

# **CHEMICAL BONDS THEORY– COVALENT BONDING**

## **❖ Learning Objectives**

1. Requirements of any satisfactory Theory of Chemical Bonding
2. QUANTUM PICTURE OF THE CHEMICAL BOND
3. MOT: Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
4. Describe traits of bonding and antibonding molecular orbitals
5. Write molecular electron configurations for some homo- and hetero-nuclear diatomic molecules
6. Relate these electron configurations to the molecules' stabilities and magnetic properties
7. Applications of MOT to  $\text{AX}_2$  and  $\text{AX}_3$  molecules
8. MOT and shapes of molecules
9. Applications of MOT to delocalized pi-bonding systems
10. Applications of MOT to solids (ionic and metallic)

# CHEMICAL BONDS THEORY– COVALENT BONDING

Requirements of any satisfactory Theory of Chemical Bonding...

It should explain...

1. Why some atoms combine to form molecules whereas *some do not*. For example,  $\text{H}_2$  stable; not  $\text{He}_2$ .
2. Why atoms form molecules in definite proportions and why there is saturation of valency. For example,  $\text{CH}_4$  is a stable molecule but not  $\text{CH}_3$ ,  $\text{CH}_2$ ...
3. The 3-dimensional shapes of molecules, bond angles, bond lengths, and bond energies.

# CHEMICAL BONDS THEORY

## □ QUANTUM PICTURE OF THE CHEMICAL BOND

- *Quantum mechanics* help to understand the *nature of chemical bonding* and *predict the structures and properties of small molecules*.
- ✓ However, for *large molecules approximate quantum mechanical* methods have been used and **even then**, *the calculations provide a lot of information* about the molecular structures and chemical properties.
- There are **two major approaches** to the calculation of molecular structure, *valence-bond theory (VB theory)* and *molecular orbital theory (MO theory)*.
- Valence bond (VB) theory gave us a qualitative picture of chemical bonding, which was useful for predicting the shapes of molecules, bond strengths, etc. It fails to describe some bonding situations accurately because *it ignores the wave nature of the electrons*.
- **Molecular orbital theory (MOT)** has the potential to be *more quantitative*. With it we can also get a picture of where the electrons are in the molecule. This can *help us understand patterns of bonding and reactivity that are otherwise difficult to explain*. **Almost all modern computational work makes use of MO theory**.

## Molecular Orbital Theory (MOT)

### Conceptual Development of Molecular Orbitals

- The simplest possible molecular system is  $\text{H}_2^+$ , the **hydrogen molecular ion**, in which a single electron bonds two protons.
- The formalism that applies to the molecular orbital method will be illustrated by considering a hydrogen molecule (but a more detailed description of both  $\text{H}_2^+$  and  $\text{H}_2$  will be given in the next sections).
- Before we consider the quantum mechanical calculations of bond formation in  $\text{H}_2^+$  in detail, let us look in a general way into **how it is possible for two protons to share an electron** and **why such sharing should lead to a lower total energy and hence to a stable system**.
- To begin our description of diatomic molecules, let us imagine that two hydrogen atoms that are separated by a relatively large distance are being brought closer together (see next Fig.).
- As the atoms approach each other, as the distance between them becomes shorter, what happens?

- We know the **phenomenon of quantum-mechanical barrier penetration**. There we saw that a ***particle can “leak” out of a box*** even *without enough energy to break through the wall* because the particle’s wave function extends beyond it. Only if the wall is infinitely strong is the wave function wholly inside the box.
- The electric field around a proton is in effect a box for an electron, and two nearby protons correspond to a pair of boxes with a wall between them.
- No mechanism in classical physics permits the electron in a hydrogen atom to jump spontaneously to a neighboring proton more distant than its parent proton.
- In quantum physics, however, such a mechanism does exist. ***There is a certain probability that an electron trapped in one box will tunnel through the wall and get into the other box***, and once there it has ***the same probability for tunneling back***. This ***situation can be described by saying the electron is shared by the protons***.
- To be sure, the ***likelihood that an electron will pass*** through the region of high potential energy—the “wall”—between two protons ***depends strongly on how far apart the protons are***.

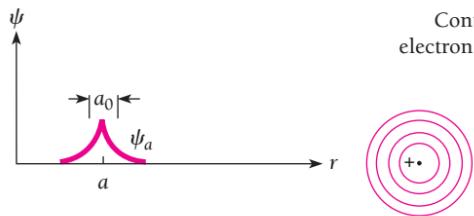
- If the proton-proton distance is 0.1 nm, the electron may be regarded as going from one proton to the other about every  $10^{-15}$  s. We ***can legitimately consider such an electron as being shared by both***. If the proton-proton distance is 1 nm, however, the electron shifts across *an average of only about once per second*, which is practically an ***infinite time on an atomic scale***.
- Since the effective radius of the 1s wave function in hydrogen is 0.053 nm, we conclude that electron sharing can take place only between atoms whose wave functions overlap appreciably.
- Granting that two protons can share an electron, a simple argument shows why the ***energy of such a system could be less than that of a separate hydrogen atom and proton***.
- According to the uncertainty principle, the smaller the region to which we restrict a particle, the greater must be its momentum and hence kinetic energy. ***An electron shared by two protons is less confined*** than one belonging to a single proton, which ***means that it has less kinetic energy***. The total energy of the electron in  $\text{H}_2^+$  is therefore less than that of the electron in  $\text{H} + \text{H}^+$ . Provided the magnitude of the proton-proton repulsion in  $\text{H}_2^+$  is not too great, then,  $\text{H}_2^+$  ought to be stable.

## THE H<sub>2</sub><sup>+</sup> MOLECULAR ION

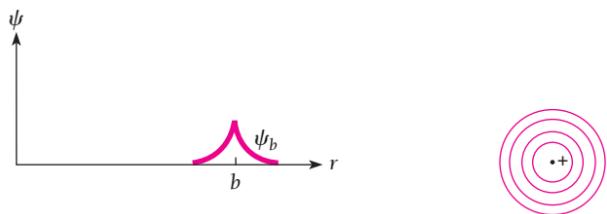
❖ Bonding requires a symmetric wave function

- What we would like to know is the wave function of the electron in H<sub>2</sub><sup>+</sup>, since from we can ***calculate the energy of the system as a function of the separation R of the protons.***
- If  $E(R)$  has a ***minimum***, we will know that a **bond can exist**, and we can also **determine the bond energy and the equilibrium spacing of the protons.**
- Solving Schrödinger's equation for is a long and complicated procedure, that will be discussed later. An intuitive approach that brings out the physics of the situation is more appropriate here.
- Let us begin by trying to predict what is when R, the distance between the protons, is large compared with ***a<sub>o</sub>, the radius of the smallest Bohr orbit*** in the hydrogen atom. In this event near each proton must closely resemble the 1s wave function of the hydrogen atom, as pictured in Fig. 8.5. The 1s wave function around proton a is called  $\psi_a$  and that around proton b is called  $\psi_b$ .

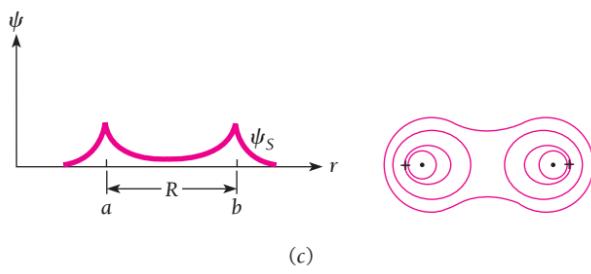
Contours of  
electron probability



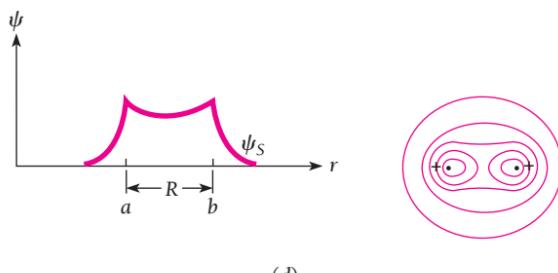
(a)



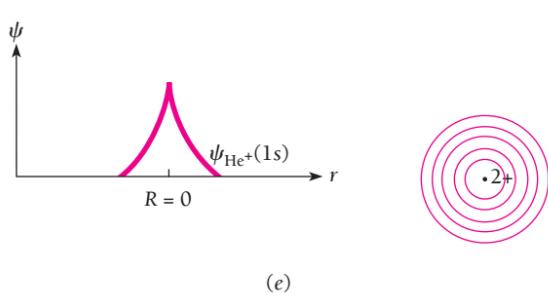
(b)



(c)



(d)



(e)

**Figure 8.5 (a)–(d)** The combination of two hydrogen-atom 1s wave functions to form the symmetric  $\text{H}_2^+$  wave function  $\psi_s$ . The result is a stable  $\text{H}_2^+$  molecular ion because the electron has a greater probability of being between the protons than outside them.

**(e)** If the protons could join together, the resulting wave function would be the same as the 1s wave function of a  $\text{He}^+$  ion.

- We also know what looks like when R is 0, that is, when the *protons are imagined to be fused together*. Here the situation is that of the  $\text{He}^+$  ion, since the electron is now near a single nucleus whose charge is  $2e$ . The 1s wave function of He has the same form as that of H but with a greater amplitude at the origin, as in Fig. 8.5e.
- Evidently is going to be something like the wave function sketched in Fig. 8.5d when R is comparable with  $a_0$ . *There is an enhanced likelihood of finding the electron in the region between the protons*, which *corresponds to the sharing of the electron* by the protons. Thus, *there is on the average an excess of negative charge between the protons*, and *this attracts the protons together*.
- *We have still to establish whether this attraction is strong enough to overcome the mutual repulsion of the protons.*
- The combination of  $\psi_a$  and  $\psi_b$  in Fig. 8.5 is **symmetric**, since exchanging a and b does not affect. However, it is also conceivable that we could have an *antisymmetric combination* of  $\psi_a$  and  $\psi_b$ , as in Fig. 8.6. Here there is a **node** between  $\psi_a$  and  $\psi_b$  where  $\psi = 0$ , which *implies a reduced likelihood of finding the electron* between the protons. Now there is *on the average a deficiency of negative charge between the protons* and in consequence *a repulsive force*. *With only repulsive forces acting, bonding cannot occur*.

- An interesting question concerns the behavior of the antisymmetric  $H_2^+$  wave function  $\psi_A$  as  $R \rightarrow 0$ . Obviously  $\psi_A$  **does not become the 1s wave function** of He when  $R \rightarrow 0$ .
- However,  $\psi_A$  **does** approach the **2p** wave function of He (Fig. 8.6e), which has a node at the origin. But the 2p state of He is an excited state whereas the 1s state is the ground state.
- **Hence  $H_2^+$  in the antisymmetric state ought to have more energy** than when it is in the symmetric state, which agrees with our inference from the shapes of the wave functions  $\psi_A$  and  $\psi_S$  that in the former case there is a repulsive force and in the latter, an attractive one.

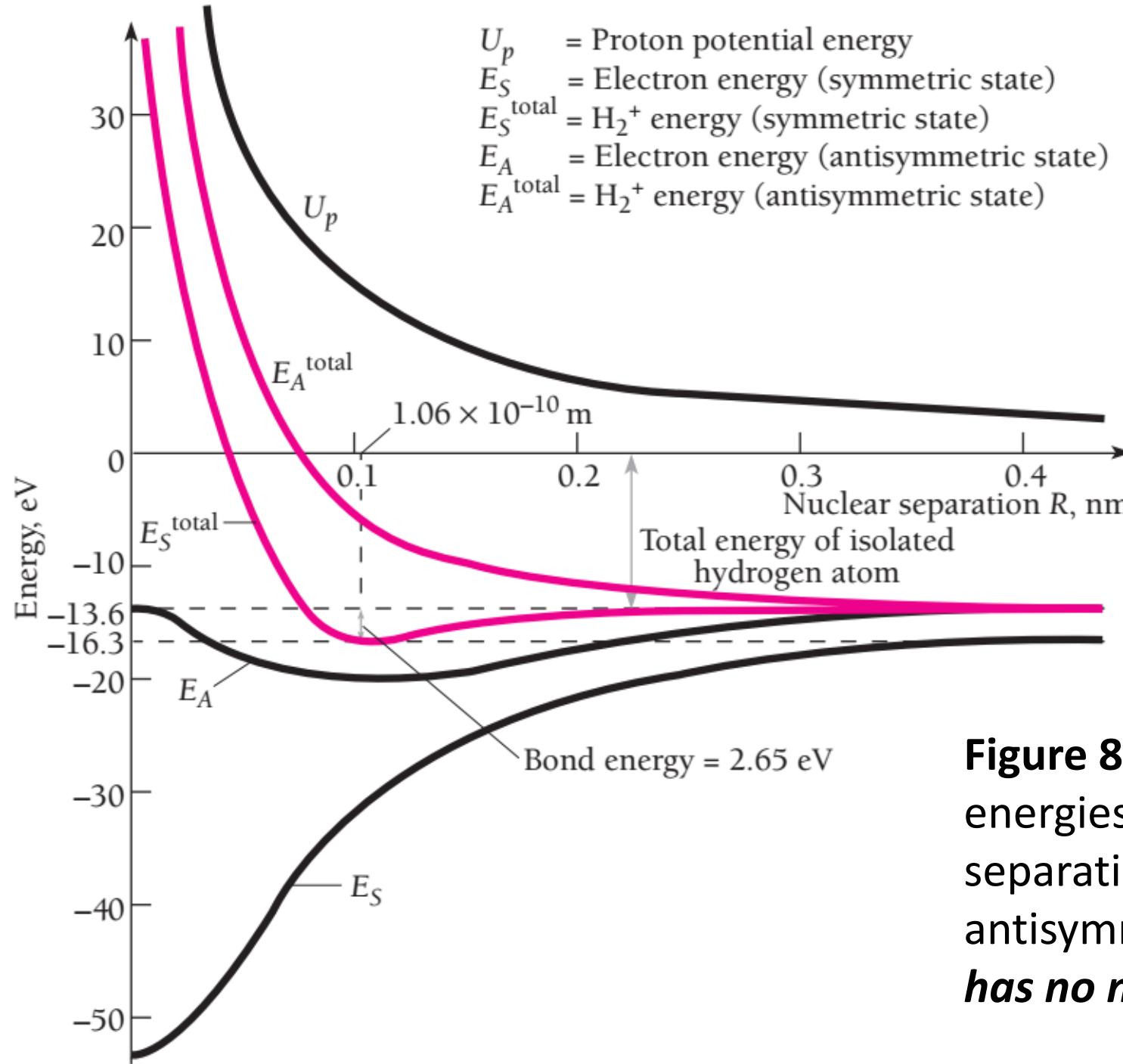
## □ System Energy

- A line of reasoning similar to the preceding one lets us estimate how the **total energy** of the  $H_2^+$  system varies with  $R$ .
- We first consider the symmetric state. When  $R$  is large, the electron energy  $E_S$  must be the -13.6-eV energy of the hydrogen atom, while the electric potential energy  $U_p$  of the protons,

$$U_p = \frac{e^2}{4\pi\epsilon_0 R}$$

falls to 0 as  $R \rightarrow \infty$ . ( $U_p$  is a positive quantity, corresponding to a repulsive force.) When  $R \rightarrow 0$ ,  $U_p \rightarrow \infty$  as  $1/R$ . At  $R = 0$ , the electron energy must equal that of the  $He^+$  ion, which is  $Z^2$ , or 4 times, that of the H atom. Hence  $E_S = -54.4$  eV when  $R = 0$ .

- Both  $E_s$  and  $U_p$  are sketched in Fig. 8.7 as functions of R. The shape of the curve for  $E_s$  can only be approximated without a detailed calculation, but we do have its value for both  $R = 0$  and  $R = \infty$  and, of course,  $U_p$  obeys the above Eq.
- The total energy  $E_s^{\text{total}}$  of the system is the ***sum of the electron energy  $E_s$  and the potential energy  $U_p$  of the protons.***
- Evidently  $E_s^{\text{total}}$  has a minimum, which ***corresponds to a stable molecular state.*** This result is confirmed by the experimental data on  $\text{H}_2^+$  which indicate a bond energy of 2.65 eV and an equilibrium separation R of 0.106 nm.
- By “bond energy” is meant the energy needed to break  $\text{H}_2^+$  into  $\text{H} + \text{H}^+$ .
- The total energy of  $\text{H}_2^+$  is the -13.6 eV of the hydrogen atom plus the -2.65-eV bond energy, or -16.3 eV in all.
- In the case of the ***antisymmetric state,*** the analysis proceeds in the same way except that the electron energy  $E_A$  when  $R = 0$  is that of the 2p state of  $\text{He}^+$ . This energy is proportional to  $Z^2/n^2$ . With  $Z = 2$  and  $n = 2$ ,  $E_A$  is just equal to the -13.6 eV of the ground-state hydrogen atom. Since  $E_A \rightarrow 13.6$  eV also as  $R \rightarrow \infty$ , we might think that the electron energy is constant, but actually there is ***a small dip at intermediate distances.*** However, the dip is ***not nearly enough*** to yield a minimum in the total energy curve for the antisymmetric state, as shown in Fig. 8.7, and ***so in this state no bond*** is formed.

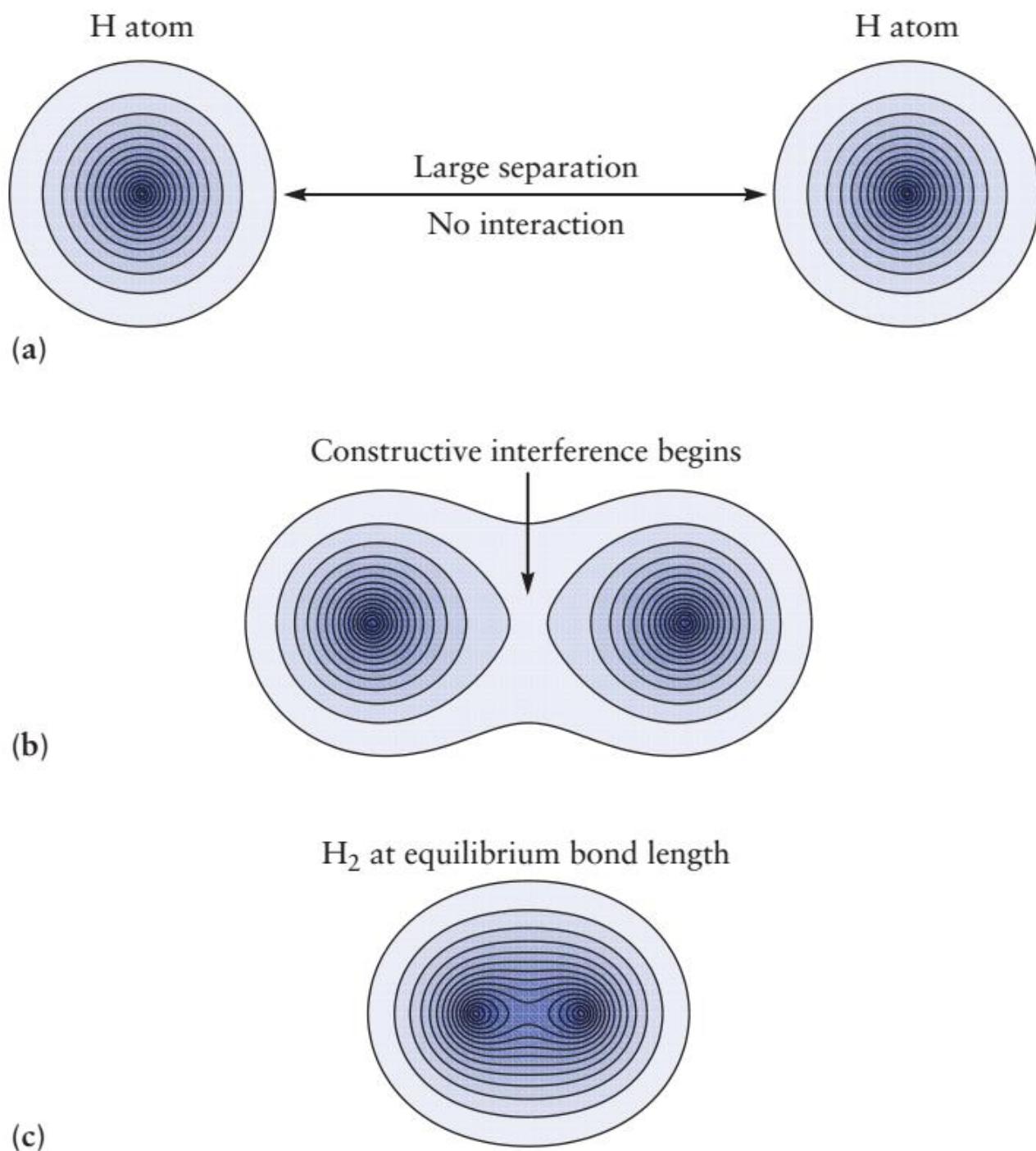


**Figure 8.7** Electron, proton repulsion, and total energies in  $H_2^+$  as a function of nuclear separation  $R$  for the symmetric and antisymmetric states. The ***antisymmetric state has no minimum*** in its ***total energy***.

## ☐ Quantum Picture of the Chemical Bond

- Visualize two H atoms (labeled A and B), initially quite far apart, as they approach one another with the possibility of forming a chemical bond.

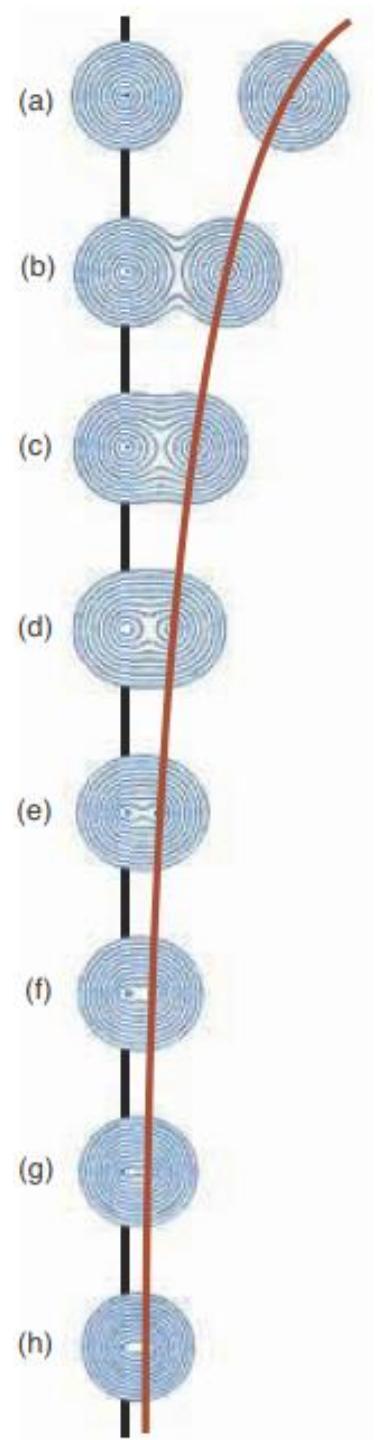
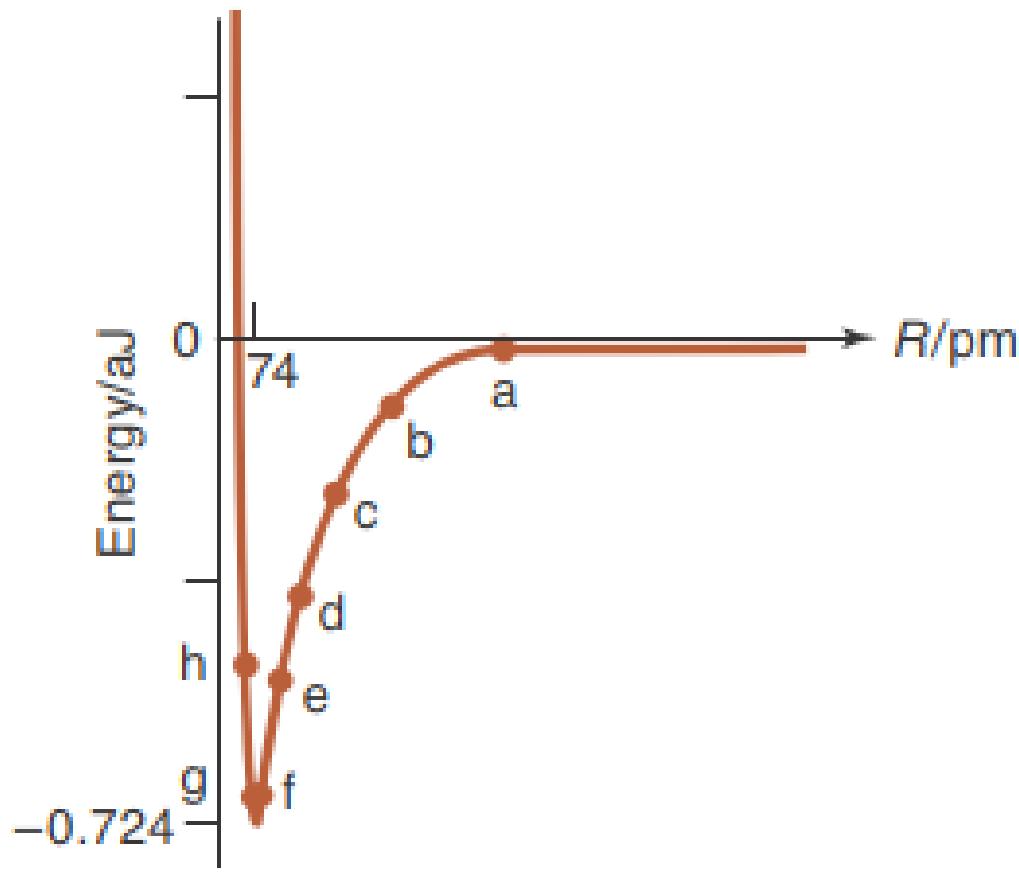
FIGURE 6.2 The probability density for finding an electron in the  $\text{H}_2$  molecule, plotted at three internuclear distances: (a)  $8a_0$ , (b)  $3.5a_0$ , and (c)  $1.4a_0$ . At the equilibrium bond length (c) significant build up of electron density between the nuclei is visible. (Courtesy of Chad Heaps, David A. Mazziotti, The University of Chicago)



- The sequence of events traced in Figure 6.2 shows us that as the two atoms draw near, their electron densities interpenetrate and form a new electron density characteristic of the molecule. Because electrons behave like waves, the two atomic electronic wave functions can interfere either constructively or destructively. If the interference is constructive, the electron density in the region between the nuclei increases. The net result of this increased negative charge density between the nuclei is to attract them toward each other and offset their mutual Coulomb repulsion so they arrive at a stable position.
- Figure 6.2 shows us the *electron density contour diagrams of two hydrogen atoms as a function of their separation*. At large separations, as in (a), the two orbitals appear simply as those of two separate atoms. ***As the atoms come together, the two separate atomic orbitals combine into one molecular orbital encompassing both nuclei***, as in (c).
- We know that a bond can form only if the resulting molecule has lower energy than the pair of isolated atoms.

**Figure 9.1** Electron density contour diagrams of two hydrogen atoms as a function of their separation (right side). At large separations, as in (a), the two orbitals appear simply as those of two separate atoms. **As the atoms come together, the two separate atomic orbitals combine into one molecular orbital encompassing both nuclei**, as in (b) through (h). The lower left part of the figure shows the energy of two hydrogen atoms as a function of their separation  $R$ . The labels (a) through (h) correspond to those in the right part of the figure.

- ✓ At large distances, the two hydrogen atoms do not interact, so their interaction energy is zero.
- ✓ As the *two atoms come together*, they *attract* each other, and so their *interaction energy becomes negative*.
- ✓ When they are less than 74 pm apart, the interaction energy increases, and *they repel each other*.
- ✓ The **bond length** of a  $\text{H}_2$  molecule is the distance *at which the energy is a minimum*, that is, 74 pm.
- ✓ The energy at this distance is  $-0.724 \text{ aJ}$ , which is the energy required to dissociate the  $\text{H}_2$  molecule into two separate hydrogen atoms.



- Let's track progress by plotting the potential energy of the atoms as the distance between them  $R_{AB}$  decreases (Figure 6.1).

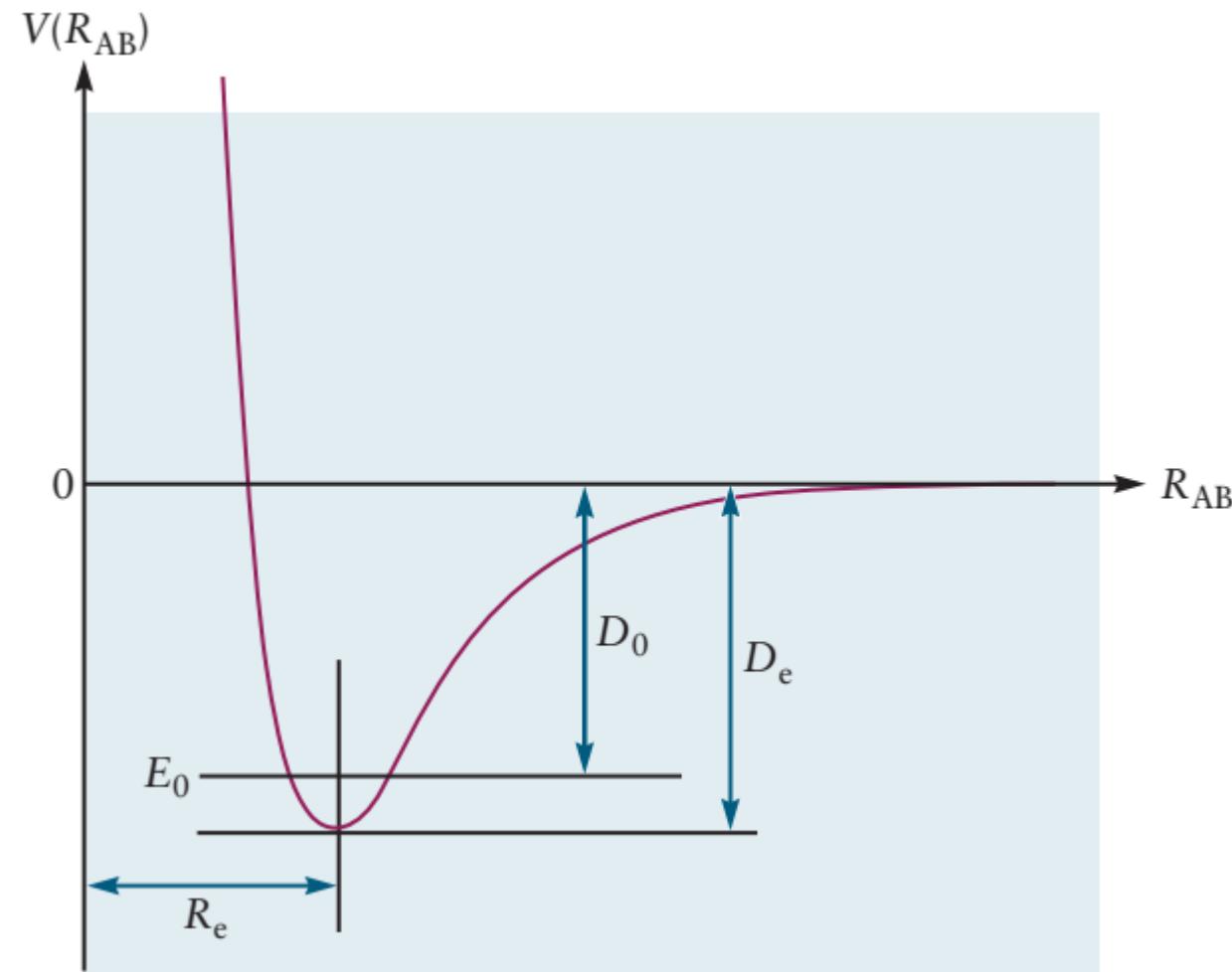


FIGURE 6.1 Schematic representation of the potential energy of two hydrogen atoms as a function of the distance between them. As distance decreases, the potential energy reaches a minimum value of  $-458 \text{ kJ mol}^{-1}$  at a distance of  $0.74 \text{ \AA}$ . The value of  $D_0$  for  $\text{H}_2$  is  $432 \text{ kJ mol}^{-1}$  or  $4.48 \text{ eV molecule}^{-1}$ .

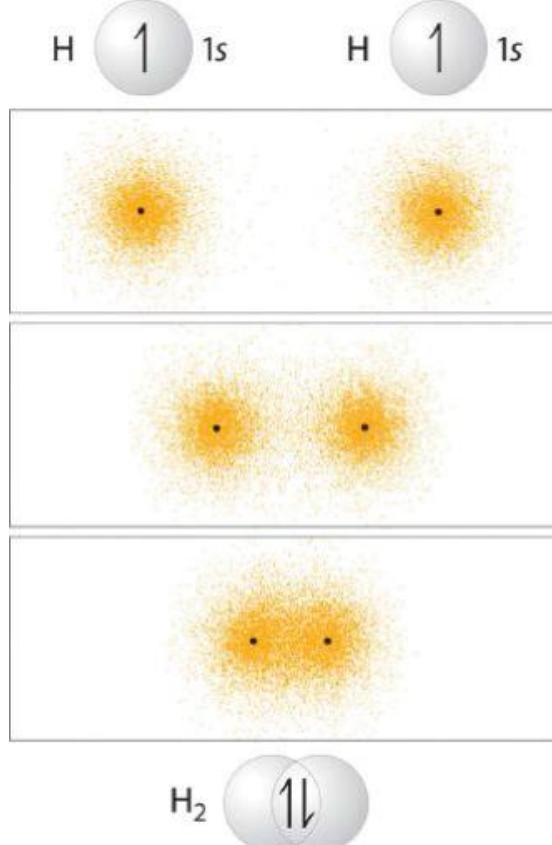


Figure: Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in  $\text{H}_2$ .  
 The formation of  $\text{H}_2$  from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an  $\text{H}_2$  molecule increases the electron density in the region between the two positively charged nuclei.

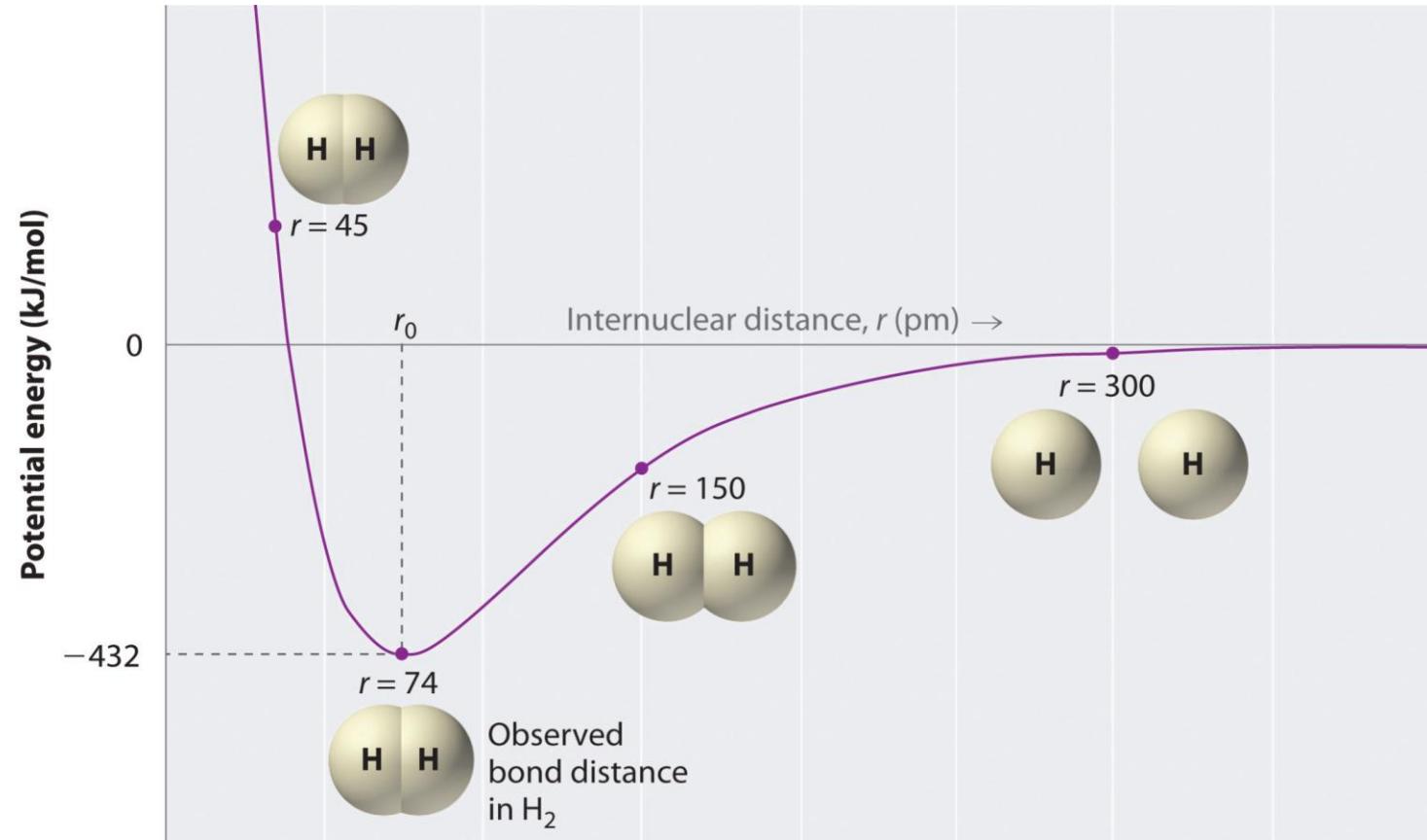


Figure: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

## Exact Molecular Orbitals for the Simplest Molecule: $\text{H}_2^+$

- Today, quantum chemistry provides very good approximate solutions to Schrödinger's equation for molecules. Perhaps more important, it provides new qualitative concepts for representing and describing chemical bonds, molecular structure, and chemical reactivity. The quantum description of the chemical bond justifies the electron pair model, shows the limits of its validity, and points the way to advances beyond the pair model. The quantum description forms the basis for all modern studies in structural chemistry.
- This topic begins with a description of the quantum picture of the chemical bond and then applies this picture to the simplest possible molecule,  $\text{H}_2^+$ , which contains only one electron.
- Schrödinger's equation for the motion of the electron in  $\text{H}_2^+$  can be solved exactly, and we use its solutions to display the general features of each molecular orbital (MO), the one-electron wave functions that describe the electronic structure of molecules.

- Just as we used the atomic orbitals (AOs) of the H atom to suggest approximate AOs for complex atoms, we let the MOs for  $\text{H}_2^+$  guide us to develop approximations for the MOs of more complex molecules.
- Guided by these insights, we then describe the two main ways to construct approximate molecular electronic wave functions from atomic orbitals, the linear combination of atomic orbitals (LCAO) method and the valence bond (VB) method.
- The LCAO method generates MOs that are delocalized over the entire molecule, and it builds up the electronic configurations of molecules using an *aufbau* principle just like the one for atoms. In contrast, the VB method describes electron pairs that are localized between a pair of atoms, and it provides a quantum mechanical foundation for the Lewis electron dot diagrams and for the valence shell electron pair repulsion (VSEPR) theory.
- We apply both of these methods to describe structure and bonding in a variety of molecules.

## MO Theory: Molecular orbital and energy

- Molecular orbital theory involves solving (approximately) the Schrödinger equation for the electrons in a molecule. This is a differential equation in which the first and second terms on the right represent the kinetic and potential energies:  $\hat{H}\psi = E\psi$     or     $(-\hbar^2/2\mu)\nabla^2\psi + V\psi = E\psi$ .
- *$\Psi$  is the molecular orbital.  $\hat{H}$  is Hamiltonian.*
- While the Schrödinger equation can be solved analytically for the hydrogen atom, the potential energy function  $V$  becomes more complicated - and the equation can then only be solved numerically - when there are many (mutually repulsive) electrons in a molecule. So, as a first approximation we will assume that the s, p, d, f, etc. orbitals of the atoms that make up the molecule are good solutions to the Schrödinger equation. We can then allow these wavefunctions to interfere constructively and destructively as we bring the atoms together to make bonds. In this way, we use the atomic orbitals (AO) as our *basis for constructing MO's*.

## Molecular Orbitals Theory: $\text{H}_2^+$ Is the Prototypical Species

- For the case where the protons in  $\text{H}_2^+$  are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other.
- The electronic wavefunction would just be  $1s_A(r)$  or  $1s_B(r)$  depending upon which proton, labeled *A* or *B*, the electron is nearby. Here  $1s_A$  denotes a 1s hydrogen atomic orbital with proton *A*.

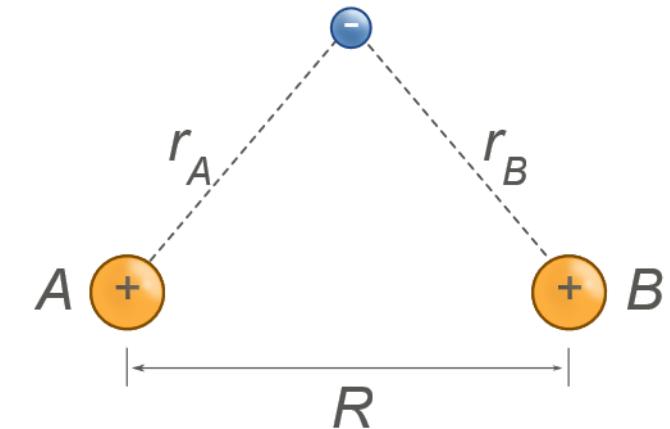


Figure 9.2.1 : Hydrogen molecular ion  $\text{H}_2^+$  with fixed nuclei *A* and *B*, internuclear distance *R*.

