

Molecular orbitals in diatomic molecules

Molecules containing two atoms of the same element are the simplest molecules to discuss. We have already seen the results for the hydrogen molecule (p. 99; Fig. 3.23) and for the linear combination of *s* and *p* orbitals (Fig. 3.24). We shall now investigate the general case for molecular orbitals formed from two atoms having atomic orbitals 1*s*, 2*s*, 2*p*, 3*s*, etc.

There are two criteria which must be met for the formation of molecular orbitals which are more stable,³⁸ i.e., lower in energy than the contributing atomic orbitals. One is that the overlap between the atomic orbitals must be positive. Furthermore, in order that there be effective interaction between orbitals on different atoms, the energies of the two atomic orbitals must be approximately the same. This topic will be discussed at greater length later (pp. 137, 144), but for now it may be concluded that molecular orbitals will form from corresponding orbitals on the two atoms (i.e., 1*s* + 1*s*; 2*s* + 2*s*; etc.). We shall see later that this is an oversimplification that can occasionally lead us astray. However, it is the simplest way to approach the topic and we can easily modify it when necessary. When we combine the atomic orbitals in this way, the energy levels shown in Fig. 3.28 are obtained. The appropriate combinations are:³⁹

$$\begin{array}{ll} \sigma_{1s} = 1s_A + 1s_B & \pi_{2py} = 2p_{yA} + 2p_{yB} \\ \sigma_{1s}^* = 1s_A - 1s_B & \pi_{2px} = 2p_{xA} + 2p_{xB} \\ \sigma_{2s} = 2s_A + 2s_B & \pi_{2py}^* = 2p_{yA} - 2p_{yB} \\ \sigma_{2s}^* = 2s_A - 2s_B & \pi_{2px}^* = 2p_{xA} - 2p_{xB} \\ \sigma_{2p} = 2p_{zA} + 2p_{zB} & \\ \sigma_{2p}^* = 2p_{zA} - 2p_{zB} & \end{array}$$

The σ_{1s} and σ_{1s}^* orbitals correspond to the molecular orbitals seen previously for the hydrogen molecule. The atomic 2*s* orbitals form a similar set of σ and σ^* orbitals. The atomic *p* orbitals can form σ bonds from direct ("head on") overlap of the p_z orbitals and two π bonds from parallel overlap of the p_y and p_x orbitals. Since the overlap is greater in the former case, we should expect the exchange energy to be greater also (p. 100), and σ bonds are generally stronger than π bonds. Hence the σ_{2p} orbital is stabilized (lowered in energy) more than the π_{2p} orbitals, and conversely the corresponding antibonding orbitals are raised accordingly.⁴⁰ By analogy with atomic electron configurations, we can write molecular electron configurations. For H₂ we have:



Using Fig. 3.28 as a guide, we can proceed to build up various diatomic molecules in much the same way as the *aufbau* principle was used to build up atoms.

³⁸ This statement applies to *bonding orbitals*, of course. *Antibonding orbitals* are always less stable than the corresponding atomic orbitals.

³⁹ Symbols A and B represent atoms. x, y, and z represent orientation of the *p* orbitals, and the asterisk (*) identifies antibonding orbitals.

⁴⁰ This discussion is somewhat oversimplified as we shall see later.

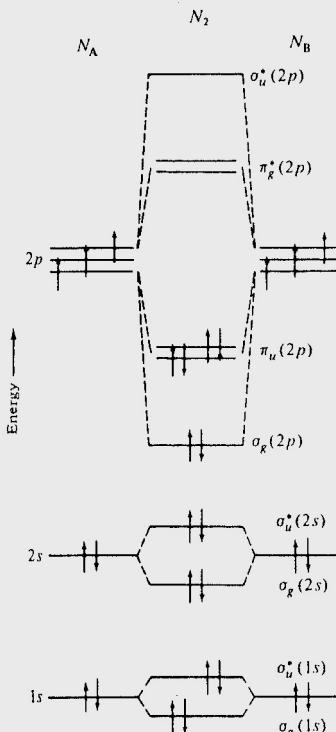


Fig. 3.28 Simplified molecular orbital energy levels assuming no mixing of *s* and *p* orbitals. The three 2*p* orbitals are degenerate, i.e., they all have the same energy and might better be shown as ——————, but the latter is more cumbersome. The molecule shown is N₂. [Adapted from M. Orchin and H. H. Jaffé, "The Importance of Antibonding Orbitals," Houghton Mifflin, Boston, 1967. Reproduced with permission.]

