

theory, and theoreticians who tend to work in the molecular orbital context sometimes question the necessity of invoking hybridization. It is an integral part of the valence-bond approach. But even in a molecular orbital context it often aids in visualizing what is actually going on in the bonding process. In this section the topic of hybridization will be discussed in some detail, beginning with the basic concepts and proceeding to some more involved arguments.

Consider the methane molecule, CH_4 . The ground state of a carbon atom is ^3P corresponding to the electron configuration of $1s^2 2s^2 2p_x^1 2p_y^1$. Carbon in this state would be divalent because only two unpaired electrons are available for bonding in the p_x and p_y orbitals.⁴⁵ Although divalent carbon is well known in methylene and carbene intermediates in organic chemistry, stable carbon compounds are tetravalent. In order for four bonds to form, the carbon atom must be raised to its *valence state*. This requires the promotion of one of the electrons from the $2s$ orbital to the formerly empty $2p$ orbital. This excited ^5S state has an electron configuration $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$. This promotion costs 406 kJ mol^{-1} . Since the valence state, V_4 , is defined as the state of an atom in a molecule, but without the addition of bonded atoms, it is necessary to supply a further quantity of energy to randomize the spins of the ^5S state, i.e., to supply enough energy to overcome the normal tendency toward parallel spins.⁴⁶ Despite all of the energy necessary to reach the valence state, the formation of two additional bonds makes CH_4 895 kJ mol^{-1} more stable than $\text{CH}_2 + 2\text{H}$.

It might be supposed that upon addition of four hydrogen atoms four bonds would form—three from overlap of the three $2p$ orbitals of carbon with hydrogen $1s$ and the fourth from the carbon $2s$ orbital. The three equivalent $2p$ bonds should be strongly directional since maximum overlap requires that the bonds lie along the axes of the three p orbitals involved. The fourth bond would be nondirectional because of the spherical symmetry of the carbon $2s$ orbital, but presumably this bond would tend to lie on the side of the carbon atom opposite to the three mutually perpendicular “ p ” bonds. It is, of course, a well-known fact that a molecule of methane answering this description has never been experimentally observed. All four bonds in methane are identical and all bond angles are $109\frac{1}{2}^\circ$; we call this process *hybridization*.

Hybridization consists of a mixing or linear combination of the “pure” s and p orbitals of an atom in such a way as to form new hybrid orbitals. Thus we say that the single $2s$ orbital plus the three $2p$ orbitals of the carbon atom have combined to form a set of four spatially and energetically equivalent sp^3 hybrid orbitals. This is illustrated in Fig. 3.34 for the conceptually simpler case of the sp hybrid formed from an s orbital and a single p orbital. Combination of the s and p orbital causes a reinforcement in the region in which the sign of the wave function is the same, cancellation where the signs are opposite.

⁴⁵ The choice of p_x and p_y here instead of, for example, p_z and p_z is, of course, completely arbitrary.

⁴⁶ The existence of this extra valence state excitation energy may be clearer if the reverse process is considered. If (in a thought experiment) four hydrogen atoms are removed from methane but the carbon is not allowed to change in any way, the resulting spins will be perfectly randomized. Energy would then be released if the spins were allowed to become parallel. See C. A. Coulson, “Valence,” 2nd ed., Oxford University Press, London, 1961, pp. 206–208. It should be noted that unlike ^3P , ^1S , etc., V_4 is not an observable spectroscopic state but is calculated by adding to the spectroscopic states energies for parallel spins.

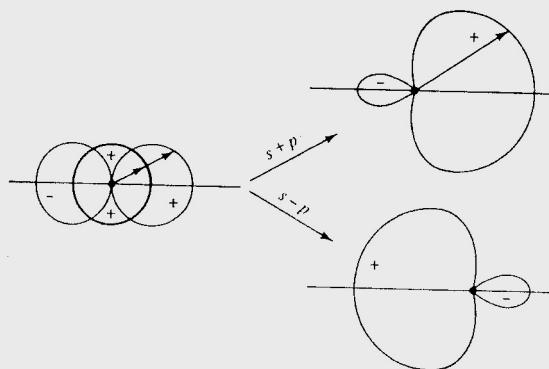


Fig. 3.34 Formation of sp hybrid orbitals by the addition and subtraction of angular wave functions.