## Molecular-Orbital Theory: $\text{H}_2^+$ Is the Prototypical Species

- *The one-electron wavefunctions obtained by solving the Schrödinger equation  $\hat{H}\psi = E\psi$  are called molecular orbitals.*
- A molecular orbital  $\psi$  gives, through the value of  $|\psi|^2$ , the distribution of the electron in the molecule. A molecular orbital extends over the molecule like how electrons in an atom occupy atomic orbitals.
- For molecules, the Schrodinger equation for the one-electron molecular ion  $\text{H}_2^+$  is solved, and the resulting orbitals are used to construct the wave functions for more complicated molecules.
- We should mention at this point that  $\text{H}_2^+$  is a stable species that has been well studied spectroscopically. It has a bond length of 106 pm ( $2.00a_0$ ) and a binding energy of  $268 \text{ kJ}\cdot\text{mol}^{-1}$  ( $0.103E_h$ ).

- Because  $\text{H}_2^+$  is a one-electron species, **the Schrodinger equation for  $\text{H}_2^+$  can be solved exactly within the Born-Oppenheimer approximation.**
- Nevertheless, the solutions are not easy to use, and their mathematical form does not give much physical insight as to how and why bonding occurs.
- Instead, it is more useful to solve  $\text{H}_2^+$  approximately and use the resultant approximate molecular orbitals to build molecular wave functions.
- *Although this approach may seem a crude way to proceed (after all, the problem can be solved exactly), it provides good physical insight into the nature of chemical bonds in molecules and yields results in good agreement with experimental observations.* Furthermore, this approach can be systematically improved to give any desired degree of accuracy.

## ❖ The construction of Molecular Orbitals of $\text{H}_2^+$

- A molecular orbital is a one-electron wavefunction that spreads throughout the molecule. The *mathematical forms of such orbitals* are highly complicated, even for such a simple species as  $\text{H}_2^+$ , and they *are unknown* in general.
- All *modern work builds approximations* to the true molecular orbital by formulating models based on *linear combinations of the atomic orbitals (LCAOs) on the atoms in the molecule*.
- According to the general principles of quantum mechanics, *if there are several possible outcomes, then the overall wavefunction is a superposition - a linear combination of the wavefunctions that represent the individual outcomes*.
- *In  $\text{H}_2^+$ , there are two possible outcomes*: an electron may be found either in an atomic orbital  $\varphi_A$  centred on A or in an atomic orbital  $\varphi_B$  centred on B.
- Then *we add two wavefunctions to get a new wavefunction*.

- The two functions can be given the same phase ( $\varphi_A + \varphi_B$ ) or opposite phases ( $\varphi_A - \varphi_B$ ) (see Figure 9.2.2).
- To write these two options formally, we have, therefore, the two possible (unnormalized) wavefunctions for molecular orbitals are

$$\Psi_{\pm} = c_A \varphi_A \pm c_B \varphi_B \quad \text{where } c_A \text{ and } c_B \text{ are numerical coefficients.}$$

- The AOs are the **basis functions** for the MO.
- In this case the **basis set**, *the atomic orbitals  $\varphi_i$  from which the molecular orbital is built, consists of two  $H_{1s}$  orbitals, one on atom A and the other on atom B.*
- However, such a small basis set is inadequate for quantitative calculations, and in solving the computational problems, one need to use much larger basis sets.

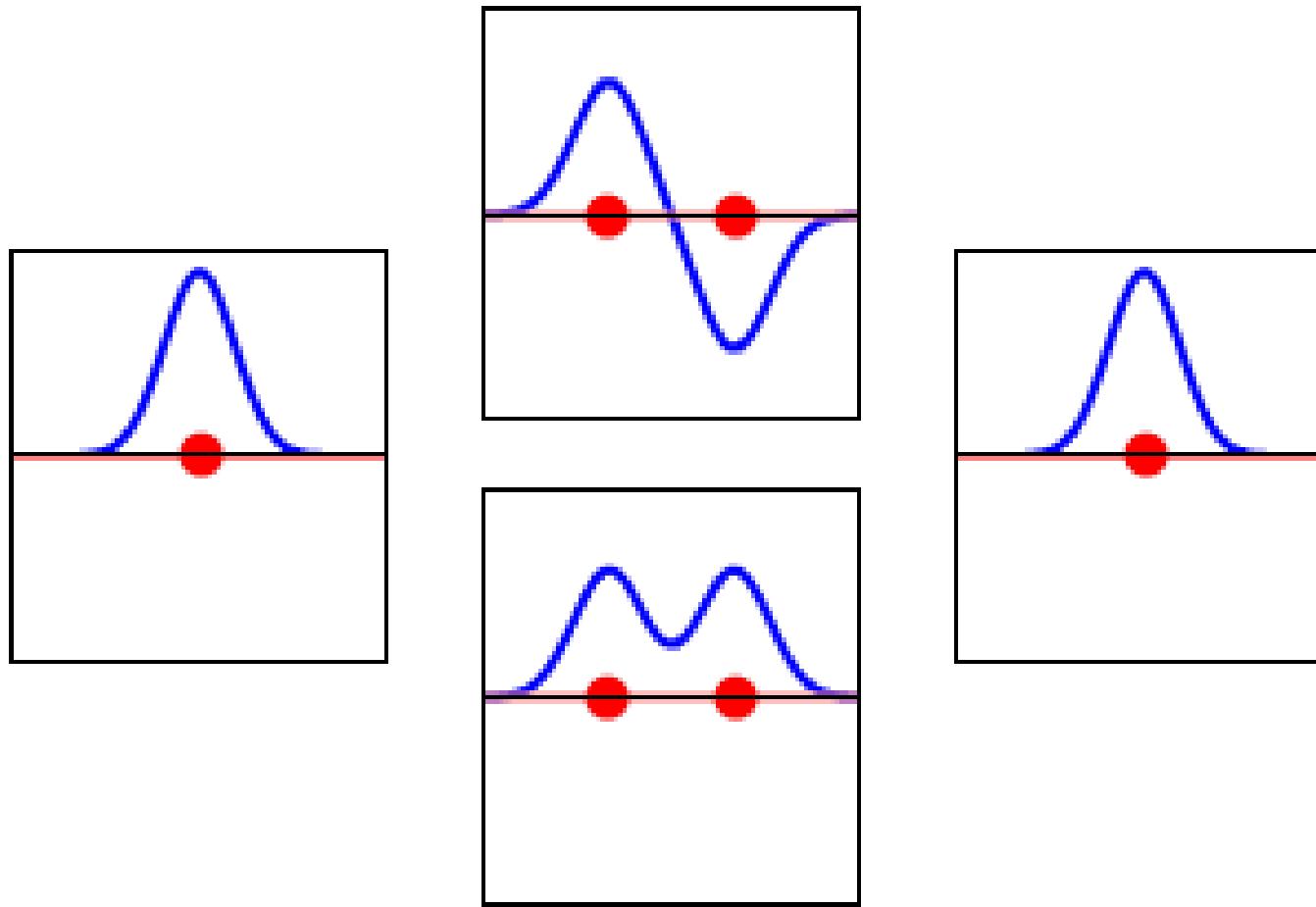


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the  $\text{H}_2^+$  ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional.)

- In general, the linear combination of atomic orbitals can be written mathematically as
- $\Psi = \sum c_i \phi_i$
- In this equation,  $\psi$  is the molecular wave function,  $\phi$  is an atomic wave function, and  $c$  is a weighting coefficient, which gives the relative weight in the “mix” of the atomic wave functions. The summation is over  $i$ , the number of atomic wave functions (number of atoms) being combined.
- If a diatomic molecule is being described, there are only two atoms involved so the equation becomes
- $\Psi = c_1 \phi_1 + c_2 \phi_2$
- Although the combination has been written as a sum, *the difference is also an acceptable linear combination.*
- The *weighting coefficients* are variables that must be determined.

Generally, when *choosing atomic orbitals for linear combination, three prerequisites* need to be fulfilled:

- • The *energies of the atomic orbitals need to be at a comparable level.*
- • Atomic orbitals need to be able to *produce sufficient overlap.*
- • The *atomic orbitals need to have the same symmetry with respect to the interatomic axis.*
- A *molecule must have as many molecular orbitals as there are atomic orbitals.*

- Finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In the  $\text{H}_2^+$  case, we have two *basis functions* in our *basis set*, the hydrogenic atomic orbitals  $1s_A$  and  $1s_B$ .  $\Psi = c_A \phi_A + c_B \phi_B = c_A 1s_A + c_B 1s_B$
- The *squares of the coefficients* ( $c_A^2$  &  $c_B^2$ ) give the *relative proportions of the atomic orbitals contributing to the molecular orbital*.
- ✓ In a homonuclear diatomic molecule (such as  $\text{H}_2$ ,  $\text{O}_2$ , or  $\text{Cl}_2$ ) an electron can be found with equal probability in orbital A or orbital B, so the squares of the coefficients must be equal ( $c_B^2 = c_A^2$ ), which implies that  $c_B = \pm c_A$ .
- Note that before we can discuss a *probability density associated with these molecular orbitals*, so  $\Psi_{\pm}$  must be normalized.
- Next by using the **approximate MO** in terms of the atomic orbitals, *one needs to minimize the MO energy with respect to the values of the AO coefficients  $c_A$  and  $c_B$* .

## MO: Energy Calculation

- First, let us identify the nature of the energy of molecular orbitals of a diatomic as a function of intermolecular distance.
  - Here we shall identify the three integrals involved in calculating the total Molecular Orbital Energy: **coulomb Integral**, **exchange integral**, and **overlap integral**.
- In quantum mechanics, it was shown that to **calculate the average value for a dynamical variable  $a$  whose operator is  $\alpha$** , it is necessary to make use of the relationship

$$\langle a \rangle = \frac{\int \psi^* \alpha \psi d\tau}{\int \psi^* \psi d\tau} \quad (3.3)$$

- If the property we wish to **determine** is the **energy ( $E$ )**, this equation becomes

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \quad (3.4)$$

- Where  $\hat{H}$  is the Hamiltonian operator, the **operator for total energy**.

- The expression shown in Eq. (3.2) is substituted for  $\psi$  in the equation above which gives

$$E = \frac{\int (a_1\phi_1^* + a_2\phi_2^*) \hat{H} (a_1\phi_1 + a_2\phi_2) d\tau}{\int (a_1\phi_1^* + a_2\phi_2^*)(a_1\phi_1 + a_2\phi_2) d\tau} \quad (3.5)$$

- When the multiplications are carried out and the constants are removed from the integrals we obtain

$$E = \frac{a_1^2 \int \phi_1^* \hat{H} \phi_1 d\tau + 2a_1 a_2 \int \phi_1^* \hat{H} \phi_2 d\tau + a_2^2 \int \phi_2^* \hat{H} \phi_2 d\tau}{a_1^2 \int \phi_1^* \phi_1 d\tau + 2a_1 a_2 \int \phi_1^* \phi_2 d\tau + a_2^2 \int \phi_2^* \phi_2 d\tau} \quad (3.6)$$

- In writing this equation, it was assumed that

$$\int \phi_1^* \hat{H} \phi_2 d\tau = \int \phi_2^* \hat{H} \phi_1 d\tau \quad (3.7)$$

- and that

$$\int \phi_1^* \phi_2 d\tau = \int \phi_2^* \phi_1 d\tau \quad (3.8)$$

- These assumptions are valid for a diatomic molecule composed of identical atoms (homo-nuclear diatomic) because  $\phi_1$  and  $\phi_2$  are identical and real in this case.
- In working with the quantities in equations such as Eq. (3.6), certain elements are frequently encountered. For simplicity, the definitions that will be adopted are as follows:

$$H_{11} = \int \phi_1^* \hat{H} \phi_1 d\tau \quad (3.9)$$

$$H_{12} = \int \phi_1^* \hat{H} \phi_2 d\tau \quad (3.10)$$

- In addition to the *integrals that represent energies*, there are ***integrals of a type in which no operator occurs***. These are represented as

$$S_{11} = \int \phi_1^* \phi_1 d\tau \quad (3.11)$$

$$S_{12} = \int \phi_1^* \phi_2 d\tau \quad (3.12)$$

- If the subscripts are identical, orbitals on the same atom are indicated, and *if the atomic wave functions are normalized*, the value of such an integral is 1.
- As a result, we can write

$$S_{11} = \int \phi_1^* \phi_1 d\tau = S_{22} = \int \phi_2^* \phi_2 d\tau = 1 \quad (3.13)$$

- On the other hand, the integrals of the type

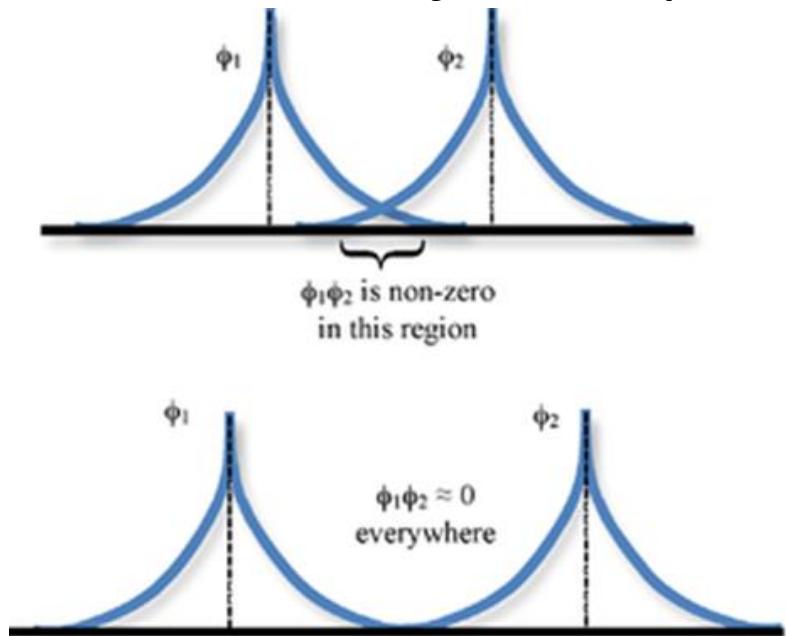
$$S_{12} = \int \phi_1^* \phi_2 d\tau = S_{21} = \int \phi_2^* \phi_1 d\tau \quad (3.14)$$

- Then the energy equation becomes:

$$E = \frac{a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22}}{a_1^2 + 2a_1 a_2 S_{12} + a_2^2} \quad (3.15)$$

- involves the product of an atomic orbital situated on nucleus 1 and one situated on nucleus 2, where the two nuclei are separated by a distance  $R$ , as in Figures 9.3.1, 10.10 & 12.1.
- This product is significant only for regions where the two atomic orbitals have a large overlap. Integrals of this type are known as **overlap integrals**, and in a general way, they represent the **effectiveness with which the orbitals overlap in a region of space**.
- Consequently,  $S_{ij}$  is called an **overlap integral** that gives the extent of overlap and is an abbreviation for  $S_{ij} = \int \varphi_i^* \varphi_j d\tau$ .

Figure 9.3.1 : The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both  $S$  is close to zero.



- If the two atoms are *separated by a large distance*, the *overlap integral approaches 0* (Figure 9.3.1: bottom).
- However, if the atoms are *closer together*, there is *some overlap* of the orbitals and  $S > 0$ . If the atoms were forced together in such a way that the two nuclei coincided (internuclear distance is 0), we would expect  $S = 1$  because the orbitals would be congruent.
- Clearly, the value of an overlap integral such as those shown in Eq. (3.14) must be somewhere *between 0 and 1*, and it must be a function of the internuclear distance. With the exchange integrals and overlap integrals both being functions of the internuclear distance, it should be possible to express one in terms of the other. We will return to this point later.
- The *overlap* is a new concept that is not encountered in atomic systems.

- The meaning of  $S$  is indicated pictorially in Figure 12.1. In words, ***it is a measure of the degree to which both of the AOs have nonzero values in the same region.***  $S$  can have values between 0 and 1 and decreases as the distance between the two nuclei increases. It has the value zero for widely separated atoms and 1 for superimposed atoms. As we will see later, *in order to have chemical bond formation it is necessary that  $S > 0$ .*
- Thus, we see that  $0 \leq S(R) \leq 1$ .

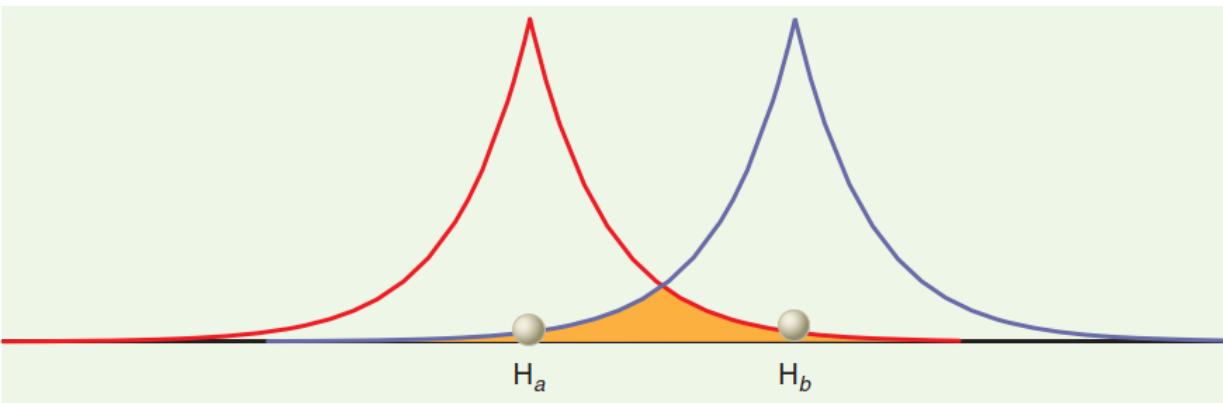


FIGURE 12.1

The amplitude of two 1s atomic orbitals is shown along an axis connecting the atoms. The overlap is appreciable only for regions in which the amplitude of both AOs is significantly different from zero. Such a region is shown schematically in orange. In reality, the overlap occurs in three-dimensional space.

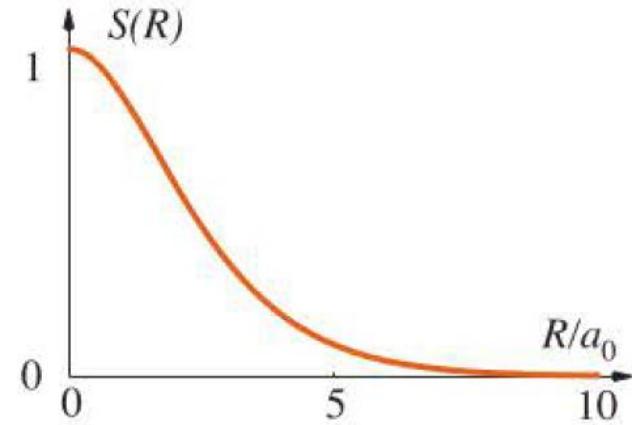


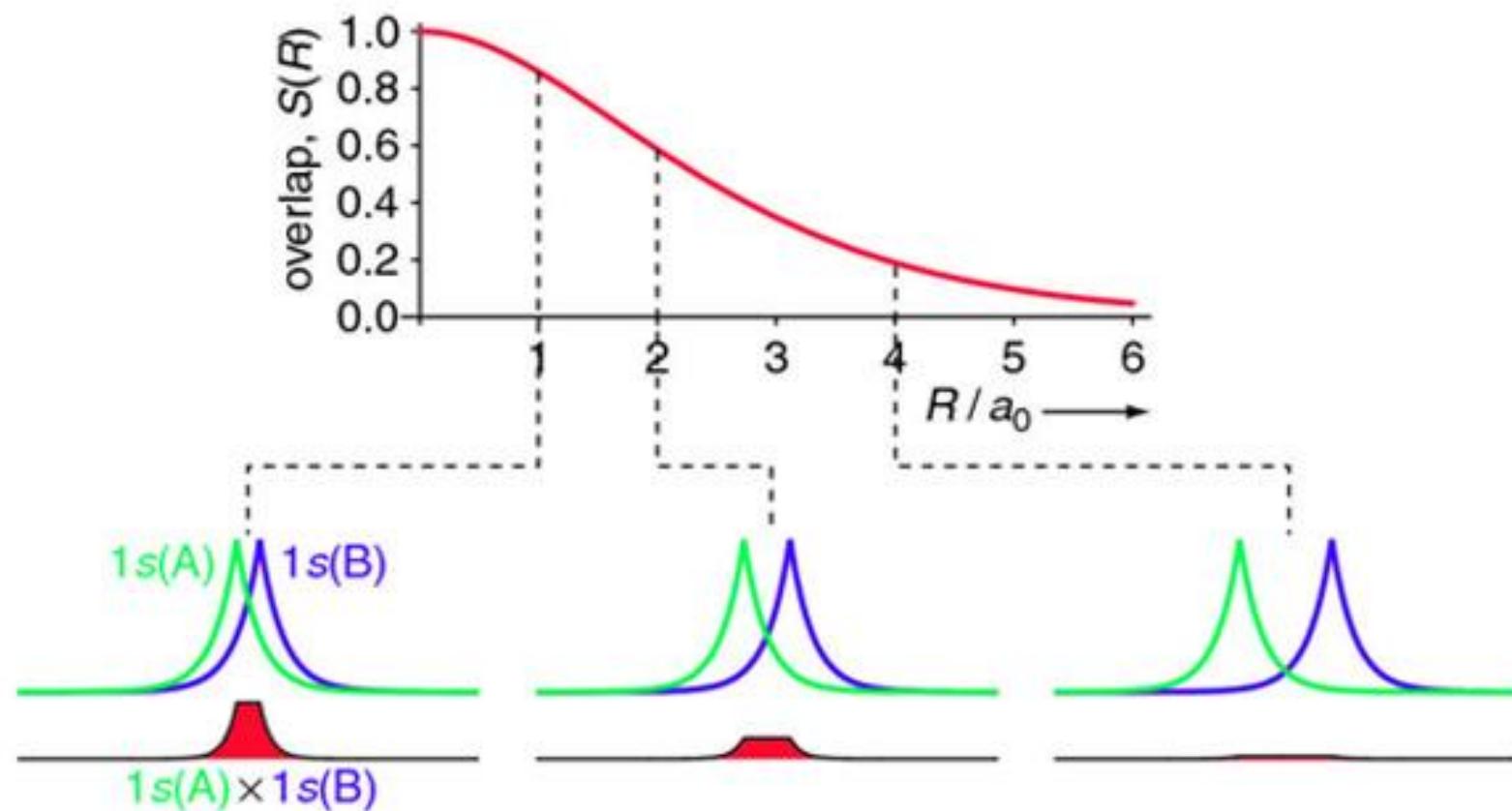
FIGURE 10.10

The overlap integral  $S(R)$ , for two hydrogen-atom 1s orbitals, plotted versus the internuclear separation in atomic units.

- **The Overlap Integral Is a Quantitative Measure of the Overlap of Atomic Orbitals Situated on Different Atoms.** For  $\text{H}_2^+$  at its equilibrium bond length,  $S \approx 0.59$ .

- For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:
- $S(R) = \int \varphi_i^* \varphi_j d\tau = e^{-R/a_0} \left( 1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right)$
- The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

Figure 9.3.2 : The overlap integral at different proton separations.



- For  $\text{H}_2^+$ , the simplest molecule, we must **determine the values for the coefficients,  $C_A$  and  $C_B$**  for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals:  $\Psi(r)=C_A 1s_A + C_B 1s_B$
- We could use the *linear variational method* to find a value for these coefficients, but for the case of  $\text{H}_2^+$  evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by  $|C_A|^2$  and  $|C_B|^2$ , respectively.
- Consider two possibilities that satisfy the condition  $|C_A|^2=|C_B|^2$
- So,  $C_A = C_B = C_+$  and  $C_A = -C_B = C_-$ .
- These two cases produce two molecular orbitals:
- $\Psi_+ = C_+(1s_A + 1s_B)$  .....bonding molecular orbital ....(9.3.1)
- and
- $\Psi_- = C_-(1s_A - 1s_B)$  .....antibonding molecular orbital. ....(9.3.2)

- Now we want to evaluate  $C_+$  and  $C_-$  and then calculate the energy.
- The bonding and antibonding character of  $\psi_+$  and  $\psi_-$  also should be reflected in the energy. If  $\psi_+$  indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts  $H_2^+$  to be stable or not and also how much energy is required to dissociate this molecule.
- The constants  $C_+$  and  $C_-$  are evaluated from the standard normalization condition:  $\int \psi_{\pm}^* \psi_{\pm} d\tau = \int |\psi_{\pm}|^2 d\tau = 1$ .

Or,  $\int C_{\pm}(1s_A \pm 1s_B) \cdot C_{\pm}(1s_A \pm 1s_B) d\tau = 1$

Or,  $|C_{\pm}|^2 \int (1s_A \pm 1s_B) \cdot (1s_A \pm 1s_B) d\tau = 1$

Or,  $|C_{\pm}|^2 [\int 1s_A 1s_A d\tau \pm \int 1s_B 1s_A d\tau \pm \int 1s_A 1s_B d\tau \pm \int 1s_B 1s_B d\tau] = 1 \quad \dots \text{Eqn. (9.3.5)}$

- In the above Eqn. the first ( $\int 1s_A 1s_A d\tau$ ) and the last ( $\int 1s_B 1s_B d\tau$ ) integrals are equal to 1, since the atomic orbitals are normalized.

- The middle two integrals ( $\int 1s_B 1s_A d\tau$  and  $\int 1s_A 1s_B d\tau$ ) are **overlap integrals** and are symbolized by  $S$  (and  $S^*$ , respectively), since one is the complex conjugate of the other.
- ***The overlap integrals are telling*** us to take the value of  $1s_B$  at a point **multiply** by the value of  $1s_A$  at that point and **sum** (integrate) such a product over all of space (Figure 9.3.1).
- If the functions do not overlap, i.e., if one is zero when the other one is not and vice versa, these integrals then will be zero.
- It is also possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.
- If the **overlap integral is zero**, for whatever reason, the functions are said to be **orthogonal**.

- Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from  $R=\infty$  to  $R=0$ . Clearly when the protons are infinite distance apart, there is no overlap, and when  $R=0$  both functions are centered on one nucleus and  $\int 1s_B 1s_A d\tau$  becomes identical to  $\int 1s_A 1s_B d\tau$ , which is normalized to 1, because  $1s_A = 1s_B$ .
- Substituting the above values, Equation 9.3.5 becomes  $|C_{\pm}|^2(1 \pm S \pm S \pm 1) = |C_{\pm}|^2(2 \pm 2S) = 1$ .
- The solution to the above Equation is given by:  $C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}}$ .
- Hence, the normalized molecular orbitals in Equations 9.3.1 and 9.3.2 are:
- $\Psi_+ = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B)$  .....bonding molecular orbital ....(9.3.1)
- and  $\Psi_- = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B)$  .....antibonding molecular orbital. ....(9.3.2)

$$\Psi_+ = \frac{1s_A + 1s_B}{\sqrt{2(1+S)}} = \Psi_b$$

$$\Psi_- = \frac{1s_A - 1s_B}{\sqrt{2(1-S)}} = \Psi_a$$

- The **probability density** of finding the electron at any point in space is given by  $|\psi^2|$  (or  $|\psi^*\psi|$ ) and the *electronic charge density* is just  $|e\psi^2|$ .
- The **important difference** between  $\psi_+^2$  and  $\psi_-^2$  is that the **charge density for  $\psi_+$  is enhanced between the two protons**, whereas it is *diminished for  $\psi_-$* .
- $\psi_-$  has a node in the middle while  $\psi_+$  corresponds to our intuitive sense of what a chemical bond must be like. The **electronic charge density is enhanced in the region between the two protons**. So  $\psi_+$  is called a **bonding molecular orbital**.
- If the electron were described by  $\psi_-$ , **the low charge density between the two protons** would not balance the Coulomb repulsion of the protons, so  $\psi_-$  is called an **antibonding molecular orbital**.
- The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

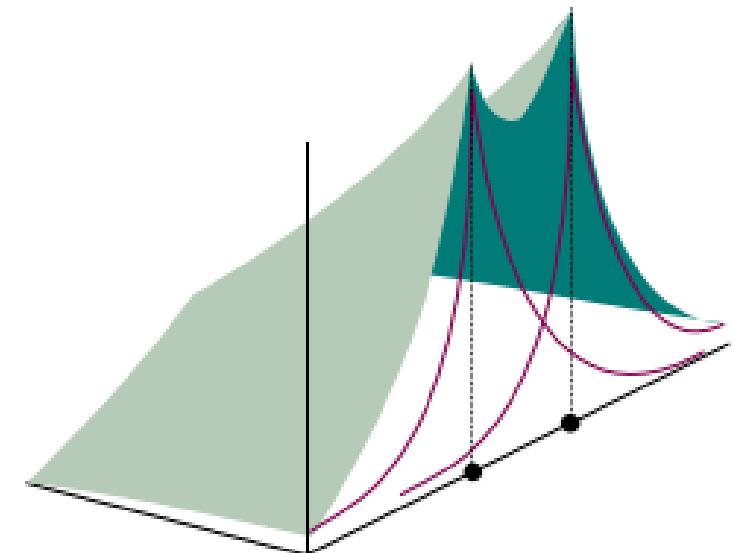
## Bonding orbitals

According to the Born interpretation, **the probability density of the electron at each point in  $H_2^+$  is proportional to the square modulus of its wavefunction at that point**. The probability density corresponding to the (real) wavefunction  $\psi_+$  is

$$\psi_+^2 \propto \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B \quad \text{Bonding probability density} \quad (9B.3)$$

This probability density is plotted in Fig. 9B.4. An important feature becomes apparent in the internuclear region, where both atomic orbitals have similar amplitudes. According to eqn. 9B.3, the total probability density is proportional to the sum of:

- $\psi_A^2$ , the probability density if the electron were confined to atom A;
- $\psi_B^2$ , the probability density if the electron were confined to atom B;
- $2\psi_A\psi_B$ , an extra contribution to the density from both atomic orbitals.



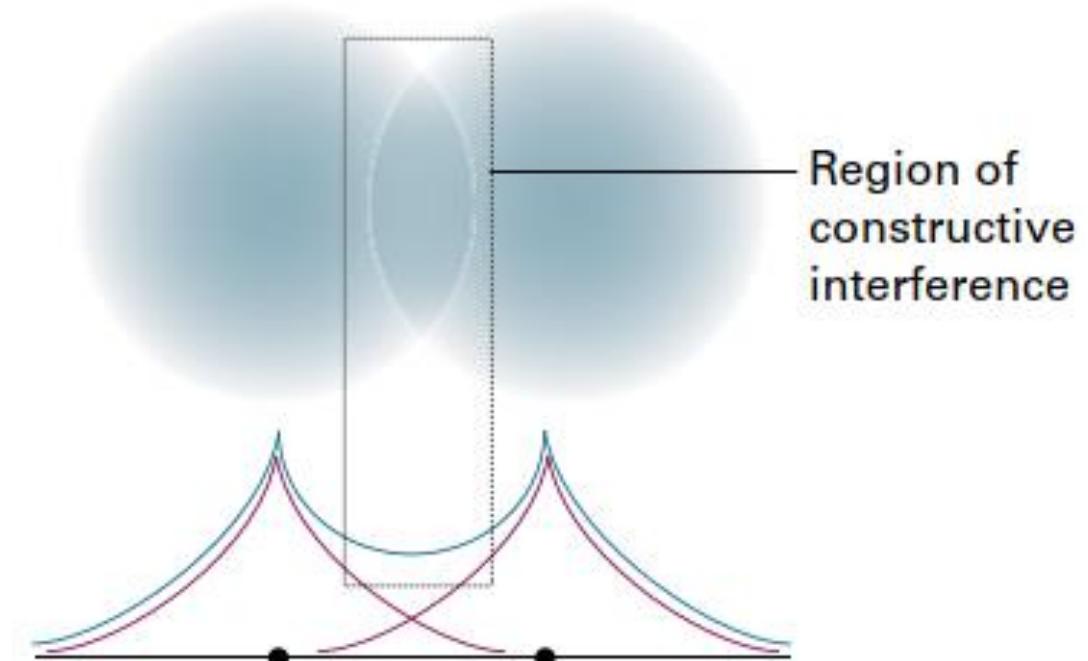
**Figure 9B.4** The electron density calculated by forming the square of the wavefunction used to construct Fig. 9B.2. Note the accumulation of electron density in the internuclear region.

□ The last contribution, **the *overlap density***, is crucial because it represents an enhancement of the probability of finding the electron in the internuclear region. The enhancement can be traced to the *constructive interference of the two atomic orbitals*: each has a positive amplitude in the internuclear region, so the total amplitude is greater there than if the electron were confined to a single atom. This observation is summarized as:

- Bonds form as a result of the build-up of electron density where atomic orbitals overlap and interfere constructively.
- ✓ All descriptions of bonding recognize the buildup of electron density in the region between the two nuclei at the expense of the regions beyond the nuclei.

$$\psi_+^2 \propto \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

Bonding probability  
density (9B.3)



**Figure 9B.7** A representation of the constructive interference (blue line) that occurs when two  $H_{1s}$  orbitals overlap and form a bonding  $\sigma$  orbital.

- The *conventional explanation* of this observation is based on the notion that *the accumulation of electron density between the nuclei puts the electron in a position where it interacts strongly with both nuclei*. Hence, *the energy of the molecule is lower than that of the separate atoms*, where each electron can interact strongly with only one nucleus.
- This *conventional explanation*, however, has been called into question, because *shifting an electron away from a nucleus into the internuclear region raises its potential energy*. The modern (and still controversial) explanation does not emerge from the simple LCAO treatment given here.
- ✓ It seems that, at *the same time as the electron shifts into the internuclear region*, the *atomic orbitals shrink*. *This orbital shrinkage improves the electron–nucleus attraction more than it is decreased by the migration to the internuclear region*, so there is *a net lowering of potential energy*. The kinetic energy of the electron is also modified because the curvature of the wave function is changed, but the change in kinetic energy is dominated by the change in potential energy.
- Throughout the following discussion the strength of chemical bonds is ascribed to the accumulation of electron density in the internuclear region. In molecules more complicated than  $\text{H}_2^+$  the true source of energy lowering may be this accumulation of electron density or some indirect but related effect.

## Antibonding orbitals

The linear combination  $\psi_-$  has higher energy than  $\psi_+$ , and for now, it is labeled  $\sigma^*$  because it is also a  $\sigma$  orbital. This orbital has a nodal plane perpendicular to the internuclear axis and passes through the mid-point of the bond where  $\psi_A$  and  $\psi_B$  cancel exactly (Figs. 9B.8 and 9B.9).

The probability density is

$$\psi_-^2 \propto \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

Antibonding  
probability density      (9B.6)

There is a reduction in probability density between the nuclei due to the term  $-2\psi_A\psi_B$  (Fig. 9B.10); in physical terms, *there is destructive interference where the two atomic orbitals overlap.*

- The  $\sigma^*$  orbital is an example of an antibonding orbital, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to the separated

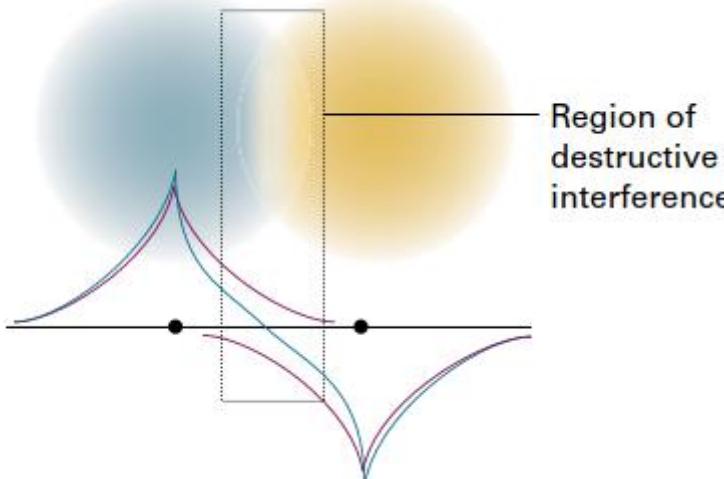
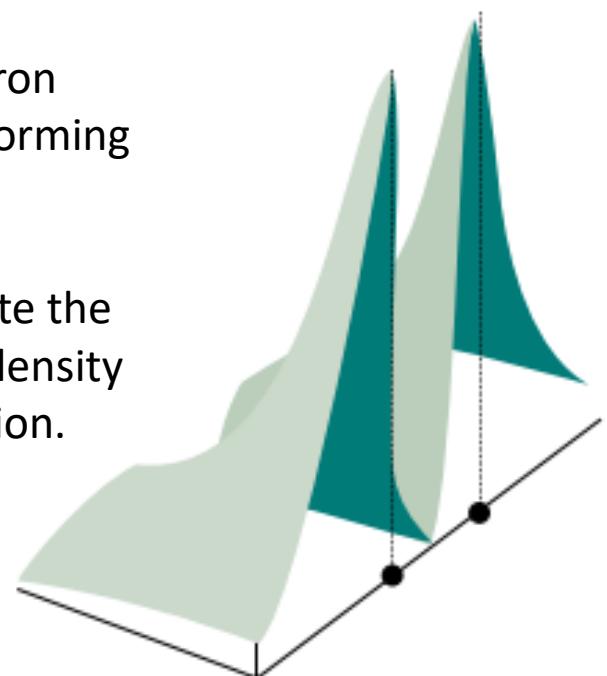


Figure 9B.8 A representation of the destructive interference that occurs when two H<sub>1s</sub> orbitals overlap and form an antibonding  $\sigma$  orbital.

Figure 9B.10 The electron density calculated by forming the square of the wavefunction used to construct Fig. 9B.9. Note the reduction of electron density in the internuclear region.



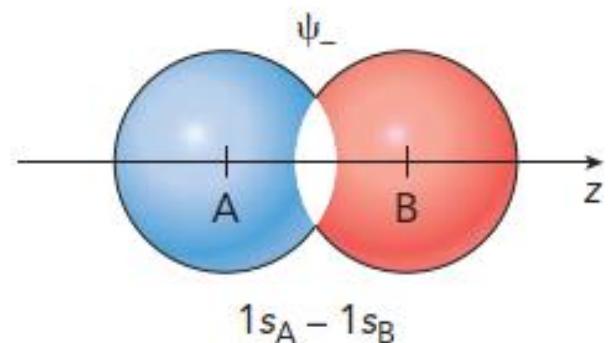
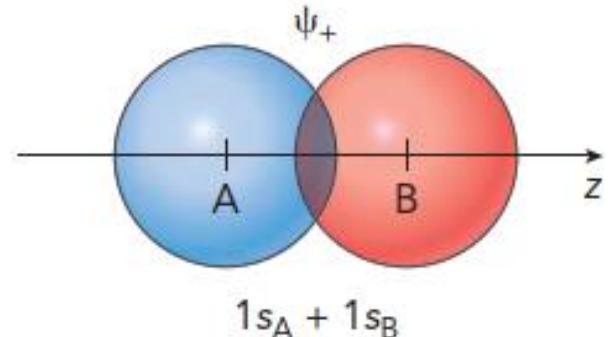
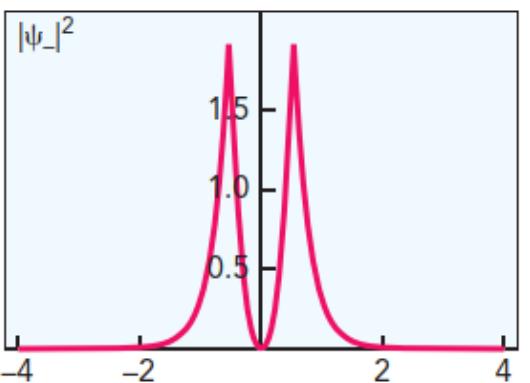
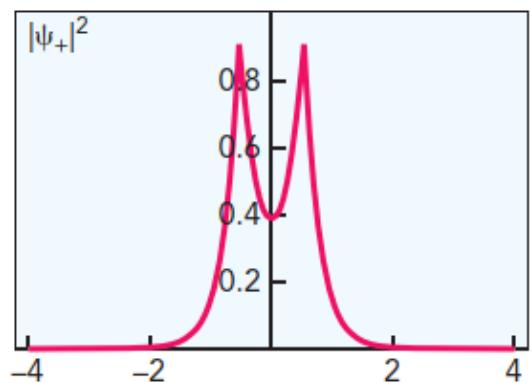
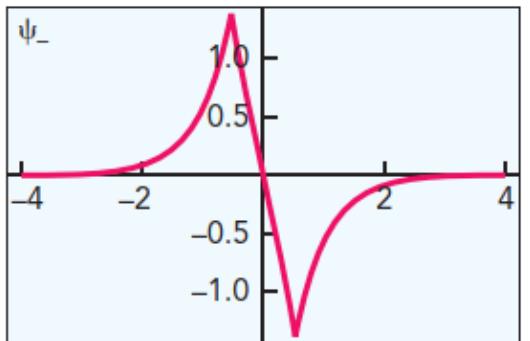
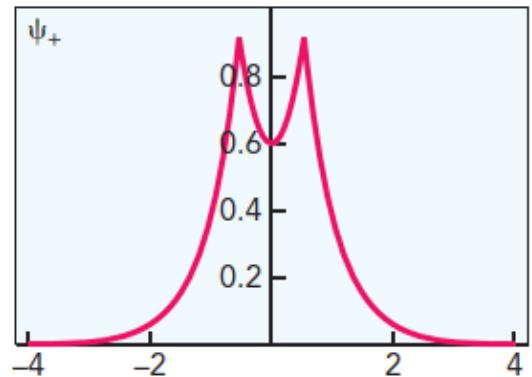


Figure 5.8. The  $\psi_+$  and  $\psi_-$  wavefunctions and probability densities, graphed as functions of  $z$ .

