roam over the entire spherical volume of the cluster, which renders this simple model rather effective. In this model, one thinks of each electron being free to roam within a sphere of radius R (i.e., having a potential that is uniform within the sphere and infinite outside the sphere). Finally, as noted above, this same spherical box model forms the basis of the so-called shell model of nuclear structure. In this model, one assumes that the protons and neutrons that make up a nucleus, both of which are fermions, occupy

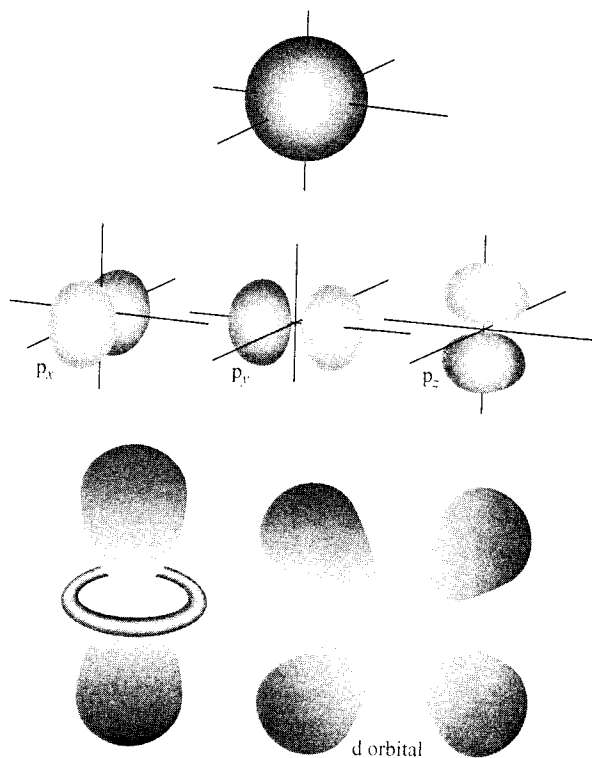
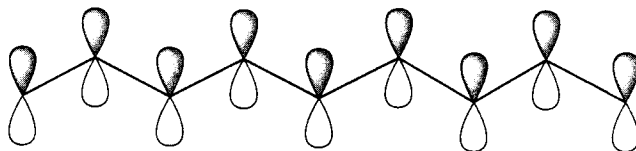


Figure 2.1 The angular shapes of s, p, and d functions.

spherical-box orbitals (one set of orbitals for protons, another set for neutrons because they are distinguishable from one another). By placing the protons and neutrons into these orbitals, two to an orbital, one achieves a description of the energy levels of the nucleus. Excited states are achieved by promoting a neutron or proton from an occupied orbital to a virtual (i.e., previously unoccupied) orbital. In such a model, especially stable nuclei are achieved when “closed-shell” configurations such as $1s^2$ or $1s^2 2s^2 2p^6$ are realized (e.g., ${}^4\text{He}$ has both neutrons and protons in $1s^2$ configurations).

The orbitals that solve the Schrödinger equation inside such a spherical box are not the same in their radial “shapes” as the s, p, d, etc. orbitals of atoms because, in atoms, there is an additional radial potential $V(r) = -Ze^2/r$ present. However, their angular shapes are the same as in atomic structure because, in both cases, the potential is independent of θ and ϕ . As the orbital plots shown above indicate, the angular shapes of s, p, and d orbitals display varying numbers of nodal surfaces. The s orbitals have none, p orbitals have one, and d orbitals have two. Analogous to how the number of nodes related to the total energy of the particle constrained to the x, y plane, the number of nodes in the angular wave functions indicates the amount of angular or rotational energy. Orbitals of s shape have no angular energy, those of p shape have less than do d orbitals, etc.

Figure 2.2 The π atomic orbitals of a conjugated chain of nine carbon atoms.



One-dimensional free particle motion provides a qualitatively correct picture for π -electron motion along the p_π orbitals of delocalized polyenes. The one Cartesian dimension then corresponds to motion along the delocalized chain. In such a model, the box length L is related to the carbon-carbon bond length R and the number N of carbon centers involved in the delocalized network $L = (N - 1)R$. In Fig. 2.2, such a conjugated network involving nine centers is depicted. In this example, the box length would be eight times the C-C bond length. The eigenstates $\psi_n(x)$ and their energies E_n represent orbitals into which electrons are placed. In the example case, if nine π electrons are present (e.g., as in the 1,3,5,7-nonatetraene radical), the ground electronic state would be represented by a total wave function consisting of a product in which the lowest four ψ s are doubly occupied and the fifth ψ is singly occupied:

$$\Psi = \psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_3\alpha\psi_3\beta\psi_4\alpha\psi_4\beta\psi_5\alpha. \quad (2.1)$$

The z -component angular momentum states of the electrons are labeled α and β as discussed earlier.