If we let Ψ_s and Ψ_p represent the wave functions of an s and a p orbital, then we combine them to make two equivalent orbitals as follows:

$$\Psi_{di_1} = \frac{1}{\sqrt{2}} (\Psi_s + \Psi_p) \quad (3.47)$$

$$\Psi_{di_2} = \frac{1}{\sqrt{2}} (\Psi_s - \Psi_p) \quad (3.48)$$

where $1/\sqrt{2}$ is the normalizing coefficient and Ψ_{di_1} and Ψ_{di_2} are the new *digonal* (*di*) or sp orbitals. If this process appears reminiscent of the formation of molecular orbitals, it is because in both cases linear combinations of atomic orbitals are being made. It should be kept in mind, however, that in the present case we are combining two or more orbitals on the *same atom* to form a new set of hybrid atomic orbitals.

Mathematically, the formation of sp^3 or tetrahedral orbitals for methane is more complicated but not basically different. The results are four equivalent hybrid orbitals, each containing one part s to three parts p in each wave function, directed to the corners of a tetrahedron. As in the case of sp hybrids, the hybridization of s and p has resulted in one lobe of the hybrid orbital being much larger than the other (see Fig. 3.35). Hybrid orbitals may be pictured in many ways: by several contour surfaces (Fig. 3.35); a single, “outside” contour surface (Fig. 3.36a); cloud pictures (Fig. 3.36b); or by simpler, diagrammatic sketches which ignore the small, nonbonding lobe of the orbital and picture the larger, bonding lobe (Fig. 3.36c). The latter, though badly distorted, are commonly used in drawing molecules containing several hybrid orbitals.

It is possible to form a third type of $s-p$ hybrid containing one s orbital and two p orbitals. This is called an sp^2 or *trigonal* (*tr*) hybrid. It consists of three identical orbitals, each of which does not differ appreciably in shape from Fig. 3.35 and is directed toward the corner of an equilateral triangle. The angles between the axes of the orbitals in a trigonal hybrid are thus all 120° .

Although promotion and hybridization are connected in the formation of methane from carbon and hydrogen, care should be taken to distinguish between them. Promotion

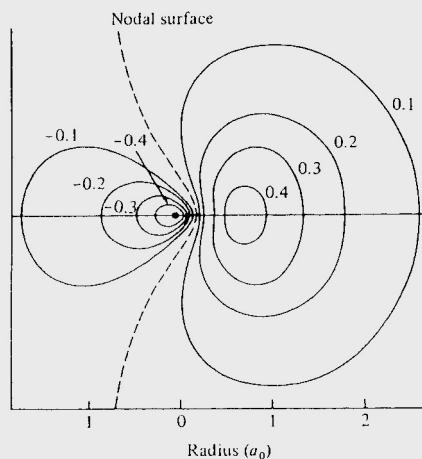


Fig. 3.35 Electron density contours for an sp^3 hybrid orbital. Note that the nodal surface does not pass through the nucleus. [Adapted from C. A. Coulson, "Valence," 2nd ed., Clarendon Press, Oxford, 1961. Reproduced with permission.]

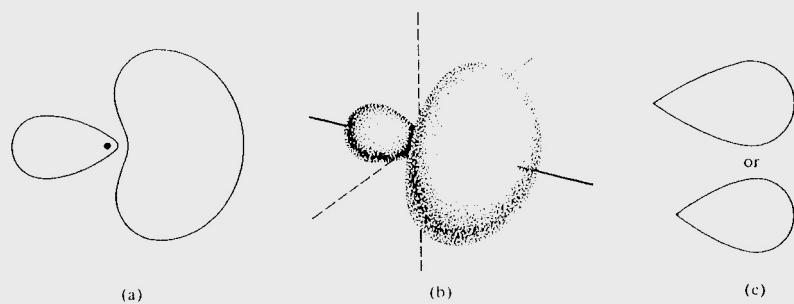
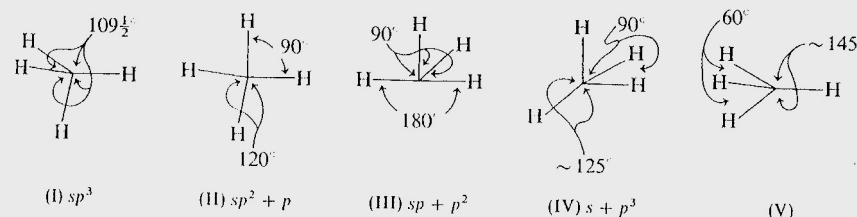


Fig. 3.36 Other ways of representing hybrid orbitals. (a) Orbital shape shown by single contour. (b) Cloud representation. (c) Simplified representation. The small back lobes have been omitted and the shape streamlined to make it easier to draw molecules containing several hybrid orbitals.

involves the addition of energy to raise an electron to a higher energy level in order that the two additional bonds may form. It is conceivable that after promotion the carbon atom could have formed three bonds with the three p orbitals and the fourth with the s orbital. That carbon forms tetrahedral bonds instead is a consequence of the greater stability of the latter, not a necessary result of promotion. Thus, although promotion and hybridization often occur together, either could occur without the other.

