

Bonding theory

The two “contenders for the throne” of bonding theory are *valence bond theory* (VBT) and *molecular orbital theory* (MOT). The allusion is an apt one since it seems that much of the history of these two theories consisted of contention between their respective proponents as to which was “best.” This is indeed unfortunate inasmuch as they are but opposite sides of the same coin. Sometimes overzealous proponents of one theory give the impression that the other is “wrong.” Granted that any theory can be used unwisely, it remains nonetheless true that neither theory can be “true” to the *exclusion* of the other since both reduce to the same common and fundamental quantum-mechanical ideas. As used in inorganic chemistry, however, they do have distinctive aspects. Given a specific question one theory may prove distinctly superior in insight, ease of calculation, or simplicity and clarity of results, but a different question may reverse the picture completely. Surely the inorganic chemist who does not become thoroughly familiar with *both* theories is like the carpenter who refuses to carry a saw because he already has a hammer! He is severely limiting his skills by limiting his tools.

VALENCE BOND THEORY

The valence bond (VB) theory grew directly out of the ideas of electron pairing by Lewis and others. In 1927 W. Heitler and F. London proposed a quantum-mechanical treatment of the hydrogen molecule. Their method has come to be known as the valence bond approach and was developed extensively by men such as Linus Pauling and J. C. Slater. The following discussion is adapted from the works of Pauling and Coulson.²⁹

Suppose we have two isolated hydrogen atoms. We may describe them by the wave functions Ψ_A and Ψ_B , each having the form given on page 16 for a 1s orbital. If the atoms are sufficiently isolated so that they do not interact, the wave function for the system of two atoms is:

$$\Psi = \Psi_{A(1)}\Psi_{B(2)} \quad (3.25)$$

where A and B designate the atoms and the numbers 1 and 2 designate electrons number 1 and 2. Now we know that when the two atoms are brought together to form a molecule they will affect each other and that the individual wave functions Ψ_A and Ψ_B will change, but we may assume that Eq. 3.25 is a good starting place as a trial function for the hydrogen molecule and then try to improve it. When we solve for energy as a function of distance, we find that the energy curve for Eq. 3.25 does indeed have a minimum (curve *a*, Fig. 3.20) of about -24 kJ mol^{-1} at a distance of about 90 pm. The actual observed bond distance is 74 pm, which is not too different from our first approximation, but the experimental bond energy of H_2 is -458 kJ mol^{-1} , almost 20 times greater than our first approximation.

²⁹ L. Pauling, “The Nature of the Chemical Bond,” 3rd ed., Cornell University Press, Ithaca, N.Y., 1960; C. A. Coulson, “Valence,” 2nd ed., Oxford University Press, London, 1961; R. McWeeny, “Coulson’s Valence,” Oxford University Press, 1979.

If we examine Eq. 3.25, we must decide that we have been overly restrictive in using it to describe a hydrogen molecule. First, we are not justified in labeling electrons since all electrons are indistinguishable from each other. Moreover, even if we could, we would not be sure that electron 1 will always be on atom A and electron 2 on atom B. We must alter Eq. 3.25 in such a way that the artificial restrictions are removed. We can do this by adding a second term in which the electrons have changed positions:

$$\Psi = \Psi_{A(1)}\Psi_{B(2)} + \Psi_{A(2)}\Psi_{B(1)} \quad (3.26)$$

This improvement was suggested by Heitler and London. If we solve for the energy associated with Eq. 3.26, we obtain curve *b* in Fig. 3.20. The energy has improved greatly (-303 kJ mol^{-1}) and also the distance has improved slightly. Since the improvement is a result of our “allowing” the electrons to exchange places, the increase in bonding energy is often termed the *exchange energy*. One should not be too literal in ascribing this large part of the bonding energy to “exchange,” however, since the lack of exchange in Eq. 3.25 was merely a result of our inaccuracies in approximating a correct molecular wave function. If a physical picture is desired to account for the exchange energy, it is probably best to ascribe the lowering of energy of the molecule to the fact that the electrons now have a larger volume in which to move. Recall that the energy of a particle in a box is inversely related to the size of the box; i.e., as the box increases in size, the energy of the particle is lowered. By providing two nuclei at a short distance from each other, we have “enlarged the box” in which the electrons are confined.