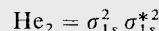
1. *Molecules containing one to four electrons.* We have already seen the H₂ molecule in which there are two electrons in the σ_{1s} orbital. Two bonding electrons constitute a chemical bond. The molecular orbital theory does not restrict itself to even numbers of bonding electrons, and so the bond order is given as one-half the difference between the number of bonding electrons and the number of antibonding electrons:

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) \quad (3.43)$$

The molecule He₂ is unknown since the number of antibonding electrons (2) is equal to the number of bonding electrons (2) and the net bond order is zero. With no bond energy to overcome⁴¹ the dispersive tendencies of entropy, two helium atoms in a "molecule" will not remain together but fly apart. If it existed, molecular helium would have the electron

⁴¹ If overlap is not neglected in the calculation, the antibonding orbital is *more* destabilizing than the bonding orbital is stabilizing and so He₂ actually has a repulsive energy forcing it apart.

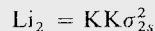
configuration:



If helium is ionized, it is possible to form diatomic helium molecule-ions, He_2^+ . Such a molecule will contain three electrons, two bonding and one antibonding, for a net bond order of one-half. Such a species, although held together with only about one-half the bonding energy of the hydrogen molecule, should be expected to exist. In fact it does, and it has been observed spectroscopically in highly energetic situations sufficient to ionize the helium. That it is not found under more familiar chemical situations as, for example, in salts, $\text{He}_2^+X^-$, is not a result of any unusual weakness in the He—He bond, but because contact with just about any substance will supply the missing fourth electron with resultant conversion into helium atoms.

Isoelectronic in a formal sense, but quite different in the energies involved is the Xe_2^+ ion believed to exist in certain very acidic solvents (see Chapter 15). The energetics of the situation are not completely understood, but presumably the much lower ionization energy of xenon can more readily be compensated by the solvation energy of the polar solvent, thus stabilizing the Xe_2^+ cation.

2. Lithium and beryllium. Two lithium atoms contain six electrons. Four will fill the σ_{1s} and σ_{1s}^* orbitals with no bonding. The last two electrons will enter the σ_{2s} orbital, giving a net bond order of one in the Li_2 molecule. The electron configuration will be:



where K stands for the K (1s) shell.⁴²

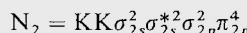
Eight electrons from two beryllium atoms fill the four lowest energy levels, σ_{1s} , σ_{1s}^* , σ_{2s} , σ_{2s}^* , yielding a net bond order of zero, as in He_2 , with an electron configuration of:



Like the latter molecule, Be_2 is not expected to exist. The experimental facts are that lithium is diatomic in the gas phase, but that beryllium is monatomic.

3. Boron and carbon. The molecules B_2 and C_2 are not commonly observed chemical species. Nevertheless, their properties are important in determining the correctness of our energy level diagram, and they will be discussed later.

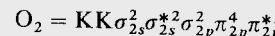
4. Nitrogen, oxygen, fluorine, and neon. The nitrogen molecule contains fourteen electrons. Four of these lie in the σ_{1s} and σ_{1s}^* orbitals, which cancel and may thus be ignored. The next four occupy the σ_{2s} and σ_{2s}^* orbitals and contribute nothing to the net bonding. The remaining six electrons form a σ bond and two π bonds. The electronic configuration for the N_2 molecule may therefore be written:



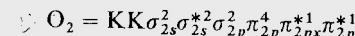
⁴² The inner shells of core electrons are often abbreviated since no net bonding takes place in them. The symbols used, K, L, M, etc., refer to the older system of designating the principal energy levels, $n = 1(\text{K})$, $n = 2(\text{L})$, etc. Thus $\text{Na}_2 = \text{KK LL} \sigma_{3s}^2$.