A second point to be made with regard to hybrids is the source of the driving force resulting in hybridization. Statements are often made to the effect that "methane is tetrahedral because the carbon is hybridized sp^3 ." This is very loose usage and gets the cart before the horse. The methane molecule is tetrahedral because the energy of the molecule is lowest in that configuration, principally because of increased bond energies and decreased

repulsion energies. For this molecule to be tetrahedral, VB theory demands that sp^3 hybridization take place. Thus it is incorrect to attribute the shape of a molecule to hybridization—the latter prohibits certain configurations and allows others but does not indicate a preferred one. For example, consider the following possibilities for the methane molecule:



The first three geometries involve the tetrahedral, trigonal, and digonal hybrids discussed above and the fourth involves the use of pure s and p orbitals as discussed on p. 114. The last structure contains three equivalent bonds at mutual angles of 60° and a fourth bond at an angle of approximately 145° to the others. It is impossible to construct $s-p$ hybrid orbitals with angles less than 90° , and so structure (V) is ruled out. In this sense it may be said that hybridization does not "allow" structure (V), but it may *not* be said that it "chooses" one of the others. Carbon hybridizes sp , sp^2 , and sp^3 in various compounds, and the choice of sp^3 in methane is a result of the fact that the tetrahedral structure is the most stable possible.

Although we shall not make explicit use of them, the reader may be interested in the form of the $s-p$ hybrids we have seen:⁴⁷

$$\Psi_{tr_1} = \frac{1}{\sqrt{3}} \Psi_s + \sqrt{\frac{2}{3}} \Psi_{p_x} \quad (3.49)$$

$$\Psi_{tr_2} = \frac{1}{\sqrt{3}} \Psi_s - \frac{1}{\sqrt{6}} \Psi_{p_x} + \frac{1}{\sqrt{2}} \Psi_{p_y} \quad (3.50)$$

$$\Psi_{tr_3} = \frac{1}{\sqrt{3}} \Psi_s - \frac{1}{\sqrt{6}} \Psi_{p_x} - \frac{1}{\sqrt{2}} \Psi_{p_y} \quad (3.51)$$

$$\Psi_{te_1} = \frac{1}{2} \Psi_s + \frac{1}{2} \Psi_{p_x} + \frac{1}{2} \Psi_{p_y} + \frac{1}{2} \Psi_{p_z} \quad (3.52)$$

$$\Psi_{te_2} = \frac{1}{2} \Psi_s - \frac{1}{2} \Psi_{p_x} - \frac{1}{2} \Psi_{p_y} + \frac{1}{2} \Psi_{p_z} \quad (3.53)$$

$$\Psi_{te_3} = \frac{1}{2} \Psi_s + \frac{1}{2} \Psi_{p_x} - \frac{1}{2} \Psi_{p_y} - \frac{1}{2} \Psi_{p_z} \quad (3.54)$$

$$\Psi_{te_4} = \frac{1}{2} \Psi_s - \frac{1}{2} \Psi_{p_x} + \frac{1}{2} \Psi_{p_y} - \frac{1}{2} \Psi_{p_z} \quad (3.55)$$

⁴⁷ The forms for common hybrids are given in Eqs. 3.49 to 3.55. The percent s and p character is proportional to the square of the coefficients since the wave function must be squared to have physical meaning. Taken from C.Y. Hsu and M. Orchin, *J. Chem. Educ.*, 1973, 50, 114.

It is not necessary to limit hybridization to *s* and *p* orbitals. The only criterion is that the radial parts of the wave functions of the orbitals being hybridized be similar; otherwise the radial wave function of the hybrid would be unsuited for bonding since the electron density would be spread too thinly. In practice this means that hybrids are formed among orbitals lying in the same principal energy level or, occasionally, in adjacent energy levels.

Some hybrid orbitals containing *s*, *p*, and *d* orbitals are listed in Table 3.10. The structural aspects of various hybrid orbitals will be discussed in Chapter 5, but the bond angles between orbitals of a given hybridization are also listed in Table 3.10 for reference.

Most sets of hybrid orbitals are equivalent and symmetric, i.e., four sp^3 orbitals directed to the corners of a regular tetrahedron, six d^2sp^3 orbitals to the corners of an octahedron, etc. In the case of sp^3d hybrids the resulting orbitals are not equivalent. In the trigonal bipyramidal arrangement three orbitals directed trigonally form one set of equivalent orbitals (these may be considered sp^2 hybrids) and two orbitals directed linearly (and perpendicular to the plane of the first three) form a second set of two (these may be considered *dp* hybrids). The former set is known as the *equatorial* orbitals and the latter as the *axial* orbitals. Because of the nature of the different orbitals involved, bonds formed from the two are intrinsically different and will have different properties even when bonded to identical atoms. For example, in molecules like PF_5 bond lengths differ for axial and equatorial bonds (see pp. 224–227).