The key feature for us here is that in the  $\psi_-$  orbital, the density goes to zero at the midpoint between the two nuclei. This is expected for a wavelike electron: with enough energy, it should be able to oscillate with a node in the middle. But this node reduces the electron charge in the binding region, causing the orbital to have the net impact of weakening the bond between the two nuclei.

Figure 5.7 The  $\psi_+$  and  $\psi_-$  MOs. We combine the two spherically symmetric 1s orbitals on nuclei A and B to get the simplest molecular orbitals.

- The appearance of Eq. (3.6) can be simply written as follows by using the notation described above. When the substitutions are made, the result is

$$E = \frac{a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22}}{a_1^2 + 2a_1 a_2 S_{12} + a_2^2} \quad (3.15)$$

- (assuming  $S_{11}$  and  $S_{22}$  are both equal to 1 because of the atomic wave functions being normalized).
- We now seek to ***find values of the weighting coefficients that make the energy a minimum.*** To find a minimum in the energy expression, we take the partial derivatives with respect to  $a_1$  and  $a_2$  and set them equal to 0.

$$\left( \frac{\partial E}{\partial a_1} \right)_{a_2} = 0 \quad \left( \frac{\partial E}{\partial a_2} \right)_{a_1} = 0 \quad (3.16)$$

- When the differentiations are carried out with respect to  $a_1$  and  $a_2$  in turn while keeping the other constant, we obtain two equations that after simplification can be written as

$$a_1(H_{11} - E) + a_2(H_{12} - S_{12}E) = 0 \quad (3.17)$$

$$a_1(H_{21} - S_{21}E) + a_2(H_{22} - E) = 0 \quad (3.18)$$

- These equations are known as the *secular equations*, and in them the weighting coefficients  $a_1$  and  $a_2$  are the unknowns.
- These equations constitute a pair of linear equations that can be written in the form

$$ax + by = 0 \quad \text{and} \quad cx + dy = 0 \quad (3.19)$$

- It can be shown that a nontrivial solution for a pair of linear equations requires that the determinant of the coefficients must be equal to 0. This means that

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{21} - S_{21}E & H_{22} - E \end{vmatrix} = 0 \quad (3.20)$$

- The molecule being described is a homonuclear diatomic, so  $H_{12} = H_{21}$  and  $S_{12} = S_{21}$ .
- If we represent  $S_{12}$  and  $S_{21}$  by  $S$  and let  $H_{11} = H_{22}$ , the expansion of the determinant yields

$$(H_{11} - E)^2 - (H_{12} - SE)^2 = 0 \quad (3.21)$$

- By equating the two terms on the left-hand side of Eq. (3.21), taking the square root gives

$$H_{11} - E = \pm(H_{12} - SE) \quad (3.22)$$

- from which we find two values for  $E$  (denoted as  $E_b$  and  $E_a$ ).

- Two values for  $E$  are denoted as  $E_b$  and  $E_a$ :

$$E_b = \frac{H_{11} + H_{12}}{1 + S} \quad \text{and} \quad E_a = \frac{H_{11} - H_{12}}{1 - S} \quad (3.23)$$

- The energy state labeled  $E_b$  is known as the ***bonding or symmetric state***, whereas that designated as  $E_a$  is called the ***antibonding or asymmetric state***.
- Quantitative calculations show that near the equilibrium distance  $R = R_e$ ,  $H_{12}$  is **negative** and  $|H_{12}| > |H_{11}|$ . Since  $H_{12}$  is negative and  $S > 0$ , therefore  $E_b$  represents the state of lower energy ( $E_b < E_a$ ).
- The bonding and antibonding states are “split” below and above the energy state of the electron in an atom, not below and above an energy of 0. The above argument also shows that ***antibonding state is raised a greater amount than the bonding state is lowered relative to the atomic orbital energy***. This can be seen from the relationships shown in Eq. (3.23) because in the first case the denominator is  $(1 + S)$ , but in the other it is  $(1 - S)$  and  $H_{12}$  is negative,  $|H_{12}| > |H_{11}|$  and  $S > 0$ .

- Fig. 3.3 shows the qualitative energy diagram for the bonding and antibonding molecular orbitals relative to the 1s atomic orbital.

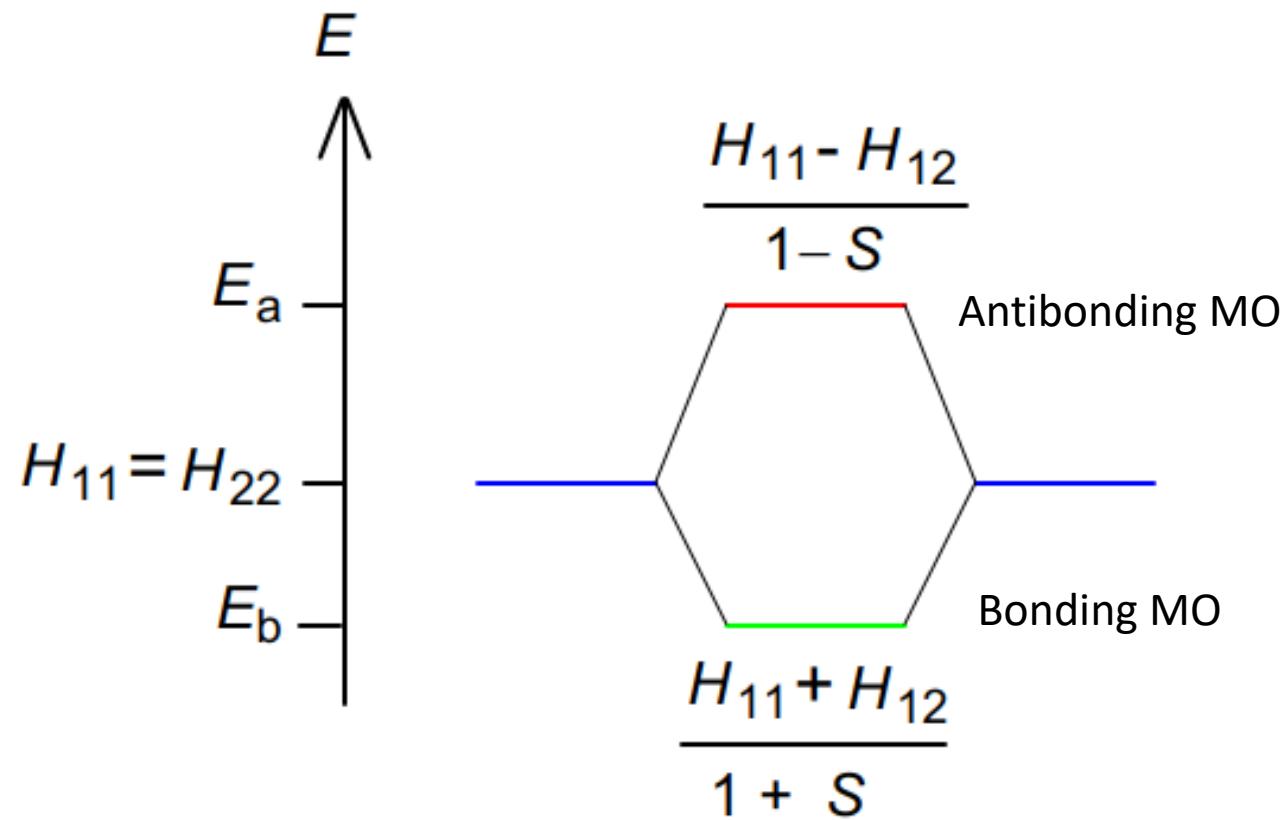


FIGURE 3.3 Combination of two  $s$  orbitals to produce *bonding* and *antibonding* orbitals.

- As shown previously, we can construct two molecular orbitals for the  $\text{H}_2^+$  system using the LCAO approximation with a basis set of two 1s atomic orbitals (i.e., the 1s orbitals on hydrogen A ( $1s_A$ ) and hydrogen B ( $1s_B$ ) in places of  $\phi_1$  and  $\phi_2$ ).
- If the  $H_{11}$  and  $H_{12}$  are known, the energies of the bonding and antibonding states  $E_b$  and  $E_a$  can be calculated.

## MOT: Hamiltonian ( $H$ ) of the Simplest Diatomic Molecular Species: $\text{H}_2^+$ and $\text{H}_2$

- As a *first step* in setting up the Schrödinger equation for  $\text{H}_2^+$  and  $\text{H}_2$  molecules, the nuclei are fixed at some given separation.
- *Then* the electrons are included, and the equation is solved to give the wave functions and energies that describe the two electrons.
- The *wavefunction* that corresponds to the lowest energy, the *ground state wavefunction*, can be used to compute *contour diagrams*, much like the maps used to show peaks and valleys in hilly terrain. These diagrams show the distribution of electron density around the two nuclei.
- For simplicity, let's consider the simplest neutral molecule,  $\text{H}_2$ . The Schrödinger equation for a  $\text{H}_2$ , like that for a hydrogen atom, gives a set of wave functions, or orbitals, and their corresponding energies. As noted earlier, these orbitals extend over both nuclei in  $\text{H}_2$  and therefore are called **molecular orbitals (MOs)**.

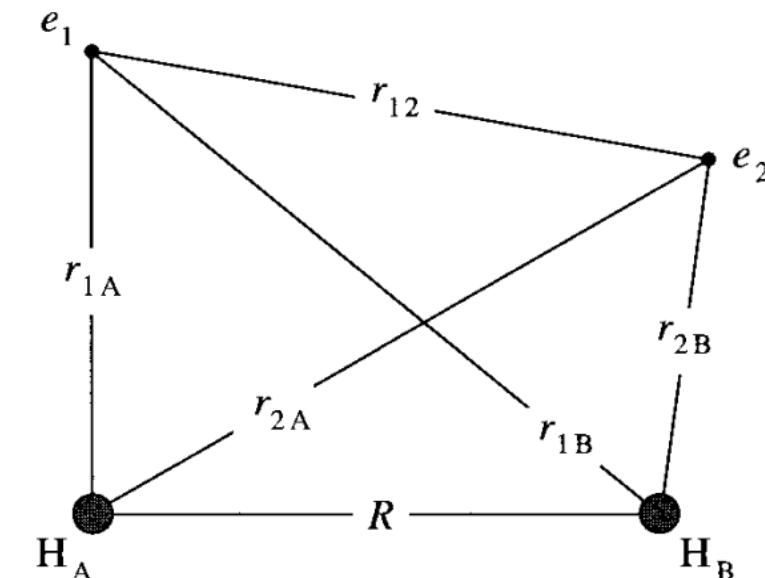
- The Hamiltonian operator for a hydrogen molecule ( $H_2$ ) is given by

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \quad (9.1)$$

- In Equation 9.1, the subscripts A and B refer to the nuclei of the individual atoms, the *subscripts 1 and 2 refer to the individual electrons*, and the various distances  $r_{1A}$ ,  $r_{1B}$ , etc. are as illustrated in Figure 9.1.

**FIGURE 9.1**

Definition of the distances between the nuclei and the electrons involved in the **Hamiltonian operator for a hydrogen molecule**.



- In these expressions  $e$  is the magnitude of the charge on the protons and the electrons,  $m_e$  and  $M$  are the masses of the electron and proton respectively and  $\epsilon_0$  is the vacuum permittivity.
- The symbol  $\nabla^2$ , which is spoken ‘del squared’ (Laplacian), is defined by:

$$\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

- The first two terms of the Hamiltonian operator in Equation 9.1 correspond to the kinetic energy of the two nuclei; the next two terms represent the kinetic energy of the two electrons; the four ensuing negative terms describe the contributions to the potential energy that arise from the attraction between the nuclei and the electrons; and the final two positive terms account for electron-electron and nuclear-nuclear repulsion, respectively.

- The total Hamiltonian operator is therefore the sum of ten terms, and we immediately recognize that it is unlikely that a solution of Schrödinger's eigenvalue-eigenfunction equation can be found, even for this, the simplest of molecules.
  - Therefore, if the theory is to be applicable, some way or ways, of simplifying the problem must be found.
- The Born-Oppenheimer (BO) Approximation**.....Separates the Nuclear and Electronic motions and simplifies Schrodinger Equation for Molecules
- All theories of molecular structure adopt the Born-Oppenheimer (BO) approximation.
  - In this approximation, it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move around them.

- Since electrons are much lighter than nuclei, electrons move much faster than nuclei in a molecule, for calculations suggest that (in classical terms) *the nuclei* in  $\text{H}_2$  **move through only about 1 pm** while the **electron speeds through 1000 pm**.
- ✓ Because of the large difference between the masses of the nuclei and the electrons, we can reasonably view the nuclei as fixed in position relative to the motion of the electrons.
- ✓ *Under such an approximation, the kinetic energy terms of the nuclei (the first two terms in the Hamiltonian operator, Equation 9.1) can be treated separately.*
- *This approximation of neglecting the nuclear motion is called the Born-Oppenheimer approximation.*
- *The nuclei can be thought of as being fixed at arbitrary locations so that the Schrodinger equation can be solved for the electrons alone.*
- *The approximation is quite good for molecules in their electronic ground states.*

- Although the *Born-Oppenheimer approximation will lead to approximate values of the energies* and *wave functions*, it can be systematically corrected using perturbation theory. For most practical purposes, however, these corrections are on the order of the mass ratio ( $\sim 10^{-3}$ ), and so the Born-Oppenheimer approximation is a very good approximation.
- The Hamiltonian operator for a hydrogen molecule ( $H_2$ ) is given by

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \quad (9.1)$$

- *Neglecting the nuclear kinetic energy terms* in Equation 9.1 gives the Hamiltonian operator for the motion of the electrons around the two nuclei fixed at an internuclear separation:

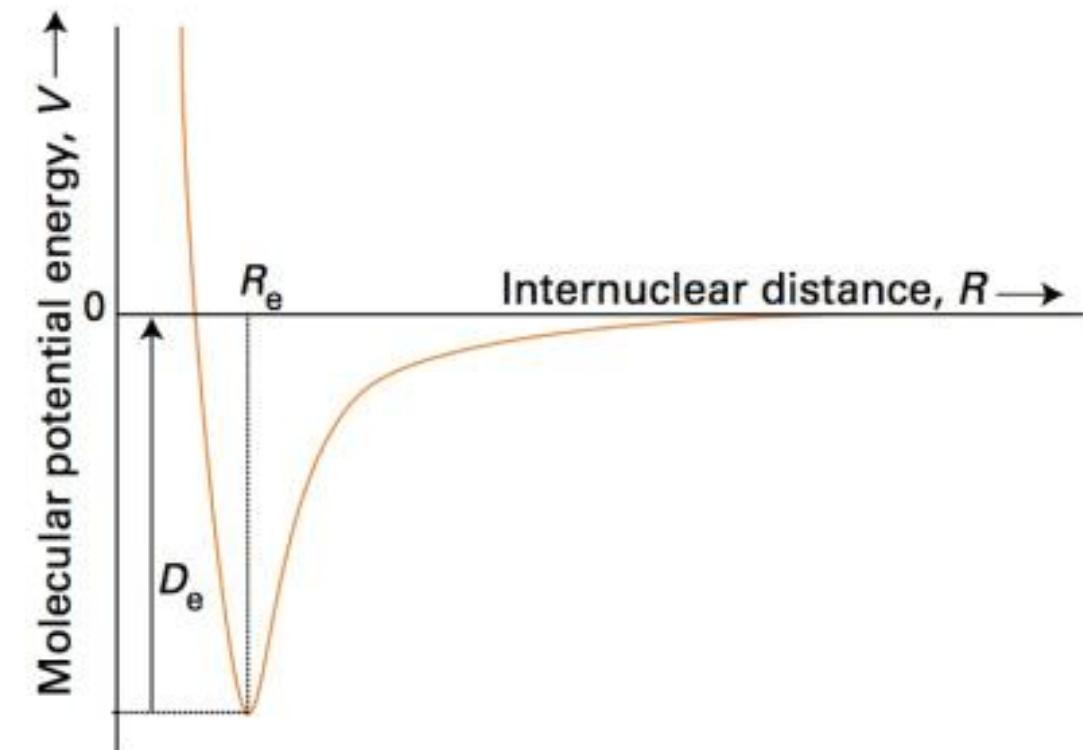
$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \quad (9.2)$$

- As usual, we will *express all our equations in atomic units* and so Equation 9.2 becomes:

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (9.3)$$

- *Because the nuclei are considered to be fixed, the quantity R in Equation 9.2 is treated as a parameter; the **energy** that we will calculate using the above Hamiltonian operator **will depend upon R**.*
- By invoking the Born-Oppenheimer approximation, the **energies** and **wavefunctions** of a diatomic molecule *can be obtained by selecting an internuclear separation and then solving the Schrodinger equation for the electrons.*
- Then the calculation can be repeated at a different internuclear separation, and so on.
- *If a stable molecule is to be formed, there must be a decrease in energy as we move towards smaller values of R* and this process will continue until the mutual repulsion of the nuclei and of the electrons begins to make itself felt and the energy begins to rise again; normally quite steeply.

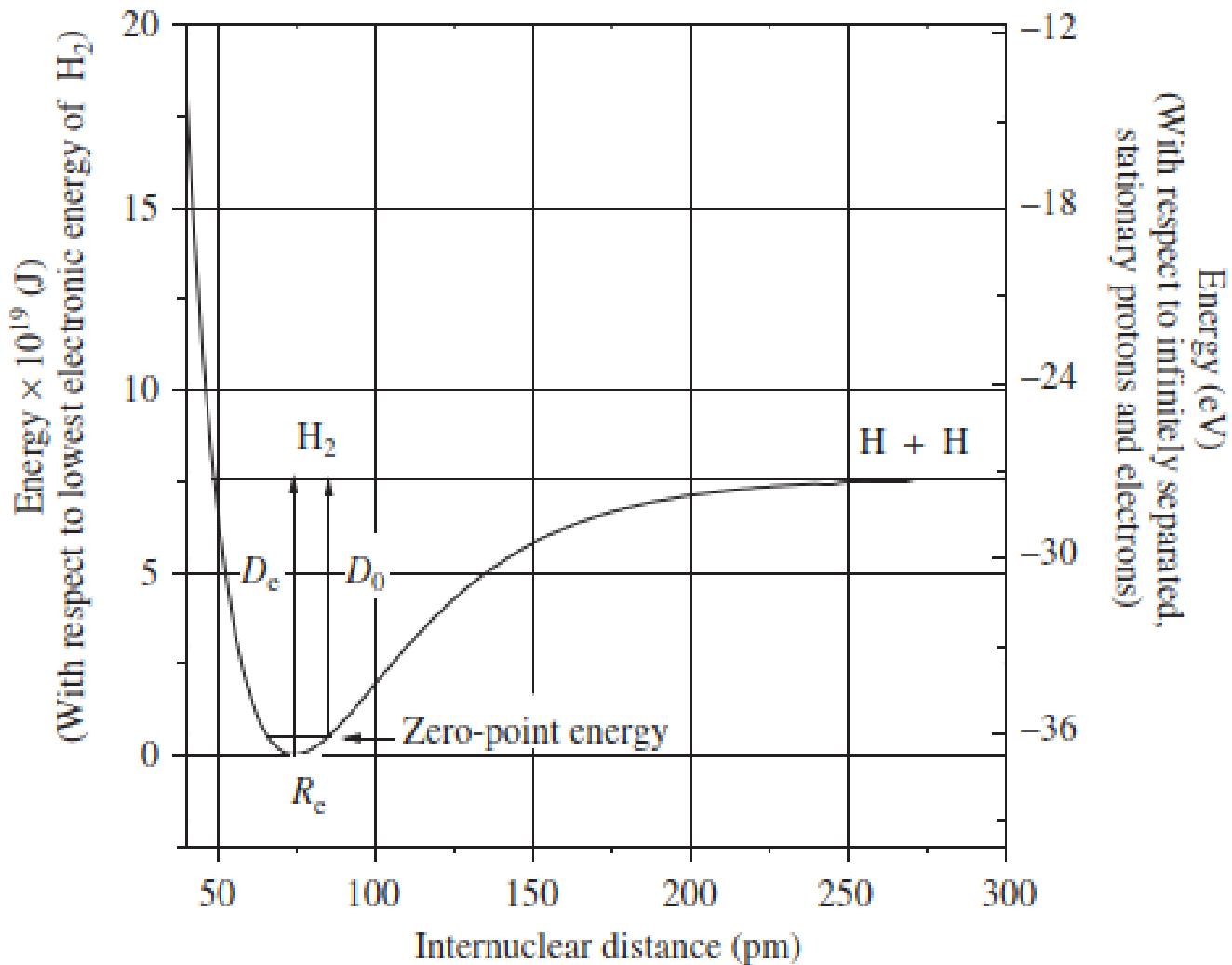
- In this way it is possible to explore **how the energy of the molecule varies with bond length** and obtain a **molecular potential energy curve**, a graph showing how the molecular energy depends on the internuclear separation (Fig. 1). The graph is called a **potential energy curve** because the nuclei are stationary and contribute no kinetic energy.
- Once the curve has been calculated, two important parameters can be identified: the **equilibrium bond length**,  $R_e$ , the internuclear separation at the minimum of the curve, and  $D_e$  the depth of the minimum below the energy of the infinitely widely separated and stationary atoms.
- Similar considerations apply to **polyatomic molecules**, where **bond angles** may be varied as well as **bond lengths**.



**Fig. 1** A molecular potential energy curve. The equilibrium bond length  $R_e$ , corresponds to the energy minimum  $D_e$ .

This distance is known as the equilibrium internuclear distance,  $R_e$ , and is found experimentally to be 74.1 pm.

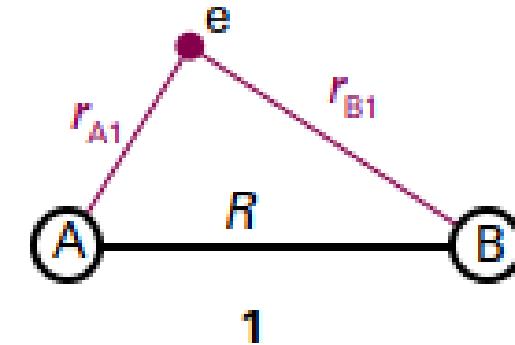
- The corresponding experimental energy is 4.747 eV ( $7.6056 \times 10^{-19}$  J) below the energy of the two, non-interacting hydrogen atoms.
- This is the energy which we shall seek to calculate by determining the difference between the electronic energy of two independent hydrogen atoms and that of the hydrogen (H–H) molecule with a bond length of  $R_e$ . The symbol for this energy difference is  $D_e$ .



**Figure 6.3** The hydrogen molecule: energy versus internuclear distance

## ❖ The Case of the Simplest Diatomic Species: Hydrogen Molecular Ion $\text{H}_2^+$ (one-electron system)

The Hamiltonian for the single electron in  $\text{H}_2^+$  is  
.....????.....



where  $r_{A1}$  and  $r_{B1}$  are the distances of the electron from the two nuclei A and B and R is the distance between the two nuclei. In the expression for V, the first two terms in parentheses are the attractive contribution from the interaction between the electron and the nuclei; the remaining term is the repulsive interaction between the nuclei.

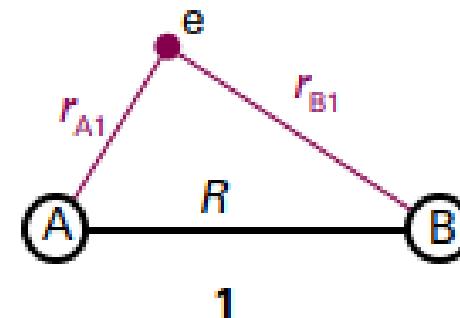
## The Simplest Diatomic Species: Hydrogen Molecular Ion $\text{H}_2^+$ (one-electron system)

A one-electron system that applies to homonuclear diatomic molecules is the hydrogen molecular ion,  $\text{H}_2^+$ , which consists of two protons and one electron. The  $\text{H}_2^+$  ion can be produced experimentally by using  $\text{H}_2(\text{g})$  in a discharge tube. It is a stable species, with a bond length of 106 pm and a bond energy of 0.423 aJ.

The Schrödinger equation for a  $\text{H}_2^+$  ion, like that for a hydrogen atom, is relatively easy to solve, and we obtain a set of wave functions, or orbitals, and their corresponding energies. As noted earlier, these orbitals extend over both nuclei in  $\text{H}_2^+$  and therefore are called **molecular orbitals**. As it was done with the various hydrogen atomic orbitals to build up the electronic structures of more complicated atoms, in the same way, we will now use the various  $\text{H}_2^+$  molecular orbitals to build up the electronic structures of more complicated diatomic molecules.

The Hamiltonian for the single electron in  $\text{H}_2^+$  is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 + V \quad V = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R} \right)$$



where  $r_{A1}$  and  $r_{B1}$  are the distances of the electron from the two nuclei A and B and R is the distance between the two nuclei. In the expression for  $V$ , the first two terms in parentheses are the attractive contribution from the interaction between the electron and the nuclei; the remaining term is the repulsive interaction between the nuclei. The collection of fundamental constant  $e^2/4\pi\epsilon_0$  occurs widely throughout this section and is denoted  $j_0$ .

- Once we know the Hamiltonians, let us examine the results of  $H_{11}$  (or  $H_{AA} = H_{22}$  or  $H_{BB}$ ) and  $H_{12}$  (or  $H_{AB} = H_{21}$ ) integrals after inserting the Hamiltonian operator for  $H_2^+$  (single electron). The electronic Hamiltonian for  $H_2^+$  is:
- $\hat{H}_{elec}(r, R) = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} + \frac{e^2}{4\pi\epsilon_0 R}$  (where  $r$  gives the coordinates of the electron, and  $R$  is the distance between the two protons.)
- $$H_{11} = \int 1s_A \left( -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} + \frac{e^2}{4\pi\epsilon_0 R} \right) 1s_A \delta\tau$$
- $$= \int 1s_A \left( -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} \right) 1s_A \delta\tau - \int 1s_A \left( \frac{e^2}{4\pi\epsilon_0 r_{B1}} \right) 1s_A \delta\tau + \int 1s_A \left( \frac{e^2}{4\pi\epsilon_0 R} \right) 1s_A \delta\tau$$
- The **first term** is just the integral for the **energy of the hydrogen atom** of the 1s orbital,  $E_H$ .
- The **last integral** is equal to **1** by normalization; the prefactor is just the Coulomb repulsion of the two protons.
- The **second integral**, including the **minus sign**, is called the **Coulomb integral**,  $J_{AB}$ . Physically it is the **potential energy of interaction** of the electron **located around proton A with proton B**.

➤ The *second integral*, including the *minus sign*, is called the **Coulomb integral**,  $J_{AB}$ . Physically it is the ***potential energy of interaction*** of the electron ***located around proton A with proton B***. It is negative because it is an attractive interaction. It is the ***average interaction energy of an electron*** described by the  $1s_A$  function with proton B.

➤  $H_{11} = E_H + J_{AB} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R}$

➤  $H_{22} = \dots ?$

➤ Now consider  $H_{12}$  ( $H_{AB}$ ): .....?

- Now consider  $H_{12}$  ( $H_{AB}$ ):
- $$H_{12} = \int 1s_A \left( -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{A1}} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{B1}} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} \right) 1s_B \delta\tau$$
- $$= \int 1s_A \left( -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{B1}} \right) 1s_B \delta\tau - \int 1s_A \left( \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{A1}} \right) 1s_B \delta\tau$$

$$+ \int 1s_A \left( \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} \right) 1s_B \delta\tau$$
- In the ***first integral*** we have the hydrogen atom Hamiltonian and the H atom function  $1s_B$ . The function  $1s_B$  is an eigenfunction of the operator with eigenvalue  $E_H$ . Since  $E_H$  is a constant, it factors out of the integral, which then becomes the overlap integral,  $S$ . The first integral therefore reduces to  $E_H S$ .
- The second term, *including the minus sign*, is given the symbol  $K_{AB}$  and is called the ***exchange integral*** because the electron is described by the  $1s_A$  orbital on one side and by the  $1s_B$  orbital on the other side of the operator. The electron changes or exchanges position in the molecule.
- The ***third term*** is just the *Coulombic (repulsion) energy* of the two protons *times the overlap integral*.

➤ In a **coulomb integral**, the electron always is in the *same orbital*; whereas, in an *Exchange Integral*, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

➤  $H_{12} = E_H S + K_{AB} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} S$

➤ Then:  $H_{11} + H_{12} = E_H + J_{AB} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} + E_H S + K_{AB} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} S$

➤  $= E_H(1 + S) + (J_{AB} + K_{AB}) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} (1 + S)$

➤  $= (1 + S) \left( E_H + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} \right) + (J_{AB} + K_{AB})$

- We know:  $E_b = \frac{H_{11} + H_{12}}{1+S}$  and  $E_a = \frac{H_{11} - H_{12}}{1-S}$
- $E_b = \frac{(1+S)\left(E_H + \frac{e^2}{4\pi\varepsilon_0 R} \frac{1}{R}\right) + (J_{AB} + K_{AB})}{1+S}$  and  $E_a = \frac{(1-S)\left(E_H + \frac{e^2}{4\pi\varepsilon_0 R} \frac{1}{R}\right) + (J_{AB} - K_{AB})}{1-S}$
- $E_b = E_H + \frac{e^2}{4\pi\varepsilon_0 R} \frac{1}{R} + \frac{(J_{AB} + K_{AB})}{1+S}$  and  $E_a = E_H + \frac{e^2}{4\pi\varepsilon_0 R} \frac{1}{R} + \frac{(J_{AB} - K_{AB})}{1-S}$
- Above Equations tell us that the energy of the  $H_2^+$  molecule is the ***energy of a hydrogen atom*** plus the ***repulsive energy of two protons*** plus ***some additional electrostatic interactions of the electron with the protons***. These additional interactions are given by the last terms
- $\frac{(J_{AB} \pm K_{AB})}{1 \pm S}$ .

- If the protons are infinitely far apart then only  $E_H$  is nonzero, which we can set to zero by subtracting off:

- $\Delta E_{\pm} = E_{\pm} - E_H = \frac{e^2}{4\pi\epsilon_0 R} + \frac{(J_{AB} \pm K_{AB})}{1 \pm S}$ . .....(9.4.13)
- To get a chemical bond and a stable  $H_2^+$  molecule  $\Delta E_{\pm}$  must be less than zero and have a minimum, i.e.,  $\frac{(J_{AB} \pm K_{AB})}{1 \pm S}$  must be *sufficiently negative* to overcome the positive repulsive energy of the two protons  $\frac{e^2}{4\pi\epsilon_0 R}$  for some value of  $R$ . For large  $R$ , **these terms** are **zero**, and for **small  $R$ , the Coulomb repulsion of the protons rises to infinity**.
- Now let us see the behavior of various parameters.

- Figure 9.4.2 shows graphs of the four terms contributing to the energy of  $\text{H}_2^+$  (Equation 9.4.13). In Figure 9.4.2 , you can see that ***as the internuclear distance  $R$  approaches zero,***
- ✓ the **Coulomb repulsion** of the two protons goes from near zero to a large positive number,
- ✓ the **overlap integral** goes from zero to one, and
- ✓ ***J and K become increasingly negative.***

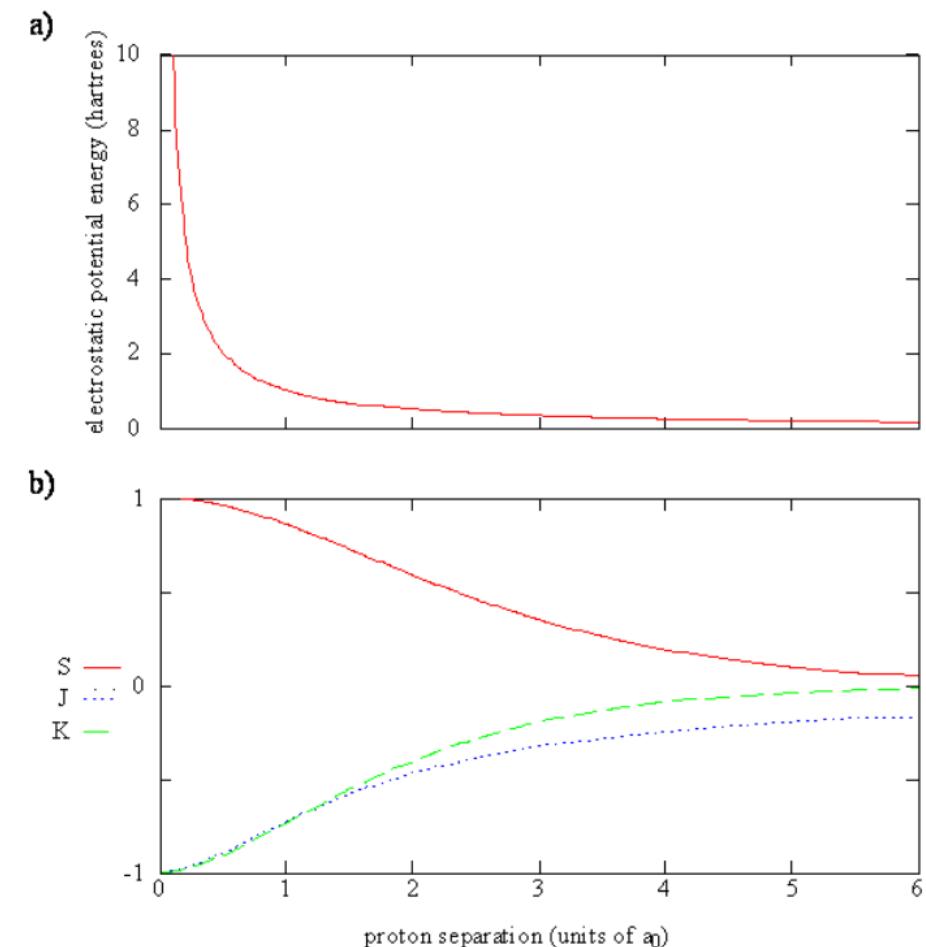
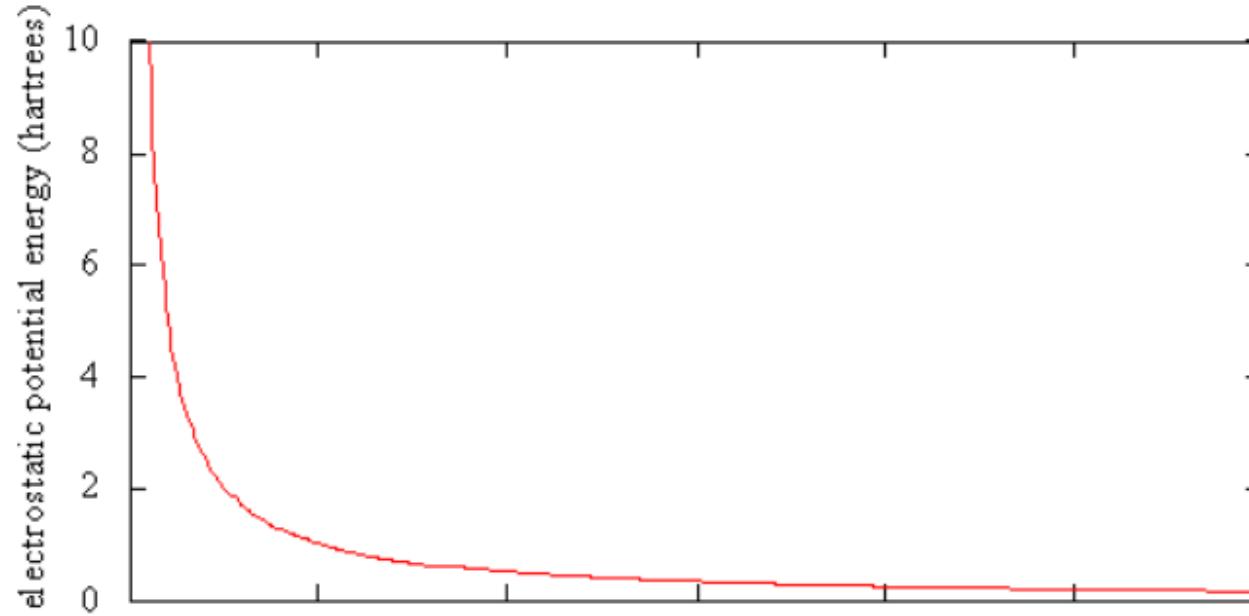


Figure 9.4.2

a)



b)

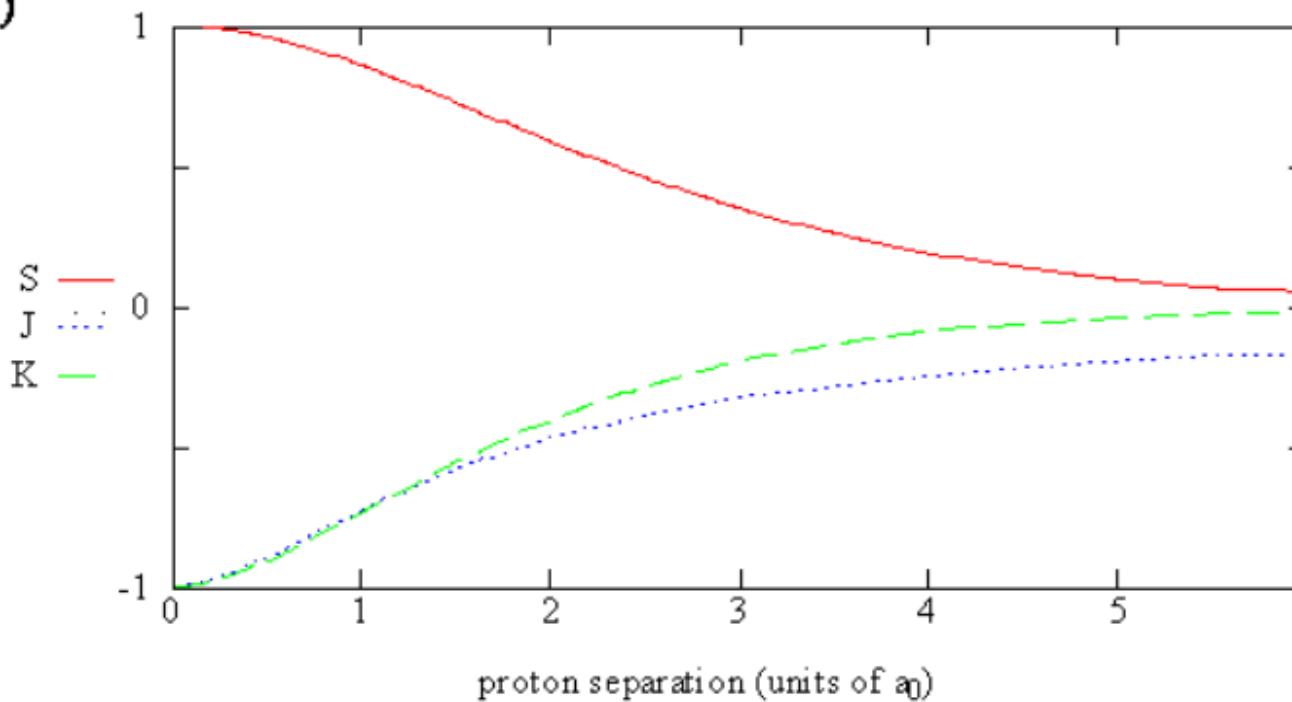


Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance  $R$  in units of the Bohr radius (52.92 pm).

(b) The overlap ( $S$ ), Coulomb ( $J$ ), and exchange ( $K$ ) integrals at different proton separations. The units for  $J$  and  $K$  are hartrees;  $S$  has no units.

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- Note that ***both J and K integrals are negative*** since all quantities in the integrands are positive.
- In the ***Coulomb integral***,  $e\varphi_{1sA}^*(r)\varphi_{1sA}(r)$  is the charge density of the electron around proton A, since  $r$  represents the coordinates of the electron relative to proton A. Since  $r_B$  is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B. **J** can be interpreted as an average potential energy of this interaction because  $e\varphi_{1sA}^*(r)\varphi_{1sA}(r)$  is the probability density for the electron at point  $r$ , and  $e^2/4\pi\epsilon_0 r_B$  is the potential energy of the electron at that point due to the interaction with proton B. **Essentially, J accounts for the attraction of proton B to the electron density of hydrogen atom A.** As the two protons get further apart, this integral goes to zero because all values for  $r_B$  become very large and all values for  $1/r_B$  become very small.

- In the **exchange integral**,  $K$ , the product of the two functions is nonzero only in the regions of space where the two functions overlap. If one function is zero or very small at some point, then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the  $1/r$  values become zero. The product  $e\varphi_{1sA}^*(r)\varphi_{1sB}(r)$  is called the ***overlap charge density***. ***Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond.*** The exchange integral,  $K$ , is the potential energy due to the interaction of the overlap charge density with one of the protons.
- While ***J*** accounts for the attraction of proton *B* to the electron density of hydrogen atom *A*, ***K*** accounts for the added attraction of the proton due the ***build-up of electron charge density*** between the two protons.

- For the electron in the  $\psi_+$  orbital, you can see that the big effect for the energy of the bonding orbital,  $E_+(R)$ , is the balance between the repulsion of the two protons  $e^2/4\pi\epsilon_0 R$  and  $J$  and  $K$ , which are both negative.
- *J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm* (i.e., the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. ***This minimum represents the formation of a chemical bond.*** The effect of  $S$  is small. It only causes the denominator in Equation 9.4.13 to increase from 1 to 2 as  $R$  approaches 0.
- For the antibonding orbital,  $-K$  is a positive quantity and essentially cancels  $J$  so there is ***not sufficient compensation for the Coulomb repulsion of the protons.*** The effect of the  $-K$  in the expression, Equation 9.4.13, for  $E_-$  ( $E_a$ ) is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for  $\psi_-$  is even lower than that given by the atomic orbitals.

- Figure 9.4.3 shows the energy of  $\text{H}_2^+$  relative to the energy of a separated hydrogen atom and a proton as given by Equation 9.4.11. For the electron in the  $\psi_-$  orbital, the energy of the molecule,  $E_{el}(R)$ , always is greater than the energy of the separated atom and proton.