A further improvement can be made if we recall that electrons shield each other (p. 36) and that the effective atomic number Z^* will be somewhat less than Z . If we adjust

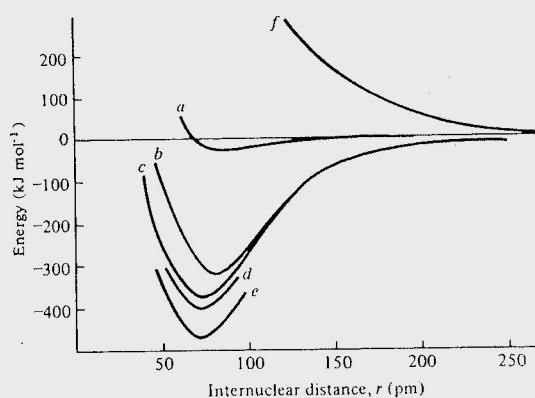
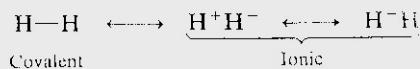


Fig. 3.20 Theoretical energy curves (*a*–*d*, *f*) for the hydrogen molecule, H_2 , compared with the experimental curve (*e*). Curves (*a*–*d*) show successive improvements in the wave function as discussed in the text. Curve (*f*) is the repulsive interaction of two electrons of like spin. [Modified from F.A. Cotton and G. Wilkinson, “Advanced Inorganic Chemistry,” 2nd ed., Wiley, New York, 1966. Reproduced with permission.]

our wave functions, Ψ_A and Ψ_B , to account for the shielding from the second electron, we obtain energy curve c—a further improvement.

Lastly, we must again correct our molecular wave function for an overrestriction which we have placed upon it. Although we have allowed the electrons to exchange in Eq. 3.26, we have demanded that they must exchange simultaneously, i.e., that only one electron can be associated with a given nucleus at a given time. Obviously this is too restrictive. Although we might suppose that the electrons would tend to avoid each other because of mutual repulsion and thus tend to stay one on each atom, we cannot go so far as to say that they will *always* be in such an arrangement. It is common to call the arrangement given by Eq. 3.26 the “covalent structure” and to consider the influence of “ionic structures” on the overall wave function:



We then write

$$\Psi = \Psi_{A(1)}\Psi_{B(2)} + \Psi_{A(2)}\Psi_{B(1)} + \lambda\Psi_{A(1)}\Psi_{A(2)} + \lambda\Psi_{B(1)}\Psi_{B(2)} \quad (3.27)$$

where the first two terms represent the covalent structure and the second two terms represent ionic structures in which both electrons are on atom A or B. Since the electrons tend to repel each other somewhat, there is a smaller probability of finding them both on the same atom than on different atoms, so the second two terms are weighted somewhat less ($\lambda < 1$). Equation 3.27 can be expressed more succinctly as

$$\Psi = \Psi_{\text{cov}} + \lambda'\Psi_{\text{H}^+\text{H}^-} + \lambda'\Psi_{\text{H}^-\text{H}^+} \quad (3.28)$$

When we investigate the energetics of the wave function in Eq. 3.27, we find further improvement in energy and distance (curve d, Fig. 3.20).

This is the first example we have had of the phenomenon of *resonance*, which we shall discuss at some length later on. It should be pointed out now, however, that the hydrogen molecule has one structure which is described by *one* wave function, Ψ . However, it may be necessary because of our approximations, to write Ψ as a combination of two or more wave functions, each of which only partially describes the hydrogen molecule. Table 3.7 lists values for the energy and equilibrium distance for the various stages of our approximation, together with the experimental values.

Now, if one wishes, additional “corrections” can be included in our wave function, to make it more nearly descriptive of the actual situation obtaining in the hydrogen molecule.^{30,31} However, the present simplified treatment has included the three important contributions to bonding: delocalization of electrons over two or more nuclei, mutual screening, and partial ionic character.

³⁰ A 100-term function (see ref. 31) has reproduced the experimental value to within 0.01 kJ mol⁻¹. See C. A. Coulson, “Valence,” 2nd ed., Oxford University Press, London, 1961, pp. 124–125. For a more rigorous discussion, see F. L. Pilar, “Elementary Quantum Chemistry,” McGraw-Hill, New York, 1968, pp. 234–249.

³¹ W. Koles and L. Wolniewicz, *J. Chem. Phys.*, 1968, 49, 404. See G. Herzberg, *J. Mol. Spectr.*, 1970, 33, 147, for the experimental value.

Table 3.7 Energies and equilibrium distances for VB wave functions

Type of wave function	Energy (kJ mol ⁻¹)	Distance (pm)
Uncorrected, $\Psi = \Psi_A\Psi_B$	24	90
“Heitler-London”	303	86.9
Addition of shielding	365	74.3
Addition of ionic contributions	388	74.9
Observed values	458.0	74.1

SOURCE: C. A. Coulson, “Valence,” 2nd ed., Oxford University Press, London, 1961, p. 125. Used with permission.