Even in the case of *s–p* orbitals it is not necessary that all the orbitals be equivalent. Consider the water molecule, in which the $H-O-H$ angle is $104\frac{1}{2}^\circ$, which does not correspond to any of the hybrids described above, but lies between the $109\frac{1}{2}^\circ$ angle for sp^3 and 90° for pure *p* orbitals. Presumably the two bonding orbitals in water are approximately tetrahedral orbitals but contain a little more *p* character, which correlates with the tendency of the bond angle to diminish toward the 90° of pure *p* orbitals. The driving forces for this effect will be discussed in Chapter 5.

The relationship between *p* or *s* character and bond angle will also be discussed in Chapter 5. For now we need only consider the possibility of *s–p* hybridization other than *sp*, *sp*², and *sp*³. If we take the ratio of the *s* contribution to the total orbital complement in these hybrids, we obtain 50%, 33%, and 25% *s* character, respectively, for

Table 3.11 Effect of hybridization on overlap and bond properties

Molecule	Hybridization	C—H bond energy (kJ mol ⁻¹)	C—H bond length (pm)
$H-C\equiv C-H$	sp	~506	106
$H_2C=CH_2$	sp^2	~444	107
CH_4	sp^3	410	109
CH radical	~ <i>p</i>	~335	112

these hybrids. A pure *s* orbital would be 100% *s*, and a *p* orbital would have 0% *s* character. Since hybrid orbitals are constructed as linear combinations of *s* and *p* orbital wave functions,

$$\phi = a\Psi_s + b\Psi_p \quad (3.56)$$

there is no constraint that *a* and *b* must have values such that the *s* character is exactly 25%, 33%, or 50%. A value of 20% *s* character is quite acceptable, for example, and indeed this happens to be the value in water. When the hybridization is defined as above, the % *p* character is always the complement of % *s*, in the case of water, 80%.

Hybridization and overlap

Both pure *s* and pure *p* orbitals provide relatively inefficient overlap compared with that of hybrid orbitals. The relative overlap of hybrid orbitals decreases in the order $sp > sp^2 > sp^3 \gg p$. The differences in bonding resulting from hybridization effects on overlap can be seen in Table 3.11. The C—H bond in acetylene is *shorter* and *stronger* than in hydrocarbons having less *s* character in the bonding orbital. The hybridization in the hydrocarbons listed in Table 3.11 is dictated by the stoichiometry and stereochemistry. In molecules where variable hybridization is possible, various possible hybridizations, overlaps, and bond strengths are possible. Other things being equal,⁴⁸ we should expect molecules to maximize bond energies through the use of appropriate hybridizations.

Molecular orbital equivalent of hybridization

Hybridization does not enter explicitly into MO theory, but mixing of orbitals does occur as in VB theory. Since several examples of the application of MO methods to molecules will be discussed in later chapters, only a very simple example will be given here—that of the linear triatomic molecule BeH_2 . The molecular orbitals for this molecule are constructed from the 1s orbitals on the hydrogen atoms (labeled H and H') and the 2s and one of the 2p orbitals of the beryllium. The remaining two 2p orbitals of the beryllium

⁴⁸ As someone has sagely remarked, "other things" are *seldom* equal, but we can expect to see the effects of the idea expressed here on the molecular properties.

Table 3.10 Bond angles of hybrid orbitals

Hybrid	Geometry	Bond angle(s)
$sp(di)$	Linear (digonal)	180
$sp^2(tr)$	Trigonal	120
$sp^3(te)$	Tetrahedral	$109\frac{1}{2}^\circ$
dsp^3	Trigonal bipyramidal or	$90^\circ, 120^\circ$
d^2sp^3	Square pyramidal ^a	$>90^\circ, <90^\circ$
	Octahedral	90°

^a Not common.