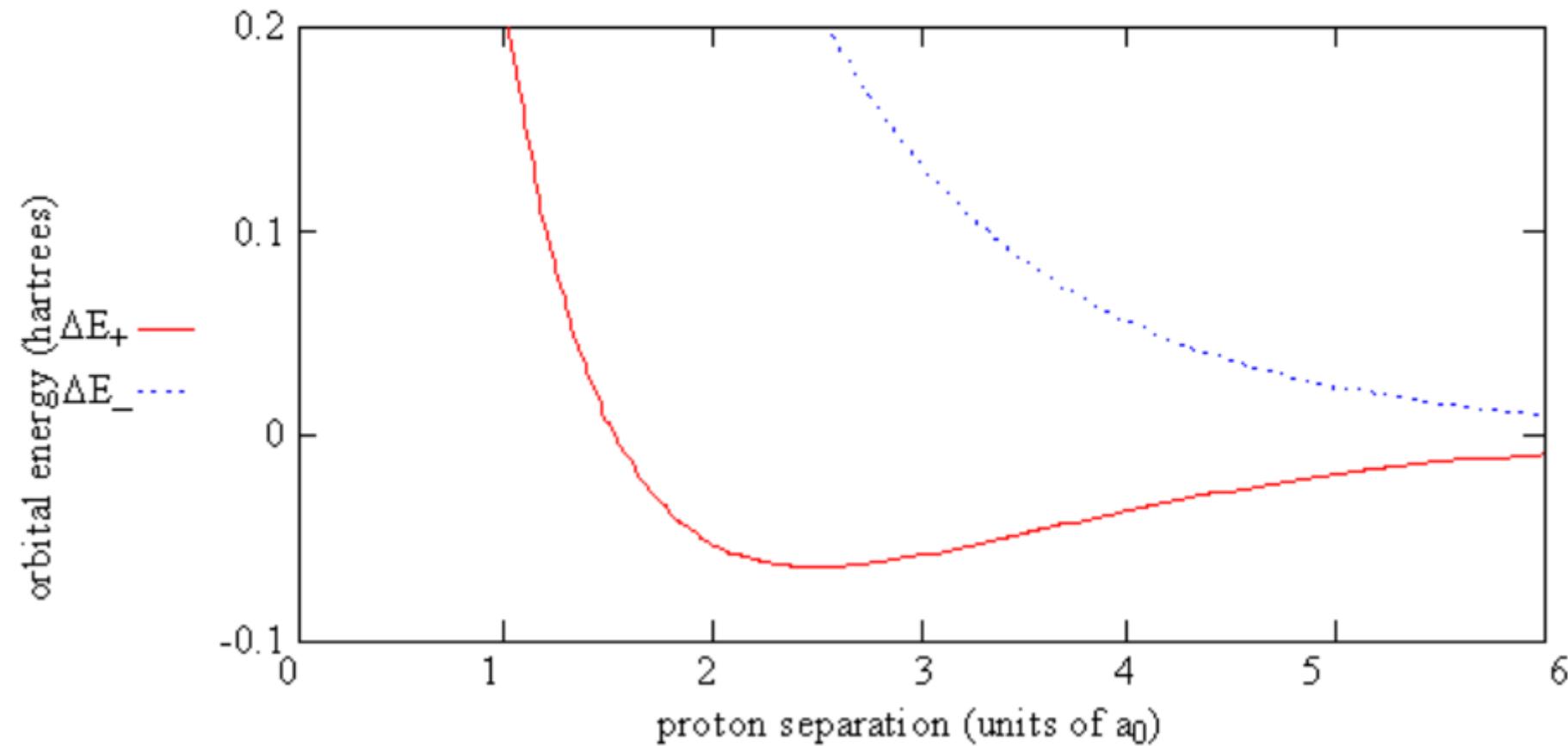
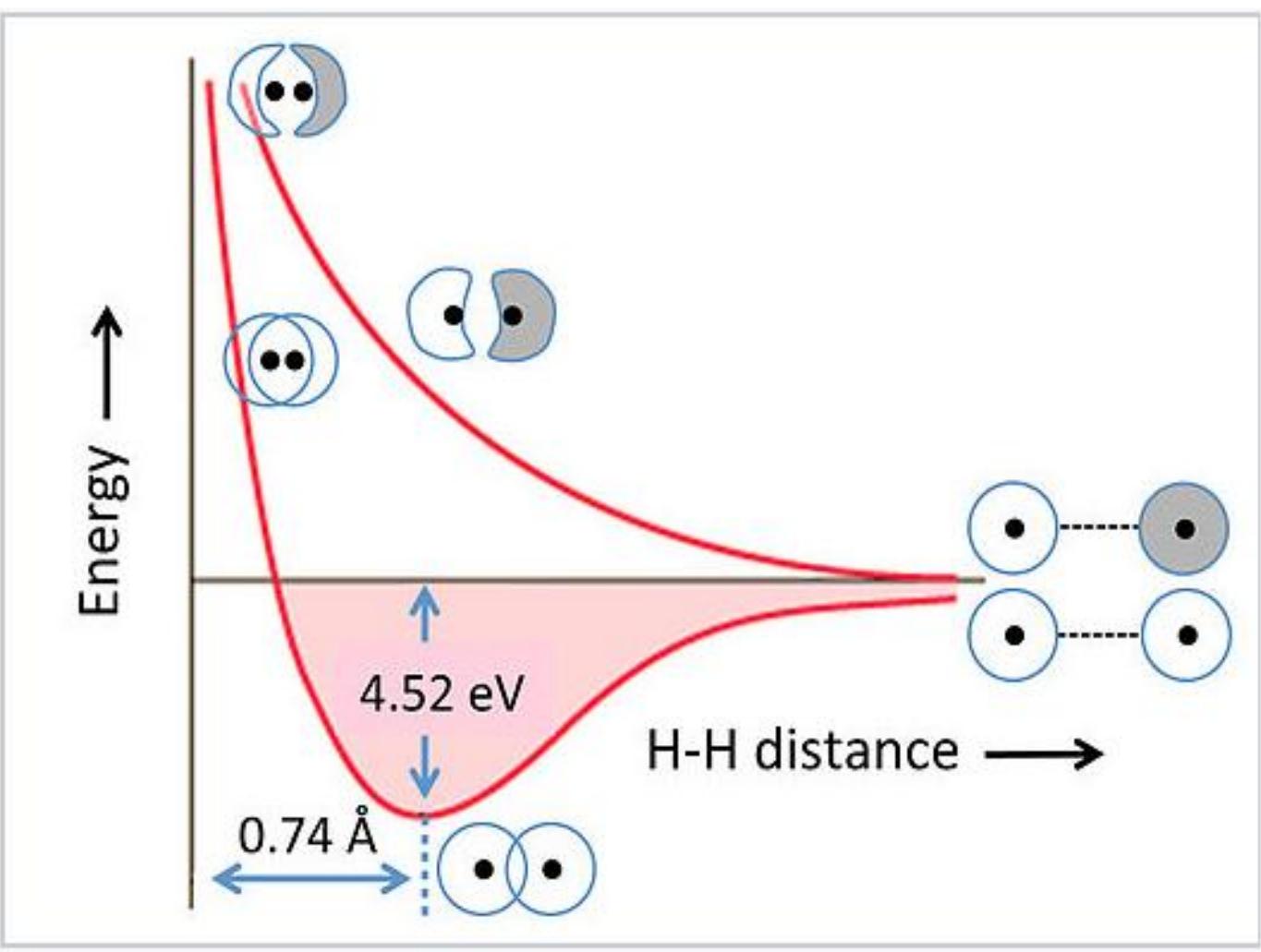


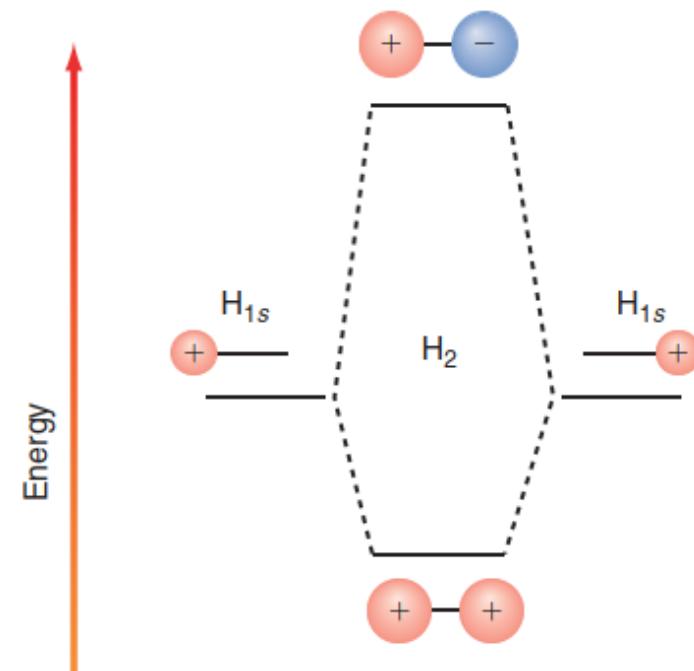
Figure 9.4.3 : Energy of the  $\text{H}_2^+$  bonding molecular orbital  $\Delta E_+$  and the antibonding molecular orbital  $\Delta E_-$ , relative to the energy of a separated hydrogen atom and proton.



**Figure 2.2.5 :** Energy *as a function of internuclear distance* for the bonding and antibonding orbitals of the  $\text{H}_2$  molecule

Figure 12.2 **summarizes** the following results of this discussion **pictorially** in a molecular orbital energy diagram using  $\text{H}_2$  as an example:

- Two **localized** AOs combine to form two **delocalized** MOs provided that  $S_{AB}$  is nonzero. This is the case if there are regions in space in which the amplitudes of both AOs are nonzero.
  - The energy of one MO is lowered and the energy of the other MO is raised relative to the AO energy. The amount by which the MO energy differs from the AO energy depends on  $H_{AB}$  and  $S_{AB}$ .
  - Because  $S_{AB} > 0$ ,  $(1 + S_{AB}) > (1 - S_{AB})$  and  $\varepsilon_2$  is raised relative to the AO energy more than  $\varepsilon_1$  is lowered.
  - The AO coefficients have the same sign (in-phase) in the lower energy MO and the opposite sign (out-of-phase) in the higher energy MO.
- In a molecular orbital energy diagram, *the energy of the orbital* rather than the total energy of the molecule is displayed. For this reason, the appropriate energy operator in calculating the MO energy is  $\hat{H}_{el}$  rather than total  $\hat{H}$ .



**FIGURE 12.2**

Molecular orbital energy diagram for a qualitative description of bonding in  $\text{H}_2$ . The atomic orbitals are shown to the left and right, and the molecular orbitals are shown in the middle. Dashed lines connect the MO with the AOs from which it was constructed. Shaded circles have a diameter proportional to the coefficients  $c_A$  and  $c_B$ . Red and blue shading signifies positive and negative signs of the AO coefficients, respectively. Interchanging red and blue does not generate a different MO.

- Fig. 3.4 shows a *more correctly scaled* energy level diagram that results for the hydrogen molecule. Note that the energy for the 1s atomic orbital of a hydrogen atom is at  $-1312 \text{ kJ mol}^{-1}$  because the ionization potential is  $1312 \text{ kJ mol}^{-1}$  ( $13.6 \text{ eV}$ ). Note also that the bonding molecular orbital has an energy of  $-1528 \text{ kJ mol}^{-1}$ , which is lower than that of the 1s atomic state.

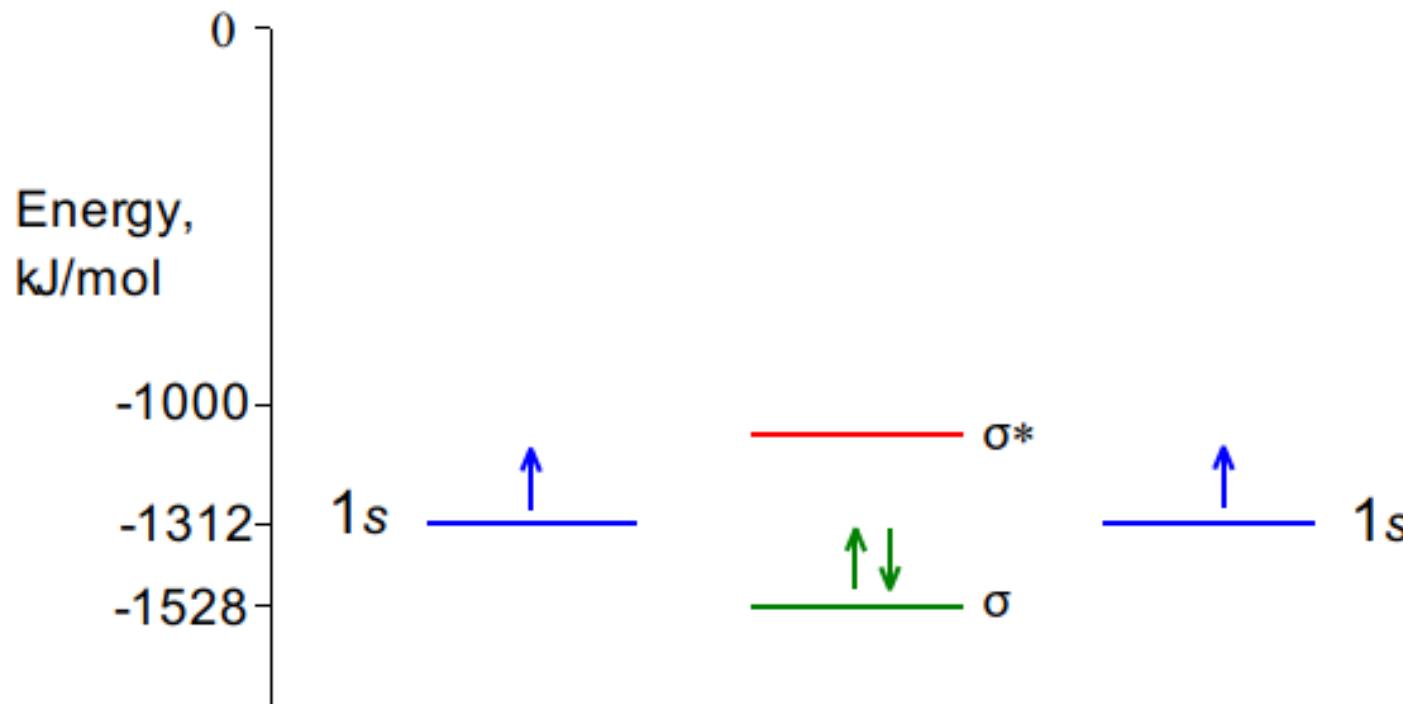


FIGURE 3.4 The energy level diagram for the  $\text{H}_2$  molecule.

- If a hydrogen molecule is separated into the two constituent atoms, the result ***is equivalent to taking the two electrons in the bonding molecular orbital and placing them back in the atomic orbitals.***
- Because there are two electrons, that energy would be  $2(1528 - 1312) = 432 \text{ kJ.mol}^{-1}$ , the **bond energy** of the  $\text{H}_2$  molecule.
- From the molecular orbital diagram, it can be seen that although the energy of the antibonding state is higher than that of the hydrogen atom, it is still very ***negative***.
- ***An energy of 0 does not result*** because even when the atoms are completely separated the energy of the system is the sum of the binding energies in the atoms which is  $2 (-1312) \text{ kJ.mol}^{-1}$ .

➤ The normalized trial function corresponding to the energy  $E_b$  is therefore

$$\Psi_+ = \Psi_b = \frac{1s_A + 1s_B}{\sqrt{2(1 + S)}}$$

➤ The normalized trial function corresponding to the energy  $E_a$  is

$$\Psi_- = \Psi_a = \frac{1s_A - 1s_B}{\sqrt{2(1 - S)}}$$

$$\Delta E_{\pm} = E_{\pm} - E_H = \frac{e^2}{4\pi\varepsilon_0 R} + \frac{(J_{AB} \pm K_{AB})}{1 \pm S}.$$

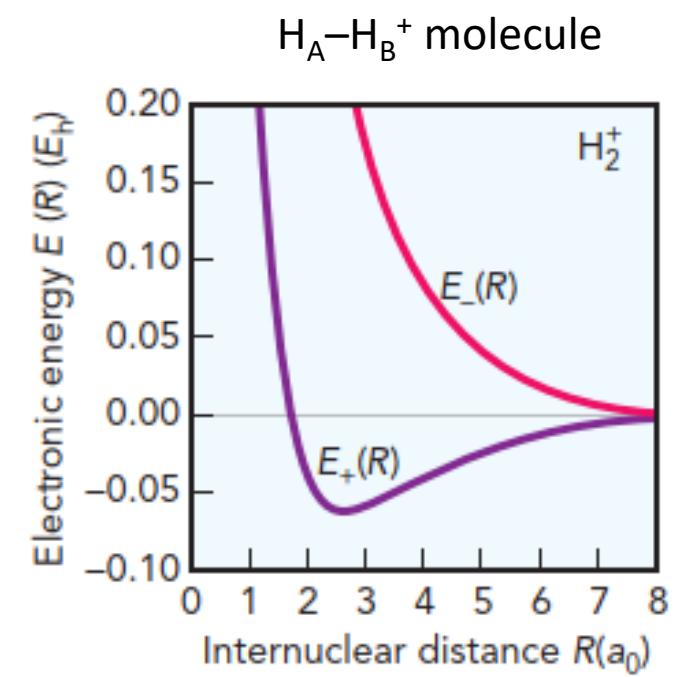
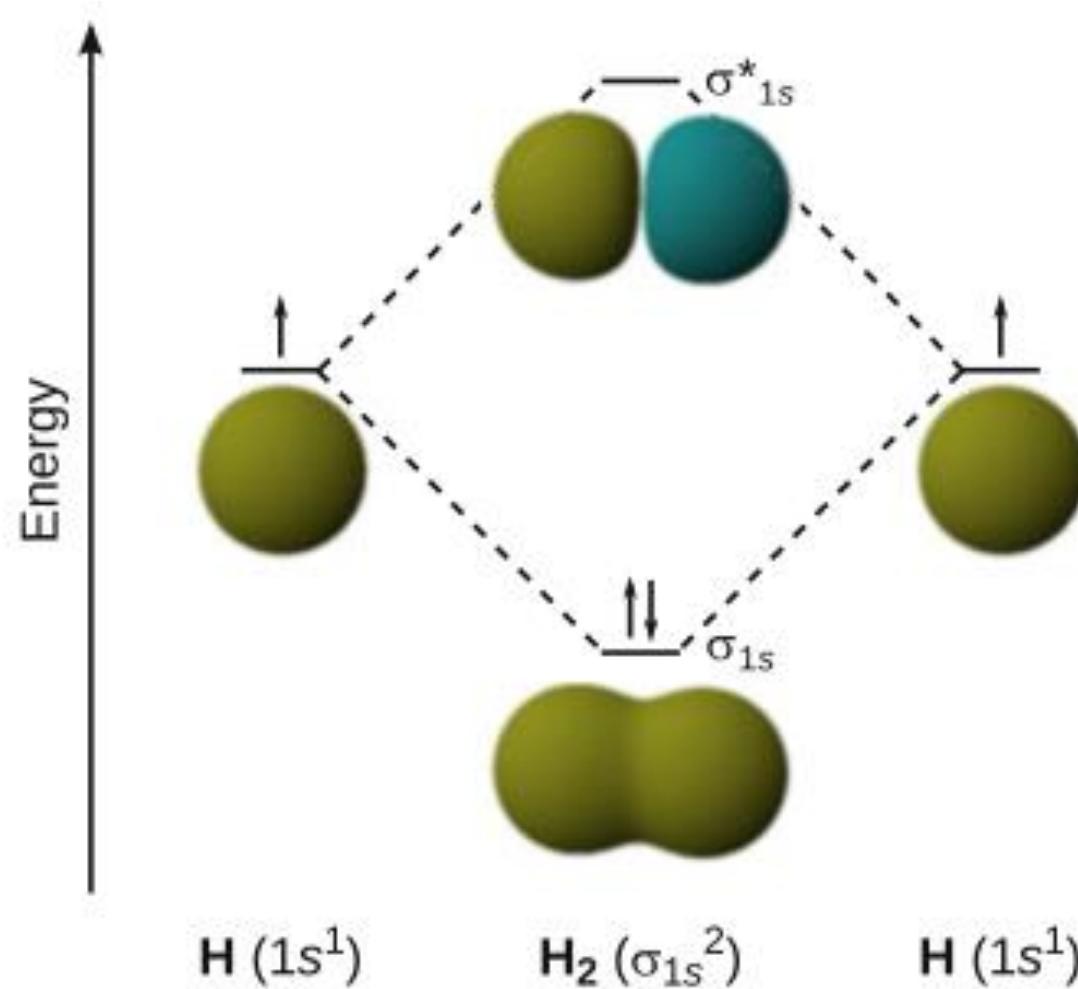


Figure 5.10 The electronic energy functions  $E_+(R)$  and  $E_-(R)$  for  $\text{H}_2^+$ .

Fig. 11.3 Linear combination of the two 1s orbitals in hydrogen leads to bonding and anti-bonding molecular orbitals of  $\text{H}_2$



When 1s orbitals are combined (added or subtracted), a **bonding orbital of lower energy** (an orbital which, if occupied, helps to bind two atoms together) and **an antibonding orbital of higher energy** (which, if occupied, weakens the bond) are formed.

A **molecular orbital that has cylindrical symmetry around the internuclear axis**, such as the one being discussed, is called a  **$\sigma$  orbital** because it resembles an s orbital when viewed along the axis and, more precisely, because it has zero orbital angular momentum around the internuclear axis. An electron that occupies a  $\sigma$  orbital is called a  $\sigma$  electron, and if that is the only electron present in the molecule (as in the ground state of  $\text{H}_2^+$ ), then the configuration of the molecule is  $\sigma^1$ .

The most important conclusions that can be drawn from this figure are that  $\sigma_{1s}$  describes a stable molecule because the energy has a well-defined minimum at  $R=R_e$  and that  $\sigma_{1s}^*$  does not describe a bound state of H and  $\text{H}^+$  because for all R, which makes the molecule unstable with respect to dissociation. Therefore, we conclude that only a molecule described by  $\sigma_{1s}$  molecular orbital is a stable molecule. The  $\psi_g$  and  $\psi_u$  wave functions are referred to as **bonding and antibonding molecular orbitals**, respectively, to emphasize their relationship to the chemical bond.

Calculations on  $\text{H}_2^+$  give  $R_e = 2.49a_0 = 132 \text{ pm}$  and  $hcD_e = 1.76 \text{ eV}$  ( $171 \text{ kJ mol}^{-1}$ ); the experimental values are 106 pm and 2.6 eV, so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong.

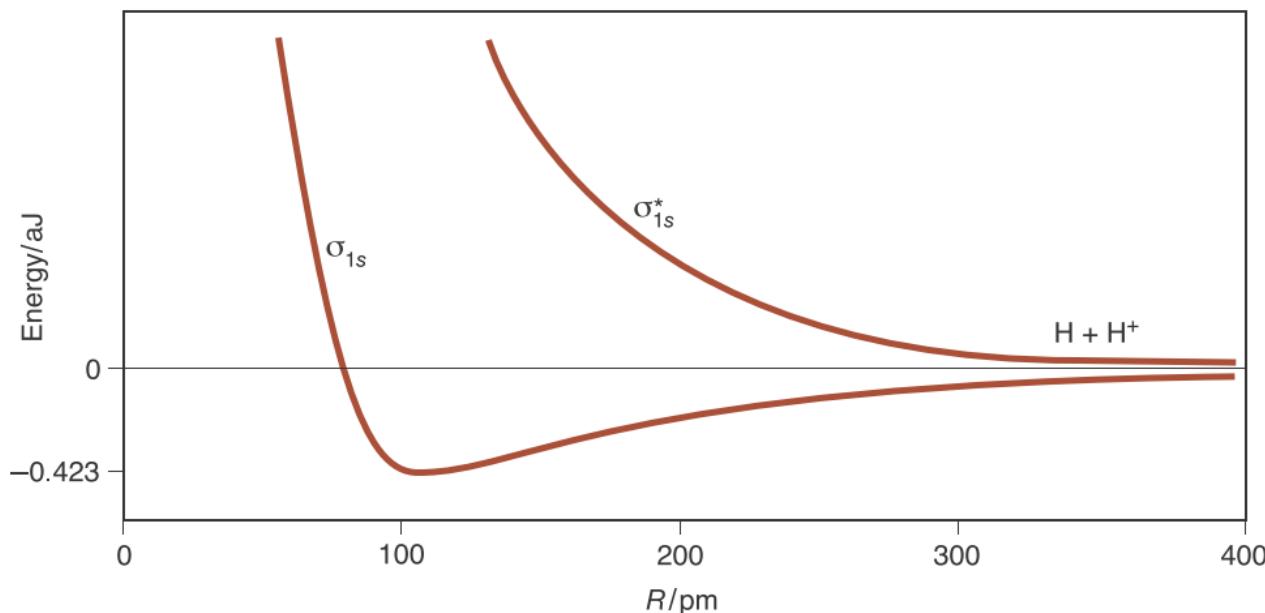


Figure 9.4 Potential energy of the  $\sigma_{1s}$  bonding molecular orbital and  $\sigma_{1s}^*$  antibonding molecular orbital for  $\text{H}_2^+$  as a function of the internuclear separation between the two hydrogen nuclei. The minimum in the lower curve represents the equilibrium nuclear separation or average bond length of the molecular ion (106 pm). This energy minimum depicts the formation of a stable bond. In contrast, the energy of the  $\sigma_{1s}^*$  orbital (upper curve) is always above that of the separated atoms, making this an antibonding orbital.

## Orbital notation

For homonuclear diatomic molecules (molecules consisting of two atoms of the same element, such as N<sub>2</sub>), it proves helpful to label a molecular *orbital according to its inversion symmetry, the behaviour of the wavefunction when it is inverted through the centre* (more formally, the centre of inversion) of the molecule. Thus, *any point on the bonding σ orbital that is projected through the centre of the molecule and out an equal distance on the other side leads to an identical value (and sign) of the wavefunction* (Fig. 9B.12).

- ✓ This so-called **gerade** symmetry (from the German word for ‘even’) is denoted by a subscript **g**, as in  $\sigma_g$ . The same procedure applied to the antibonding  $\sigma^*$  orbital results in the same amplitude but *opposite sign of the wavefunction*. This **ungerade** symmetry (‘odd symmetry’) is denoted by a subscript **u**, as in  $\sigma_u$ .
- ✓ The inversion symmetry classification is **not applicable to heteronuclear diatomic molecules** (diatomic molecules formed by atoms from two different elements, such as CO) because these molecules do not have a centre of inversion.

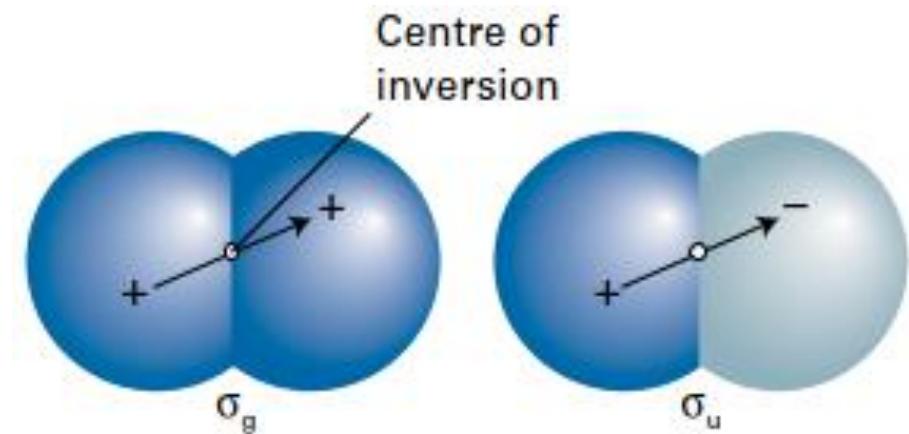


Figure 9B.12 The parity of an orbital is even (**g**) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (**u**) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the **g, u** classification is irrelevant.

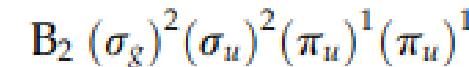
Although the subject of symmetry has not yet been discussed, it is true that  $\sigma$  orbitals that are bonding in character have “g” symmetry because the wave functions are symmetric with respect to the center of the bond. Essentially, this means that if  $\psi(x,y,z)$  is equal to  $\psi(-x,-y,-z)$ , the function is said to be an even function or to have *even parity*. This is signified by “g,” which comes from the German word *gerade* meaning even.

If  $\psi(x,y,z)$  is equal to  $-\psi(-x,-y,-z)$  the function has odd parity and is indicated by “u,” which comes from the word *ungerade* meaning *uneven*. An atomic  $s$  orbital is g, whereas a  $p$  orbital is u in symmetry.

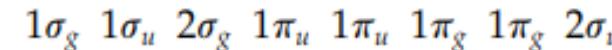
Although a bonding  $\sigma$  orbital is g,  $\pi$  bonding orbitals have “u” symmetry because they are antisymmetric with respect to the internuclear axis.

Antibonding molecular orbitals of each type have the symmetry labels reversed.

Sometimes the symmetry character of the molecular orbital is indicated by means of a subscript. When this is done, the representation for  $B_2$  is



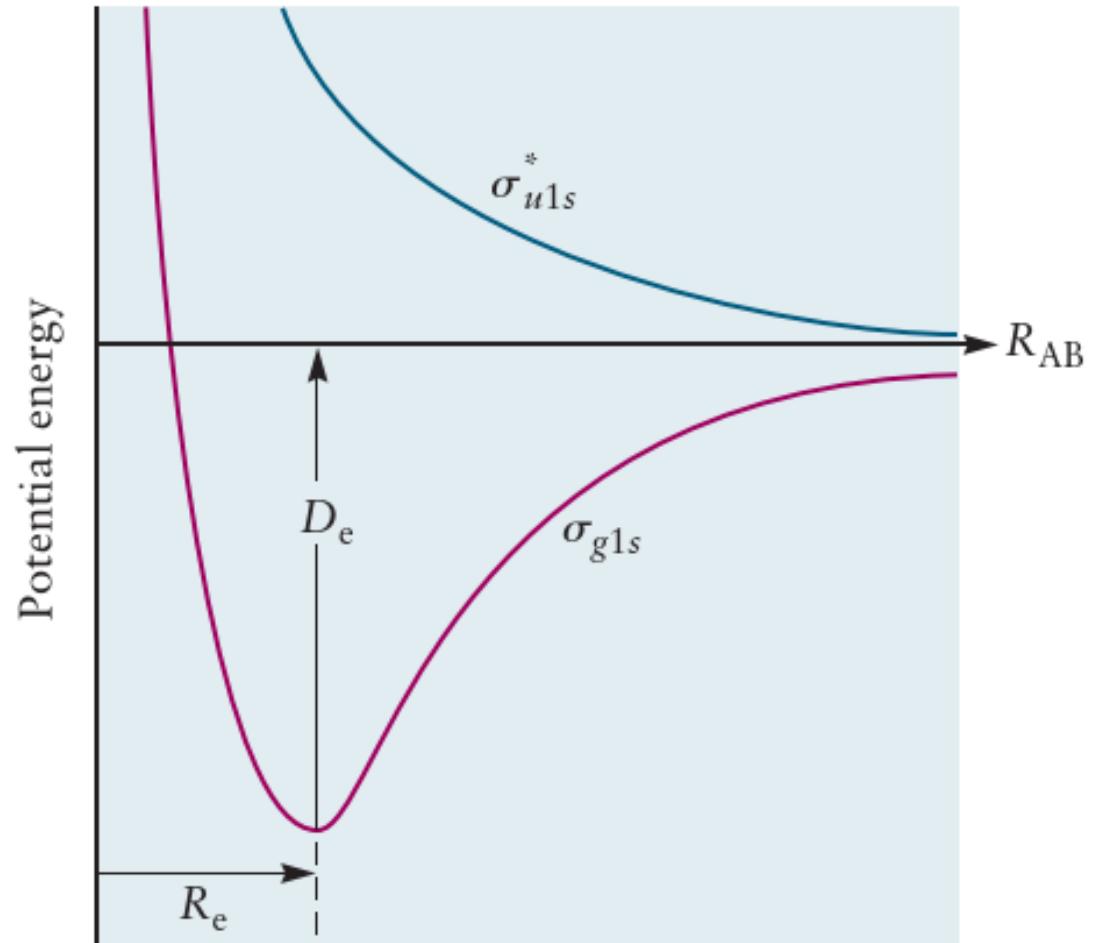
Molecular orbitals are sometimes given numerical prefixes to show the order in which the orbitals having those type and symmetry designations are encountered. When this is done, the order of filling the molecular orbitals for the second-row elements is shown as



In this case, “1” indicates the first instance where an orbital of that type is encountered. A “2” indicates the second time an orbital having the designation following the number is encountered.

The various ways to identify molecular orbitals are shown here because different schemes are sometimes followed by different authors.

FIGURE 6.9 Effective potential energy of the protons in  $\text{H}_2^+$  when the electron is in a  $\sigma_{g1s}$  (bonding) and  $\sigma_{g1s}^*$  (antibonding) molecular orbital, shown as a function of internuclear separation  $R_{AB}$  in the LCAO approximation.



The energy-level diagram within the LCAO approximation is given by a correlation diagram (Fig. 6.11), which shows that two 1s atomic orbitals have been combined to give a  $\sigma_{g1s}$  MO with energy lower than the atomic orbitals and a  $\sigma^*_{u1s}$  MO with higher energy than the atomic orbitals. This diagram is a purely qualitative representation of the same information contained in Figure 6.9. The actual energy level values will depend on the distance between the fixed nuclei (as shown in Figure 6.9) and must be determined from calculations.

Even without the results shown in Figure 6.9, we would know that an electron in an antibonding orbital has higher energy than one in a bonding orbital because the antibonding orbital has a node.

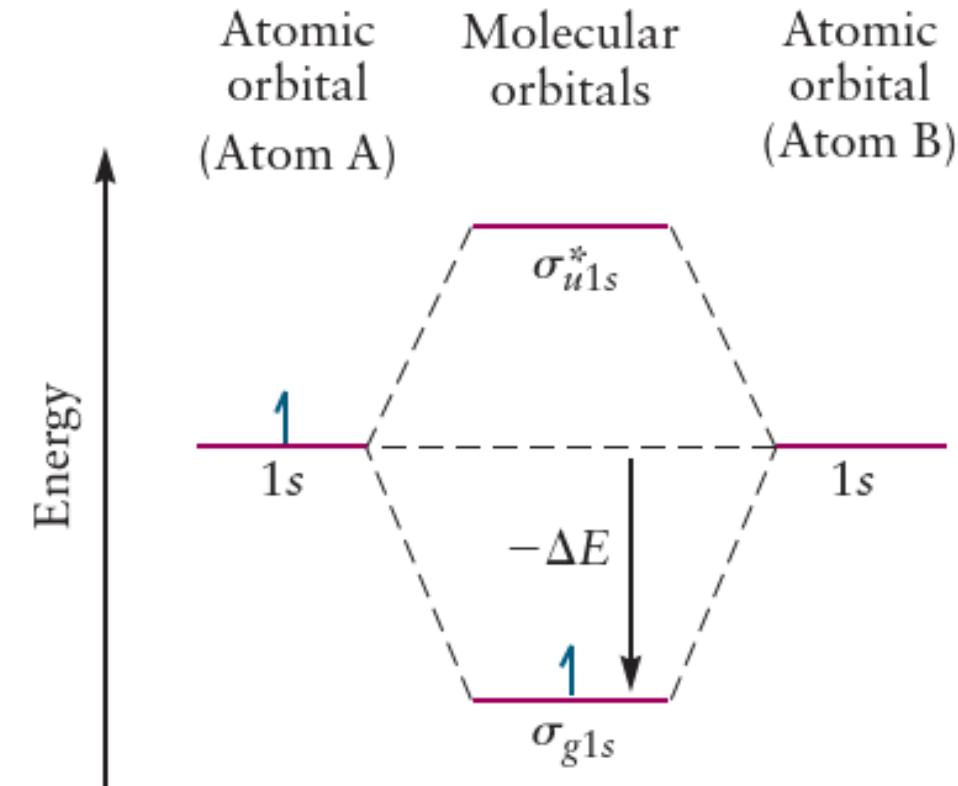
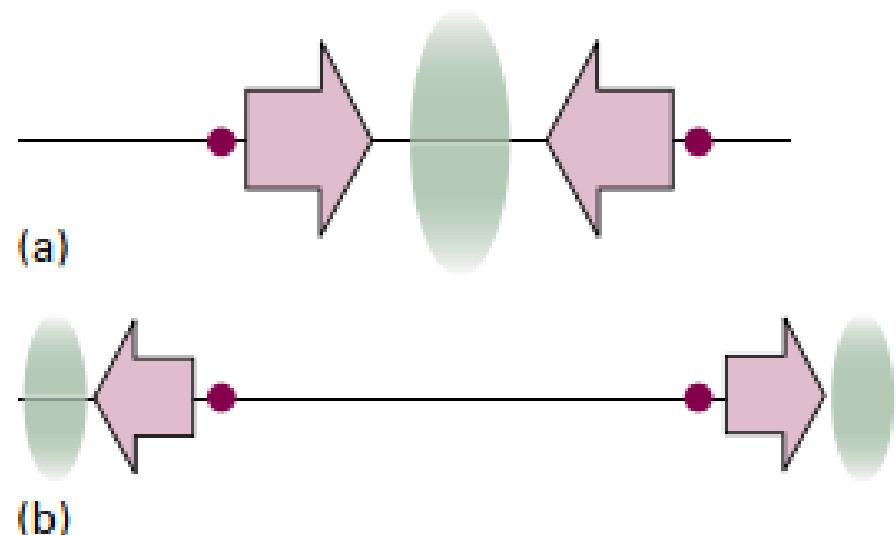


FIGURE 6.11 Correlation diagram for  $\text{H}_2^+$  in the linear combination of atomic orbitals (LCAO) approximation. The bonding orbital is stabilized relative to the noninteracting system.  
 $E_{1s} + (-\Delta E) = E_{\sigma g1s}$  so  $\Delta E$  is a positive number.

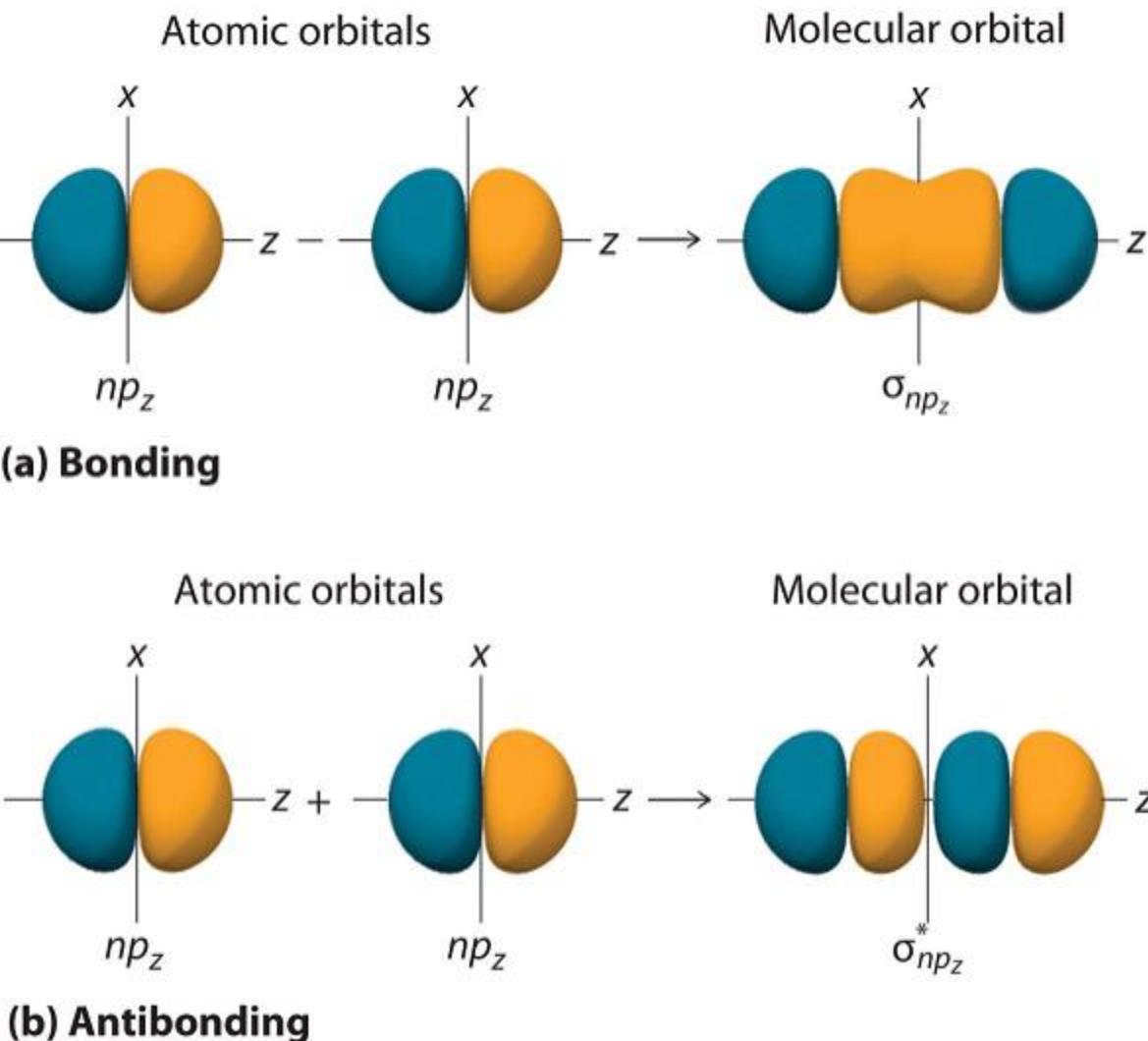
- The variation of  $E\sigma^*$  with  $R$  shows the destabilizing effect of an antibonding electron. The effect is partly due to the fact that an *antibonding electron is excluded from the internuclear region* and hence is distributed largely outside the bonding region. In effect, whereas **a bonding electron pulls two nuclei together, an antibonding electron pulls the nuclei apart** (Fig. 9B.11).
- The illustration also shows another feature drawn on later:  $|E\sigma^* - EH_{1s}| > |E\sigma - EH_{1s}|$ , which indicates that the antibonding orbital is more antibonding than the bonding orbital is bonding. *This important conclusion stems in part from the presence of the nucleus–nucleus repulsion: this contribution raises the energy of both molecular orbitals.*

Figure 9B.11 A partial explanation of the origin of bonding and antibonding effects. (a) In a bonding orbital, the nuclei are attracted to the accumulation of electron density in the internuclear region. (b) In an antibonding orbital, the nuclei are attracted to an accumulation of electron density outside the internuclear region.