The reader may question the apparently *ad hoc* corrections for shielding and ionic contributions and wonder if it is not possible to “overcorrect” for a given physical factor. The answer is given by the *variation principle* which states that any trial wave function can never yield a lower energy (i.e., give a greater bonding energy) than the true energy of the system. All of our adjustments allow us to approach the true wave function for the molecule; we can never surpass it. As each adjustment is made (i.e., for shielding, etc.) the parameters in the trial function can be adjusted to yield the best energy. In fact, it is not necessary even to make the adjustments in terms of exchange, shielding, or ionicity—introduction of sufficient parameters can improve the wave function to any desired degree of accuracy. Again, this should remind us of the artificiality of such things as “exchange energy.”

There is an implicit assumption contained in all of the above: *The two bonding electrons are of opposite spin*. If two electrons are of parallel spin, no bonding occurs, but repulsion instead (curve f, Fig. 3.20). This is a result of the Pauli exclusion principle. Because of the necessity for pairing in each bond formed, the valence bond theory is often referred to as the electron pair theory, and it forms a logical quantum-mechanical extension of Lewis’s theory of electron pair formation.

Molecular orbital theory

A second approach to bonding in molecules is known as the molecular orbital (MO) theory. The assumption here is that if two nuclei are positioned at an equilibrium distance, and electrons are added, they will go into molecular orbitals that are in many ways analogous to the atomic orbitals discussed in Chapter 2. In the atom there are s, p, d, f, . . . orbitals determined by various sets of quantum numbers and in the molecule we have $\sigma, \pi, \delta, \dots$ orbitals determined by quantum numbers. We should expect to find the Pauli exclusion principle and Hund’s principle of maximum multiplicity obeyed in these molecular orbitals as well as in the atomic orbitals.

When we attempt to solve the Schrödinger equation to obtain the various molecular orbitals, we run into the same problem found earlier for atoms heavier than hydrogen. We are unable to solve the Schrödinger equation exactly and therefore must make some approximations concerning the form of the wave functions for the molecular orbitals.

Of the various methods of approximating the correct molecular orbitals, we shall discuss only one, the linear combination of atomic orbitals (LCAO) method. We assume that we can approximate the correct molecular orbitals by combining the atomic orbitals

of the atoms that form the molecule. The rationale is that most of the time the electrons will be nearer and hence "controlled" by one or the other of the two nuclei, and when this is so, the molecular orbital should be very nearly the same as the atomic orbital for that atom. We therefore combine the atomic orbitals, Ψ_A and Ψ_B , to obtain two molecular orbitals:³²

$$\Psi_b = \Psi_A + \Psi_B \quad (3.29)$$

$$\Psi_a = \Psi_A - \Psi_B \quad (3.30)$$

The one-electron molecular orbitals thus formed consist of a *bonding* molecular orbital (Ψ_b) and an *antibonding* molecular orbital (Ψ_a).³³ If we allow a single electron to occupy the bonding molecular orbital (as in H_2^+ , for example), the approximate wave function for the molecule is

$$\Psi = \Psi_{b(1)} = \Psi_{A(1)} + \Psi_{B(1)} \quad (3.31)$$

For a two-electron system such as H_2 , the total wave function is the product of the wave functions for each electron:

$$\Psi_t = \Psi_{b(1)} \Psi_{b(2)} = [\Psi_{A(1)} + \Psi_{B(1)}] [\Psi_{A(2)} + \Psi_{B(2)}] \quad (3.32)$$

$$\Psi = \Psi_{A(1)} \Psi_{A(2)} + \Psi_{B(1)} \Psi_{B(2)} + \Psi_{A(1)} \Psi_{B(2)} + \Psi_{A(2)} \Psi_{B(1)} \quad (3.33)$$

The results for the MO treatment are similar to those obtained by VB theory. Equation 3.33 is the same (when rearranged) as Eq. 3.27 except that the ionic terms ($\Psi_{A(1)}\Psi_{A(2)}$ and $\Psi_{B(1)}\Psi_{B(2)}$) are weighted as heavily as the covalent ones ($\Psi_{A(1)}\Psi_{B(2)}$ and $\Psi_{A(2)}\Psi_{B(1)}$). This is not surprising, since we did not take into account the repulsion of electrons in obtaining Eq. 3.32. This is a general result: Simple molecular orbitals obtained in this way from the linear combination of atomic orbitals (LCAO-MO theory) tend to exaggerate the ionicity of molecules, and the chief problem in adjusting this simple method to make the results more realistic consists of taking into account *electron correlation*. As in the case of VB theory it is possible to optimize the wave function by the addition of correcting terms. Some typical results for the hydrogen molecule are listed in Table 3.8.