A product wave function is appropriate because the total Hamiltonian involves the kinetic plus potential energies of nine electrons. To the extent that this total energy can be represented as the sum of nine separate energies, one for each electron, the Hamiltonian allows a separation of variables

$$H \cong \sum_j H(j) \quad (2.2)$$

in which each $H(j)$ describes the kinetic and potential energy of an individual electron. Recall that when a partial differential equation has no operators that couple its different independent variables (i.e., when it is separable), one can use separation of variables methods to decompose its solutions into products. Thus, the (approximate) additivity of H implies that solutions of $H\Psi = E\Psi$ are products of solutions to

$$H(j)\psi(\mathbf{r}_j) = E_j\psi(\mathbf{r}_j). \quad (2.3)$$

The two lowest π -excited states would correspond to states of the form

$$\Psi^* = \psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_3\alpha\psi_3\beta\psi_4\alpha\psi_5\beta\psi_5\alpha, \quad (2.4)$$

$$\text{and } \Psi'^* = \psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_3\alpha\psi_3\beta\psi_4\alpha\psi_4\beta\psi_6\alpha, \quad (2.5)$$

where the spin-orbitals (orbitals multiplied by α or β) appearing in the above products depend on the coordinates of the various electrons. For example,

$$\psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_3\alpha\psi_3\beta\psi_4\alpha\psi_5\beta\psi_5\alpha \quad (2.6)$$

denotes

$$\psi_1\alpha(\mathbf{r}_1)\psi_1\beta(\mathbf{r}_2)\psi_2\alpha(\mathbf{r}_3)\psi_2\beta(\mathbf{r}_4)\psi_3\alpha(\mathbf{r}_5)\psi_3\beta(\mathbf{r}_6)\psi_4\alpha(\mathbf{r}_7)\psi_5\beta(\mathbf{r}_8)\psi_5\alpha(\mathbf{r}_9). \quad (2.7)$$

The electronic excitation energies from the ground state to each of the above excited states within this model would be

$$\begin{aligned} \Delta E^* &= \pi^2 \frac{\hbar^2}{2m} \left[\frac{5^2}{L^2} - \frac{4^2}{L^2} \right] \\ \text{and } \Delta E'^* &= \pi^2 \frac{\hbar^2}{2m} \left[\frac{6^2}{L^2} - \frac{5^2}{L^2} \right]. \end{aligned} \quad (2.8)$$

It turns out that this simple model of π -electron energies provides a qualitatively correct picture of such excitation energies. Its simplicity allows one, for example, to easily suggest how a molecule's color (as reflected in the complementary color of the light the molecule absorbs) varies as the conjugation length L of the molecule varies. That is, longer conjugated molecules have lower-energy orbitals because L^2 appears in the denominator of the energy expression. As a result, longer conjugated molecules absorb light of lower energy than do shorter molecules.

This simple particle-in-a-box model does not yield orbital energies that relate to ionization energies unless the potential "inside the box" is specified. Choosing the value of this potential V_0 such that $V_0 + [\pi^2\hbar^2/2m][5^2/L^2]$ is equal to minus the lowest ionization energy of the 1,3,5,7-nonatetraene radical, gives energy levels (as $E = V_0 + [\pi^2\hbar^2/2m][n^2/L^2]$) which can then be used as approximations to ionization energies.

The individual π -molecular orbitals

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad (2.9)$$

are depicted in Fig. 2.3 for a model of the 1,3,5-hexatriene π -orbital system for which the "box length" L is five times the distance R_{CC} between neighboring pairs of carbon atoms. The magnitude of the k th C-atom centered atomic orbital in the n th π -molecular orbital is given by $(2/L)^{1/2} \sin(n\pi k R_{CC}/L)$. In this figure, positive amplitude is denoted by the clear spheres, and negative amplitude is shown by the darkened spheres. Where two spheres of like shading overlap, the wave function has enhanced amplitude; where two spheres of different shading overlap, a node occurs. Once again, we note that the number of nodes increases as one ranges from the lowest energy orbital to higher energy orbitals. The reader is once again encouraged to keep in mind this ubiquitous characteristic of quantum mechanical wave functions.

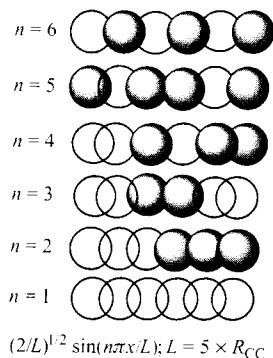


Figure 2.3 The phases of the six molecular orbitals of a chain containing six atoms.