- The basic principles dealing with the molecular orbital description of the bonding in diatomic molecules have been presented in the previous section. Atomic orbitals other than  $ns$  orbitals can also interact to form molecular orbitals. Because individual  $p$ ,  $d$ , and  $f$  orbitals are not spherically symmetrical, however, we need to define a coordinate system, so we know which lobes are interacting in three-dimensional space.
- Recall that for each  $np$  subshell, for example, there are  $np_x$ ,  $np_y$ , and  $np_z$  orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.
- Just as with  $ns$  orbitals, we can form ***molecular orbitals from np orbitals*** by taking their mathematical sum and difference.
- When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two  $np$  atomic orbitals in part (a) in Figure 10.7.5, it is the ***mathematical difference of their wave functions that results in constructive interference***, which in turn increases the electron probability density between the two atoms.

- The difference therefore corresponds to a molecular orbital called a ***bonding molecular orbital*** because, just as with the  $\sigma$  orbitals discussed previously, it is *symmetrical about the internuclear axis* (in this case, the z-axis):
- $\sigma_{npz} = n_{pz}(A) - n_{pz}(B)$
- The other possible combination of the two np orbitals is the mathematical sum:  $\sigma_{npz} = n_{pz}(A) + n_{pz}(B)$ . In this combination, shown in part (b) in Figure 10.7.5, the positive lobe of one  $np_z$  atomic orbital overlaps the negative lobe of the other, leading to *destructive interference* of the two waves and creating a node between the two atoms. Hence this is an ***antibonding molecular orbital***. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a  $\sigma_{npz}$  antibonding molecular orbital.
- Whenever orbitals combine, the bonding combination is always lower in energy (more stable) than the atomic orbitals from which it was derived, and the antibonding combination is higher in energy (less stable).

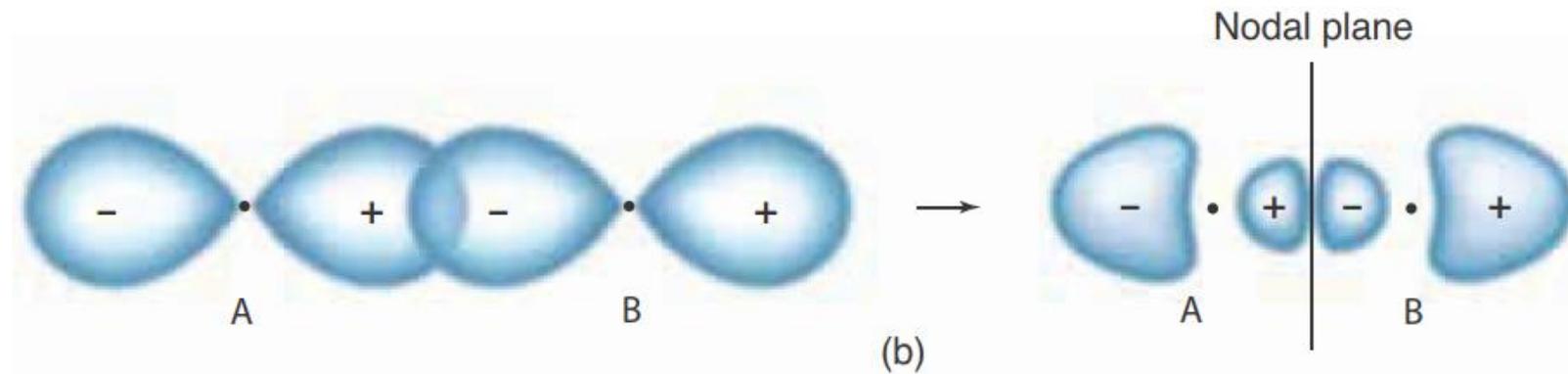


**Figure 10.7.5 Formation of Molecular Orbitals from  $np$  Atomic Orbitals on Adjacent Atoms.**

(a) By convention, in a linear molecule or ion, the  $z$ -axis always corresponds to the internuclear axis, with  $+z$  to the right. As a result, the signs of the lobes of the  $np$  atomic orbitals on the two atoms alternate  $- + - +$ , from left to right. *In this case, the  $\sigma$  (bonding) molecular orbital corresponds to the mathematical difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei.

(b) In contrast, the  $\sigma^*$  (antibonding) molecular orbital corresponds to the *mathematical sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

➤  $n_{pz}(A) + n_{pz}(B)$



➤  $n_{pz}(A) - n_{pz}(B)$

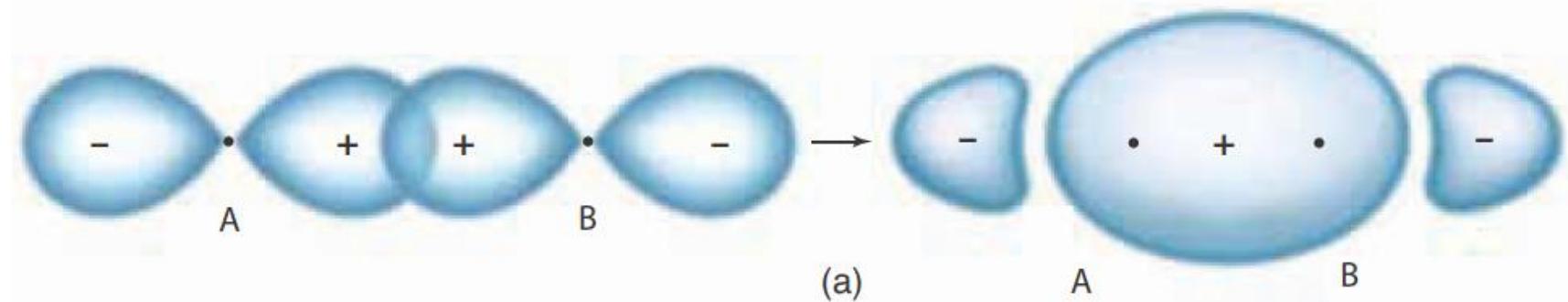


Figure 9.7 The combination of 2p orbitals that lie along the internuclear (z) axis. One lobe of a p orbital has a positive sign and the other a negative sign, as indicated in the figure. In (a), the  $2p_z$  orbitals are combined such that the lobes having the same sign overlap, resulting in a bonding  $\sigma_{2p_z}$  orbital. In (b), they are combined such that lobes of different signs overlap, resulting in an antibonding  $\sigma^*_{2p_z}$  orbital.

- The remaining  $p$  orbitals on each of the two atoms,  $np_x$  and  $np_y$ , do not point directly toward each other. Instead, they are perpendicular to the internuclear axis.
- The two  $p$  orbitals have their lobes extending either above/below or in front/behind of the internuclear axis.
- Overlap of those  $p$  orbitals therefore leads to electron density between the two atoms above/below or in front/behind of the inter-nuclear axis. Such orbitals are called  $\pi$  orbitals. As before, constructive and destructive interference is possible, giving rise to two molecular orbitals upon interaction,  $\pi$  and  $\pi^*$ .
- If we arbitrarily label the axes as shown in Figure 10.7.6, we see that we have two pairs of  $np$  orbitals: the two  $np_x$  orbitals lying in the plane of the page, and two  $np_y$  orbitals perpendicular to the plane.
- Although these two pairs are equivalent in energy, the  $np_x$  orbital on one atom can interact with only the  $np_x$  orbital on the other, and the  $np_y$  orbital on one atom can interact with only the  $np_y$  on the other.

- These interactions are *side-to-side* rather than the head-to-head interactions characteristic of  $\sigma$  orbitals.
- Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference.
- The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi ( $\pi$ ) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel  $np$  atomic orbitals).
- The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star ( $\pi^*$ ) orbital.

- An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel np atomic orbitals, creating a nodal plane perpendicular to the internuclear axis.
  - $\pi_{np_x} = np_x(A) + np_x(B)$
  - $\pi_{np_x}^* = np_x(A) - np_x(B)$
- The two  $np_y$  orbitals can also combine using side-to-side interactions to produce a bonding molecular orbital and an antibonding molecular orbital. Because the np and np atomic orbitals interact in the same way (side-to-side) and have the same energy, the and molecular orbitals are a degenerate pair, as are the and molecular orbitals.
- Notably, the  $\pi/\pi^*$  orbitals do not possess rotational symmetry, as the sign of those orbitals changes when rotating 180° around the inter-nuclear axis.

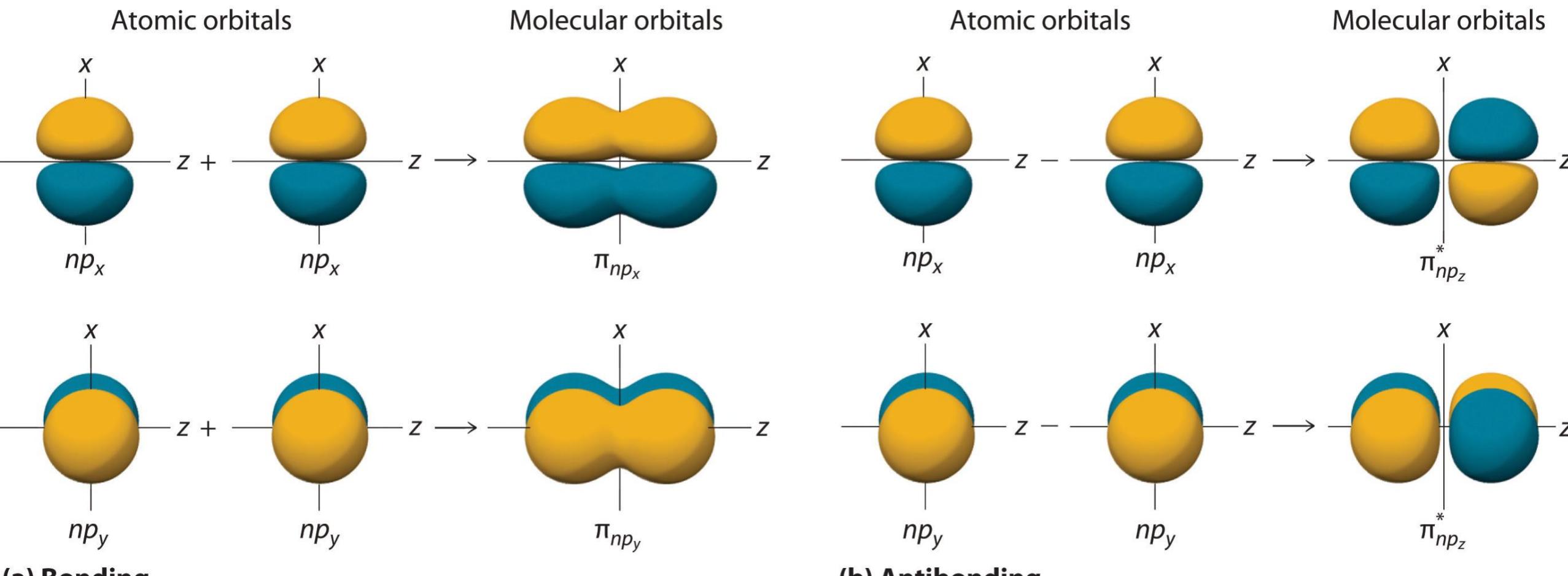


Figure 10.7.6: Formation of  $\pi$  Molecular Orbitals from  $np$  and  $np$  Atomic Orbitals on Adjacent Atoms. (a) Because the signs of the lobes of both the  $np$  and the  $np$  atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a  $\pi$  (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a  $\pi^*$  (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

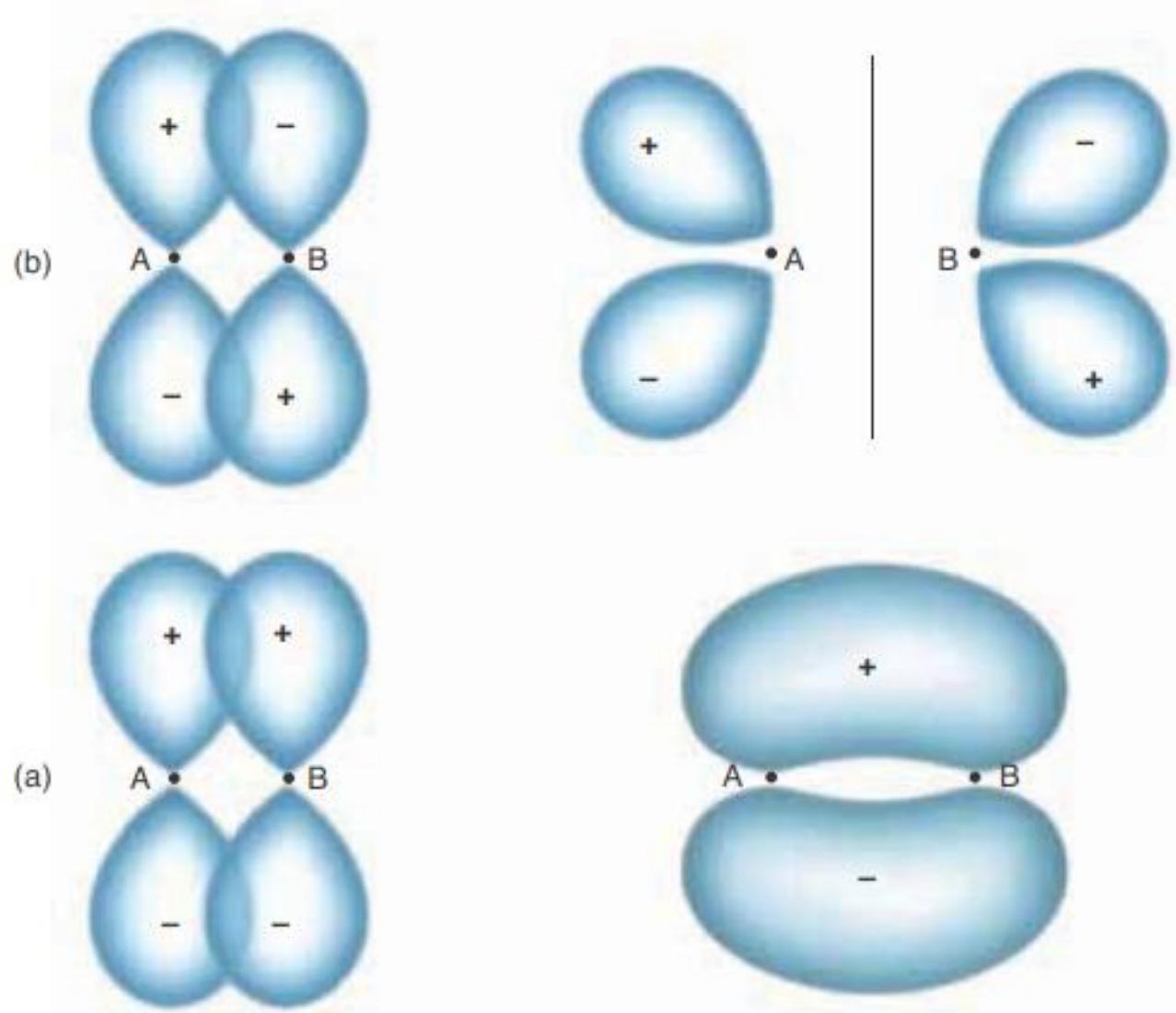


Figure 9.8 The combination of 2p orbitals that lie perpendicular to the internuclear axis. In (a), the  $p_y$  orbitals are combined such that lobes of the same sign overlap, resulting in a bonding  $\pi_{2py}$  orbital. In (b), the  $p_y$  orbitals are combined such that lobes of opposite sign overlap, resulting in an antibonding  $\pi^*_{2py}$  orbital. There is a similar picture for the  $p_z$  orbitals.

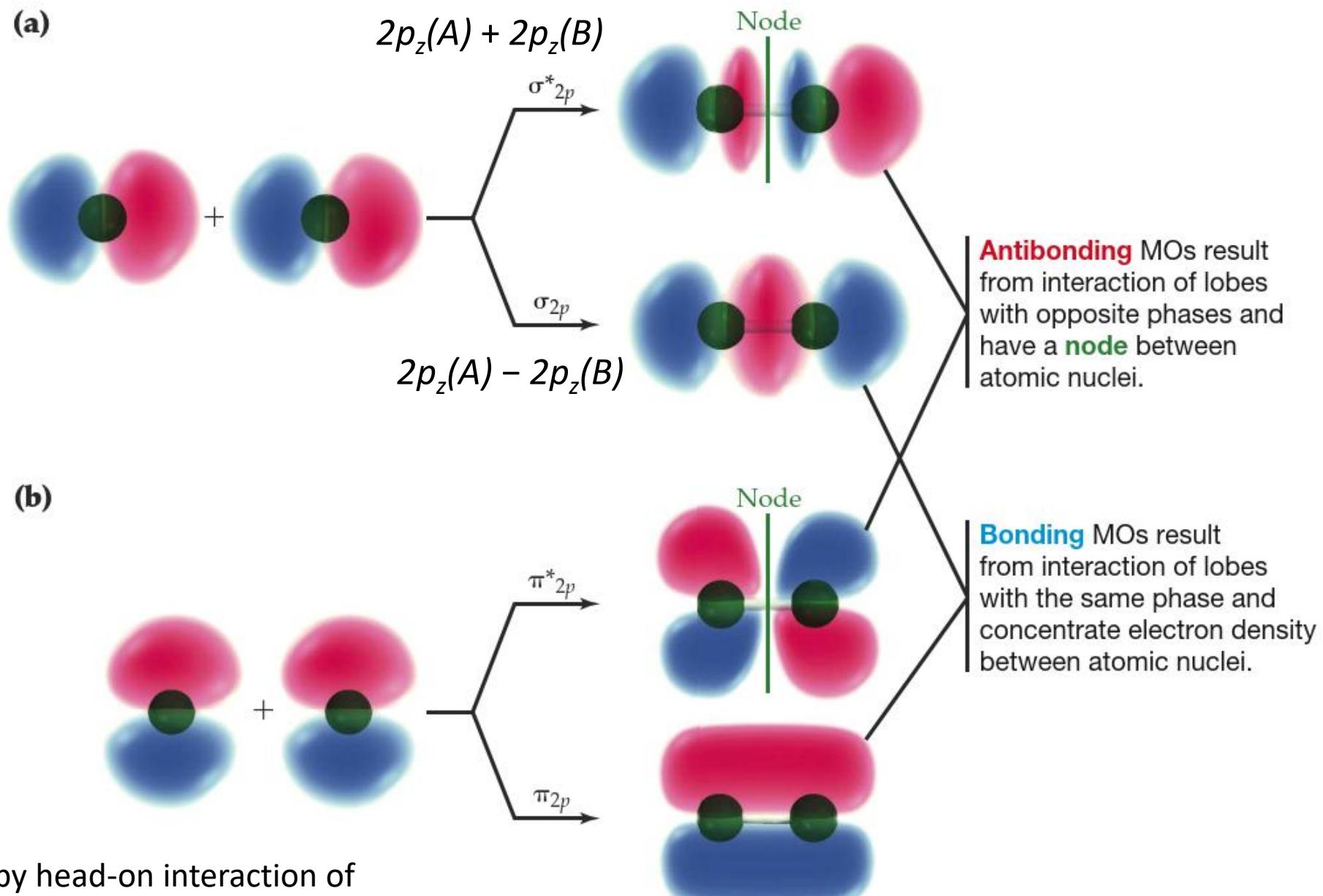


FIGURE 5.13

Formation of (a)  $\sigma_{2p}$  and  $\sigma^*_{2p}$  MOs by head-on interaction of two p atomic orbitals, and (b)  $\pi_{2p}$  and  $\pi^*_{2p}$  MOs by sideways interaction of two p orbitals.

- Figure 10.7.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three np atomic orbitals each.
- There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding.
- The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond.
- Conversely, the antibonding molecular orbitals are higher in energy, as shown.
- *The energy difference between the  $\sigma$  and  $\sigma^*$  molecular orbitals is significantly greater* than the difference between the two  $\pi$  and  $\pi^*$  sets.

The *reason for this is that the atomic orbital overlap and thus the strength of the interaction is greater for a  $\sigma$  bond* than a  $\pi$  bond, which means that the  $\sigma$  molecular orbital is more stable (lower in energy) than the  $\pi$  molecular orbitals.

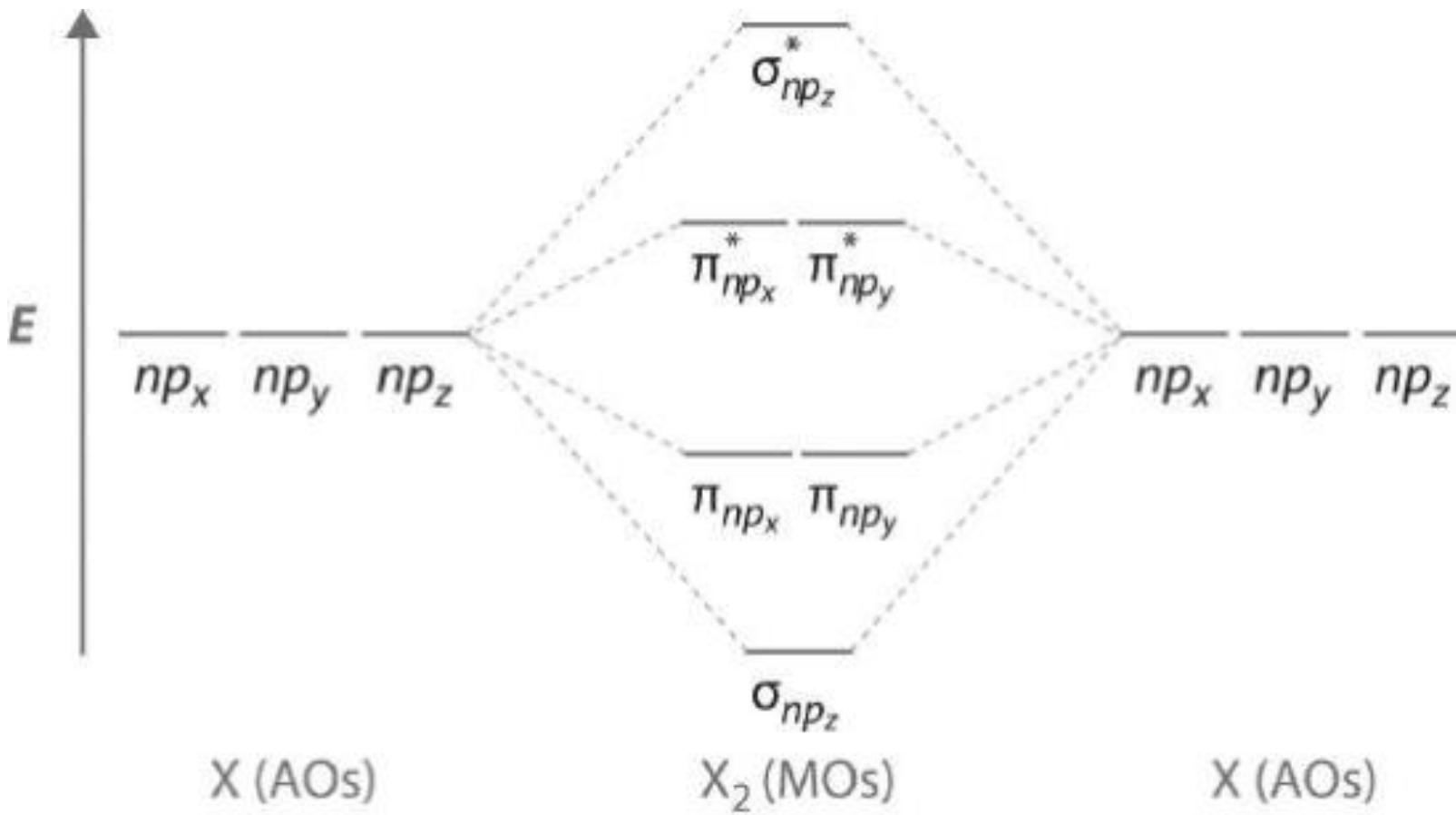
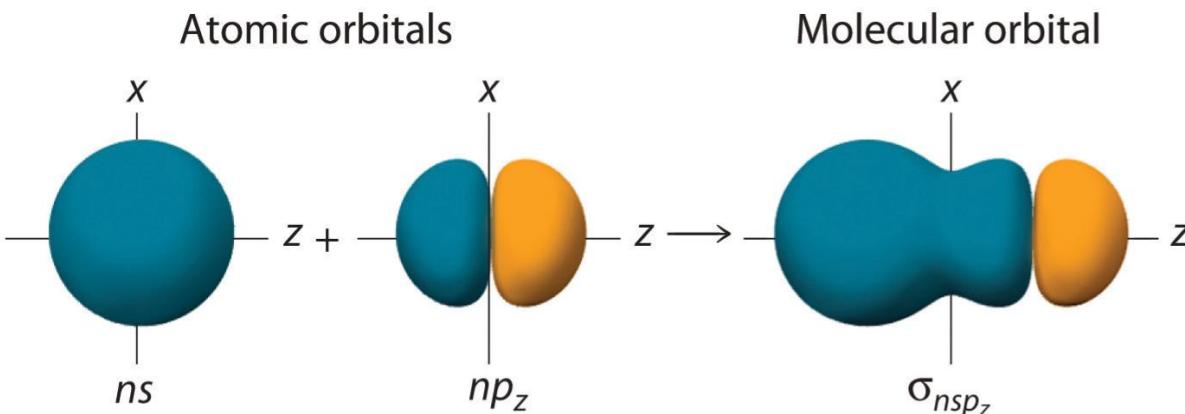
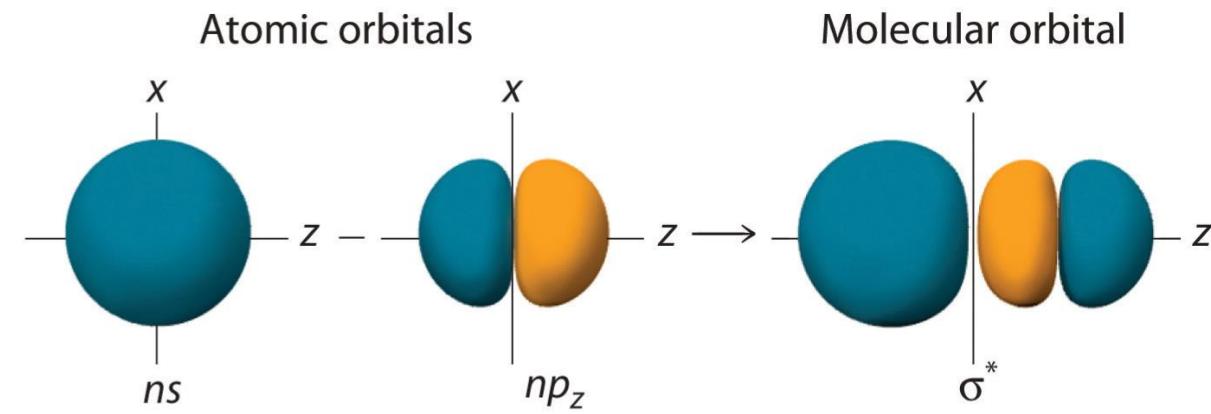


Figure 10.7.7: The Relative Energies of the  $\sigma$  and  $\pi$  Molecular Orbitals Derived from  $np_z$ ,  $np_x$ , and  $np_y$  Orbitals on Identical Adjacent Atoms. Because the two  $np_z$  orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the  $\sigma$  and  $\sigma^*$  molecular orbitals is greater than the energy difference between the  $\pi$  and  $\pi^*$  orbitals.

- Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an  $ns$  atomic orbital on one atom with an  $np_z$  atomic orbital on another.
- As shown in Figure 10.7.8, the sum of the two atomic wave functions ( $ns + np_z$ ) produces a  $\sigma$  bonding molecular orbital. Their difference ( $ns - np_z$ ) produces a  $\sigma^*$  antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.



**(a) Bonding**



**(b) Antibonding**

Figure 10.7.8: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np Atomic Orbital on an Adjacent Atom.

- (a) The mathematical sum results in a  $\sigma$  (bonding) molecular orbital, with increased probability density between the nuclei.
- (b) The mathematical difference results in a  $\sigma^*$  (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

- The essential idea is that orbital lobes of the same sign can lead to favorable overlap (the overlap integral has a value  $> 0$ ).
- This can occur between orbitals of different types in several ways.
- Fig. 3.6 shows a few types of orbital overlap that lead to bonding.
- Figure 3.7 shows types of orbital interactions that do not lead to bond formation.

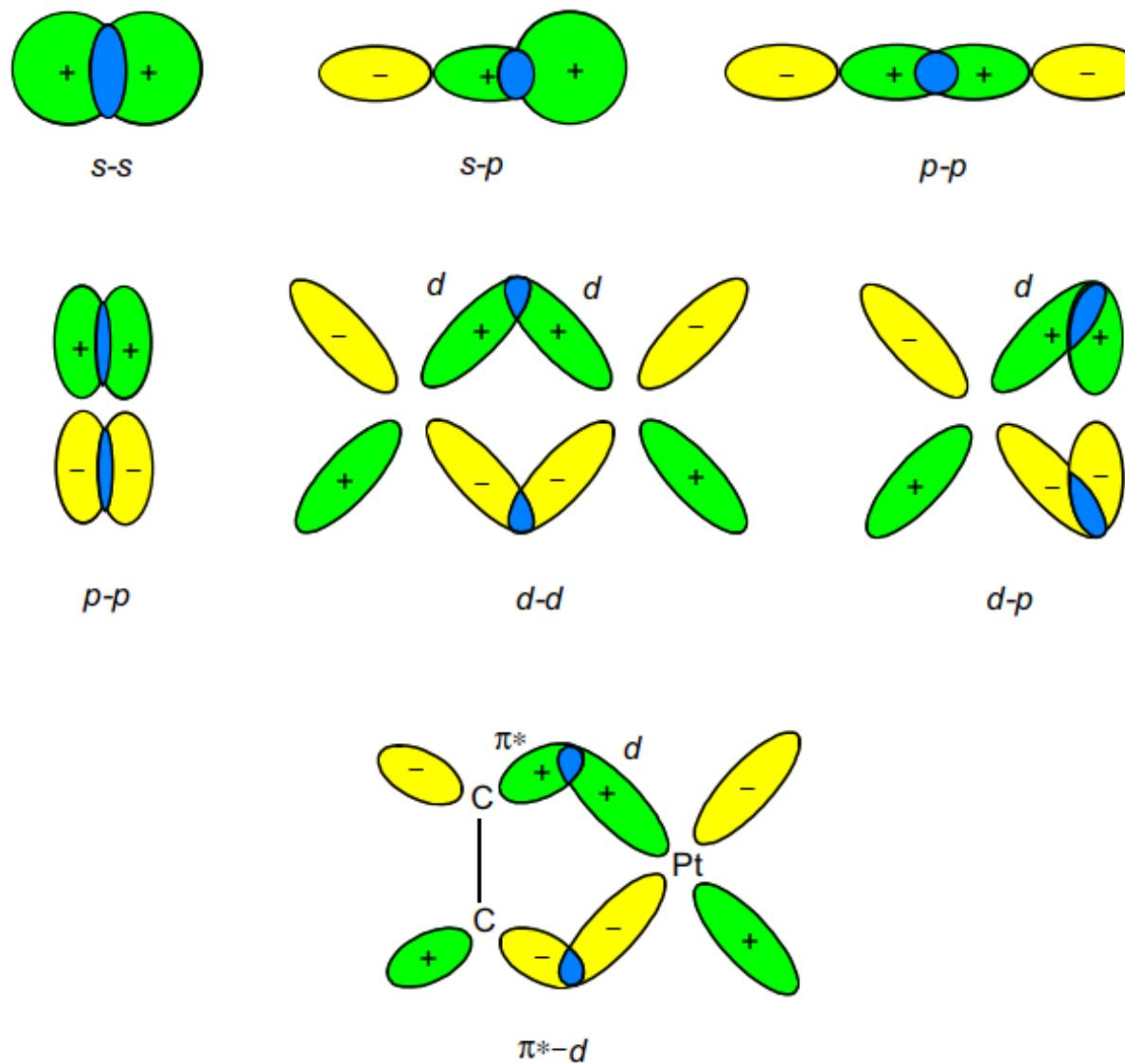
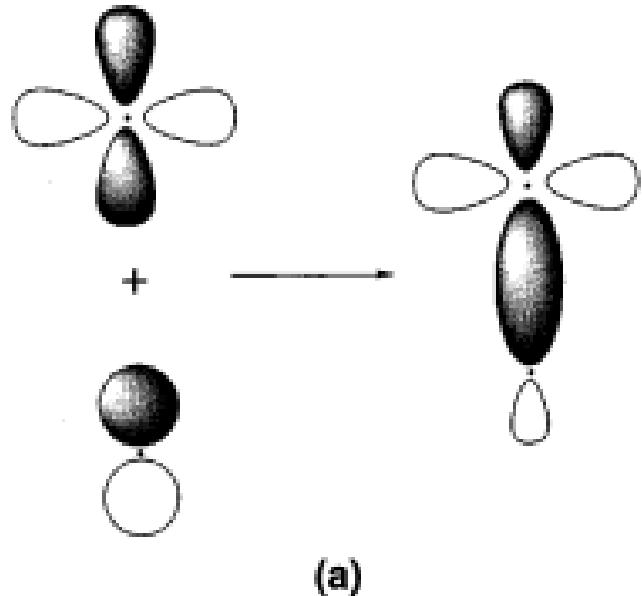
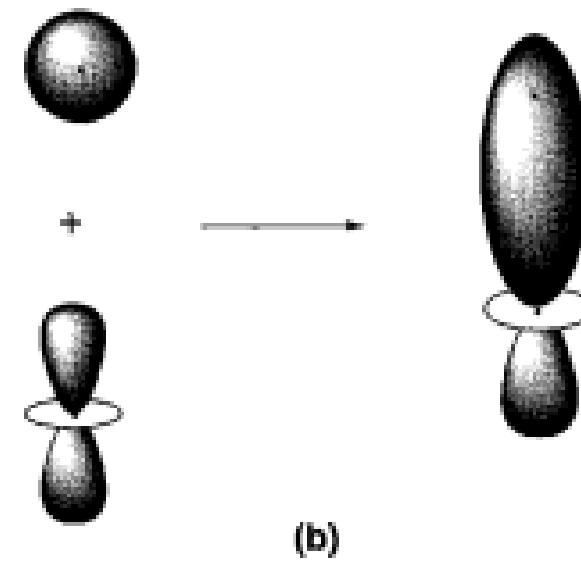


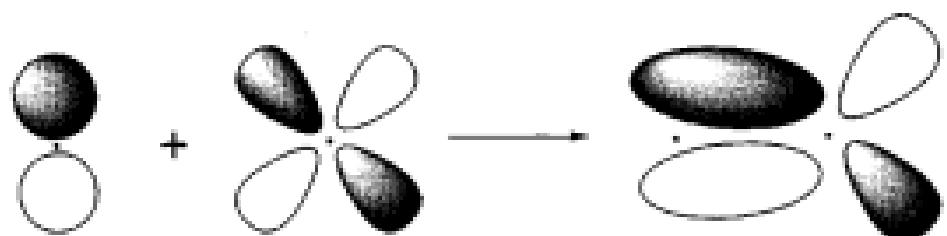
FIGURE 3.6 Some types of orbital overlap that lead to energetically favorable interactions (overlap integral  $> 0$ ).



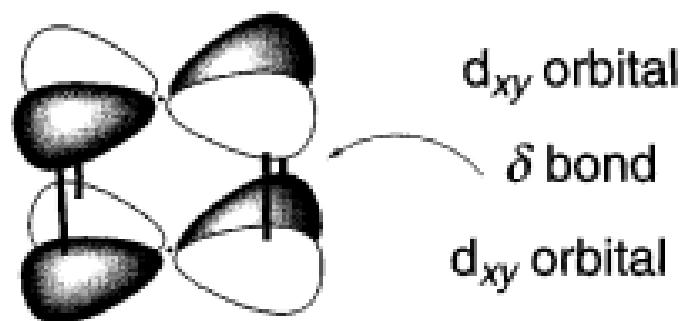
(a)



(b)



(c)



(d)

FIG. 3.1 4 Molecular orbitals involving d orbitals. These diagrams indicate the formation of  $\sigma$ ,  $\pi$  and  $\delta$  bonds, involving d orbitals. (a)  $\sigma$  bond between  $p_y$  and  $d_{x^2-y^2}$ , (b)  $\sigma$  bond between  $s$  and  $d_z^2$ , (c)  $\pi$  bond between  $p_y$  and  $d_{xy}$ , (d)  $\delta$  bond between two  $d_{xy}$  orbitals.

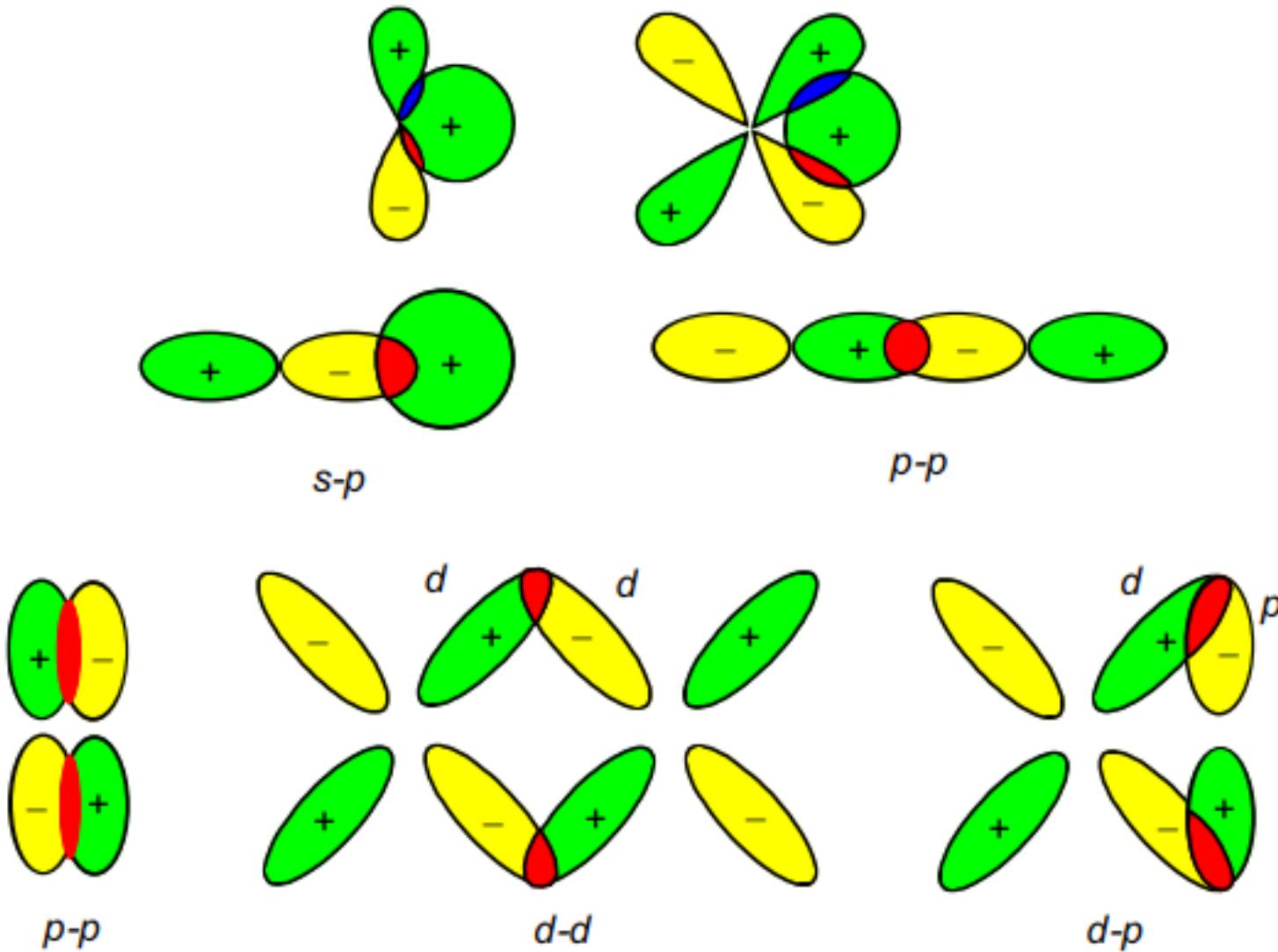
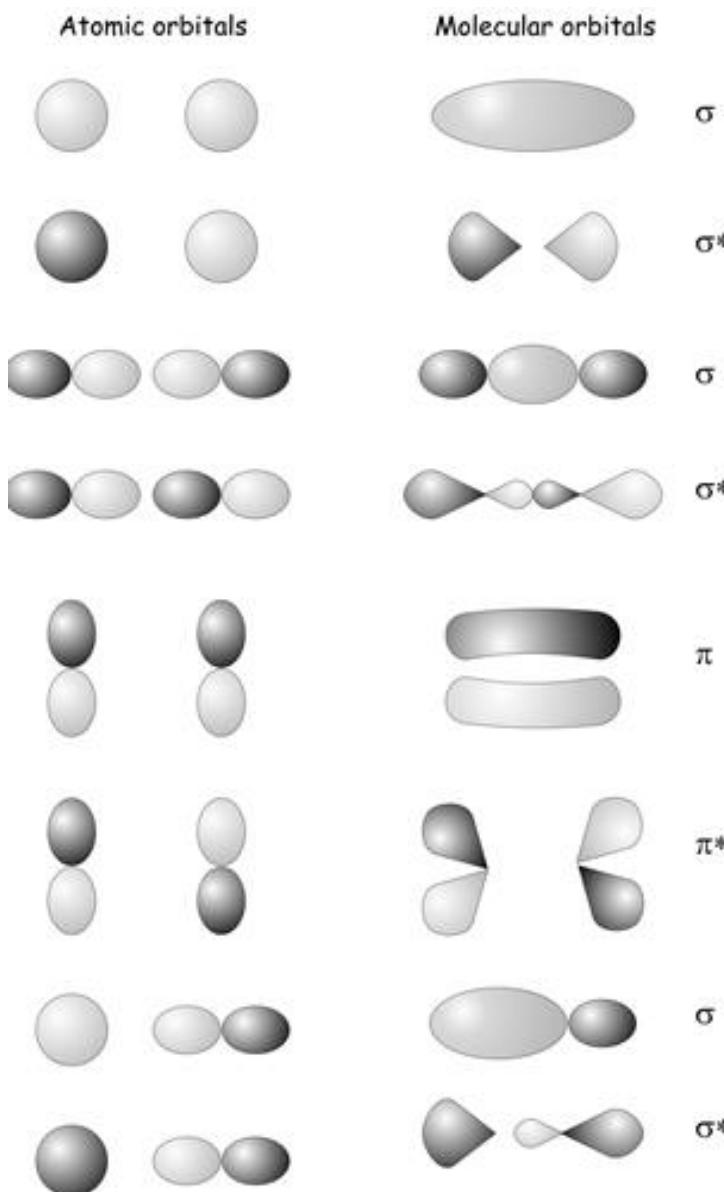


FIGURE 3.7 Patterns of orbital overlap that **do not** lead to bonds.