The two orbitals Ψ_b and Ψ_a differ from each other as follows. In the bonding molecular orbital the wave functions for the component atoms reinforce each other in the region between the nuclei (Fig. 3.21a, b), but in the antibonding molecular orbital they cancel, forming a node between the nuclei (Fig. 3.21d). We are, of course, interested in learning of the *electron distribution* in the hydrogen molecule, and will therefore be interested in the *square* of the wave functions:

$$\Psi_b^2 = \Psi_A^2 + 2\Psi_A\Psi_B + \Psi_B^2 \quad (3.34)$$

$$\Psi_a^2 = \Psi_A^2 - 2\Psi_A\Psi_B + \Psi_B^2 \quad (3.35)$$

³² The combination $\Psi_B - \Psi_A$ does not represent a third MO, but is another form of Ψ_a .

³³ Note that the subscripts a, b and A, B bear no relation to one another; the former refer to antibonding and bonding whereas the latter merely identify the atomic orbitals on the atoms forming the molecule.

Table 3.8 Energies and equilibrium distances for MO wave functions

Type of wave function	Energy (kJ mol ⁻¹)	Distance (pm)
Uncorrected, $\Psi = \Psi_A + \Psi_B$	260	85
Addition of shielding	337	73
Addition of electron-electron repulsions	397	71
Observed values	458.0	74.1

SOURCE: C. A. Coulson, "Valence," 2nd ed., Oxford University Press, London, 1961, p. 125. Used with permission.

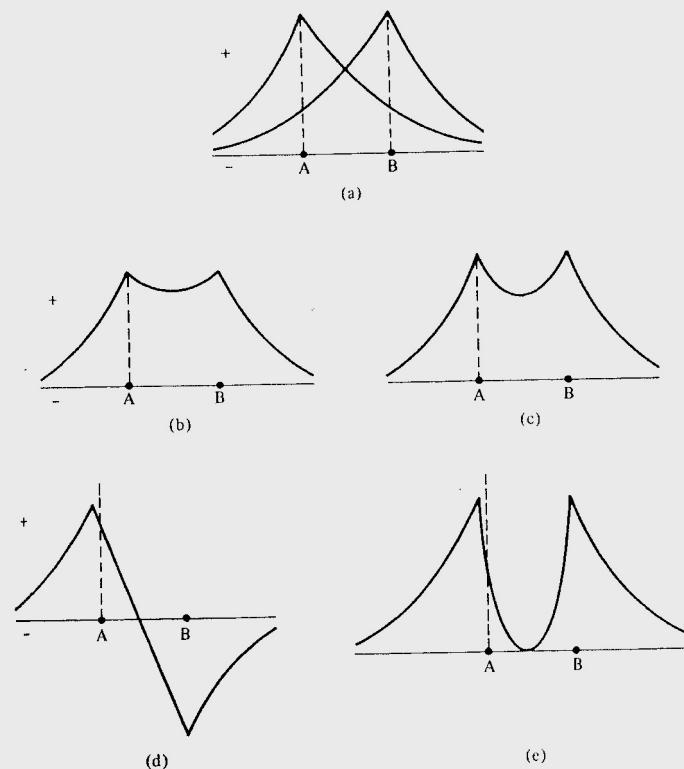


Fig. 3.21 (a) Ψ_A and Ψ_B for individual hydrogen atoms (cf. Fig. 2.3). (b) $\Psi_b = \Psi_A + \Psi_B$. (c) Probability function for the bonding orbital, Ψ_b^2 . (d) $\Psi_a = \Psi_A - \Psi_B$. (e) Probability function for the antibonding orbital, Ψ_a^2 . Note that the bonding orbital increases the electron density between the nuclei (c) but that the antibonding orbital decreases the electron density between the nuclei (e). [Adapted from H. H. Jaffé, in "Comprehensive Biochemistry," M. Florkin and E. H. Stotz, eds., Elsevier, Amsterdam, 1961. Reproduced with permission.]

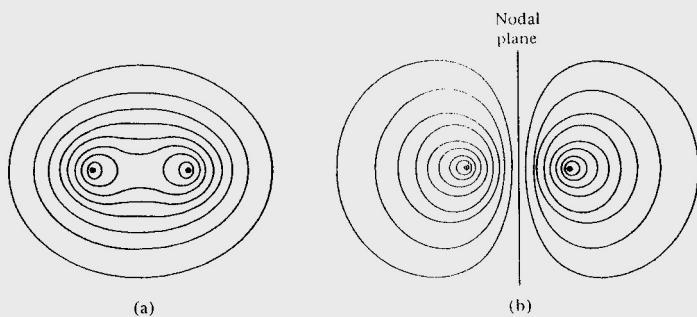


Fig. 3.22 Electron density contours for the H_2^+ ion: bonding (a) and antibonding (b) orbitals. [From D. R. Bates et al., *Phil. Trans. Roy. Soc.*, 1953, 246, 215. Reproduced with permission.]