The bond order is three (one σ and two π bonds) agreeing with the experimentally observed large dissociation energy of 942 kJ mol^{-1} .

The oxygen molecule was one of the first applications of the molecular orbital theory in which it proved more successful than the simple valence bond theory. The oxygen molecule contains two more electrons than the N_2 molecule. The electron configuration is therefore:

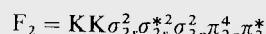


However, examination of the energy level diagram in Fig. 3.28 indicates that the π_{2p}^* level is doubly degenerate from the two equivalent π orbitals π_{2py}^* and π_{2px}^* . Hund's rule of maximum multiplicity predicts that the two electrons entering the π^* level will occupy two different orbitals, so the electronic configuration can be written more explicitly as:



This has no effect on the bond order, which is still two [$\frac{1}{2}(6 - 2)$], as anticipated by valence bond theory. The difference lies in the *paramagnetism* of molecular oxygen resulting from the two unpaired electrons. (In this regard O_2 is analogous to atomic carbon in which the last two electrons remained unpaired by entering different, degenerate orbitals.) The simple valence bond theory predicts that all electrons in oxygen will be paired; in fact, the formation of two bonds *demands* that the maximum number of electrons be paired. This is the first case of several we shall encounter in which the stress placed on *paired bonding electrons* is exaggerated by the valence bond theory. The molecular orbital theory does not require such pairing as it merely counts the number of bonding versus antibonding electrons. The experimentally measured paramagnetism of O_2 confirms the accuracy of the MO treatment.

For the fluorine molecule, there will be a total of 18 electrons distributed:



The net bond order is one, corresponding to the σ bond, and agreeing with the valence bond picture.

The addition of two more electrons to form the Ne_2 molecule will result in filling the last antibonding orbital, the σ_{2p}^* orbital. This will reduce the bond order to zero and Ne_2 , like He_2 , will not exist.

The results of this brief discussion of molecular orbitals in diatomic molecules are summarized in Table 3.9 along with appropriate experimental data.

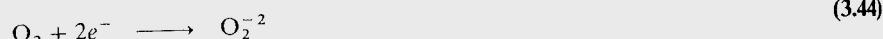
Ionization of diatomic molecules, energetics, and bond length

Further support for the advantages of the MO viewpoint comes from investigation of the bond lengths in some diatomic molecules and ions. For example, consider the oxygen molecule. As we have seen previously, it contains a double bond resulting from two σ -bonding electrons, four π -bonding electrons, and two π -antibonding electrons. The bond

Table 3.9 Selected diatomic molecules

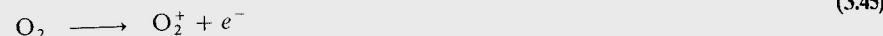
Molecule	Molecular orbital predictions			Experimental data		
	Electrons	Net bonds	Unpaired electrons	Bond energy (kJ mol ⁻¹)	Dia- or paramagnetic	Bond length (pm)
H ₂	2	1σ	0	432.00	D	74.2
He ₂	4	0	0	0	—	—
Li ₂	6	1σ	0	105	D	267.2
Be ₂	8	0	0	—	—	—
N ₂	14	1σ, 2π	0	941.69	P	120.7
O ₂	16	1σ, 1π	2	493.59	D	141.8
F ₂	18	1σ	0	155	—	—
Ne ₂	20	0	0	0	—	—

length is 121 pm. Addition of two electrons to the oxygen molecule results in the well-known peroxide ion, O₂⁻²:



According to Fig. 3.28 these two electrons will enter the π* orbitals, decreasing the bond order to one. Since the compressive forces (bond energy) are reduced and the repulsive forces (nonbonding electron repulsions) remain the same, the bond length is increased to 149 pm. If only one electron is added to an oxygen molecule, the superoxide ion, O₂⁻, results. Since there is one less antibonding electron than in O₂⁻², the bond order is 1½ and the bond length is 126 pm.