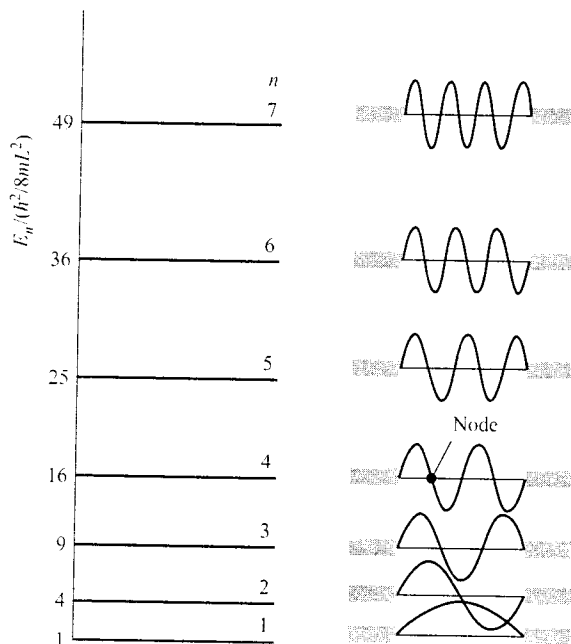


Figure 2.4 The nodal pattern for a chain containing seven atoms.

This simple model allows one to estimate spin densities at each carbon center and provides insight into which centers should be most amenable to electrophilic or nucleophilic attack. For example, radical attack at the C_5 carbon of the nine-atom nonatetraene system described earlier would be more facile for the ground state Ψ than for either Ψ^* or Ψ'^* . In the former, the unpaired spin density resides in ψ_5 , which has non-zero amplitude at the C_5 site $x = L/2$. In Ψ^* and Ψ'^* , the unpaired density is in ψ_4 and ψ_6 , respectively, both of which have zero density at C_5 . These densities reflect the values $(2/L)^{1/2} \sin(n\pi k R_{CC}/L)$ of the amplitudes for this case in which $L = 8 \times R_{CC}$ for $n = 5, 4$, and 6 , respectively. Plots of the wave functions for n ranging from 1 to 7 are shown in another format in Fig. 2.4 where the nodal pattern is emphasized. I hope that by now the student is not tempted to ask how the electron “gets” from one region of high amplitude, through a node, to another high-amplitude region. Remember, such questions are cast in classical Newtonian language and are not appropriate when addressing the wave-like properties of quantum mechanics.

2.2 Bands of orbitals in solids

Not only does the particle-in-a-box model offer a useful conceptual representation of electrons moving in polyenes, but it also is the zeroth-order model of band structures in solids. Let us consider a simple one-dimensional “crystal” consisting

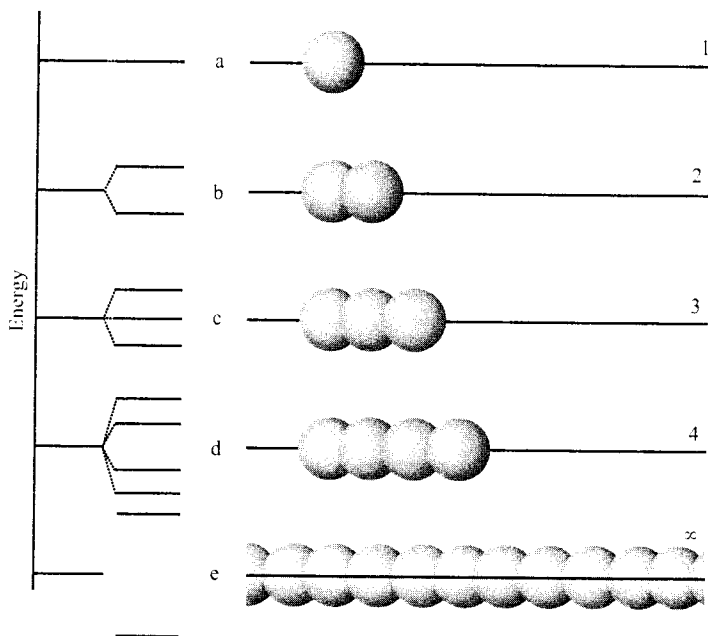


Figure 2.5 The energy levels arising from 1, 2, 3, 4, and an infinite number of orbitals.

of a large number of atoms or molecules, each with a single orbital (the spheres shown) that it contributes to the bonding. Let us arrange these building blocks in a regular "lattice" as shown in Fig. 2.5. In the top four rows of this figure we show the case with 1, 2, 3, and 4 building blocks. To the left of each row, we display the energy splitting pattern into which the building blocks' orbitals evolve as they overlap and form delocalized molecular orbitals. Not surprisingly, for $n = 2$, one finds a bonding and an antibonding orbital. For $n = 3$, one has one bonding, one non-bonding, and one antibonding orbital. Finally, in the bottom row, we attempt to show what happens for an infinitely long chain. The key point is that the discrete number of molecular orbitals appearing in the 1–4 orbital cases evolves into a continuum of orbitals called a band. This band of orbital energies ranges from its bottom (whose orbital consists of a fully in-phase bonding combination of the building block orbitals) to its top (whose orbital is a fully out-of-phase antibonding combination). In Fig. 2.6 we illustrate these fully bonding and fully antibonding band orbitals for two cases – the bottom involving s-type building block orbitals, and the top involving p-type orbitals. Notice that when the energy gap between the building block s and p orbitals is larger than is the dispersion (spread) in energy within the band of s or band of p orbitals, a band gap occurs between the highest member of the s band and the lowest member of the p band. The splitting between the s and p orbitals is a property of the individual atoms comprising the solid and varies among the elements of the periodic table. The dispersion in energies that a given band of orbitals is split into as these atomic