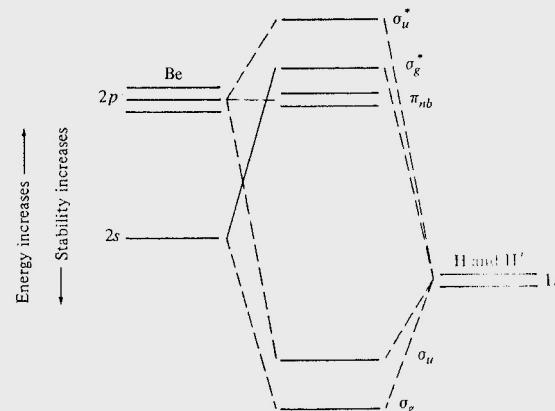


Fig. 3.37 Molecular orbital energy levels in the BeH_2 molecule.

cannot enter into bonding because they have zero overlap with the hydrogen orbitals. Since four atomic orbitals enter into the bonding, we anticipate the formation of four molecular orbitals. The bonding molecular orbitals are formed by linear combination of the atomic orbitals to give maximum overlap:

$$\Psi_g = a\Psi_{2s} + b(\Psi_H + \Psi_{H'}) = \sigma_g \quad (3.57)$$

$$\Psi_u = c\Psi_{2p} + d(\Psi_H - \Psi_{H'}) = \sigma_u \quad (3.58)$$

$$\Psi_g^* = b\Psi_{2s} - a(\Psi_H + \Psi_{H'}) = \sigma_g^* \quad (3.59)$$

$$\Psi_u^* = d\Psi_{2p} - c(\Psi_H - \Psi_{H'}) = \sigma_u^* \quad (3.60)$$

The subscripts *g* and *u* refer to the symmetry of the molecular orbitals (see p. 103) but may be considered useful labels. The parameters *a*, *b*, *c*, and *d* are weighting coefficients and are necessary because of differences in electronegativity between Be and H. They will be discussed in the section on heteropolar bonds. The energies of these molecular orbitals are shown in Fig. 3.37 and electron density boundary surfaces are sketched in Fig. 3.38. Both of the bonding molecular orbitals are *delocalized* over all three atoms. This is a general result of the MO treatment of polyatomic molecules. It is possible to convert these two delocalized molecular orbitals into localized molecular orbitals that resemble those obtained from VB treatment.⁴⁹ In any event, the mixing of the atomic orbitals occurs naturally in MO treatment. Prior hybridization of the atomic orbitals is not necessary but may be a convenience. Whether one goes through the formal step of hybridization or not, one should not lose sight of the fact that terms such as “25% *s* character” are just as appropriate in MO treatments as in VB treatments.

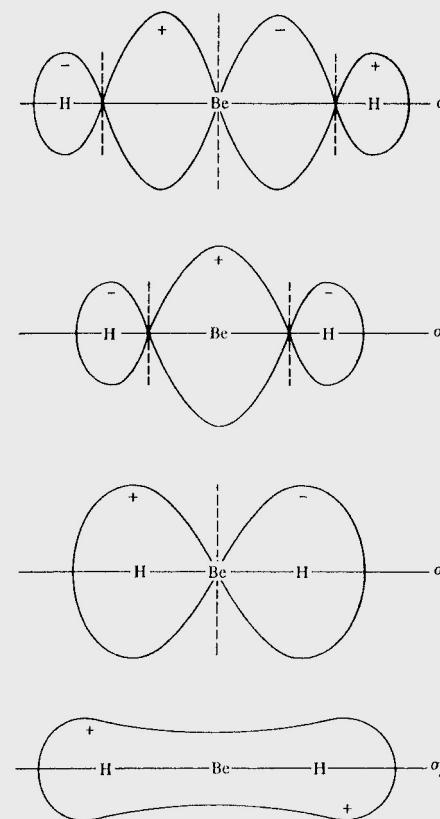


Fig. 3.38 Antibonding (top) and bonding (bottom) molecular orbitals in the BeH_2 molecule.

DELOCALIZATION

Resonance

When using valence bond theory it is often found that more than one acceptable structure can be drawn for a molecule or, more precisely, more than one wave function can be written. We have already seen in the case of the hydrogen molecule that we could formulate it either as $\text{H}-\text{H}$ or as H^+H^- . Both are acceptable structures, but the second or ionic form would be considerably higher in energy than the “covalent” structure (because of the high ionization energy and low electron affinity of hydrogen). However, we may write the wave function for the hydrogen molecule as a linear combination of the ionic and covalent functions:

$$\Psi = (1 - \lambda)\Psi_{\text{cov}} + \lambda\Psi_{\text{ion}} \quad (3.61)$$

⁴⁹ W. A. Bennett, *J. Chem. Educ.*, 1969, 46, 746; I. Cohen and J. Del Bene, *J. Chem. Educ.*, 1969, 46, 487; D. K. Hoffman et al., *J. Chem. Educ.*, 1977, 54, 590.