By considering the symmetries of s and p orbitals on two atoms, we can form bonding and antibonding combinations labeled as having either  $\sigma$  or  $\pi$  symmetry depending on whether they resemble s or p orbitals when viewed along the bond axis (see diagram below). In all of the cases shown, only atomic orbitals that have the same symmetry when viewed along the bond axis z can form a chemical bond e.g. two s orbitals, two pz orbitals , or an s and a pz can form a bond, but a pz and a px or an s and a px or a py cannot. It turns out that the rule that determines whether or not two atomic orbitals can bond is that they must belong to the same symmetry species within the point group of the molecule.

## d orbitals

➤ Recall the shapes and orientations of the five d orbitals. Three of the d orbitals ( $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ ) have electron density between the axes and nodes along the axes. Two of the d orbitals ( $d_z^2$  and  $d_{x^2-y^2}$ ) have electron density along the axes. ***Only the latter two d orbitals can possibly form sigma bonds.*** These will be similar to sigma bonds formed from p orbitals, when two lobes of the same phase overlap the electron density between the two nuclei increases and sigma bond is formed as shown in Figure 3.7A.3.

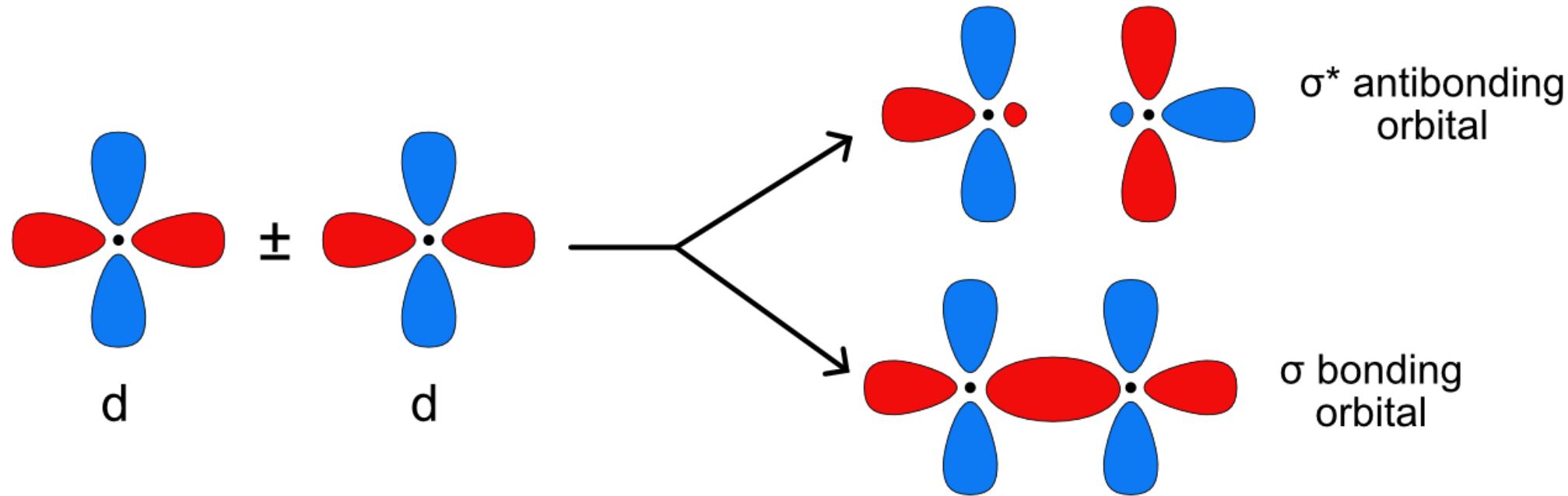


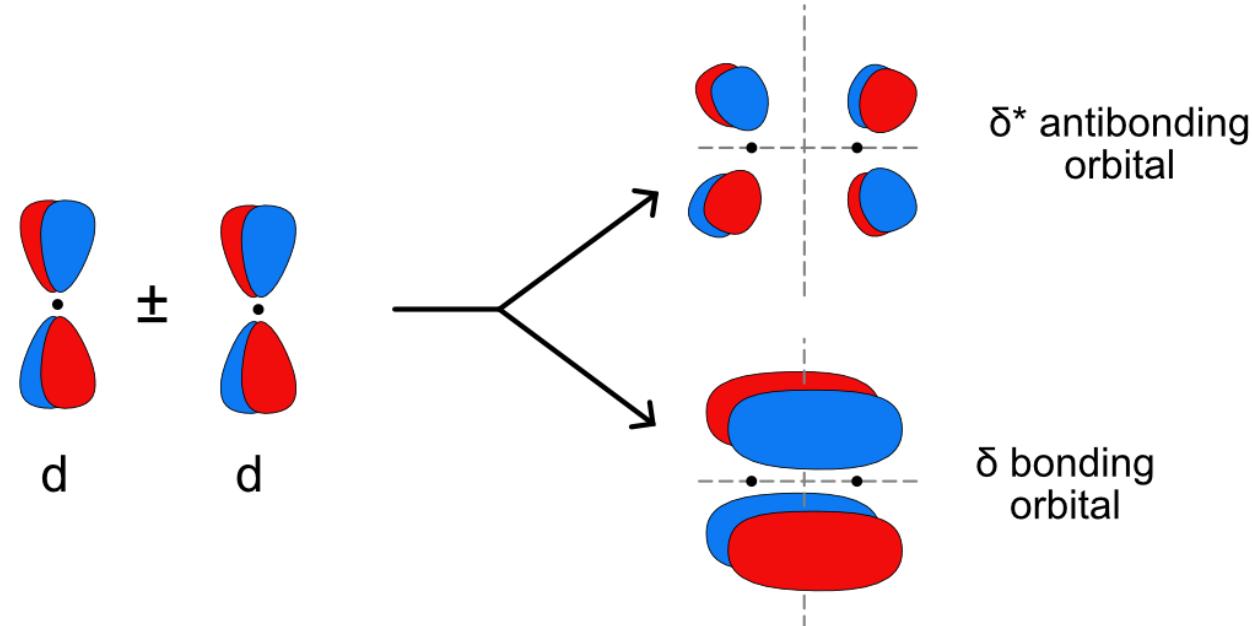
Figure 3.7A.3: Sigma ( $\sigma$ ) and sigma antibonding ( $\sigma^*$ ) molecular orbitals formed from two  $d_{x^2-y^2}$  orbitals.

## Delta ( $\delta$ ) Molecular Orbitals

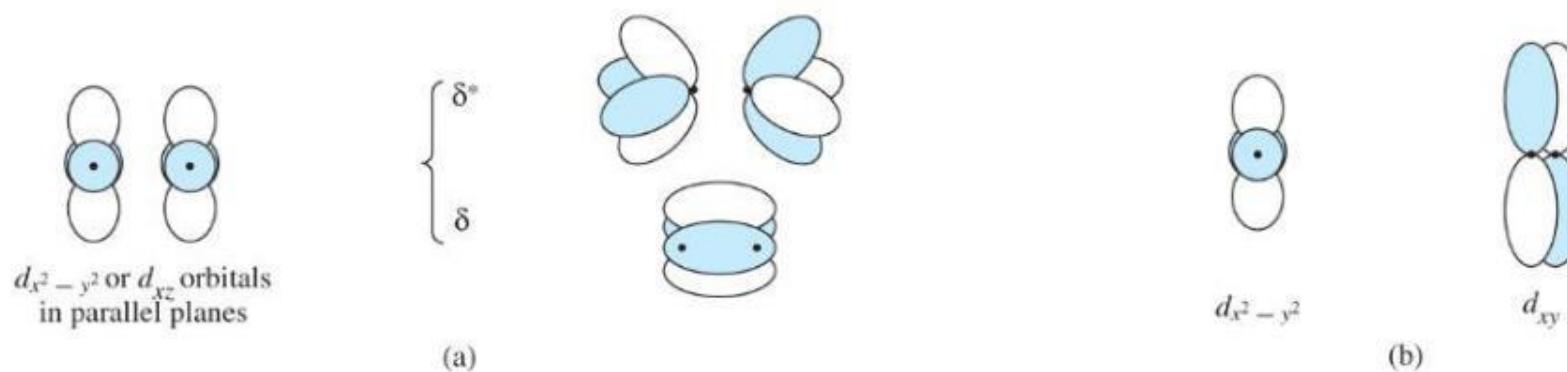
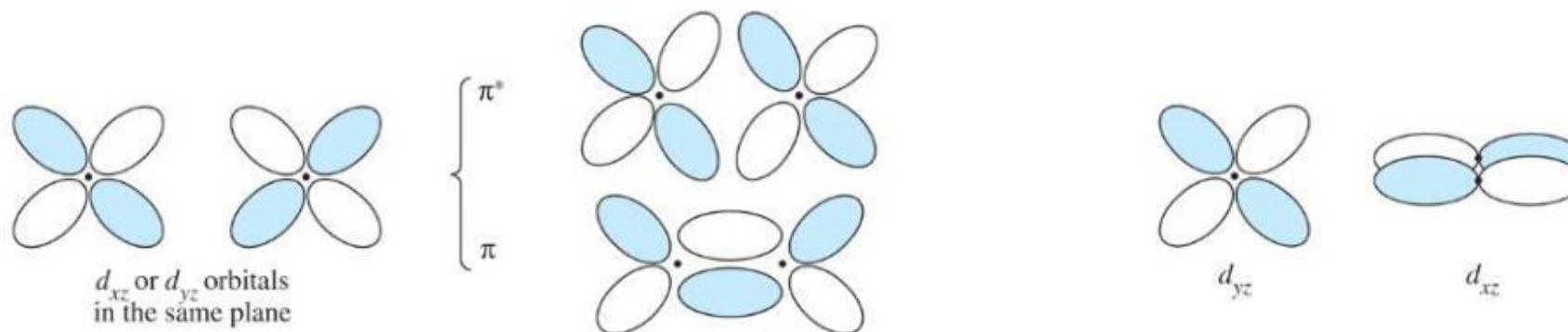
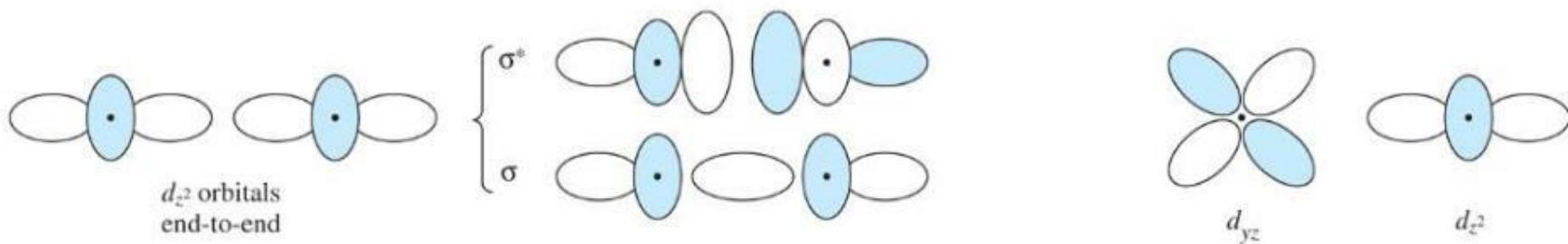
➤ In main group chemistry only sigma and pi bonds are possible. When two metal atoms are bonded together, a third type of bond, a delta bond, is possible. Two d orbitals orientated face-to-face along the internuclear bond axis (( $d_{xy}$  or  $d_{x^2-y^2}$  if the bond is on the z axis) will overlap to form delta bonding and antibonding orbitals as shown in Figure 3.7A.5. The in-phase bonding combination has four areas of electron density above and below the two nuclei, with a vertical and a horizontal node along the internuclear bond axis. In the out-of-phase combination there is a third node bisecting the internuclear axis. With delta bonding it is possible to have *quadruple* or even *quintuple* (five) bonds between two metal centers, although in practice quintuple bonds are exceedingly rare and have only been observed in a few chromium and molybdenum dimers.

- A delta ( $\delta$ ) orbital is one that **has two nodes** containing the internuclear bond axis. Only d (or f) orbitals can form delta bonds so they are only possible between two metal atoms.

**Figure 3.7A.5:** Delta ( $\delta$ ) and delta antibonding ( $\delta^*$ ) molecular orbitals are formed by the combination of two face-to-face d atomic orbitals. The grey dashed lines indicate the two nodes containing the internuclear bond axis.



# Interactions of two d orbitals



## ❖ Multiple Bonds

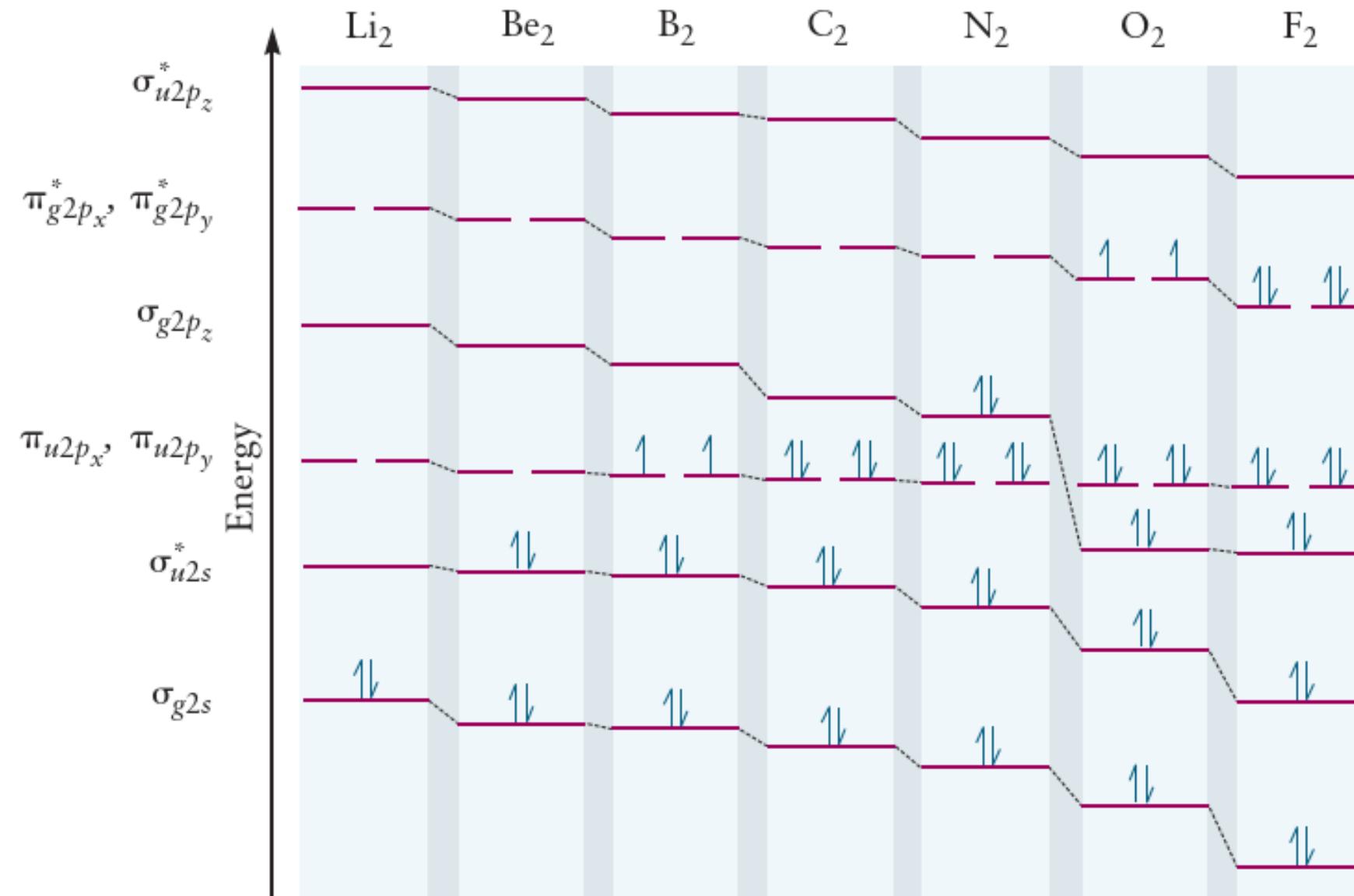
- Single bonds are formed from 1 sigma bond
- Double bonds are formed from 1 sigma bond and 1 pi bond
- Triple bonds are formed from 1 sigma bond and 2 pi bonds
- Quadruple bonds (only found between two metal atoms) are formed from 1 sigma bond, 2 pi bonds and 1 delta bond
- Quintuple bonds (only found between two metal atoms) are formed from 1 sigma bond, 2 pi bonds and 2 delta bonds

## The Electronic Structure of Many-Electron Molecules: DIATOMIC MOLECULES

- Once the MO energy levels have been calculated, a molecular configuration is obtained by putting two electrons in each MO, in order of increasing orbital energy, until all electrons have been accommodated.
- If the degeneracy of an energy level is greater than one, Hund's first rule is followed, and the electrons are placed in the MOs in such a way that the total number of unpaired electrons is maximized.
- Recall that the order of the energies of the orbitals for multielectron atoms does not follow the order of the energies of the hydrogen atomic orbitals.
- ✓ For instance, the energy of the 4s orbital is less than that of the 3d orbitals for multielectron atoms. A similar thing happens when we use the  $\text{H}_2^+$  molecular orbitals that we have constructed from the combination of hydrogen atomic orbitals.

- ✓ The ordering of the molecular orbitals depends on  $Z$  ( $Z$  is the atomic number or number of protons in an atom). *For  $Z > 7$ , the  $\sigma_{2p}$  and  $\pi_{2p}$  orbitals interchange energies so that the energy of the  $\sigma_{2p}$  orbital is less than that of the  $\pi_{2p}$  orbitals.*
- The ordering of the energies of the molecular orbitals that we use to write electron configuration of the second-row homonuclear diatomic molecules  $\text{Li}_2$  through  $\text{Ne}_2$  is shown in Figure 9.11.
- ✓ Observe that the order of the  $\sigma_{2p}$  and  $\pi_{2p}$  orbitals changes in going from  $\text{N}_2$  to  $\text{O}_2$  molecules.

➤ The relative order of  $\sigma$ - and  $\pi$  orbitals arising from linear combination of 2p orbitals is shown below.



**Figure 9.11** The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules  $\text{Li}_2$  through  $\text{F}_2$ . Notice that for  $\text{O}_2$  through  $\text{Ne}_2$  the energy of the  $\sigma_g 2p_z$  orbital is below that of the  $\pi_u 2p$  orbitals.

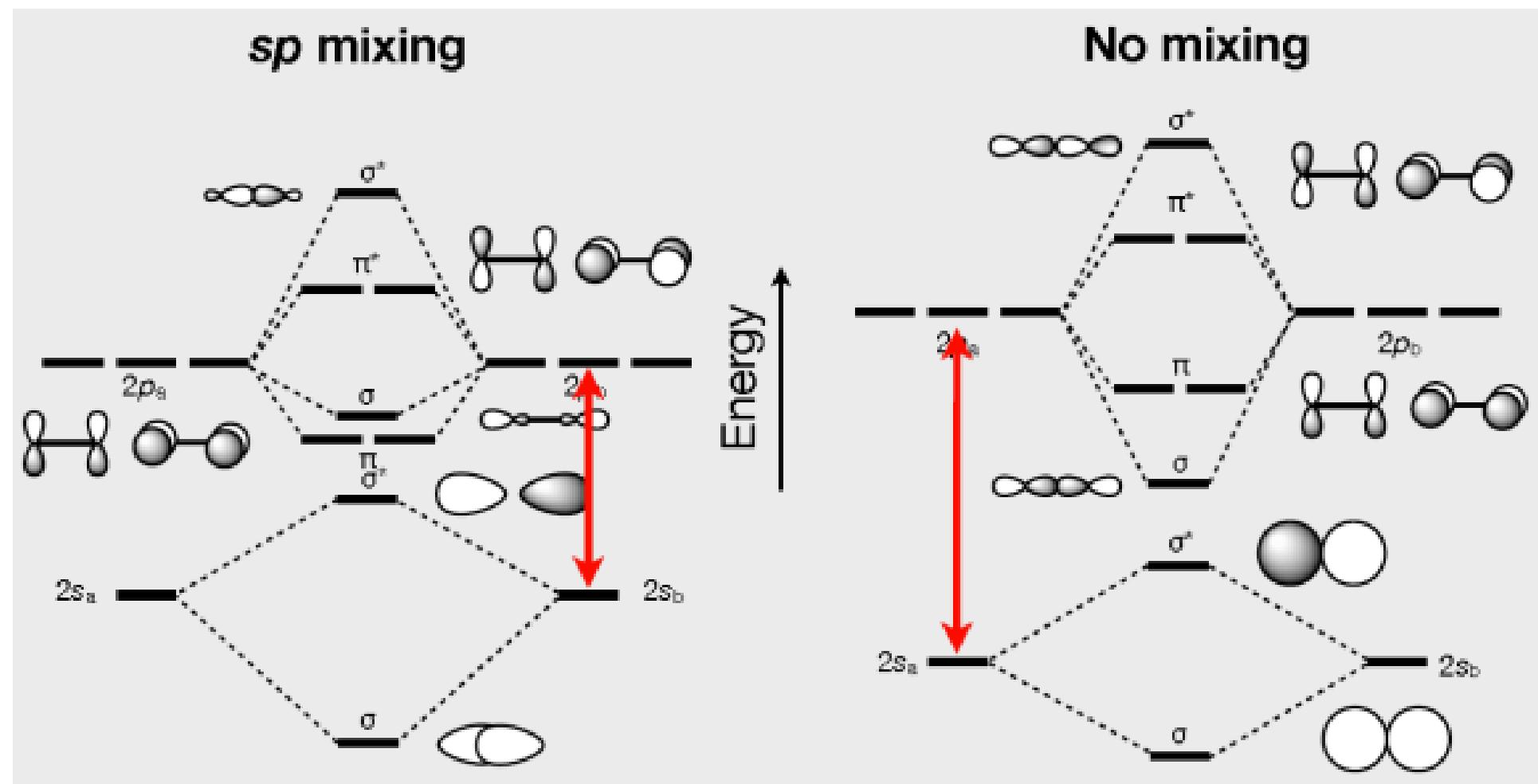
*Spectroscopic evidence shows that in  $\text{O}_2$  (and in  $\text{F}_2$ ) the  $\sigma_g 2p_z$  MO is lower in energy than the  $\pi_u 2p$  MO.*

➤ Note: As Electronegativity increases, the MO energy decreases.

- This difference is based on experimental measurements of molecular orbital energies by photoelectron spectroscopy. While the energy of the  $\pi_u$ 2p(x,y) molecular orbital remains nearly constant as we move across Period 2, the energy of the  $\sigma_g$ 2pz molecular orbital lies above  $\pi_u$ 2p(x,y) in the first part of the period and falls below it for the later elements O, F, and Ne.
- This behavior is borne out by advanced calculations of the energies for these two molecular orbitals.
- A simplified physical interpretation relates this result to the extent to which the 2s and 2pz atomic orbitals can mix while contributing to the molecular orbital. The 2s AOs have the right symmetry to mix with 2pz AOs to form a  $\sigma$  molecular orbital directed along the z-axis. In the first part of Period 2 the 2s and 2p are sufficiently close in energy that mixing occurs and increases the energy of the nominal  $\sigma_g$ 2pz orbital while decreasing the energy of the nominal  $\sigma_g$ 2s orbital. In the latter part the energy separation of 2p and 2s AOs is too great for mixing to occur. Because the 2s and 2px and 2py AOs do not have the right symmetry to mix and form a p molecular orbital, the energy of the  $\pi_u$ 2p(x,y) MO remains nearly constant across the period even when the 2s and 2p AOs are close together in energy.

## MOs of Homonuclear Diatomic Molecules: **Orbital Mixing**

- ❖ The MO picture of homonuclear diatomic molecules depends on the amount of ***sp* mixing**.

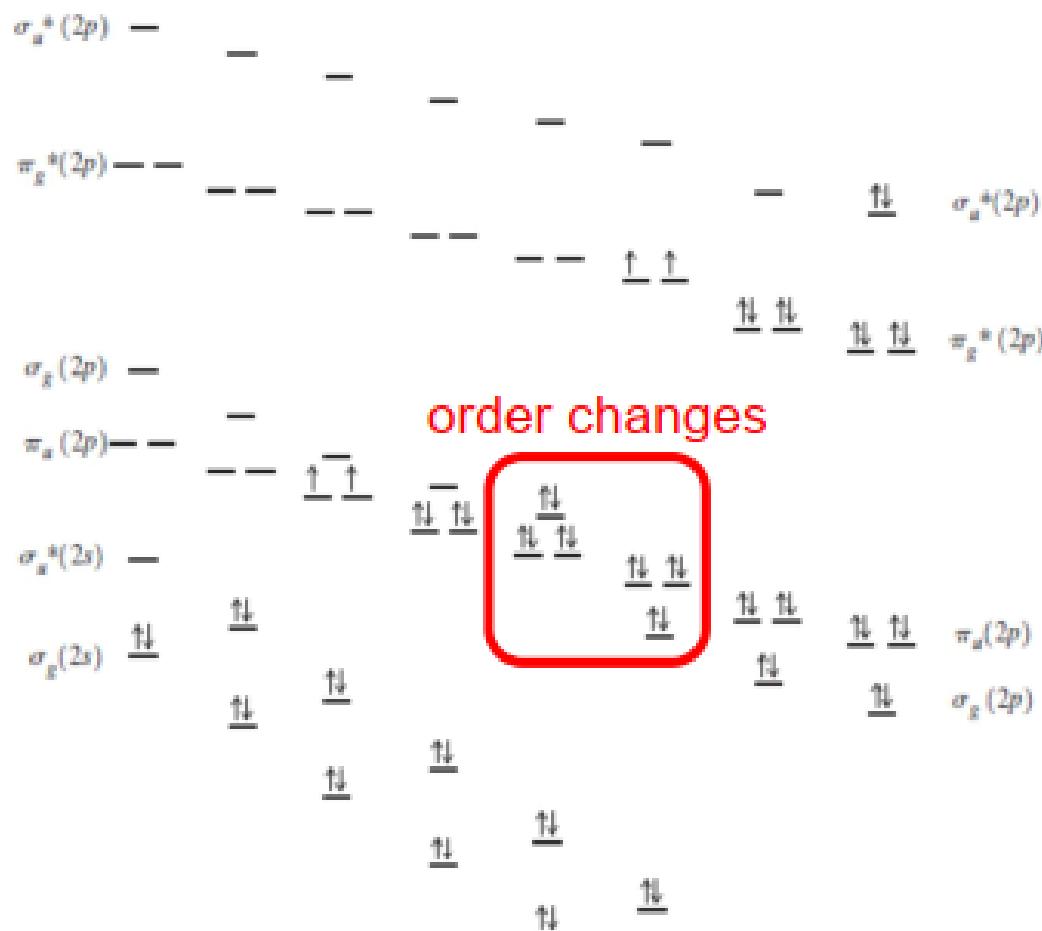


$\text{Li}_2, \text{Be}_2, \text{B}_2, \text{C}_2, \text{N}_2$

$\text{O}_2, \text{F}_2, \text{Ne}_2$

# Orbital Mixing

**The size of the effect depends on the 2s-2p energy difference.**



small  $Z_{\text{eff}} =$   
small energy  
difference =  
large *sp* mixing

	Li <sub>2</sub>	Be <sub>2</sub>	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
Bond order	1	0	1	2	3	2	1	0
Unpaired $e^-$	0	0	2	0	0	2	0	0

large  $Z_{\text{eff}} =$   
large energy  
difference =  
small *sp* mixing

- Photoelectron spectroscopy and detailed computation (the numerical solution of the Schrödinger equation for the molecules) enable us to build the orbital energy schemes shown above. As we see there, from  $\text{Li}_2$  to  $\text{N}_2$  the arrangement of orbitals is that shown in the Fig., whereas for  $\text{O}_2$  and  $\text{F}_2$  the order of the  $s$  and  $p$  orbitals is reversed.
- The reversal of order can be traced to the increasing separation of the  $2s$  and  $2p$  orbitals that occurs on going to the right across Period 2. A general principle of quantum mechanics is that the mixing of wavefunctions is strongest if their energies are similar; mixing is not important if their energies differ by more than about 10 eV. When the  $s,p$  energy separation is small, each molecular orbital is a mixture of  $s$  and  $p$  character on each atom. As the  $s$  and  $p$  energy separation increases, the molecular orbitals become more purely  $s$ -like and  $p$ -like.

- The question then arises as to why the mixing MO diagram is necessary in some cases, but not in others. *As one proceeds from left to right across the second period of the periodic table, the energies of the 2s and 2p AOs both decrease as a result of the increased effective nuclear charge across the row.*
- *Because the 2p orbitals are shielded to a certain extent by the 2s orbitals, the energies of the 2s orbitals decrease more precipitously than those of the 2p orbitals*, as shown in Table 10.7.

**TABLE 10.7** The experimentally determined energy gap between the 2s and 2p orbitals for the second period elements.

**TABLE 10.7** The experimentally determined energy gap between the 2s and 2p orbitals for the second period elements.

Element	Li	Be	B	C	N	O	F
- $E(2s)$ , eV	5.39	9.32	12.9	16.6	20.3	28.5	37.8
- $E(2p)$ , eV	3.54	6.59	8.3	11.3	14.5	13.6	17.4
$[E(2p) - E(2s)]$ , eV	1.85	2.73	4.6	5.3	5.8	14.9	20.4

Element	Li	Be	B	C	N	O	F
- $E(2s)$ , eV	5.39	9.32	12.9	16.6	20.3	28.5	37.8
- $E(2p)$ , eV	3.54	6.59	8.3	11.3	14.5	13.6	17.4
$[E(2p) - E(2s)]$ , eV	1.85	2.73	4.6	5.3	5.8	14.9	20.4

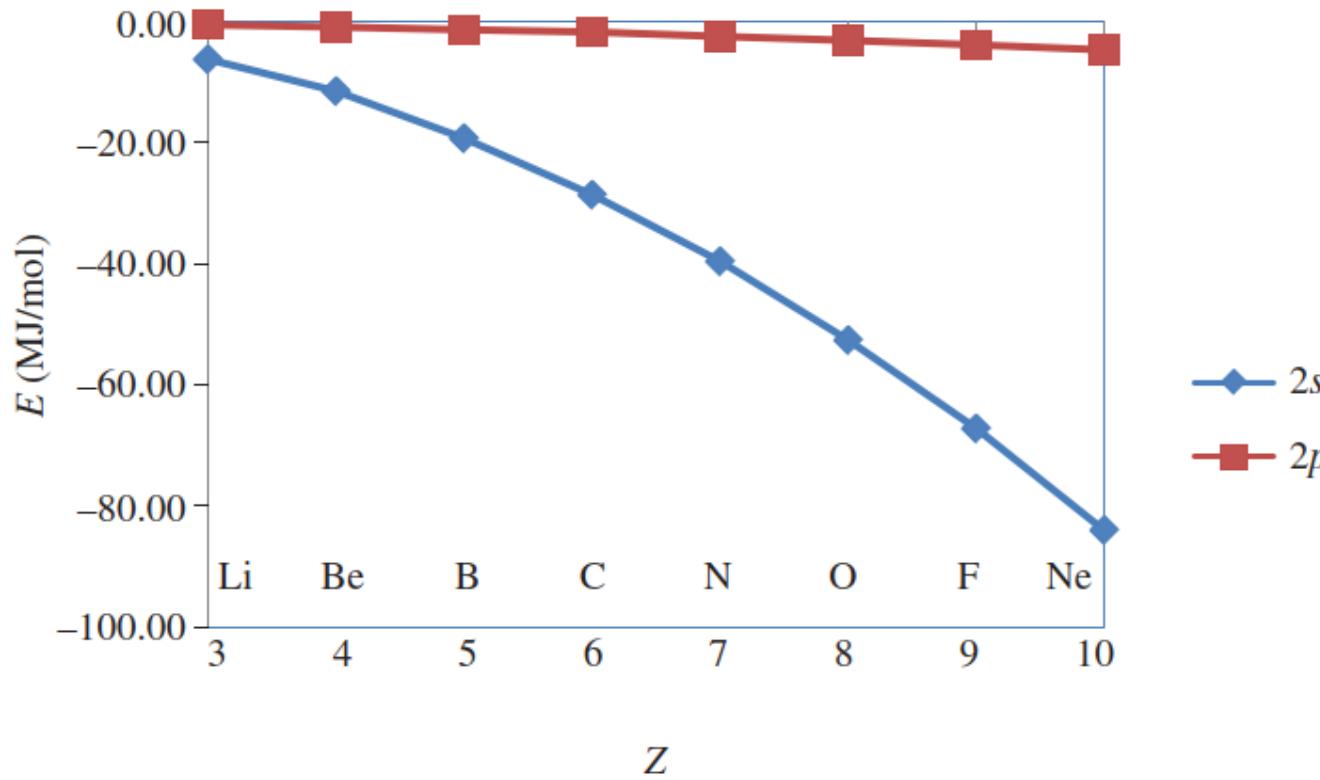


FIGURE 10.27. Relative energies of the valence MOs for the Period 2 homonuclear diatomics.

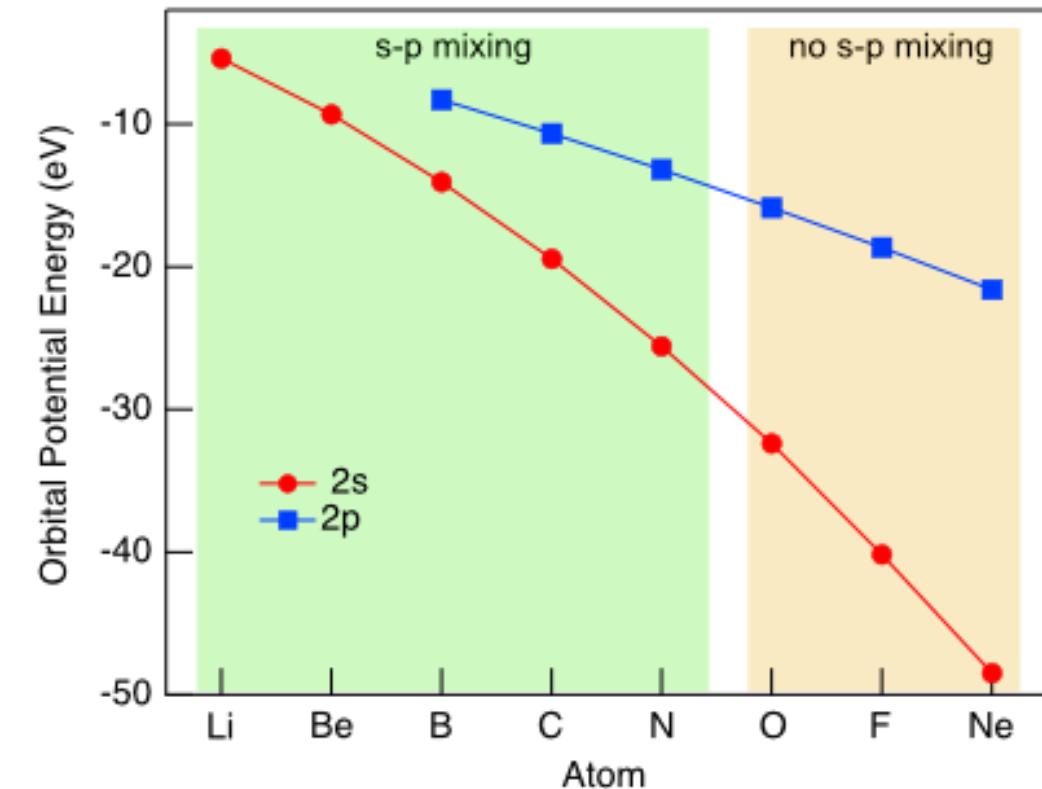


Figure 3.7B.4: Trends in the 2s (red circle) and 2p (blue square) atomic orbital potential energies for second period elements. Energies from Meissler, G. L.; Fischer, P. J.; Tarr, D. A. Inorganic Chemistry, 5th Ed.

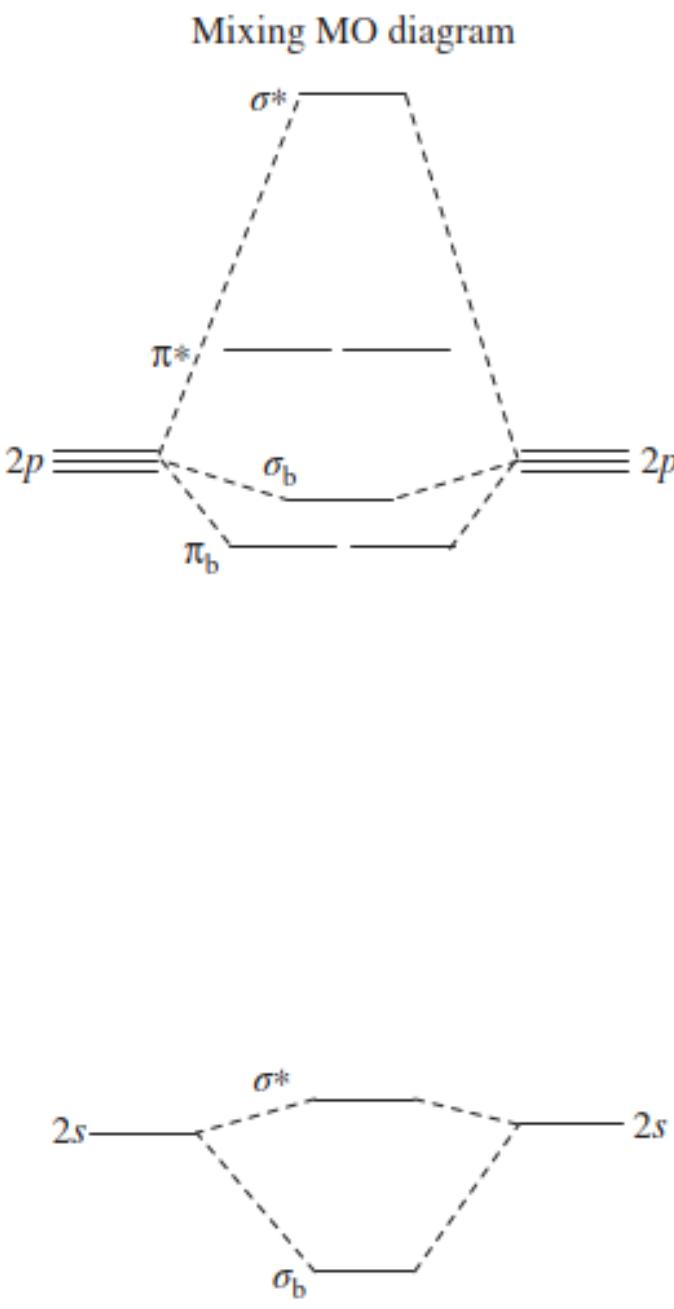
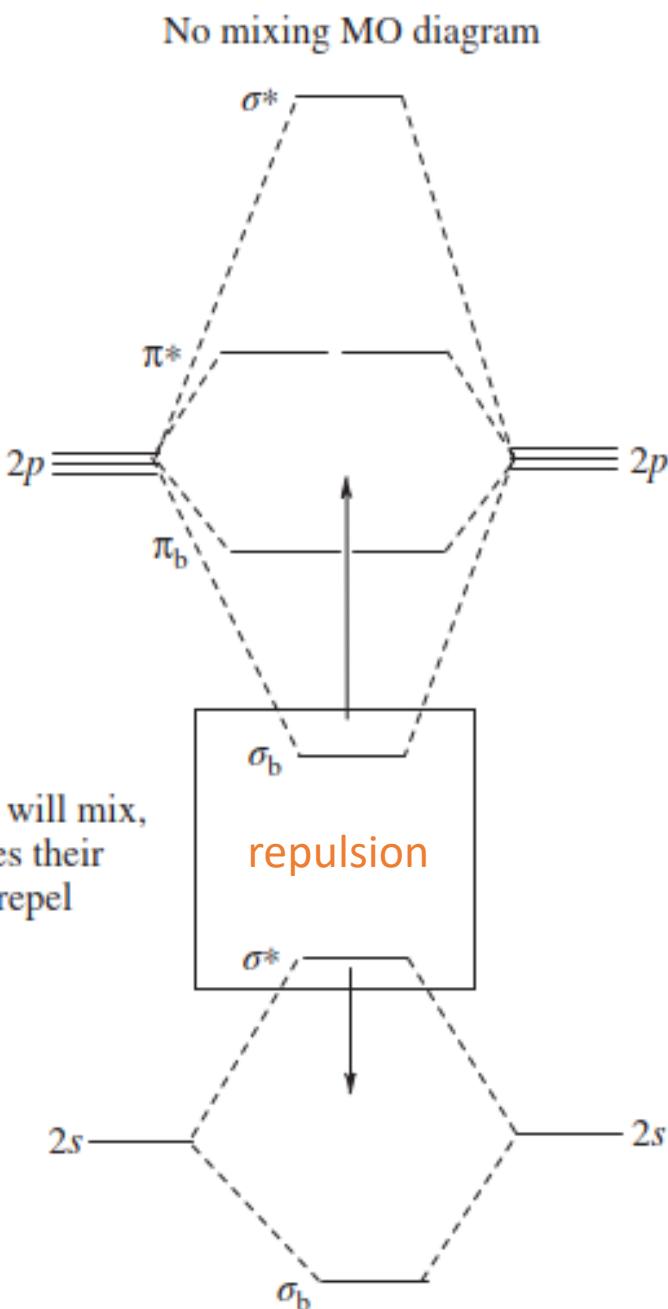
- As a result, those elements on the left-hand side of the periodic table have their 2s and 2p AOs closer in energy to one another than elements from the right-hand side. Thus, *there will be considerably more mixing in elements from the left-hand side because the energies of the interacting MOs derived from these AOs will be closer together.*
- Notice how the energy gap between the 2s and the 2p orbitals is much larger for O and F than it is for Li, Be, B, C, and N. As a result, mixing will occur in  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ , and  $\text{N}_2$  but not in  $\text{O}_2$  and  $\text{F}_2$ , as shown in Figure 10.27.
- Further *evidence that mixing occurs in  $\text{N}_2$* , which lies close to the mixing/nonmixing border, is supported by the PES spectrum of  $\text{N}_2$ , which shows that the four  $\pi^b$  electrons are ionized at slightly higher energies than the two  $\sigma^b$  ( $2\text{p}_z$ ) electrons.