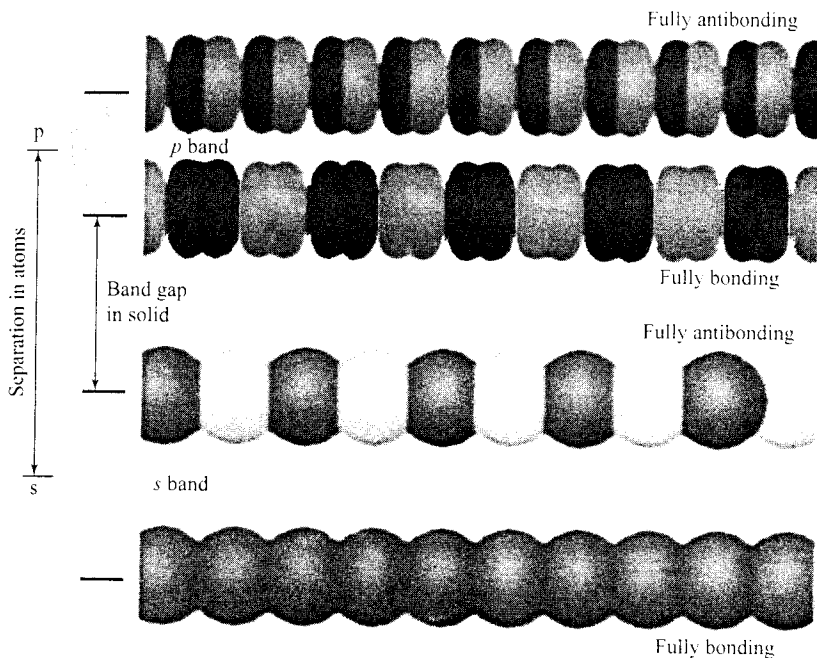


Figure 2.6 The bonding through antibonding energies and band orbitals arising from s and from p orbitals.

orbitals combine to form a band is determined by how strongly the orbitals on neighboring atoms overlap. Small overlap produces small dispersion, and large overlap yields a broad band.

Depending on how many valence electrons each building block contributes, the various bands formed by overlapping the building block orbitals of the constituent atoms will be filled to various levels. For example, if each orbital shown above has a single valence electron in an s orbital (e.g., as in the case of the alkali metals), the s-band will be half filled in the ground state with α and β paired electrons. Such systems produce very good conductors because their partially filled bands allow electrons to move with very little (e.g., only thermal) excitation among other orbitals in this same band. On the other hand, for alkaline earth systems with two s electrons per atom, the s band will be completely filled. In such cases, conduction requires excitation to the lowest members of the nearby p-orbital band. Finally, if each building block were an Al ($3s^2 3p^1$) atom, the s band would be full and the p band would be half-filled. Systems whose highest energy occupied band is completely filled and for which the gap in energy to the lowest unfilled band is large are called insulators because they have no way to easily (i.e., with little energy requirement) promote some of their higher energy electrons from orbital to orbital and thus effect conduction. If the band gap between a filled band and an unfilled band is small, it may be possible for thermal excitation (i.e., collisions with neighboring atoms or molecules) to cause excitation of electrons

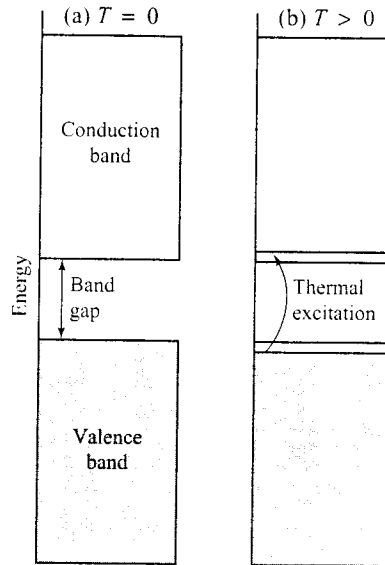


Figure 2.7 The valence and conduction bands and the band gap.

from the former to the latter thereby inducing conductive behavior. An example of such a case is illustrated in Fig. 2.7. In contrast, systems whose highest energy occupied band is partially filled are conductors because they have little spacing among their occupied and unoccupied orbitals.

To form a semiconductor, one starts with an insulator as shown in Fig. 2.8 with its filled (dark) band and a band gap between this band and its empty (clear) upper band. If this insulator material were synthesized with a small amount of “dopant” whose valence orbitals have energies between the filled and empty bands of the insulator, one may generate a semiconductor. If the dopant species has no valence electrons (i.e., has an empty valence orbital), it gives rise to an empty band lying between the filled and empty bands of the insulator as shown in Fig. 2.8a. In this case, the dopant band can act as an electron acceptor for electrons excited (either thermally or by light) from the filled band into the dopant band. Once electrons enter the dopant band, charge can flow and the system becomes a conductor. Another case is illustrated in Fig. 2.8b. Here, the dopant has its own band filled but lies close to the empty band of the insulator. Hence excitation of electrons from the dopant band to the empty band can induce current to flow.