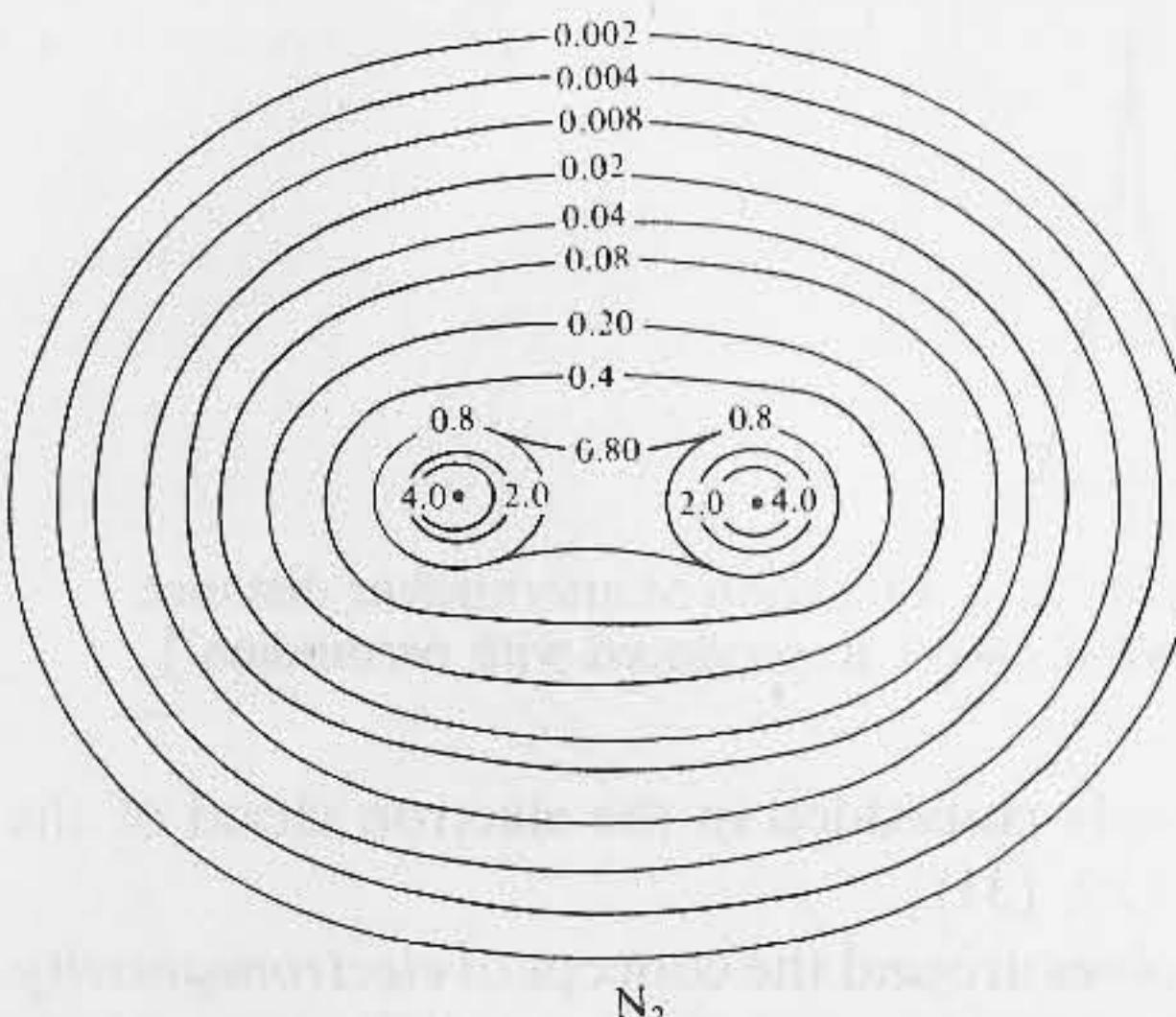


Fig. 3.52 Total charge density contours for the nitrogen molecule. [From R. F. W. Bader and A. D. Bandrauk, *J. Chem. Phys.*, 1968, 49, 1653. Reproduced with permission.]

in contrast to the symmetrical distribution in the N_2 molecule (Fig. 3.52). For homonuclear diatomic molecules we have seen that the molecular orbitals are

$$\Psi_b = \Psi_A + \Psi_B \quad (3.76)$$

$$\Psi_a = \Psi_A - \Psi_B \quad (3.77)$$

Both orbitals contribute equally. Now if one atomic orbital is lower in energy than the other, it will contribute *more* to the bonding orbital:

$$\Psi_b = a\Psi_A + b\Psi_B \quad (3.78)$$

where $b > a$ if atom B is more electronegative than atom A. Conversely, the more stable orbital contributes *less* to the antibonding orbital:

$$\Psi_a = b\Psi_A - a\Psi_B \quad (3.79)$$

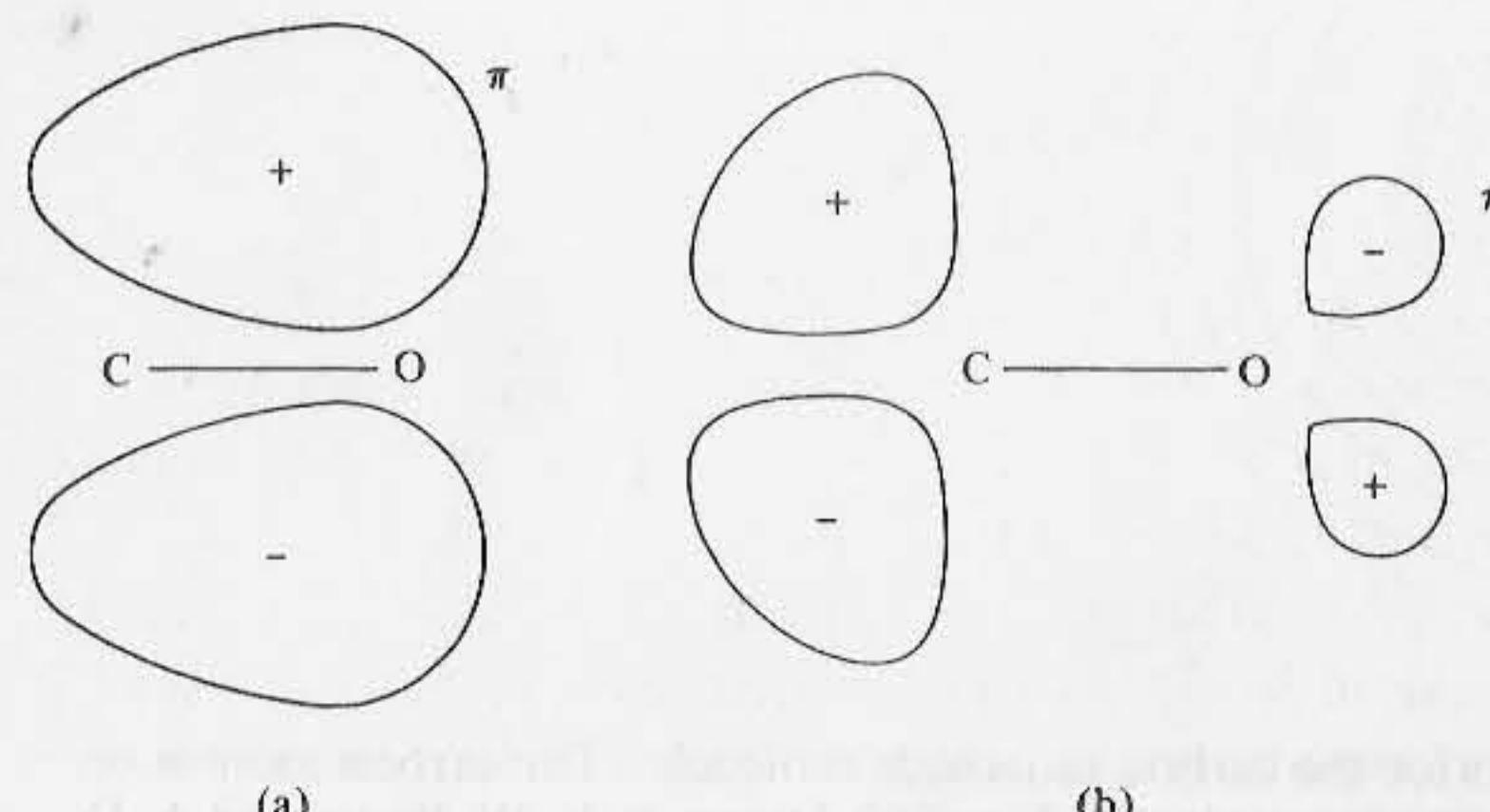


Fig. 3.53 Diagrammatic sketches of the molecular orbitals in carbon monoxide: (a) one π bonding orbital; (b) one π antibonding orbital.

In carbon monoxide the bonding molecular orbitals will resemble the atomic orbitals of oxygen more than they resemble those of carbon. The antibonding orbitals resemble the least electronegative element more, in this case the carbon (see Fig. 3.53). This results from what might be termed the conservation of orbitals. The number of molecular orbitals obtained is equal to the total number of atomic orbitals combined, and each orbital must be used to the same extent. Thus, if the carbon atomic orbital contributes less to the bonding molecular orbital, it must contribute *more* to the antibonding molecular orbital. The energy level diagram for CO is shown in Fig. 3.54.