The difference between the two probability functions lies in the cross term $2\Psi_A\Psi_B$. The integral $\int \Psi_A\Psi_B d\tau$ is known as the *overlap integral*, S , and is very important in bonding theory. In the bonding orbital the overlap is positive and the electron density between the nuclei is *increased*, whereas in the antibonding orbital the electron density between the nuclei is *decreased*. (See Fig. 3.21c, e.) In the former case the nuclei are shielded from each other and the attraction of both nuclei for the electrons is enhanced. This results in a *lowering* of the energy of the molecule and is therefore a *bonding* situation. In the second case the nuclei are partially bared toward each other and the electrons tend to be in those regions of space in which mutual attraction by both nuclei is severely reduced. This is a repulsive, or *antibonding*, situation. An electron density map for the hydrogen molecule ion, H_2^+ , is shown in Fig. 3.22 illustrating the differences in electron densities between the bonding and antibonding conditions.³⁴

We have postponed normalization of the molecular orbitals until now. Since $\int \Psi^2 d\tau = 1$ for the probability of finding an electron somewhere in space, Eq. 3.34 becomes

$$\int N_b^2 \Psi_b^2 d\tau = N_b^2 \left[\int \Psi_A^2 d\tau + \int \Psi_B^2 d\tau + 2 \int \Psi_A \Psi_B d\tau \right] = 1 \quad (3.36)$$

where N_b is the *normalizing constant*. If we let S be the overlap integral, $\int \Psi_A \Psi_B d\tau$, we have

$$\int \Psi_b^2 d\tau = \left[\int \Psi_A^2 d\tau + \int \Psi_B^2 d\tau + 2S \right] \quad (3.37)$$

Now since the atomic wave functions Ψ_A and Ψ_B were previously normalized, $\int \Psi_A^2 d\tau$ and $\int \Psi_B^2 d\tau$ each equal one. Hence

$$N_b^2 = \frac{1}{2 + 2S} \quad (3.38)$$

$$N_b = \sqrt{\frac{1}{2 + 2S}} \quad (3.39)$$

³⁴ The electron density map is easier to obtain for H_2^+ than for H_2 because of the lack of necessity for correction of electron interactions. The differences are not great.

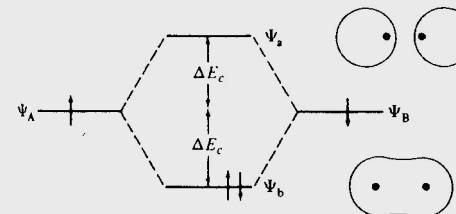


Fig. 3.23 Energy levels for the H_2 molecule with neglect of overlap. The quantity of ΔE_c represents the difference in energy between the energy levels of the separated atoms and the bonding molecular orbital. It is equal to 458 kJ mol^{-1} .

and

$$N_b = \sqrt{\frac{1}{2 - 2S}} \quad (3.40)$$

For most simple calculations the value of the overlap integral, S , is numerically rather small and may thus be neglected without incurring too great an error. This simplifies the algebra considerably and is sufficiently accurate for most purposes. With complete neglect of overlap, our molecular wave functions become

$$\Psi_b = \frac{1}{\sqrt{2}} (\Psi_A + \Psi_B) \quad (3.41)$$

$$\Psi_a = \frac{1}{\sqrt{2}} (\Psi_A - \Psi_B) \quad (3.42)$$

The idea of “complete neglect of overlap” is one which may readily lead to confusion. It is a common simplification often encountered in molecular orbital calculations. Yet in the next section great stress will be placed on the importance of overlap, and the generalization will be made that the strength of a bond is roughly proportional to overlap, and that if overlap is zero or negative, a bond will not form. This seeming paradox may be resolved as follows: The bond energy, ΔE_c , is proportional to the extent that the atomic orbitals overlap. Hence, in our qualitative attempts to rationalize covalent bonds we shall need to pay exceedingly close attention to the symmetry of orbitals and their overlap. “Neglect of overlap” simply means that the numerical value of the overlap integral, S , is neglected in the *normalization* procedure. If the overlap had been included in the calculation the normalization coefficients would have been: $N_a = 1.11$ and $N_b = 0.56$ instead of $N_a = N_b = 0.71$. Other molecules have less overlap than H_2 , and so the effect is less.