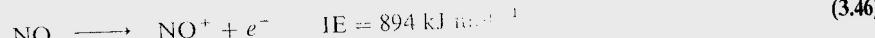
Furthermore, ionization of O₂ to a cation:



causes a decrease in bond length to 112 pm. The electron ionized is a π* antibonding electron and the bond order in O₂⁺ is 2½.

The nitric oxide molecule, NO, has a bond length of 115 pm and a bond order of 2½. Ionization to the nitrosyl ion, NO⁺, removes an antibonding π* electron and results in a bond order of three (isoelectronic with N₂) and a shortening of the bond length to 106 pm. In contrast, addition of an electron (to a π* orbital) causes a decrease in bond order and an increase in bond length.

The fact that the formation of the nitrosyl ion results from the removal of an *antibonding electron* makes the ionization energy (IE) for the reaction



lower than would otherwise be the case for the unbound atoms of nitrogen (IE = 1402 kJ mol⁻¹) and oxygen (IE = 1314 kJ mol⁻¹). The nitrosyl ion is thus stabilized and exists in several compounds, such as NO⁺HSO₄⁻ and NO⁺BF₄⁻.

A comparison of the ionization energies of molecular oxygen and nitrogen illustrates the same point. The ionization energy of molecular nitrogen is 1503 kJ mol⁻¹, greater than that of atomic nitrogen, in agreement with Fig. 3.28 that a *bonding* (and therefore more stable) electron is removed. In contrast, the ionization energy of molecular oxygen is 1164 kJ mol⁻¹, less than that of atomic oxygen. In this case the ionized electron is removed from an antibonding orbital, requiring less energy.

Closer look at diatomic energy levels

Thus far we have employed the simple energy level diagram of Fig. 3.28 with considerable success in accounting for magnetic properties, bond energies, and ionization energies of various diatomic molecules. Nevertheless, some molecules indicate that the order of energy levels shown in Fig. 3.28 is not quite right. According to Fig. 3.28, the B₂ molecule would be predicted to have a single σ bond and be diamagnetic. Experimentally the B₂ molecule is found to have two unpaired electrons. The C₂ molecule would be predicted to have an electron configuration KKσ_{2s}²σ_{2s}*²σ_{2p}²π_{2p}¹π_{2p}¹ and be paramagnetic. The experimental evidence indicates that the ground state of C₂ is diamagnetic.

The problem here is that in constructing Fig. 3.28 mixing was allowed only between orbitals on atoms A and B which were identical in energy. Actually, mixing will take place between *all* orbitals of proper symmetry, inhibited only by the fact that if the mismatch between orbitals is large, mixing will be reduced. We are therefore justified in dismissing mixing between the 1s and 2s orbitals. The energy difference between the 2s and 2p orbitals is less and varies with the effective atomic number of the element. With a larger effective atomic number, as in fluorine, the difference between s and p orbitals is more pronounced, and the mixing may be sufficiently small to be neglected.⁴³ The difference in energy between the 2s and 2p levels dramatically increases from about 200 kJ mol⁻¹ in the lithium atom to about 2500 kJ mol⁻¹ in the fluorine atom. In the case of the elements to the left of the series, the lower effective nuclear charge allows the 2s and 2p orbitals to come sufficiently close to mix. This phenomenon is the equivalent of hybridization in the valence bond theory discussed in the next section.

We shall not investigate the details of s–p mixing, but merely perform a thought experiment that indicates the nature of the results. We have seen above that Fig. 3.28 is approximately true if the energy gap between the s and p orbitals is large, as in F₂. Consider narrowing the gap between the 2s and 2p orbitals. As this gap narrows, mixing (hybridization) of the s and p orbitals becomes energetically feasible. However, more important in terms of the final energy-level diagram, molecular orbitals of the same symmetry will interact with one another, with the lower-energy orbital becoming more stabilized and the higher-energy orbital being destabilized. This is a result of the “no-crossing rule” (Fig. 3.29). In the present circumstance, as the σ_g(2s) and the σ_g(2p) orbitals approach (because of the lessening difference in energy between 2s and 2p) they interact. Because of the mixing of the

⁴³ There is no experimental evidence confirming or denying this possibility.