A second feature of heteronuclear molecular orbitals which has been mentioned previously is the diminished covalent bond energy of bonds formed from atomic orbitals of different energies. Specifically the exchange energy is reduced if the energies of the atomic orbitals do not match. This may be shown qualitatively by comparing Fig. 3.55

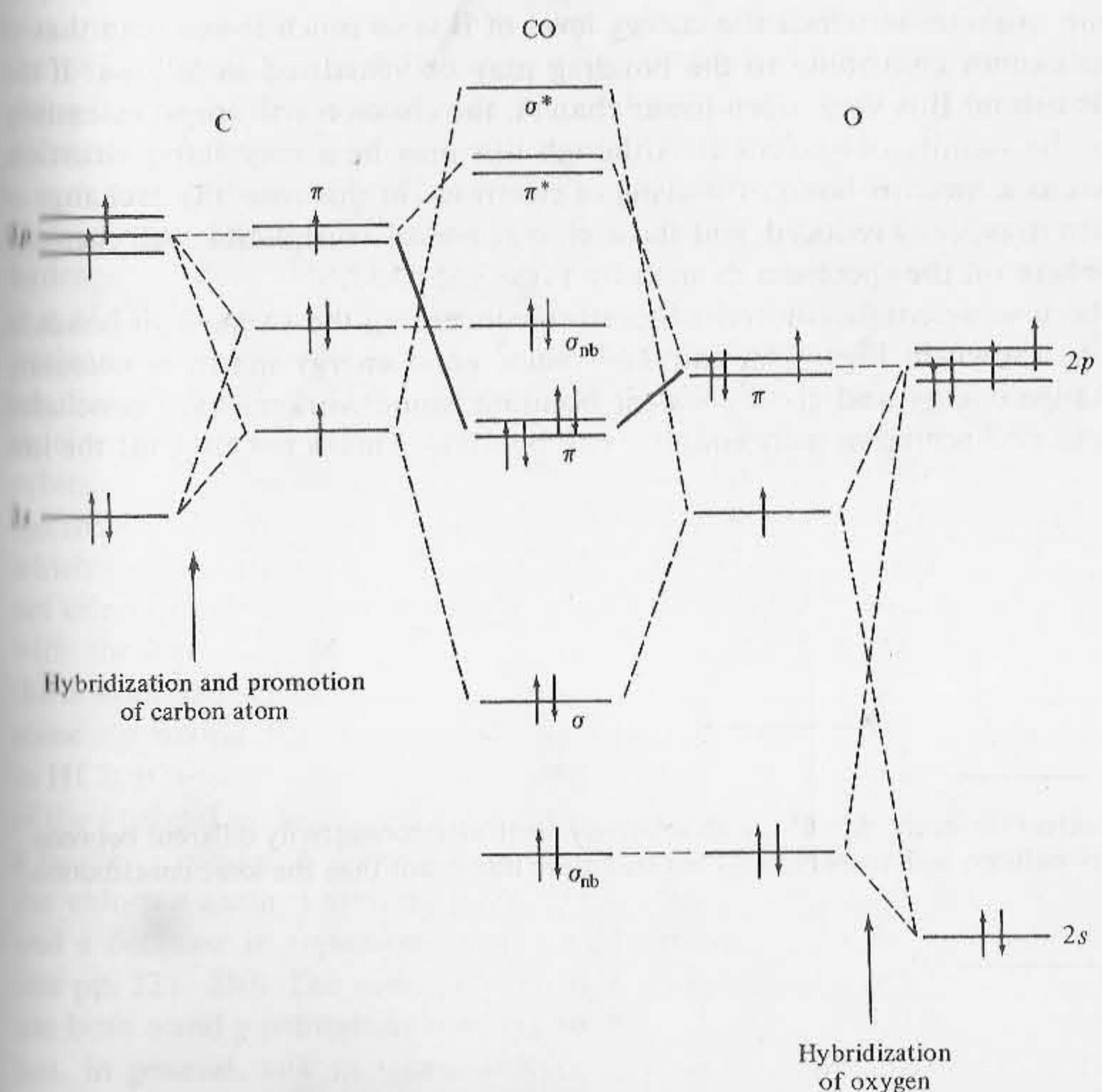


Fig. 3.54 Energy level diagram for the molecular orbitals of carbon monoxide. Note that upon bond formation electrons occupy orbitals that are more oxygen-like than carbon-like. Note carefully the bond order: The lowest and the fifth MOs are essentially nonbonding since they do not combine with orbitals on the opposite atom and do not change energy. The bond order, as in the N_2 molecule (Fig. 3.28) is three. [From H. H. Jaffé and M. Orchin, *Tetrahedron*, 1960, 10, 212. Reproduced with permission of Pergamon Press.]