2.3 Densities of states in one, two, and three dimensions

When a large number of neighboring orbitals overlap, bands are formed. However, the nature of these bands is very different in different dimensions.

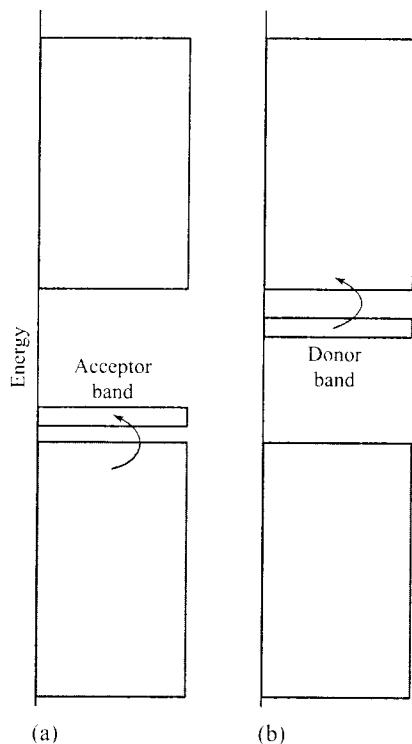


Figure 2.8 The filled and empty bands, the band gap, and empty acceptor or filled donor bands.

Before leaving our discussion of bands of orbitals and orbital energies in solids, I want to address the issue of the density of electronic states and the issue of what determines the energy range into which orbitals of a given band will split. First, let's recall the energy expression for the one- and two-dimensional electron in a box case, and let's generalize it to three dimensions. The general result is

$$E = \sum_j n_j^2 \pi^2 \hbar^2 / (2mL_j^2), \quad (2.10)$$

where the sum over j runs over the number of dimensions (one, two, or three), and L_j is the length of the box along the j th direction. For one dimension, one observes a pattern of energy levels that grows with increasing n , and whose spacing between neighboring energy levels also grows. However, in two and three dimensions, the pattern of energy level spacing displays a qualitatively different character at high quantum number.

Consider first the three-dimensional case and, for simplicity, let's use a "box" that has equal length sides L . In this case, the total energy E is $(\hbar^2 \pi^2 / 2mL^2)$ times $(n_x^2 + n_y^2 + n_z^2)$. The latter quantity can be thought of as the square of the length of a vector \mathbf{R} having three components n_x, n_y, n_z . Now think of three Cartesian axes labeled $n_x, n_y,$ and n_z and view a sphere of radius R in this space. The volume of the 1/8 sphere having positive values of $n_x, n_y,$ and n_z and having

radius R is $1/8(4/3\pi R^3)$. Because each cube having unit length along the n_x , n_y , and n_z axes corresponds to a single quantum wave function and its energy, the total number $N_{\text{tot}}(E)$ of quantum states with positive n_x , n_y , and n_z and with energy between zero and $E = (\hbar^2\pi^2/2mL^2)R^2$ is

$$N_{\text{tot}} = \frac{1}{8} \left(\frac{4}{3}\pi R^3 \right) = \frac{1}{8} \left(\frac{4}{3}\pi \left[\frac{2mEL^2}{\hbar^2\pi^2} \right]^{3/2} \right). \quad (2.11)$$

The number of quantum states with energies between E and $E + dE$ is $(dN_{\text{tot}}/dE)dE$, which is the density $\Omega(E)$ of states near energy E :

$$\Omega(E) = \frac{1}{8} \left(\frac{4}{3}\pi \left[\frac{2mL^2}{\hbar^2\pi^2} \right]^{3/2} \frac{3}{2} E^{1/2} \right). \quad (2.12)$$

Notice that this state density increases as E increases. This means that, in the three-dimensional case, the number of quantum states per unit energy grows; in other words, the spacing between neighboring state energies decreases, very unlike the one-dimensional case where the spacing between neighboring states grows as n and thus E grows. This growth in state density in the three-dimensional case is a result of the degeneracies and near-degeneracies that occur. For example, the states with $n_x, n_y, n_z = 2, 1, 1$ and $1, 1, 2$, and $1, 2, 1$ are degenerate, and those with $n_x, n_y, n_z = 5, 3, 1$ or $5, 1, 3$ or $1, 3, 5$ or $1, 5, 3$ or $3, 1, 5$ or $3, 5, 1$ are degenerate and nearly degenerate to those having quantum numbers $4, 4, 1$ or $1, 4, 4$, or $4, 1, 4$.