## ☐ Orbital Mixing

- The MOs derived from the 2s and  $2p_z$  AOs *both have sigma symmetry*, they can “mix” with each other.
- In other words, all four AOs will form linear combinations to make the four sigma MOs.
- *For the lowest energy  $\sigma_b$  MO, the coefficients for the 2s wavefunctions will be significantly larger than those for the  $2p_z$  wavefunctions in the linear combination trial function because the 2s orbitals lie closest in energy on the MO diagram to the lowest energy  $\sigma_b$  MO.*
- Likewise, for the highest energy  $\sigma^*$  MO, the coefficients for the  $2p_z$  wavefunctions will be much greater than those for the 2s wavefunctions.

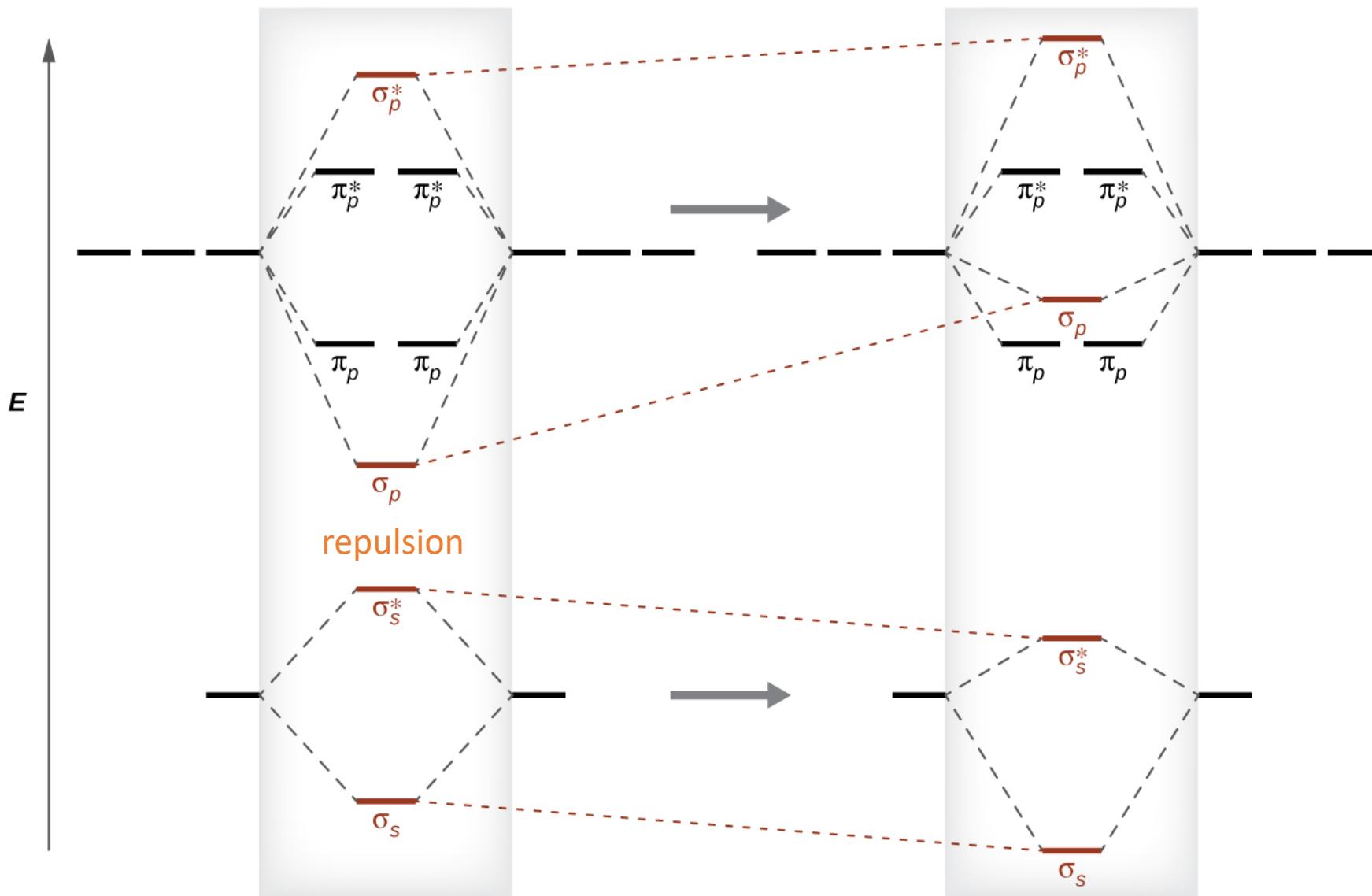
- However, for the  $\sigma^*$  and  $\sigma_b$  MOs that are intermediate in energy on the MO diagram (and close in energy to each other), the coefficients for all four atomic orbital basis functions will be similar. This MO concept of mixing is therefore very similar to the VB concept of hybridization.
- Whenever two MOs have the *same symmetry and similar energies*, the *electrons* occupying those orbitals will *lie in similar regions of space* and will therefore *repel one another*.
- This causes the two intermediate sigma MOs on the MO diagram to repel each other, as shown in Figure 10.26.
- The result of the mixing is the modified MO diagram shown below.

# Orbital Mixing

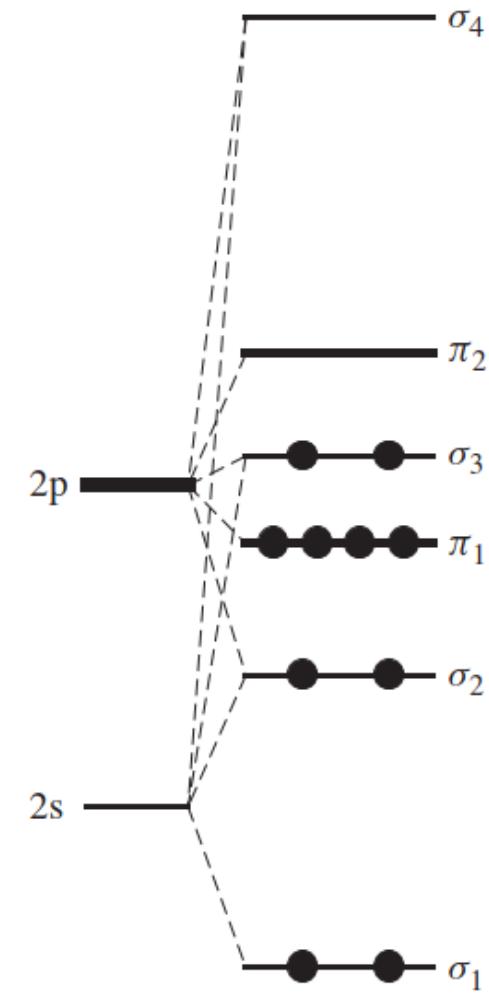
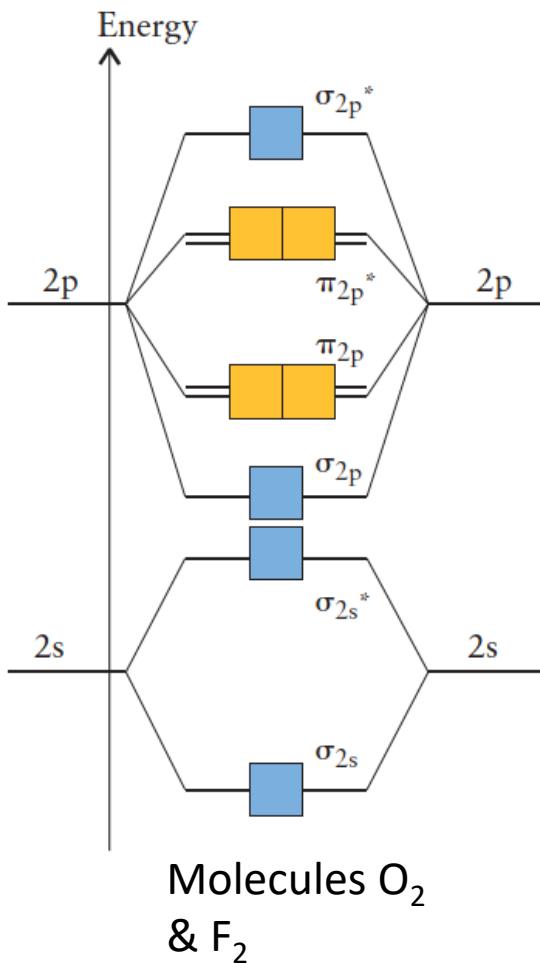
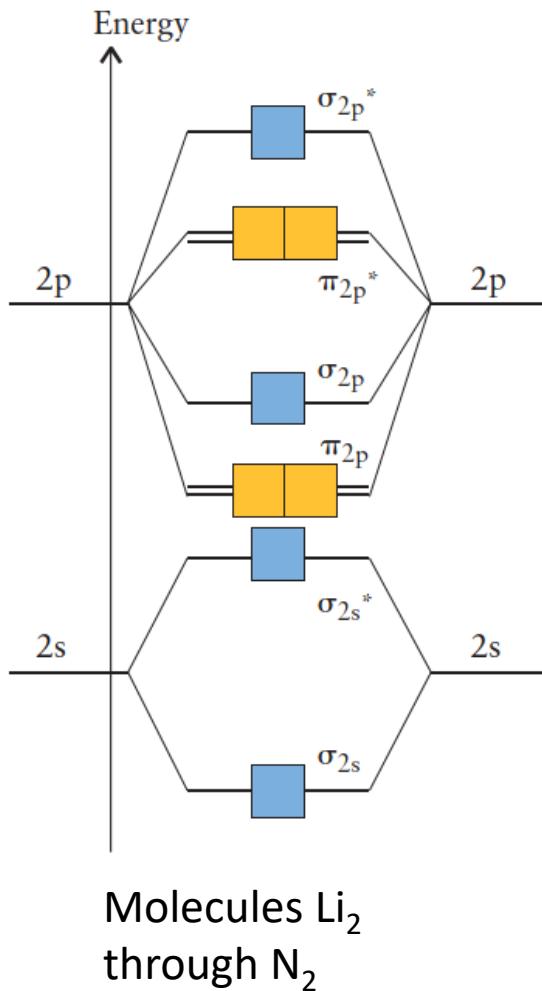


Orbitals of similar but unequal energies can interact if they have the same symmetry. The 2s and 2p<sub>z</sub> orbitals form MOs with the same sigma symmetry (σ<sub>g</sub> and σ<sub>u</sub>). s-p mixing causes the σ<sub>g</sub> and σ<sub>u</sub> MOs to be pushed apart in energy:

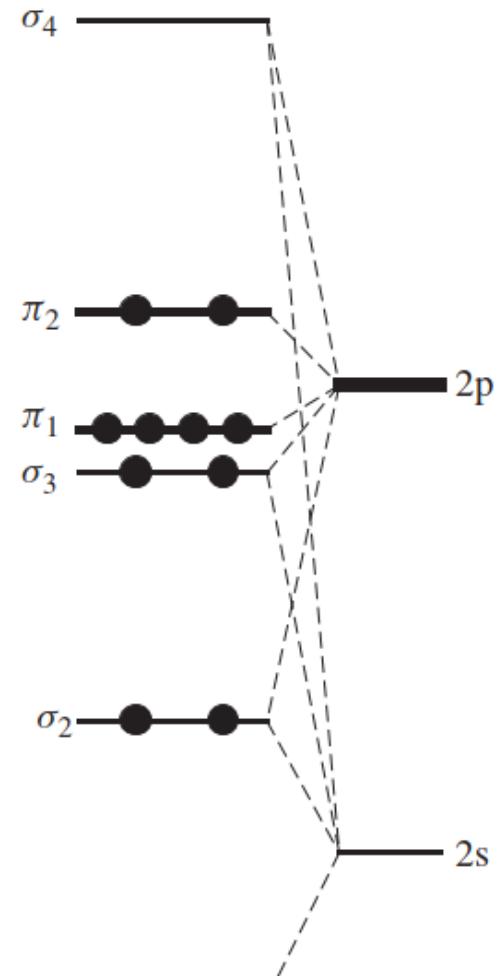
**FIGURE 10.26**  
Whenever two MOs have the same symmetry and similar energies, they will mix with each other; in extreme cases, this can lead to the MO diagram shown at right.



## Molecular Orbital theory Predicts the Electron Configurations of Diatomic Molecules



(a)  
Lithium to nitrogen



(b)  
Oxygen and fluorine

Figure 6.9 Molecular orbital energy-level schemes for homonuclear diatomic molecules of the first row of the periodic table.

- To make our theory more quantitative, we can define a quantity called bond order by the equation:

$$\text{bond order} = \frac{\left( \begin{array}{c} \text{number of} \\ \text{electrons in} \\ \text{bonding orbitals} \end{array} \right) - \left( \begin{array}{c} \text{number of} \\ \text{electrons in} \\ \text{antibonding orbitals} \end{array} \right)}{2} \quad (9.1)$$

- A bond order of  $\frac{1}{2}$  indicates a one-electron bond (one-half of an electron pair); a bond order of 1 indicates a single bond (one pair of electrons); a bond order of 2 indicates a double bond (two pairs of electrons); and so on.

Table 9.1 summarizes the properties of the molecular species,  $\text{H}_2^+$ ,  $\text{H}_2$ ,  $\text{He}_2^+$ , and  $\text{He}_2$ .

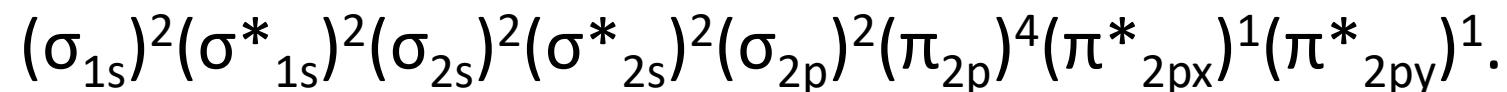
**TABLE 9.1** Molecular properties of  $\text{H}_2^+$ ,  $\text{H}_2$ ,  $\text{He}_2^+$ , and  $\text{He}_2$

Species	Number of electrons	Ground state configuration	Bond order	Bond length/pm	Bond energy/aJ
$\text{H}_2^+$	1	$(\sigma_{1s})^1$	$\frac{1}{2}$	106	0.423
$\text{H}_2$	2	$(\sigma_{1s})^2$	1	74	0.724
$\text{He}_2^+$	3	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	$\frac{1}{2}$	108	0.400
$\text{He}_2$	4	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	not observed	not observed

- ❖ *Bonding MOs produce charge buildup between the nuclei, whereas antibonding MOs produce charge depletion between the nuclei. Hence removal of an electron from a bonding MO usually decreases  $D_e$  (dissociation energy), whereas the removal of an electron from an antibonding MO increases  $D_e$ .*
- ❖ Note that **as  $R_e$  decreases, the energies of bonding MOs decrease**, while the energies of antibonding MOs increase.
- ✓ For example, the highest filled MO in  $\text{N}_2$  is bonding, and in going from the ground state of  $\text{N}_2$  to that of  $\text{N}_2^+$  the dissociation energy decreases (and the bond length increases).
- ✓ In contrast, the highest filled MO of  $\text{O}_2$  is antibonding, and in going from  $\text{O}_2$  to  $\text{O}_2^+$  the dissociation energy increases (and  $R_e$  decreases).
- The designation of bonding or antibonding is not relevant to the effect of the electrons on the total energy of the molecule. Energy is always required to ionize a stable molecule, no matter which electron is removed. Hence *both bonding and antibonding electrons in a stable molecule decrease the total molecular energy.*

- One of the *most impressive aspects of molecular orbital theory is its ability to predict that oxygen molecules are paramagnetic*. This property means that oxygen is weakly attracted to a region between the poles of a magnet.
- Most substances are **diamagnetic**, meaning that they are slightly repelled by a magnetic field.
- Let's see how the paramagnetism of O<sub>2</sub>(g) is related to its electron structure.
- The **Lewis formula** of an O<sub>2</sub> molecule does not account for the paramagnetism of O<sub>2</sub>(g). According to the octet rule, we should write the Lewis formula of an O<sub>2</sub> molecule as ::, but this formula **implies incorrectly** that **all the electrons are paired**.
- The oxygen molecule is **an exception to the utility of Lewis formulas**, whereas the more fundamental molecular orbital theory is able to account successfully for the distribution of the electrons in molecular oxygen.

- Each oxygen atom has eight electrons; thus, an O<sub>2</sub> molecule has a total of 16 electrons.
- When the 16 electrons are placed according to the molecular orbital diagram given in Figure 9.11, the last two go into the π\*<sub>2p</sub> orbitals. As in the atomic case, we apply Hund's rule.
- Because the two π\*<sub>2p</sub> orbitals have the same energy (degenerate), we place one electron in each π\*<sub>2p</sub> orbital such that the two electrons have unpaired spins, as shown in Figure 9.11.
- The ground state electron configuration of an O<sub>2</sub> molecule is:



- According to Hund's rule, each π\*<sub>2p</sub> orbital is occupied by one electron and the spins are unpaired, we get a **triplet** term. By Hund's rule this is the ground term.

- Therefore, *an oxygen molecule has a net electron spin and so acts like a tiny magnet*. Thus, O<sub>2</sub>(g) is attracted into a region between the poles of a magnet.
- This explanation of the paramagnetism of O<sub>2</sub> was one of the early triumphs of MO theory.
- The amount of oxygen in air can be monitored by measuring its paramagnetism. *Because oxygen is the only major component of air that is paramagnetic*, the measured *paramagnetism of air is directly proportional to the amount of oxygen present*. Linus Pauling developed a method using the paramagnetism of oxygen to monitor oxygen levels in submarines and airplanes in World War II.
- The *highly reactive nature of molecular oxygen* as compared to N<sub>2</sub> can be rationalized as resulting from *the readiness of the two π\* electrons, unpaired and in different regions of space, to find additional bonding partners in other molecules*.

## Spin Barriers

The magnetic properties of O<sub>2</sub> are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> in an exothermic reaction. ***Fortunately*** for us, however, ***this reaction is very, very slow***. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O<sub>2</sub> with organic compounds to give H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> would require that at least one of the electrons on O<sub>2</sub> change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a ***spin barrier***.

- Note, the bond order for the  $O_2$  molecule is  $(8 - 4)/2 = 2$ , and we say that a bond order of **2 is equivalent to a double bond**.
- If an electron is removed from an oxygen molecule, the species  $O_2^+$  results, and the **electron removed comes from the highest occupied orbital, which is a  $\pi^*$**  (antibonding) orbital. The bond order for  $O_2^+$  is  $(8 - 3)/2 = 2.5$ , which is higher than that of the  $O_2$  molecule; **removing the one electron actually gives us a more stable species**. *Because of this, it is not at all unreasonable to expect there to be some reactions in which an oxygen molecule reacts by losing an electron to form  $O_2^+$ , the dioxygenyl cation.*
- Of course, such a reaction **would require the reaction of oxygen with a very strong oxidizing agent**. One such oxidizing agent is  $PtF_6^-$ , which contains platinum in the +6-oxidation state.
- The reaction with oxygen can be written as
  - $PtF_6 + O_2 \rightarrow O_2^+ + PtF_6^-$ .

- ***This constitutes a very good test of our model of bonding and antibonding orbitals.*** Although this reaction shows the formation of  $O_2^+$ , in the same way, it is also possible to add one electron to the  $O_2$  molecule to produce  $O_2^-$ , the ***superoxide*** ion, or two electrons to form  $O_2^{2-}$ , the ***peroxide*** ion.
- Adding an electron to  $O_2$  results in a weakening of the bond, as evidenced by the lower bond energy of  $O_2^-$ . The bond energy in this ion is not known, but the length of the bond is greater, and this is indicative of a lower bond energy. These two ***dioxygen ions***, by the way, are highly reactive and can be observed only in the gas phase.
- In each case, the electrons are added to the antibonding  $\pi^*$  orbitals, which reduces the bond order from the value of 2 in the  $O_2$  molecule.
- For  $O_2^-$  the bond order is 1.5, but it is only 1 for  $O_2^{2-}$ , the peroxide ion.
- The O–O bond energy in the peroxide ion has a strength of only  $142\text{ kJ}\cdot\text{mol}^{-1}$  and, as expected, most peroxides are very reactive compounds.
- The superoxide ion is produced by the reaction:  $K + O_2 \rightarrow KO_2$

## Heteronuclear Diatomic Molecules

- Molecular orbital theory can also be applied to **heteronuclear diatomic molecules** (diatomic molecules in which the two atoms are different).
- A heteronuclear diatomic molecule is a diatomic molecule formed from atoms of *two different elements*; two examples are CO and HCl. Heteronuclear diatomic ions, such as CN<sup>-</sup>, are also important in chemistry.
- *In order to sketch the one-electron MO diagrams for heteronuclear diatomics, some understanding of the relative energies of the combining AOs must be known* in advance in order to determine which AOs are close enough in energy to form linear combinations where the MO wavefunction is not simply that of a single AO.
- The *ordinary energy-level scheme* can be used *if the atomic numbers of the two atoms in the molecule differ by only one or two atomic numbers*.

➤ The ground state electron configurations of the following three species are:



with bond orders of  $\frac{1}{2}$ , 3, and  $\frac{1}{2}$ , respectively. Thus, we predict that a CO molecule has the shortest bond, which is correct.

Homonuclear	$1\sigma_g$	$1\sigma_u^*$	$2\sigma_g$	$2\sigma_u^*$	$1\pi_u$	$3\sigma_g$	$1\pi_g^*$	$3\sigma_u^*$	....
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Heteronuclear	$1\sigma$	$2\sigma$	$3\sigma$	$4\sigma$	$1\pi$	$5\sigma$	$2\pi$	$6\sigma$	....
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## ❖ Criteria for Covalent Interactions

- **Symmetry Criterion:** If there is a combination of atomic orbitals with bonding and the antibonding interactions that do not cancel out then there is a bonding interaction.
- **Overlap Criterion:** The better the atomic orbitals overlap the stronger the covalent interaction.
- **Energy Criterion:** The closer the atomic orbitals in energy the stronger the covalent interaction.

### □ The Overlap Criterion

- Let us now look at each criterion in more detail. Let us start with the one we can probably most easily understand, the overlap criterion. The greater the overlap the greater the covalent interaction. The overlap can be estimated according to three rules.
- **Rule 1: Distance**
- The first rule says that the overlap is the greater the smaller the distance between the two orbitals. This means that a small distance between the orbital leads to a strongly bonding and a strongly anti-bonding orbital, respectively while a large distance leads to a weakly bonding and a weakly anti-bonding orbital. When the distance is small then there is a large energy

- difference between the bonding and the anti-bonding molecular orbital, when the distance is large then the energy difference is small (Figure 3.7A.6).

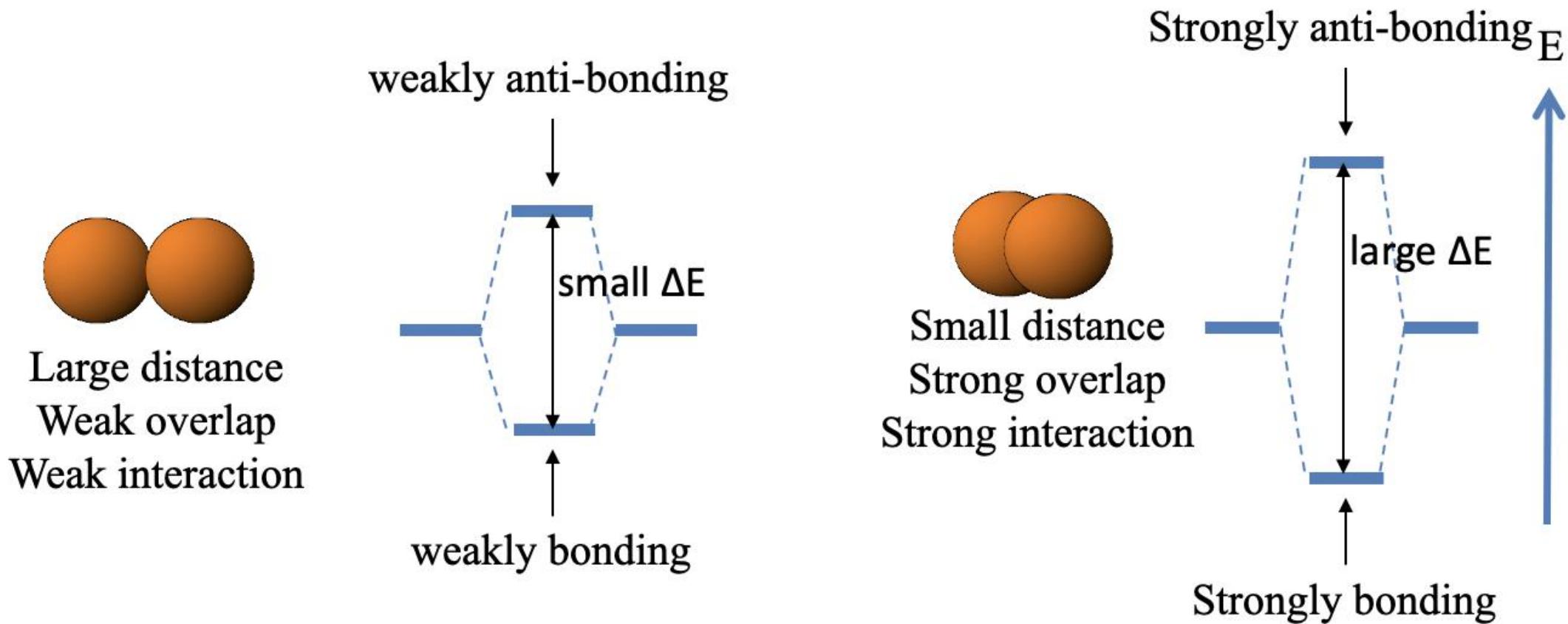


Figure 3.7A.6 The effect of the distance between atomic orbitals on the energy difference of the resulting molecular orbitals.

## Rule 2: Size

➤ Rule 2 states that a large diffuse orbital tends to overlap better (interact more strongly) with another orbital when this orbital is also a large diffuse orbital. A small, less diffuse orbital tends to interact more strongly with another small orbital. If we combine a large orbital with a small orbital however, then this typically does not lead to good overlap and thus weak interaction. We can qualitatively understand this by looking at the image below (Figure 3.7A.7).

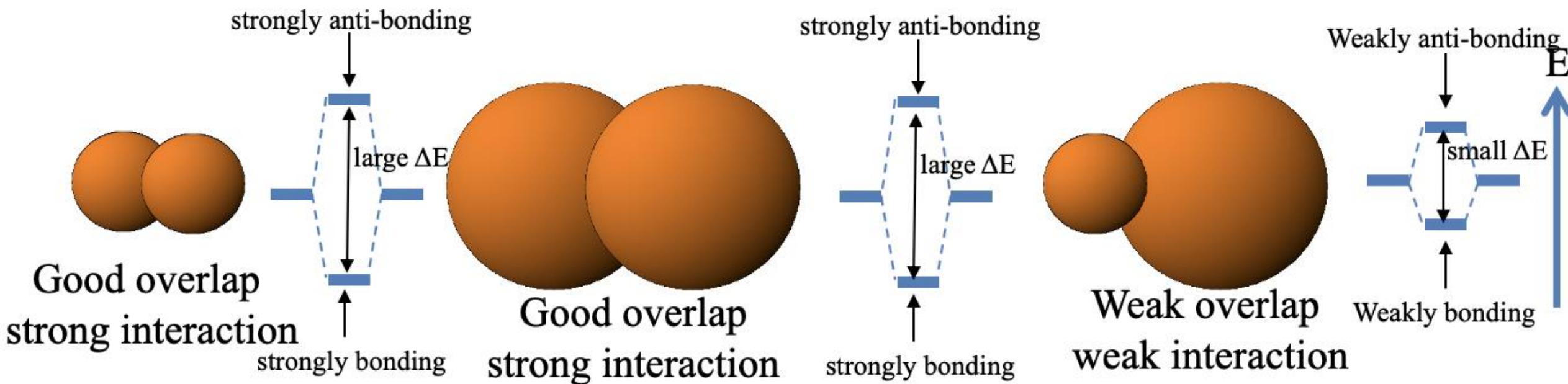


Figure 3.7A.7 Relationships between orbital size and covalent interactions.

- Only a small volume fraction of the large orbital can overlap with the small orbital due to the small size of the small orbital. Due to that small overlap the bonding orbital is only weakly bonding, and the anti-bonding is only weakly anti-bonding. The energy difference between the bonding and the anti-bonding MO is small. In the other two cases, the bonding orbitals tend to be strongly bonding, and the anti-bonding ones strongly anti-bonding. The energy differences between the MOs tend to be large.

### Rule 3: Orientation

- Rule 3 says that orbitals that overlap in  $\sigma$ -fashion tend to interact more strongly than orbitals that overlap in  $\pi$ -fashion, which interact more strongly than overlap in  $\delta$ -fashion. One can see easily from the image below that two p orbitals that have the same distance d from each other overlap much more when they overlap in  $\sigma$ -fashion compared to  $\pi$ -fashion (Figure 3.7A.8).

This is because in the first case they point toward each other, and the orbital overlap is on the bond axis, while in the latter case they are oriented parallel to each other, and the orbital overlap is above and below the bond axis. This implies that  $\sigma$ -overlap leads to more strongly bonding and anti-bonding orbitals with a larger energy gap between them compared to  $\pi$ -overlap and  $\pi$ -overlap leads to more strongly bonding and anti-bonding orbitals compared to  $\delta$ -overlap.

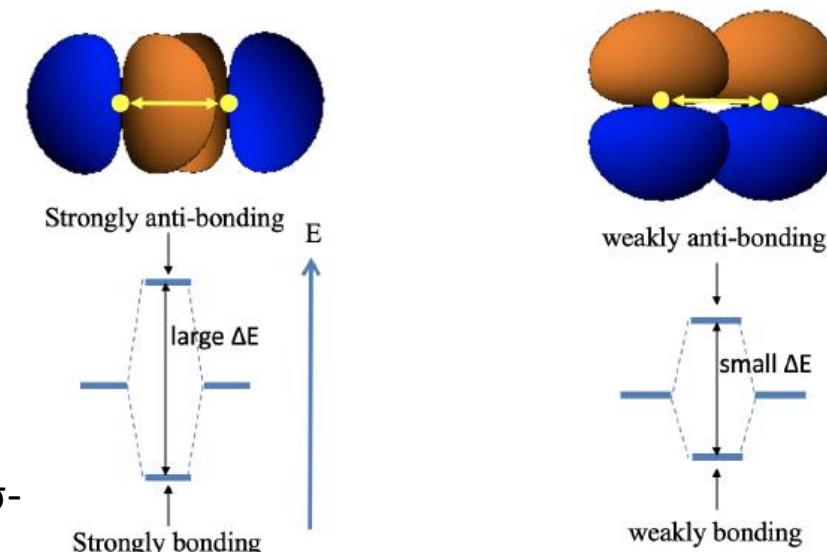


Figure 3.7A.8 Visual representation of orbitals overlapping in  $\sigma$ -fashion vs orbitals overlapping in  $\pi$ -fashion

## The Energy Criterion

- The energy criterion states that ***the covalent interaction between atomic orbitals is larger the smaller the energy difference is between the atomic orbitals.*** We can understand this qualitatively when considering that orbitals are waves, and waves of similar energy interfere more significantly with each other than waves with different energies. Just imagine two waves with very different wavelengths associated with very different energies. Would they interfere effectively? No, they wouldn't. Rather, two waves with very similar wavelengths would interfere better. Because greater energy difference means less interaction, molecular orbitals that result from the interaction of two atomic orbitals with large energy difference are much more similar in shape, size, and location compared to molecular orbitals that result from atomic orbitals with similar energy.
- The greatest covalent interaction is expected when the energy between the two orbitals is exactly the same. This is only possible when two, same orbitals A of the two same atoms overlap. In this case we form a perfect covalent bond with electrons exactly equally shared between the orbitals. The maximum of the amplitude of the bonding molecular orbital is exactly in the middle between the two atoms. Electrons the bonding (or antibonding) MO are equally shared between the atoms (Figure 3.7A.9).

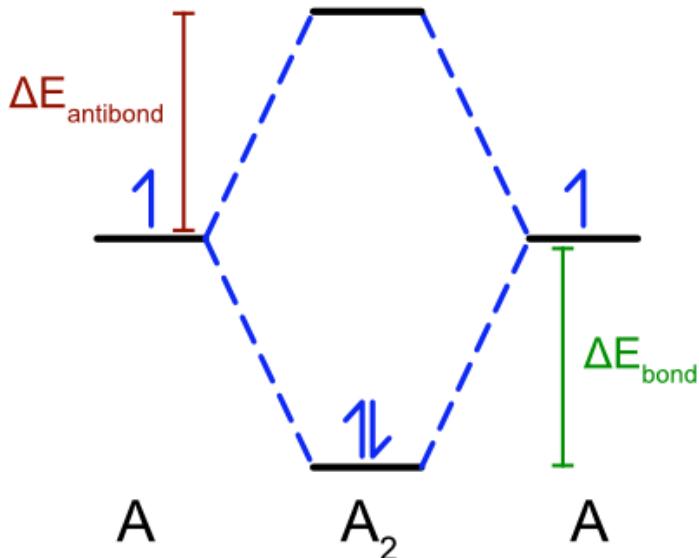


Figure 3.7A.9 Covalent interaction occurring when the energy between the two atomic orbitals is exactly the same.

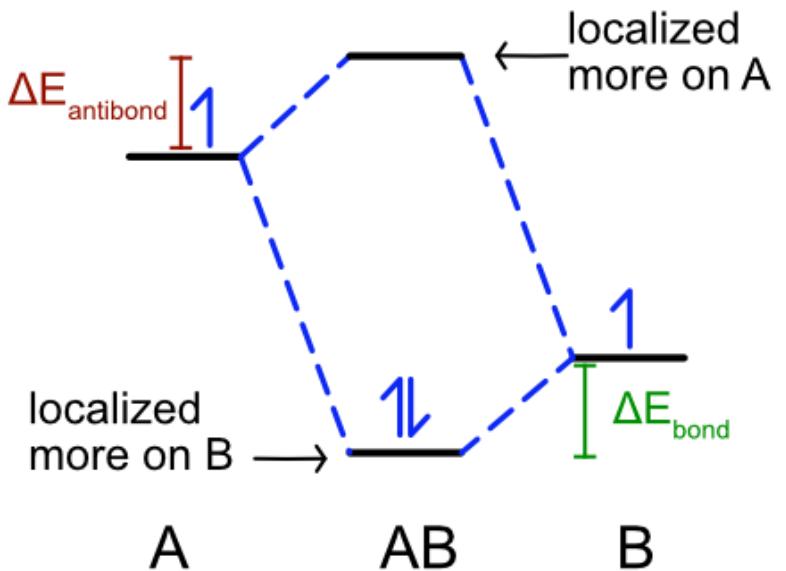


Figure 3.7A.10 An example of covalent interaction occurring when the energy between the two atomic orbitals is somewhat different

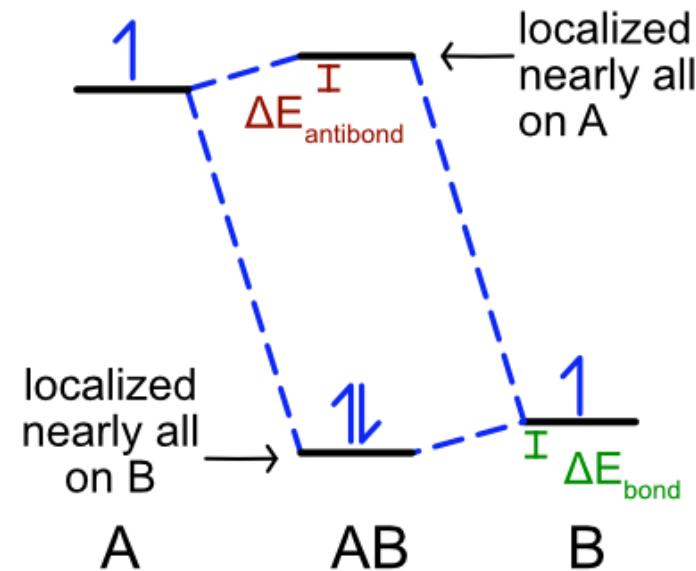


Figure 3.7A.11 Covalent interaction occurring when the energy difference between two atomic orbitals is very large.

- Now let us make the energy of the two atomic orbitals somewhat different. Because they are different we denote the atomic orbitals A and B now, whereby we choose the energy of orbital A to be somewhat higher than that of orbital B. Overlap between the atomic orbital still produces covalent interaction yielding a bonding and an anti-bonding molecular orbital. However, the energy difference of the molecular orbitals to the two atomic orbitals is no longer the same. The antibonding MO is now closer to the atomic orbital with the higher energy, and the bonding MO is now closer in energy to the atomic orbital with the lower energy. This has another consequence. The bonding molecular orbital is now localized primarily at atom A, and the anti-bonding orbital is located primarily at atom B. An electron in the bonding MO is now primarily localized at atom B. This means the bond is a polar covalent bond which is polarized toward atom B (Figure 3.7A.10).
- Now let us make the energy difference between the two atomic orbitals of the atoms A and B very large (Figure 3.7A.11). In this case, the bonding MO is energetically very close to the atomic orbital of atom B, and is localized almost exclusively at atom B. Actually, the bonding MO closely resembles the atomic orbital of atom B in shape, size and localization. In other words, the atomic orbital of B has hardly changed due to the very weak covalent interaction resulting from the large energy difference between the atomic orbitals. Vice versa, the antibonding orbital is energetically very close to the atomic orbital of atom A, and is localized

almost completely at atom A. The antibonding MO is very close to the atomic orbital in shape, size, and location. Due to the weak covalent interaction, there is almost no change to the atomic orbital of A.

- Another conclusion that we can draw is that bonding electrons are located closer to the atom with the atomic orbital of lower energy, and antibonding electrons are located closer to the atoms with the atomic orbital of higher energy. Orbital energy is correlated with electronegativity. For orbitals of the same type and the same elements, orbitals with higher electronegativity have lower energy. For example, a 2s orbital of fluorine has a lower energy than a 2s orbital of oxygen because the electronegativity of fluorine is higher. Bonding electrons are therefore located primarily at the more electronegative atom, while anti-bonding electrons are located primarily at the less electronegative atom. When there are enough anti-bonding orbitals occupied it is possible that the overall polarity in the molecule is such that the dipole moment points toward the more electro-positive atom. An example is carbon monoxide which is slightly polarized toward the carbon atom. We will discuss the MO diagram of the carbon monoxide in detail later.