The relative energies (assuming neglect of overlap) of the two molecular orbitals are shown in Fig. 3.23. The bonding orbital is stabilized relative to the energy of the isolated atoms by the quantity ΔE_c . The antibonding orbital is destabilized by an equivalent quantity.³⁵

³⁵ If overlap is included in the calculation, the antibonding orbital is somewhat more destabilized than the bonding orbital is stabilized. This is an extremely important phenomenon which we shall encounter over and over, from the nonexistence of He_2 to various atomic repulsions.

The quantity ΔE_c is termed the *exchange energy* and corresponds to the exchange energy we observed previously in VB theory (p. 93). Here, too, one should be cautious about trying to interpret it literally as resulting from "exchange" or a "resonance."

SYMMETRY AND OVERLAP³⁶

As we have seen from Eqs. 3.34 and 3.35 the only difference between the electron distribution in the bonding and antibonding molecular orbitals and the atomic orbitals is in those regions of space for which both Ψ_A and Ψ_B have appreciable values, so that their product ($S = \int \Psi_A \Psi_B d\tau$) has an appreciable nonzero value. Furthermore, for bonding, $S > 0$, and for antibonding, $S < 0$. The condition $S = 0$ is termed *norbonding* and corresponds to no interaction between the orbitals. We may make the generalization that the strength of a bond will be roughly proportional to the extent of the overlap of the atomic orbitals. This is known as the *overlap criterion of bond strength* and indicates that bonds will form in such a way as to maximize overlap.

In *s* orbitals the sign of the wave function is everywhere the same (with the exception of small, intranodal regions for $n > 1$), and so there is no problem with matching the sign of the wave functions to achieve positive overlap. With *p* and *d* orbitals, however, there are several possible ways of arranging the orbitals, some resulting in positive overlap, some in negative overlap, and some in which the overlap is exactly zero (Fig. 3.24). Bonding can take place only when the overlap is positive.

It may occur to the reader that it is always possible to bring the orbitals together in such a way that the overlap is positive. For example, in Fig. 3.24g, h if negative overlap is obtained, one need only invert one of the atoms to achieve positive overlap. This is true for diatomic molecules or even for polyatomic linear molecules. However, when we come to cyclic compounds, we no longer have the freedom arbitrarily to invert atoms to obtain proper overlap matches. One example will suffice to illustrate this.

There is a large class of compounds, the phosphonitrilic halides ($X = F, Cl, Br$), containing the phosphazene ring system, $(PNX_2)_n$ (see Chapter 14). The trimer, $P_3N_3X_6$, is illustrated in Fig. 3.25. Note the resemblance to benzene in the alternating single and double bonds. Like benzene, the phosphonitrilic trimer is aromatic, i.e., the π electrons are delocalized over a conjugated system with resonance stabilization.³⁷ Unlike benzene, however, there is a node in the lowest lying molecular orbital which tends to disrupt the aromaticity and decrease the resonance energy of the system. This is illustrated in Fig. 3.26, which represents the phosphonitrilic ring split open and arranged linearly for clarity. We start on nitrogen atom number one (N_1) and assume an arbitrary assignment of the positive and negative lobes of the *p* orbital. The phosphorus atom π bonds through its *d* orbitals, and so for the P_1 atom we draw a *d* orbital with appropriate symmetry such that the overlap between N_1 and P_1 is greater than zero. We continue with N_2 , P_2 , N_3 , and P_3 , each time matching the orbital symmetries to achieve positive overlap. However, when we come to the overlap between

³⁶ A minimum of symmetry is presented here to allow discussion of overlap. The reader is encouraged to turn to Appendix B for a more lengthy discussion of the subject.

³⁷ A number of new terms are used here such as π electrons, aromaticity, delocalization, etc. If the reader is not familiar with these terms from previous work (e.g., organic chemistry) it will be easiest simply to note the mismatch in orbital symmetry and return to this discussion after completing the chapter.