In the two-dimensional case, degeneracies also occur and cause the density of states to possess an interesting E dependence. In this case, we think of states having energy $E = (\hbar^2\pi^2/2mL^2)R^2$, but with $R^2 = n_x^2 + n_y^2$. The total number of states having energy between zero and E is

$$N_{\text{total}} = 4\pi R^2 = 4\pi E \left(\frac{2mL^2}{\hbar^2\pi^2} \right). \quad (2.13)$$

So, the density of states between E and $E + dE$ is

$$\Omega(E) = \frac{dN_{\text{total}}}{dE} = 4\pi \left(\frac{2mL^2}{\hbar^2\pi^2} \right). \quad (2.14)$$

That is, in this two-dimensional case, the number of states per unit energy is constant for high E values (where the analysis above applies best).

This kind of analysis for the one-dimensional case gives

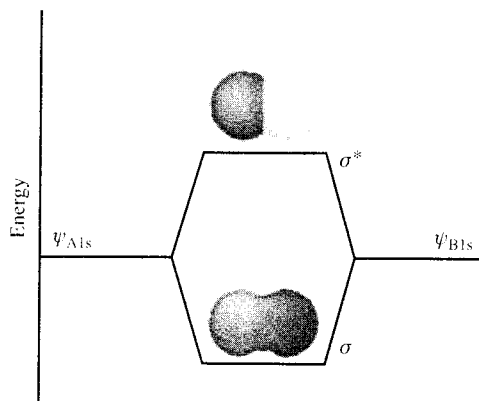
$$N_{\text{total}} = R = \left(\frac{2mEL^2}{\hbar^2\pi^2} \right)^{1/2}. \quad (2.15)$$

so the state density between E and $E + dE$ is

$$\Omega(E) = 1/2 \left(\frac{2mL^2}{\hbar^2\pi^2} \right)^{1/2} E^{-1/2}, \quad (2.16)$$

which clearly shows the widening spacing, and thus lower density, as one goes to higher energies.

Figure 2.9 Two 1s orbitals combine to produce a σ bonding and a σ^* antibonding molecular orbital.



These findings about densities of states in one, two, and three dimensions are important because, in various problems one encounters in studying electronic states of extended systems such as solids and surfaces, one needs to know how the number of states available at a given total energy E varies with E . Clearly, the answer to this question depends upon the dimensionality of the problem, and this fact is what I want the students reading this text to keep in mind.

2.4 The most elementary model of orbital energy splittings: Hückel or tight-binding theory

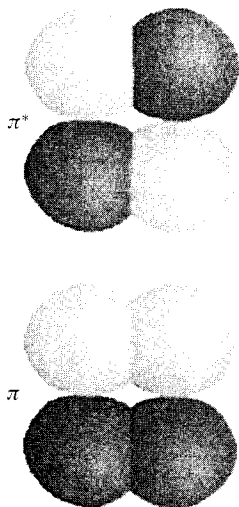


Figure 2.10 Two atomic p_π orbitals form a bonding π and antibonding π^* molecular orbital.

Now let's examine what determines the energy range into which orbitals (e.g., p_π orbitals in polyenes or metal s or p orbitals in a solid) split. To begin, consider two orbitals, one on an atom labeled A and another on a neighboring atom labeled B; these orbitals could be, for example, the 1s orbitals of two hydrogen atoms, such as Fig. 2.9 illustrates. However, the two orbitals could instead be two p_π orbitals on neighboring carbon atoms such as are shown in Fig. 2.10 as they form bonding and π^* antibonding orbitals. In both of these cases, we think of forming the molecular orbitals (MOs) ϕ_K as linear combinations of the atomic orbitals (AOs) χ_a on the constituent atoms, and we express this mathematically as follows:

$$\phi_K = \sum_a C_{K,a} \chi_a, \quad (2.17)$$

where the $C_{K,a}$ are called linear combination of atomic orbitals to form molecular orbital (LCAO-MO) coefficients. The MOs are supposed to be solutions to the Schrödinger equation in which the Hamiltonian H involves the kinetic energy of the electron as well as the potentials V_L and V_R detailing its attraction to the left and right atomic centers:

$$H = -\hbar^2/2m\nabla^2 + V_L + V_R. \quad (2.18)$$

In contrast, the AOs centered on the left atom A are supposed to be solutions of the Schrödinger equation whose Hamiltonian is $H = -\hbar^2/2m\nabla^2 + V_L$, and the AOs on the right atom B have $H = -\hbar^2/2m\nabla^2 + V_R$. Substituting $\phi_K = \sum_a C_{K,a} \chi_a$ into the MO's Schrödinger equation $H\phi_K = \varepsilon_K \phi_K$ and then multiplying on the left by the complex conjugate of χ_b and integrating over the r, θ and ϕ coordinates of the electron produces

$$\sum_a \langle \chi_b | -\hbar^2/2m\nabla^2 + V_L + V_R | \chi_a \rangle C_{K,a} = \varepsilon_K \sum_a \langle \chi_b | \chi_a \rangle C_{K,a}. \quad (2.19)$$

Recall that the Dirac notation $\langle a | b \rangle$ denotes the integral of a^* and b , and $\langle a | \text{op} | b \rangle$ denotes the integral of a^* and the operator op acting on b .