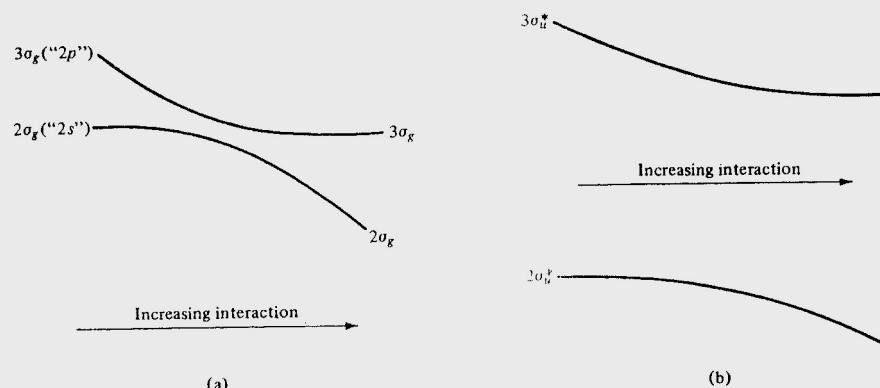


Fig. 3.29 Effects of the no-crossing rule. (a) Strong interaction between orbitals of the same symmetry. (b) Weak interaction between orbitals of the same symmetry.

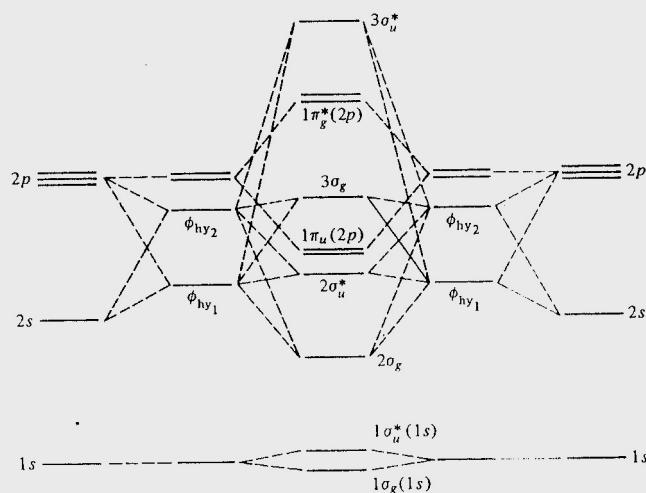


Fig. 3.30 Correct molecular orbital energy levels. Some mixing (hybridization) has occurred between the $2s$ and $2p$ orbitals. Note that it is somewhat more difficult to "keep books" and determine the bond order here than in Fig. 3.28: $2\sigma_g$ and $1\pi_u$ ($2p$) are clearly bonding (they lie below the atomic orbitals contributing to them); $2\sigma_u^*$ and $3\sigma_g$ are essentially nonbonding since they lie between the atomic orbitals contributing to them and roughly symmetrically spaced about the "center of gravity." The maximum net bond order is therefore one σ bond plus two π bonds. [Adapted from M. Orchin and H. H. Jaffé, "The Importance of Antibonding Orbitals," Houghton Mifflin, Boston, 1967. Reproduced with permission.]

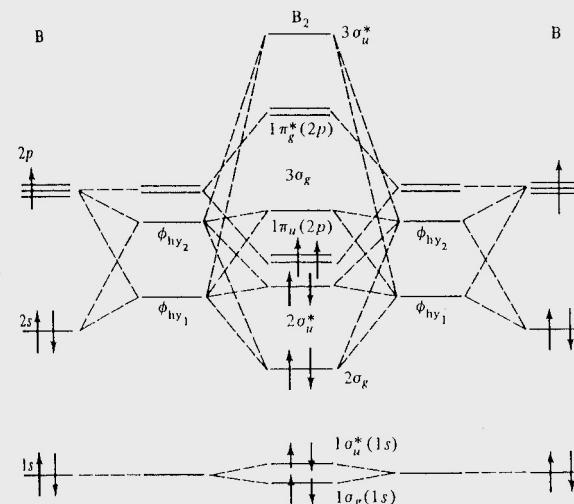


Fig. 3.31 Energy levels in the B_2 molecule. Note unpaired π electrons. [Adapted from M. Orchin and H. H. Jaffé, "The Importance of Antibonding Orbitals," Houghton Mifflin, Boston, 1967. Reproduced with permission.]