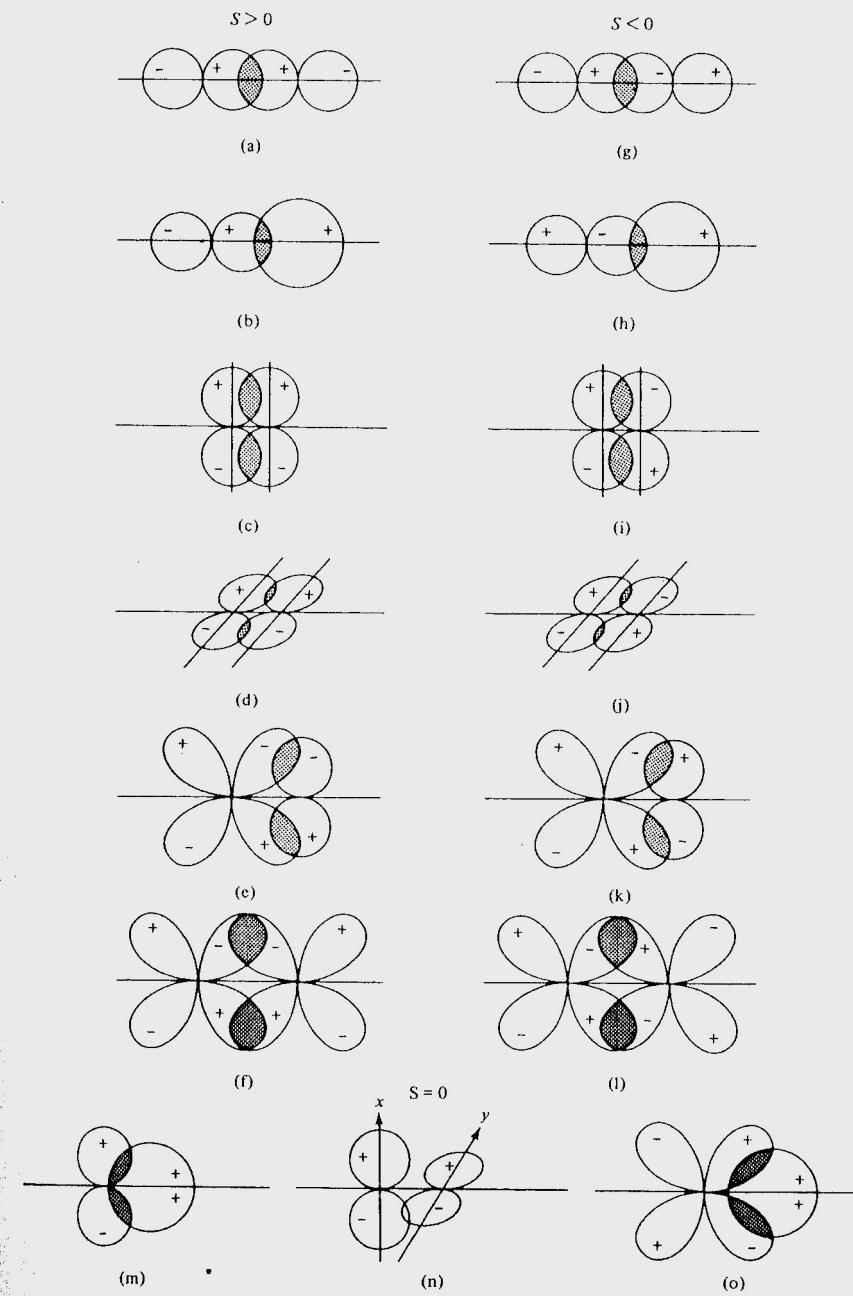


Fig. 3.24 Arrangements of atomic orbitals resulting in positive (a–f), negative (g–l), and zero (m–o) overlap.

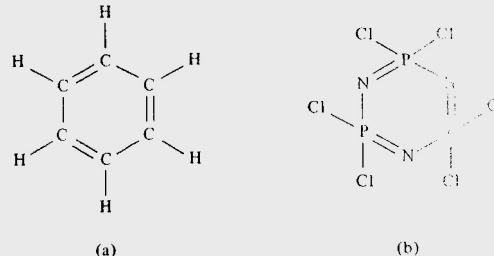


Fig. 3.25 Comparison of bonding in the ring systems of (a) benzene and (b) phosphonitrilic chloride trimer.

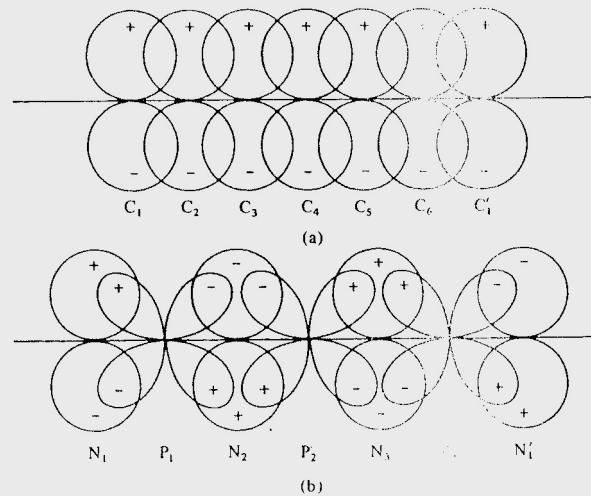


Fig. 3.26 Overlay of orbitals in the $p-p \pi$ system in benzene (a) and $p-d \pi$ system in the phosphonitrilic ring (b). Note the mismatch of orbital symmetry in the latter.