In what is known as the Hückel model in organic chemistry or the tight-binding model in solid-state theory, one approximates the integrals entering into the above set of linear equations as follows:

- (i) The diagonal integral $\langle \chi_b | -\hbar^2/2m\nabla^2 + V_L + V_R | \chi_b \rangle$ involving the AO centered on the right atom and labeled χ_b is assumed to be equivalent to $\langle \chi_b | -\hbar^2/2m\nabla^2 + V_R | \chi_b \rangle$, which means that net attraction of this orbital to the left atomic center is neglected. Moreover, this integral is approximated in terms of the binding energy (denoted α , not to be confused with the electron spin function α) for an electron that occupies the χ_b orbital: $\langle \chi_b | -\hbar^2/2m\nabla^2 + V_R | \chi_b \rangle = \alpha_b$. The physical meaning of α_b is the kinetic energy of the electron in χ_b plus the attraction of this electron to the right atomic center while it resides in χ_b . Of course, an analogous approximation is made for the diagonal integral involving χ_a : $\langle \chi_a | -\hbar^2/2m\nabla^2 + V_L | \chi_a \rangle = \alpha_a$.
- (ii) The off-diagonal integrals $\langle \chi_b | -\hbar^2/2m\nabla^2 + V_L + V_R | \chi_a \rangle$ are expressed in terms of a parameter $\beta_{a,b}$ which relates to the kinetic and potential energy of the electron while it resides in the "overlap region" in which both χ_a and χ_b are non-vanishing. This region is shown pictorially in Fig. 2.10 as the region where the left and right orbitals touch or overlap. The magnitude of β is assumed to be proportional to the overlap $S_{a,b}$ between the two AOs: $S_{a,b} = \langle \chi_a | \chi_b \rangle$. It turns out that β is usually a negative quantity, which can be seen by writing it as $\langle \chi_b | -\hbar^2/2m\nabla^2 + V_R | \chi_a \rangle + \langle \chi_b | V_L | \chi_a \rangle$. Since χ_a is an eigenfunction of $-\hbar^2/2m\nabla^2 + V_R$ having the eigenvalue α_a , the first term is equal to α_a (a negative quantity) times $\langle \chi_b | \chi_a \rangle$, the overlap S . The second quantity $\langle \chi_b | V_L | \chi_a \rangle$ is equal to the integral of the overlap density $\chi_b(r)\chi_a(r)$ multiplied by the (negative) Coulomb potential for attractive interaction of the electron with the left atomic center. So, whenever $\chi_b(r)$ and $\chi_a(r)$ have positive overlap, β will turn out negative.
- (iii) Finally, in the most elementary Hückel or tight-binding model, the overlap integrals $\langle \chi_a | \chi_b \rangle = S_{a,b}$ are neglected and set equal to zero on the right side of the matrix eigenvalue equation. However, in some Hückel models, overlap between neighboring orbitals is explicitly treated, so in some of the discussion below we will retain $S_{a,b}$.

With these Hückel approximations, the set of equations that determine the orbital energies ε_K and the corresponding LCAO-MO coefficients $C_{K,a}$ are written for the two-orbital case at hand as in the first 2×2 matrix equations shown below:

$$\begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \varepsilon \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix}. \quad (2.20)$$

which is sometimes written as

$$\begin{bmatrix} \alpha - \varepsilon & \beta - \varepsilon S \\ \beta - \varepsilon S & \alpha - \varepsilon \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}. \quad (2.21)$$

These equations reduce with the assumption of zero overlap to

$$\begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \varepsilon \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix}. \quad (2.22)$$

The α parameters are identical if the two AOs χ_a and χ_b are identical, as would be the case for bonding between the two 1s orbitals of two H atoms or two $2p_\pi$ orbitals of two C atoms or two 3s orbitals of two Na atoms. If the left and right orbitals were not identical (e.g., for bonding in HeH^+ or for the π bonding in a C–O group), their α values would be different and the Hückel matrix problem would look like:

$$\begin{bmatrix} \alpha & \beta \\ \beta & \alpha' \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \varepsilon \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix}. \quad (2.23)$$

To find the MO energies that result from combining the AOs, one must find the values of ε for which the above equations are valid. Taking the 2×2 matrix consisting of ε times the overlap matrix to the left-hand side, the above set of equations reduces to Eq. (2.21). It is known from matrix algebra that such a set of linear homogeneous equations (i.e., having zeroes on the right-hand sides) can have non-trivial solutions (i.e., values of C that are not simply zero) only if the determinant of the matrix on the left side vanishes. Setting this determinant equal to zero gives a quadratic equation in which the ε values are the unknowns:

$$(\alpha - \varepsilon)^2 - (\beta - \varepsilon S)^2 = 0. \quad (2.24)$$

This quadratic equation can be factored into a product

$$(\alpha - \beta - \varepsilon + \varepsilon S)(\alpha + \beta - \varepsilon - \varepsilon S) = 0, \quad (2.25)$$

which has two solutions

$$\varepsilon = (\alpha + \beta)/(1 + S), \quad \text{and} \quad \varepsilon = (\alpha - \beta)/(1 - S). \quad (2.26)$$