s and p orbitals it is no longer appropriate to use the $2s$ and $2p$ labels, so we merely label the orbitals according to their symmetry and in order from the most stable. Of the two σ_g orbitals, the stabilized one becomes the $2\sigma_g$, and the fact that it is lowered stabilizes the molecule considerably. The destabilization of $3\sigma_g$ does not effect the lighter molecules, such as B_2 and C_2 , since it is not populated until N_2 . There is some interaction between the $\sigma_u^*(2s)$ and the $\sigma_u^*(2p)$ to form the $2\sigma_u^*$ and $3\sigma_u^*$, but because these orbitals do not approach each other closely, the interaction is negligible. The correct energy-level diagram, including both s-p mixing and orbital interaction, is shown in Fig. 3.30.

For most molecules discussed previously, such as Li_2 , N_2 , O_2 , and F_2 , the differences between electron configurations based on Figs. 3.28 and 3.30 are only qualitative and not susceptible to experimental verification. In the case of B_2 (Fig. 3.31) and C_2 , the arrangement based on mixing of orbitals accounts for the experimentally observed magnetic properties. There is also some evidence indicating that in N_2^+ the odd electron is in a σ orbital indicating that the alternative set of energy levels is more realistic.

Electron density in molecules Li_2 through F_2

The approximate shapes of molecular orbitals have been given previously (Fig. 3.27). These give a general idea of the electron distribution in diatomic molecules. Wahl⁴⁴ has computed electron density contours for the molecular orbitals of diatomic molecules for

⁴⁴ A. C. Wahl, *Science*, 1966, 151, 961.

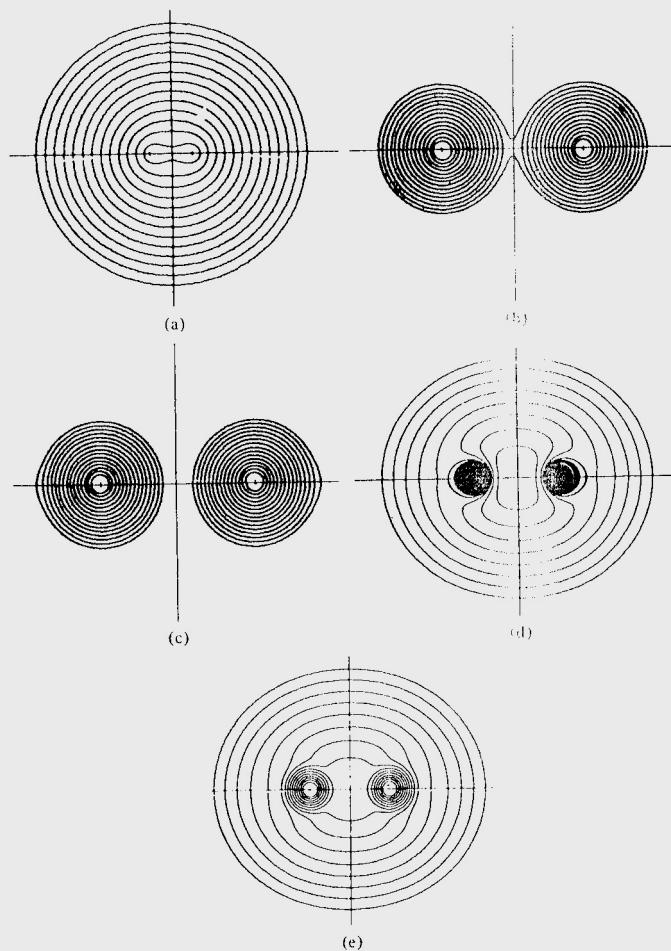


Fig. 3.32 Electron density contours for (a) H_2 ; (b) Li_2 core; (c) $\text{Li}_2 \sigma_{1s}$ core; (d) $\text{Li}_2 \sigma_{2s}^*$; (e) Li_2 total electron density. [From A. C. Wahl, *Science*, 1966, 151, 961. Copyright © 1966 by the American Association for the Advancement of Science. Reproduced with permission.]