P_3 and N_1 (to close the ring) we find that we would like to have the N_1 orbital lie as shown on the right, but we have previously assigned it the arrangement shown on the left. It is impossible to draw the six orbitals in such a way as to avoid a mismatch or node in the system.

Symmetry of molecular orbitals

Some of the possible combinations of atomic orbitals are shown in Fig. 3.27. Those orbitals which are cylindrically symmetrical about the internuclear axis are called σ orbitals, analogous to an s orbital, the atomic orbital of highest symmetry. If the internuclear axis lies in a nodal plane, a π bond results. In δ bonds the internuclear axis lies in two mutually perpendicular nodal planes. All antibonding orbitals possess an additional

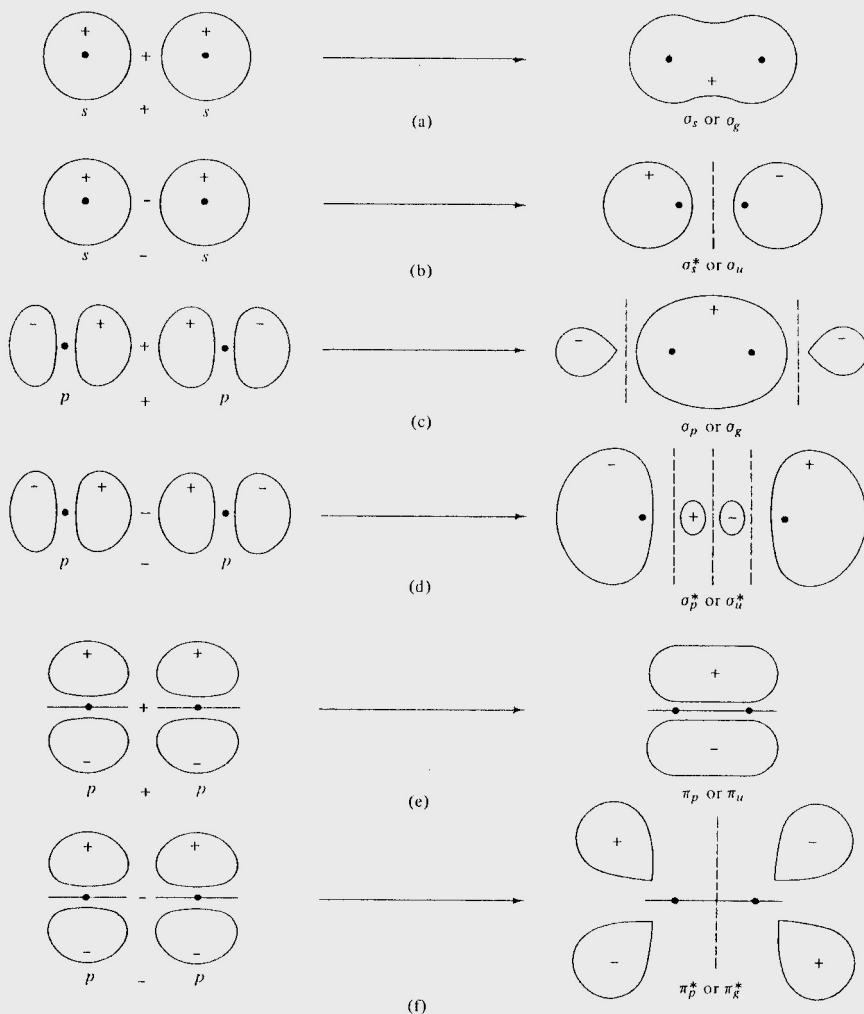


Fig. 3.27 Symmetry of molecular orbitals formed from atomic orbitals illustrating σ (a–d) and π (e, f) orbitals, and bonding (a, c, e) and antibonding (b, d, f) orbitals. The orbitals are depicted by electron density sketches with the sign of Ψ superimposed.

nodal plane perpendicular to the internuclear axis and lying between the nuclei. In addition to the presence or absence of one or more nodal planes, we shall also be interested in the symmetry with respect to inversion about the center of the molecule (see p. 24). Of interest in this regard are π_{p-p} orbitals, which are *ungerade*, and π_{p-p}^* orbitals, which are *gerade*.