As discussed earlier, it turns out that the β values are usually negative, so the lowest energy such solution is the $\varepsilon = (\alpha + \beta)/(1 + S)$ solution, which gives the

energy of the bonding MO. Notice that the energies of the bonding and antibonding MOs are not symmetrically displaced from the value α within this version of the Hückel model that retains orbital overlap. In fact, the bonding orbital lies less than β below α , and the antibonding MO lies more than β above α because of the $1 + S$ and $1 - S$ factors in the respective denominators. This asymmetric lowering and raising of the MOs relative to the energies of the constituent AOs is commonly observed in chemical bonds; that is, the antibonding orbital is more antibonding than the bonding orbital is bonding. This is another important thing to keep in mind because its effects pervade chemical bonding and spectroscopy.

Having noted the effect of inclusion of AO overlap effects in the Hückel model, I should admit that it is far more common to utilize the simplified version of the Hückel model in which the S factors are ignored. In so doing, one obtains patterns of MO orbital energies that do not reflect the asymmetric splitting in bonding and antibonding orbitals noted above. However, this simplified approach is easier to use and offers qualitatively correct MO energy orderings. So, let's proceed with our discussion of the Hückel model in its simplified version.

To obtain the LCAO-MO coefficients corresponding to the bonding and antibonding MOs, one substitutes the corresponding α values into the linear equations

$$\begin{bmatrix} \alpha - \varepsilon & \beta \\ \beta & \alpha - \varepsilon \end{bmatrix} \begin{bmatrix} C_L \\ C_R \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (2.27)$$

and solves for the C_a coefficients (actually, one can solve for all but one C_a , and then use normalization of the MO to determine the final C_a). For example, for the bonding MO, we substitute $\varepsilon = \alpha + \beta$ into the above matrix equation and obtain two equations for C_L and C_R :

$$-\beta C_L + \beta C_R = 0. \quad (2.28)$$

$$\beta C_L - \beta C_R = 0. \quad (2.29)$$

These two equations are clearly not independent; either one can be solved for one C in terms of the other C to give

$$C_L = C_R. \quad (2.30)$$

which means that the bonding MO is

$$\phi = C_L(\chi_L + \chi_R). \quad (2.31)$$

The final unknown, C_L , is obtained by noting that ϕ is supposed to be a normalized function $\langle \phi | \phi \rangle = 1$. Within this version of the Hückel model, in which the overlap S is neglected, the normalization of ϕ leads to the following condition:

$$1 = \langle \phi | \phi \rangle = C_L^2(\langle \chi_L | \chi_L \rangle + \langle \chi_R | \chi_R \rangle) = 2C_L^2, \quad (2.32)$$

with the final result depending on assuming that each χ is itself also normalized. So, finally, we know that $C_L = (1/2)^{1/2}$, and hence the bonding MO is

$$\phi = (1/2)^{1/2}(\chi_L + \chi_R). \quad (2.33)$$

Actually, the solution of $1 = 2C_L^2$ could also have yielded $C_L = -(1/2)^{1/2}$ and then we would have

$$\phi = -(1/2)^{1/2}(\chi_L + \chi_R). \quad (2.34)$$

These two solutions are not independent (one is just -1 times the other), so only one should be included in the list of MOs. However, either one is just as good as the other because, as shown very early in this text, all of the physical properties that one computes from a wave function depend not on ψ but on $\psi^*\psi$. So, two wave functions that differ from one another by an overall sign factor, as we have here, have exactly the same $\psi^*\psi$ and thus are equivalent.

In like fashion, we can substitute $\varepsilon = \alpha - \beta$ into the matrix equation and solve for the C_L and C_R values that are appropriate for the antibonding MO. Doing so gives us

$$\phi^* = (1/2)^{1/2}(\chi_L - \chi_R) \quad (2.35)$$

or, alternatively,

$$\phi^* = (1/2)^{1/2}(\chi_R - \chi_L). \quad (2.36)$$

Again, the fact that either expression for ϕ^* is acceptable shows a property of all solutions to any Schrödinger equations; any multiple of a solution is also a solution. In the above example, the two "answers" for ϕ^* differ by a multiplicative factor of (-1) .

Let's try another example to practice using Hückel or tight-binding theory. In particular, I'd like you to imagine two possible structures for a cluster of three Na atoms (i.e., pretend that someone came to you and asked what geometry you think such a cluster would assume in its ground electronic state), one linear and one an equilateral triangle. Further, assume that the Na–Na distances in both such clusters are equal (i.e., that the person asking for your theoretical help is willing to assume that variations in bond lengths are not the crucial factor in determining which structure is favored). In Fig. 2.11, I show the two candidate clusters and their 3s orbitals.

Figure 2.11 Linear and equilateral triangle structures of sodium trimer.