H_2 to Ne_2 . Some examples are shown in Figs. 3.32 and 3.33. Note particularly that: (1) Bonding orbitals cause an increase in electron density between the nuclei; (2) anti-bonding orbitals have nodes and reduced electron density between nuclei; and (3) inner shells (1s in Li, for example) are so contracted from the higher effective nuclear charge that they are nearly spherical with almost no overlap and thus contribute little to the overall bonding. We are thus justified in ignoring these core electrons in determining the molecular electron configuration (p. 106).

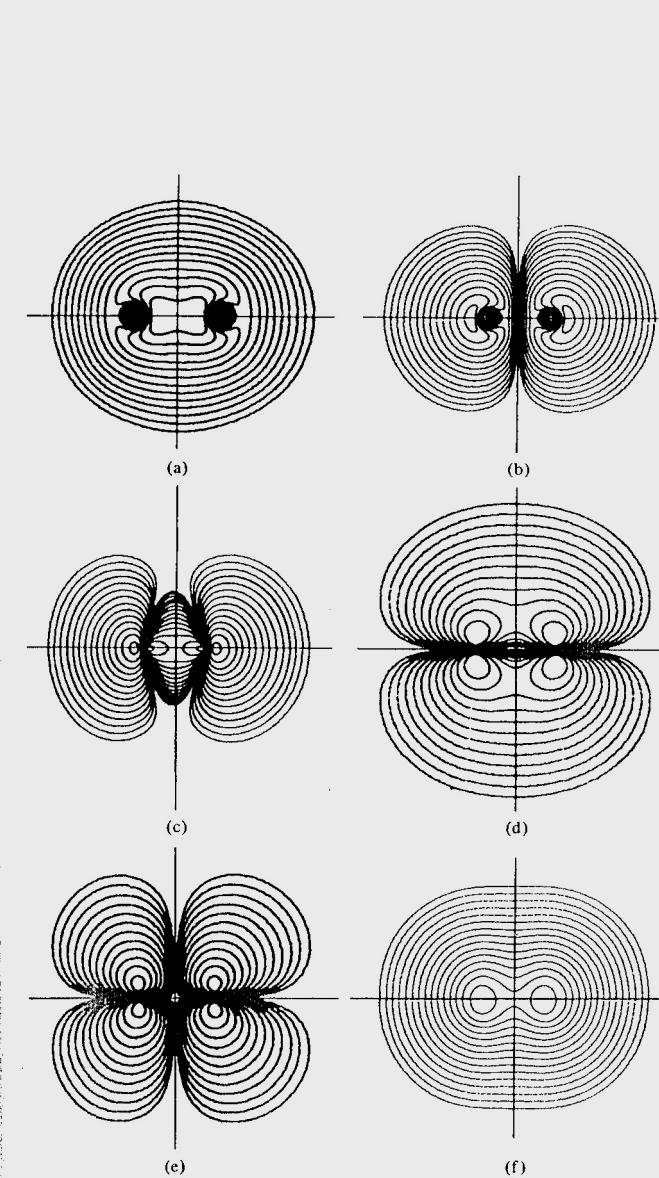


Fig. 3.33 Electron density contours for various orbitals in the O_2 molecule. (a) σ_{2s} ; (b) σ_{2s}^* ; (c) σ_{2p} ; (d) π_{2p} ; (e) π_{2p}^* ; (f) total electron density. [From A. C. Wahl, *Science*, 1966, 151, 961. Copyright © 1966 by the American Association for the Advancement of Science. Reproduced with permission.]

HYBRIDIZATION

Until now, our discussion of the formation of bonds has involved only one type of orbital on an atom at a time, e.g., an $s + s \rightarrow \sigma + \sigma^*$, $p + p \rightarrow \pi + \pi^*$. We have seen the results of “mixing” of orbitals in molecular orbital theory, and hybridization has been mentioned but left unexplained. The mixing of orbitals enters automatically in molecular orbital