## The Symmetry Criterion

- Lastly, let us look at the symmetry criterion. The symmetry criterion tells us if a covalent interaction between orbitals is possible based on the relative orientation of the orbitals. Only if the bonding and antibonding interactions do not cancel out, a bonding interaction is possible, and we can construct molecular orbitals from atomic orbitals. Bonding and antibonding interactions cancel out when positive and negative interferences due to orbital overlap are exactly equal. This can be determined by inspection of orbital overlap.
- For example, let us look at the orbital overlap between the 1s orbitals of hydrogen and the 2pz orbital of oxygen in the water molecule (Figure 3.7A.12)

➤ In the water molecule the orbitals are oriented to each other in a specific way because of the bent structure of the water molecule. Due to the bent structure of the water molecule the 1s orbitals overlap differently with the two lobes of the  $2p_z$  molecule. The lobe that points downward overlaps more strongly than the lobe that points upward and the two lobes have different phases. Now we choose the phases of 1s orbitals so that bonding is maximized. We can see that the overlap of the 1s with the  $2p_z$  orbital produces more constructive than destructive interferences. This is equivalent to saying that bonding and anti-bonding interactions do not cancel out. Therefore, the symmetry is “right”, we can construct molecular orbitals from this combination of atomic orbitals.

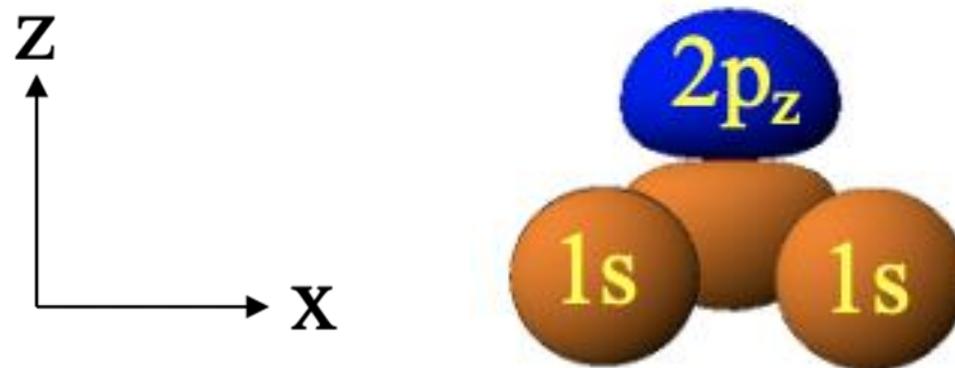
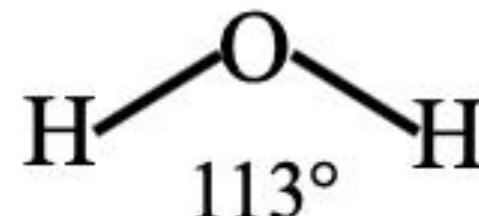
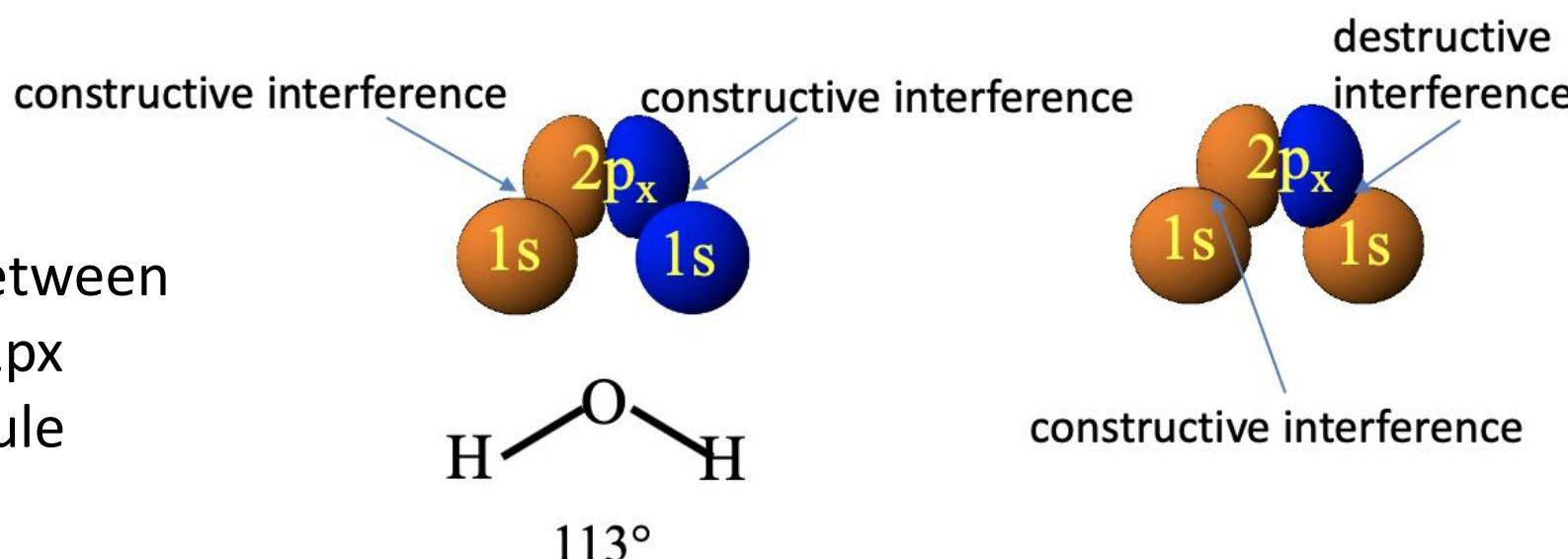


Figure 3.7A.12 The orbital overlap between the 1s orbitals of hydrogen and the  $2p_z$  orbital of oxygen in the water molecule.



➤ ***Can the  $2p_x$  orbital of oxygen also combined with the 1s orbitals of the hydrogen atom to form molecular orbitals?*** The  $2p_x$  orbital is oriented differently relative to the 1s orbitals in the  $\text{H}_2\text{O}$  molecule (Figure 3.7A.13). In this case, we must choose ***the phases of the two 1s orbitals to be different so that bonding interactions are possible.*** The bonding and the antibonding interactions only do not cancel out if the left 1s orbital has the same phase as the left lobe of the  $2p_x$  orbital and the right 1s orbital has the same phase as the right lobe of the  $2p_x$  orbital. If, for instance, we chose both 1s orbitals to be the same phase then the bonding interactions between the left lobe and the left 1s orbital would be canceled out by the equally strong anti-bonding interactions between the right lobe and the right 1s orbital. Overall, we see however, that if we select the phase of the 1s orbitals appropriately then the symmetry is “right” and we can create molecular orbitals from the atomic orbitals.

Figure 3.7A.13 The orbital overlap between the 1s orbitals of hydrogen and the  $2p_x$  orbital of oxygen in the water molecule shown in two different orientations



➤ What about the interactions between the 1s orbitals and the 2p<sub>y</sub> orbital (Figure 3.7A.14)?

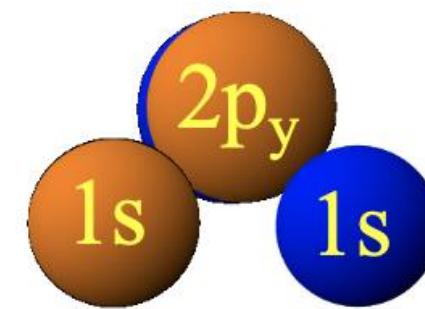
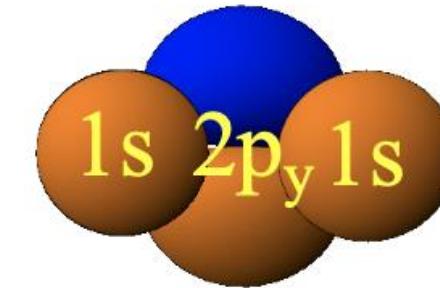
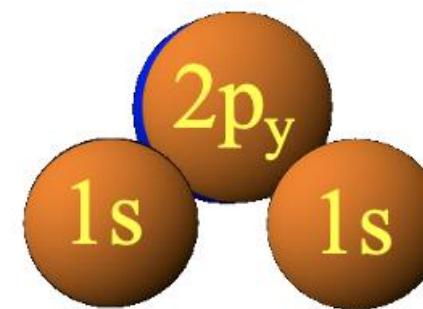
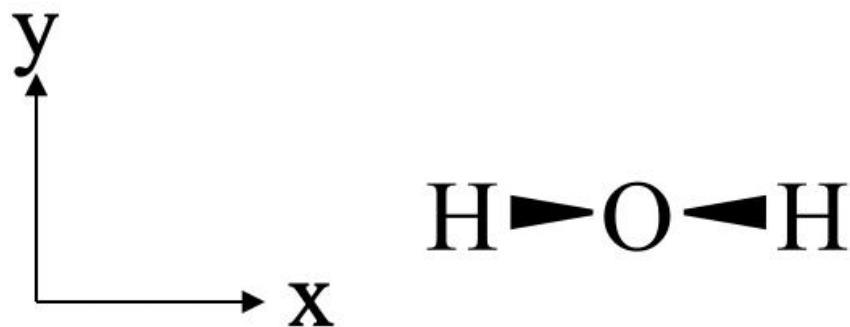
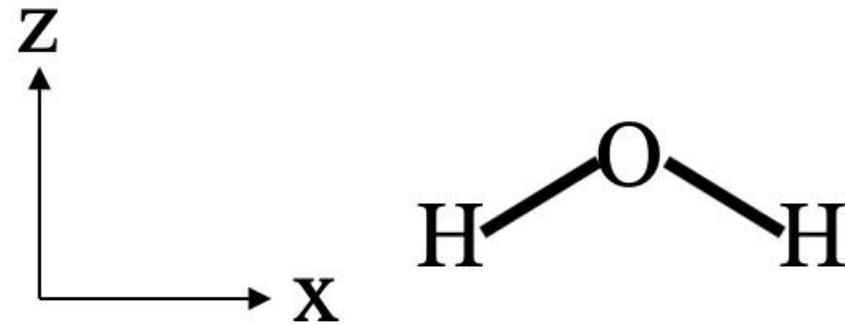


Figure 3.7A.14 The orbital overlap between the 1s orbitals of hydrogen and the 2p<sub>y</sub> orbital of oxygen in the water molecule shown in two different orientations

➤ In this case, the two 1s orbitals are in the plane of the page and the  $2p_y$  orbital stands perpendicular to it. That makes the 1s orbitals overlap equally with both lobes of the  $2p_y$  orbital. Because the two lobes of a  $2p_y$  orbital must have different phases, the constructive and the destructive interferences will cancel out, no matter how we chose the phases of our 1s orbitals. That means ***there is no possibility to create orbital overlap*** in which bonding and anti-bonding interactions do not cancel out. Therefore, we cannot produce molecular orbitals from a combination of 1s and  $2p_y$  orbitals. The  **$2p_y$  must remain non-bonding**. You may be able to see the cancellation of the bonding and antibonding orbital overlap better if you choose your coordination system differently. Let us have the y-axis point up, and the x-axis point right (Figure 3.7A.9, bottom). Now we look at the  $H_2O$  molecule from the bird perspective, and the  $2p_y$  orbital is oriented vertically. The 1s orbitals are still on the x-axis. You can see the overlap between the 1s orbitals and the  $2p_y$  orbital more clearly now. No matter how we choose the phase of our orbitals, the bonding and the anti-bonding interactions cancel out.

- We have seen thus far that it is possible to decide about “right” and “wrong” symmetries by inspection, but this is not trivial. Generally, the more complex a molecule gets the more difficult it is to decide about “right” and “wrong” symmetry.
- One should use group theory as a tool to help decide about “right” and “wrong” symmetry for orbital overlap in more complex molecules.
- In this course we will limit our discussion of molecular orbital theory to cases where we can determine symmetry by visual inspection only.

## ☐ MOT and Polar bonds

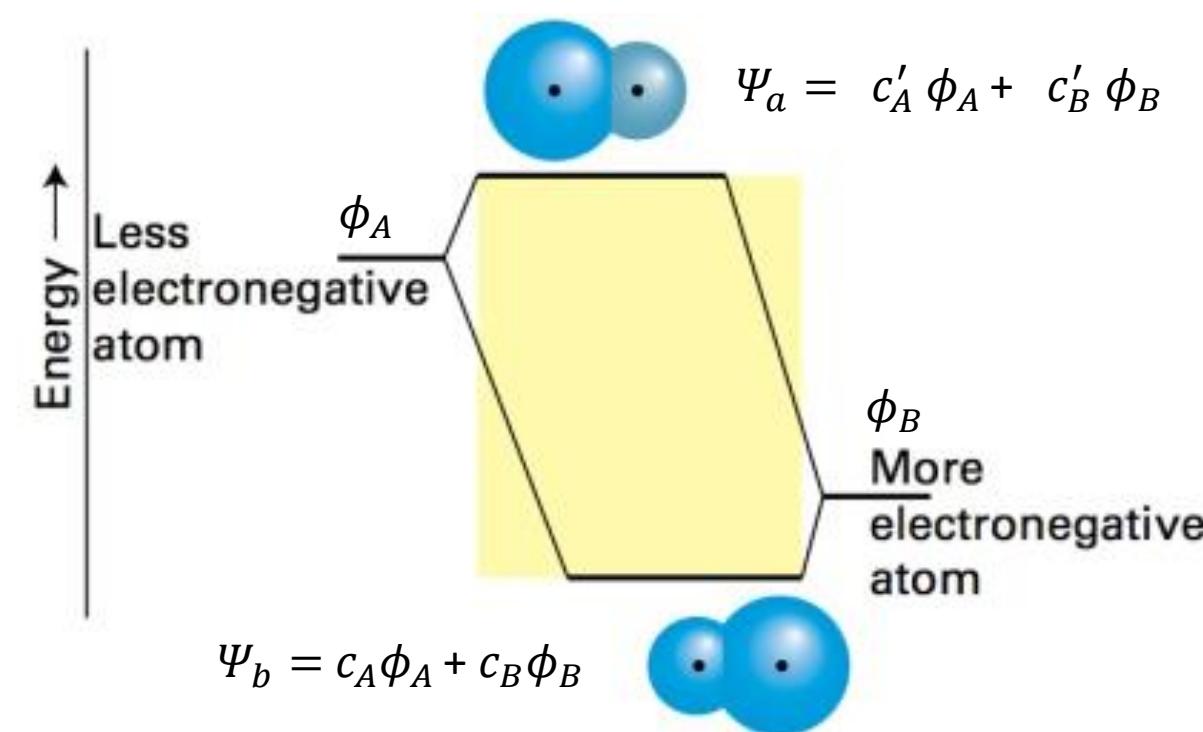
- In a **heteronuclear species** the electron distribution between the atoms is not symmetrical because it is energetically favorable for a bonding electron pair to be found closer to one atom rather than the other. This imbalance results in a **polar bond**, which is a covalent bond in which the electron pair is shared unequally by the two atoms.
- Molecular orbital theory takes polar bonds into their stride. A polar bond consists of two electrons in an orbital of the form  $\psi = c_A \psi_A + c_B \psi_B$  A general LCAO (1)
- with  $c_B^2$  not equal to  $c_A^2$ .
- If  $c_B^2 > c_A^2$ , the electrons have a greater probability of being found on B than on A and the molecule is **polar** in the sense  ${}^{\delta+}A-B{}^{\delta-}$ .
- A **nonpolar bond**, a covalent bond in which the electron pair is shared equally between the two atoms and there are zero partial charges on each atom, has  $c_B^2 = c_A^2$ .
- A **pure ionic bond**, in which one atom has obtained virtually sole possession of the electron pair (as in  $Cs^+F^-$ , to a first approximation), has one coefficient zero (so that  $A^+B^-$  would have  $c_A^2 = 0$  and  $c_B^2 = 1$ ).

□ It will be familiar from introductory chemistry that the unequal sharing of electrons is related to the **electronegativity**,  $\chi$  (chi), of an element, its power to draw electrons to itself when it is part of a compound. ***A general feature of molecular orbitals between dissimilar atoms is that the atomic orbital with the higher electronegativity makes the larger contribution to the lower energy molecular orbital.*** The opposite is true of the orbital with higher energy (the antibonding orbital), for which the principal contribution comes from the atomic orbital with higher energy (the less electronegative atom):

- ✓ Bonding orbitals: for  $\chi_B > \chi_A$ ,  $c_B^2 > c_A^2$
- ✓ Anti bonding orbitals: for  $\chi_B > \chi_A$ ,  $c_B'^2 < c_A'^2$

Figure 1 shows a schematic representation of this point.

Fig. 1 A schematic representation of the relative contributions to bonding and antibonding molecular orbitals of atoms of different electronegativities (energies). In the bonding orbital, the more electronegative atom makes the greater contribution (represented by the larger sphere), and the electrons of the bond are more likely to be found on that atom. The opposite is true of an antibonding orbital. A part of the reason why an antibonding orbital is of high energy is that the electrons that occupy it are likely to be found on the less electronegative atom.

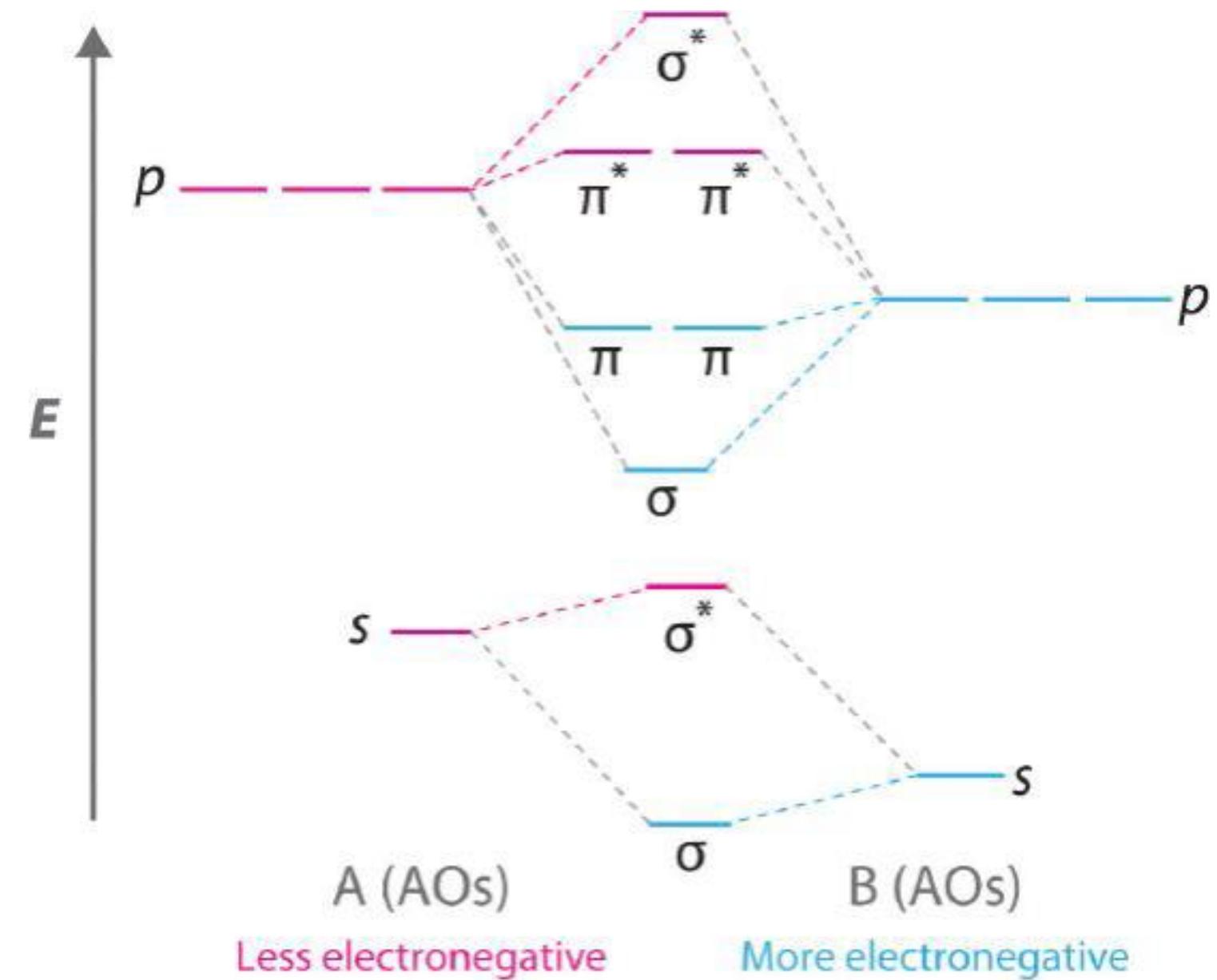


- A molecular orbital energy-level diagram is *always skewed toward the more electronegative atom.*

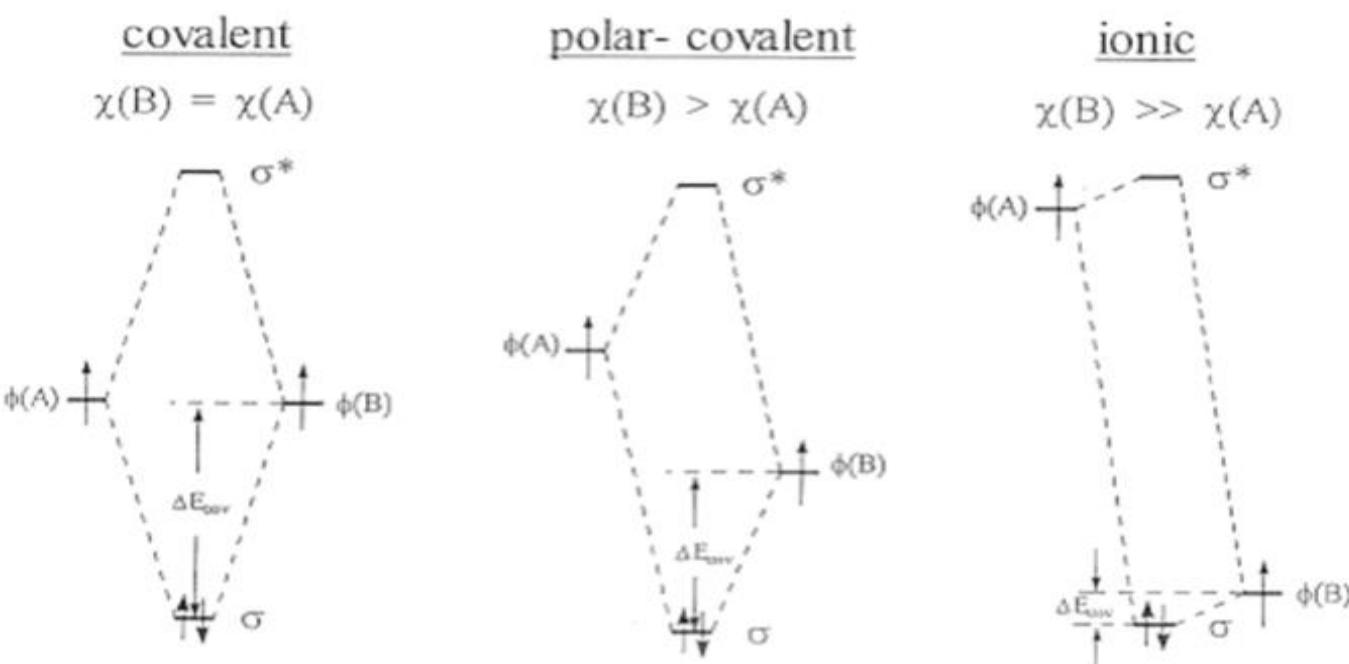
Figure 10.8.4: Molecular Orbital Energy-Level Diagram for a *Heteronuclear Diatomic Molecule AB, where  $\chi_B > \chi_A$ .*

The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom.

Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. *On average, they are closer to the B atom, resulting in a polar covalent bond.*



# MO Description of A-B Covalent, Polar-Covalent, and Ionic Bonds

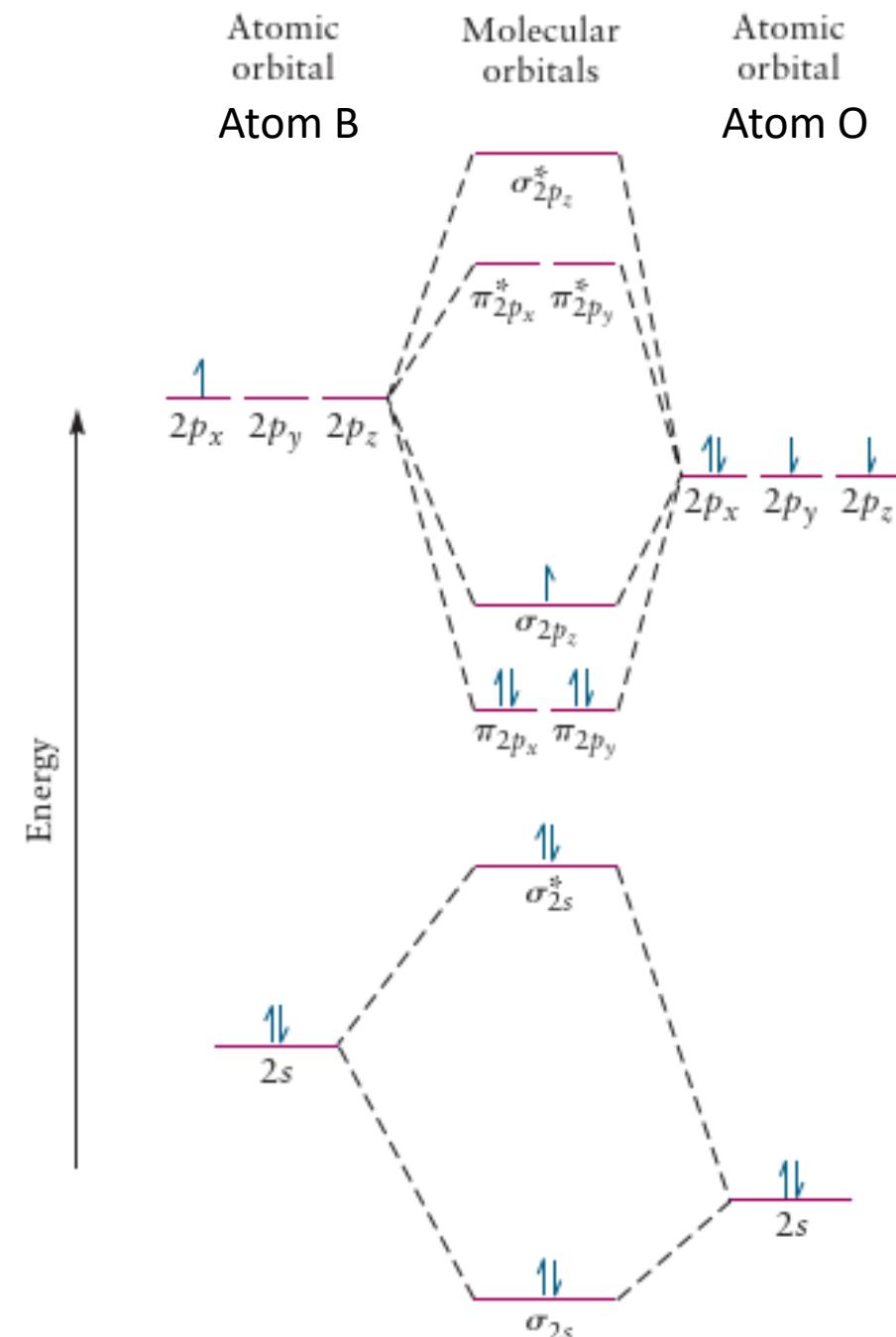


## Key Features:

- 1) The diatomic MO's are:  $\psi_b(\sigma) = a\phi(A) + b\phi(B)$   
 $\psi_a(\sigma^*) = b\phi(A) - a\phi(B)$
- 2) Since each AO *must be fully utilized*, ( $a^2 + b^2 = 1$ ),
  - i) If  $\chi(B) = \chi(A)$ , then  $b = a$
  - ii) If  $\chi(B) > \chi(A)$ , then  $b > a$
  - iii) If  $\chi(B) \gg \chi(A)$ , then  $b \sim 1$ , and:  
 $\psi_b(\sigma) \sim \phi(B)$ ,  $\psi_a(\sigma^*) \sim \phi(A)$

- To illustrate the differences between homonuclear and heteronuclear diatomic molecules, first we consider **boron monoxide (BO)** molecule.

**FIGURE 6.21** Correlation diagram for heteronuclear diatomic molecule, **boron monoxide (BO)**. The atomic orbitals for the more electronegative atom (O) are displaced downward because they have lower energies than those for B. The orbital filling shown is that for BO.



- Next, we **consider HF molecule** to illustrate the differences between homonuclear and heteronuclear diatomic molecules.
- HF is a **polar molecule** (F atom negative center) and has **3 unshared pairs of electrons**.
- This molecule illustrates the case in which **the valence electrons on the combining atoms occupy different electron shells**: the 1s AO on H and the 2s and 2p AOs on F. The **energies** of the valence electrons in the 2s and 2p atomic orbitals on fluorine are  $-1.477 E_h$  (-40.2 eV) and  $-0.684E_h$  (-18.7 eV), respectively. The energy of the valence electron in the 1s atomic orbital on hydrogen is  $-0.500E_h$  (-13.6 eV).
- *Because the 2p atomic orbitals on fluorine are the closest in energy to the 1s orbital on hydrogen, a first approximation to the molecular orbital would be to consider linear combinations of these two different types of atomic orbitals.*

➤ But which 2p atomic orbital should be used? *Defining the z-axis* as the internuclear axis, Figure 9.18 shows the ***overlap*** of the fluorine 2p<sub>z</sub> and 2p<sub>x</sub> orbitals with the hydrogen 1s orbital.

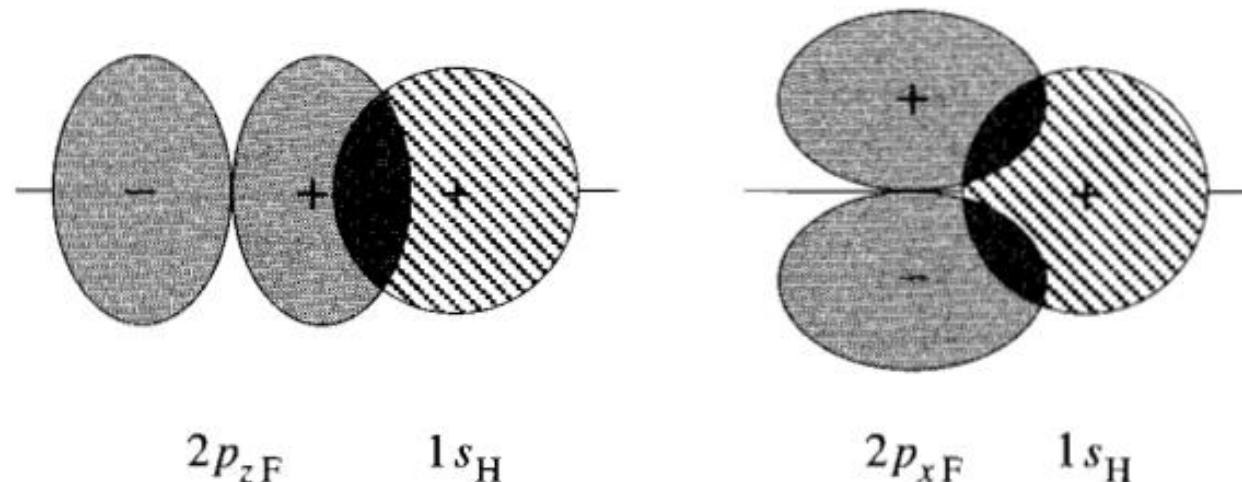


FIGURE 9.18

The overlap of the fluorine 2p<sub>z</sub> and 2p<sub>x</sub> atomic orbitals with the hydrogen 1s atomic orbital. Because of the change in sign of the 2p<sub>x</sub> wave function, the net overlap between the 2p<sub>x</sub> and hydrogen 1s is zero for all internuclear distance. A set of two molecular orbitals result from the overlap of the fluorine 2p<sub>z</sub> atomic orbital and the hydrogen 1s atomic orbital. The bonding  $\sigma$  orbital,  $\sigma_b$ , is the one shown.

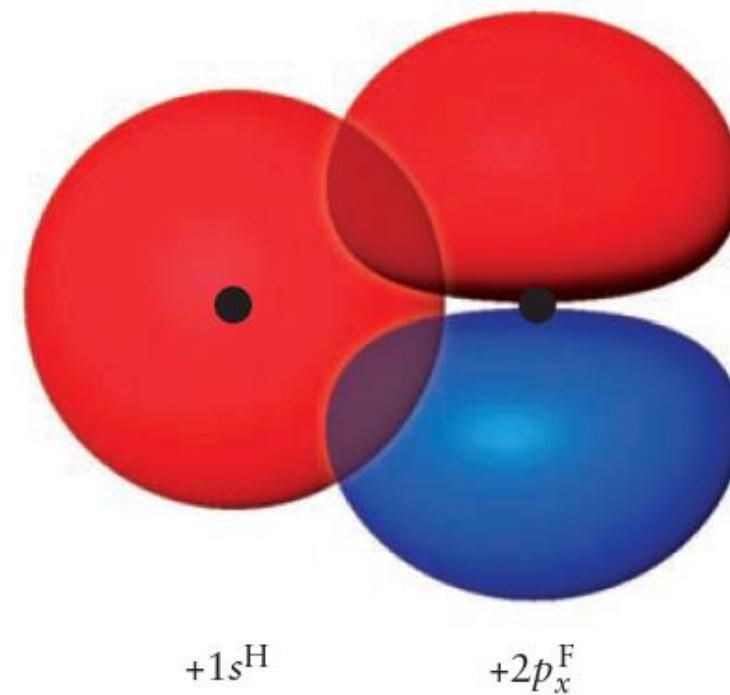


FIGURE 6.22 The H 1s and F 2p<sub>x</sub> (or 2p<sub>y</sub>) orbitals have no net overlap in HF.

- The fluorine  $2p_y$  atomic orbital overlaps the hydrogen 1s atomic orbital in a similar manner as the  $2p_x$  orbital except that it is directed along the y-axis instead of the x-axis.
- *The hydrogen 1s and fluorine  $2p_z$  orbitals overlap constructively, so we can use linear combinations of these two orbitals.* However, because of the change in sign of the wave function for the  $2p_x$  ( $2p_y$ ) atomic orbital with respect to the y-z plane (x-z plane) and the constant sign of the hydrogen 1s atomic orbital, the net overlap between the  $2p_x$  ( $2p_y$ ) on fluorine and the 1s on hydrogen is zero for all internuclear distances.
- Thus, a first approximation to the molecular orbital would be the linear combinations of the fluorine  $2p_z$  and hydrogen 1s atomic orbitals.
- The molecular orbitals are symmetric about the internuclear axis, so both are  $\sigma$  molecular orbitals (one bonding,  $\sigma_b$ , and one antibonding,  $\sigma_a$ ).
- Figure 3.4.8.2 shows the molecular-orbital energy-level diagram for HF. (The  $1s_F$  orbital is not shown.)

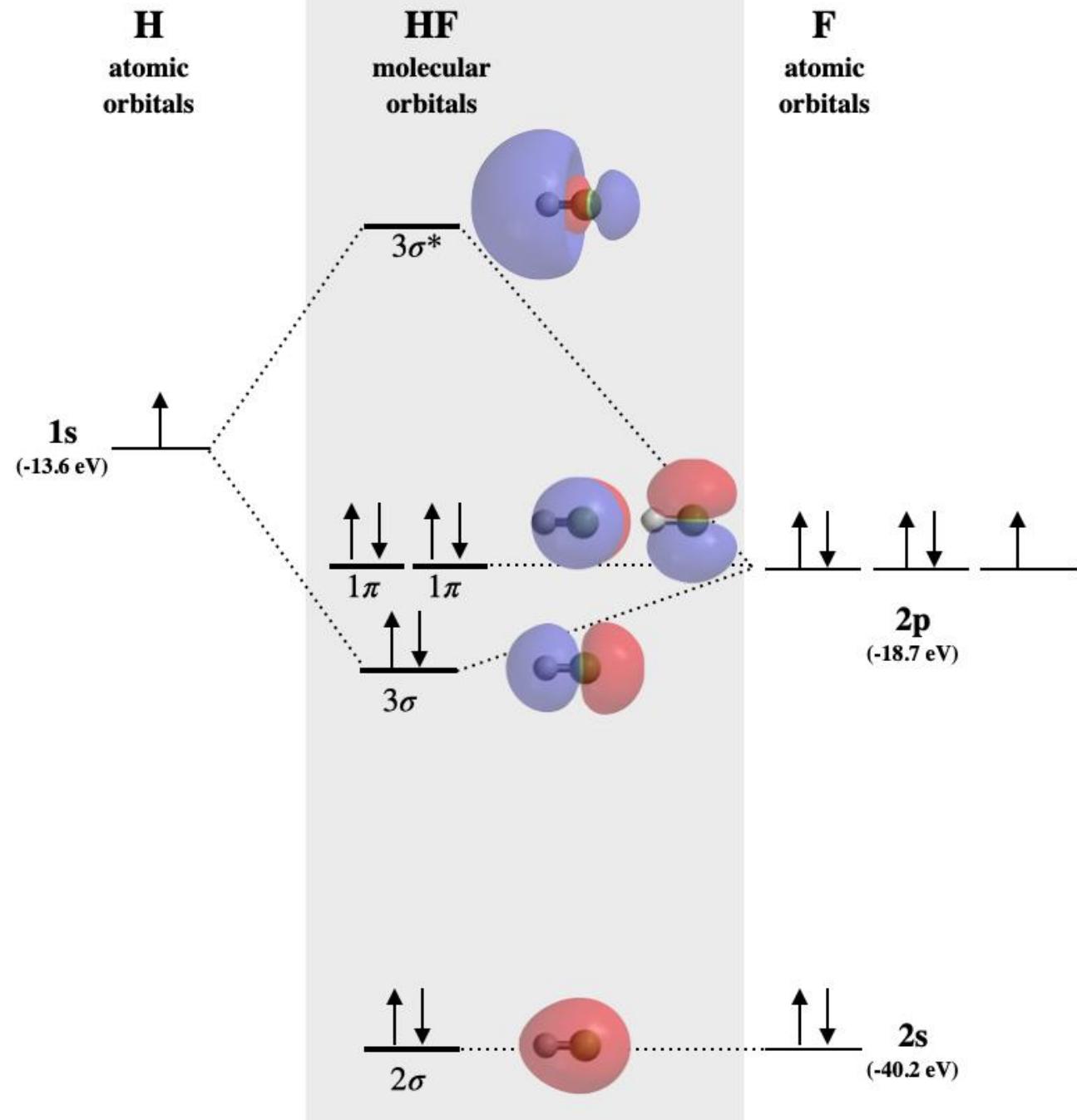


Figure 3.4.8.2: Molecular Orbital diagram of **hydrogen fluoride (HF)**. Molecular orbitals calculated using Spartan software.

The five valence orbitals available for molecular orbital formation are the 1s orbital of H and the 2s and 2p orbitals of F; there are  $1 + 7 = 8$  valence electrons to accommodate in the five molecular orbitals that can be constructed from the five basis orbitals.

- The  $1\sigma$  bonding orbital is predominantly F2s in character as the energy difference between it and the H1s orbital is large. *It is, therefore, confined mainly to the F atom and essentially nonbonding.*
- The  $2\sigma$  orbital is more bonding than the  $1\sigma$  orbital and has both H1s and F2p character.
- The  $3\sigma^*$  orbital is antibonding, and principally H1s in character: the 1s orbital has a relatively high energy (compared with the fluorine orbitals) and hence contributes predominantly to the high-energy antibonding molecular orbital.
- Two of the eight valence electrons enter the  $2\sigma$  orbital, forming a bond between the two atoms. *Six more enter the  $1\sigma$  and  $1\pi$  orbitals; these two orbitals are largely nonbonding and confined mainly to the F atom.* This is consistent with the *conventional model* of *three lone pairs on the fluorine atom.*

- The ***eight valence electrons*** occupy the four lowest energy orbitals in accord with the Pauli Exclusion Principle, so the ***ground-state valence electron configuration*** of HF is :  $(2s_F)^2(\sigma_b)^2(2p_{xF})^2(2p_{yF})^2$ .
- ***Another way*** to write the configuration of the molecule is  $2\sigma^23\sigma^21\pi^4$ .
- The  $2s_F(2\sigma)$ ,  $2p_{xF}$  and  $2p_{yF}$  ( $1\pi$ ) orbitals are ***non-bonding orbitals*** (*almost no change in energy w.r.t. AOs*), so the **bond order** of HF is **one**.
- ***One important feature to note*** is that ***all the electrons occupy orbitals that are predominantly on the F atom***. It follows that we can expect the ***HF molecule to be polar, with a partial negative charge on the F atom***, which is found experimentally.

The calculated molecular orbital energy diagram for HF is shown in Figure 12.22. The AOs on the two atoms that give rise to the MOs are shown on the right side of the diagram, with the size of the orbital proportional to its coefficient in the MO. Numerical calculations show that the 1s electrons are almost completely localized on the F atom.

The  $1\pi$  electrons are completely localized on the F atom because the  $2p_x$  and  $2p_y$  orbitals on F have a zero net overlap with the 1s orbital on H. **Electrons in MOs localized on a single atom are referred to as *nonbonding electrons*.** The mixing of 2s and 2p AOs in the  $3\sigma$  and  $4\sigma^*$  MOs changes the electron distribution in the HF molecule somewhat when compared with a homonuclear diatomic molecule. **The  $3\sigma$  MO has less bonding character and the  $4\sigma^*$  MO has less antibonding character.** Note that the total bond order is approximately one because the  $2\sigma$  MO is largely localized on the F atom, the  $3\sigma$  MO is not totally bonding, and the  $1\pi$  MOs are completely localized on the F atom. The MO energy diagram depicts the MOs in terms of their constituent AOs.

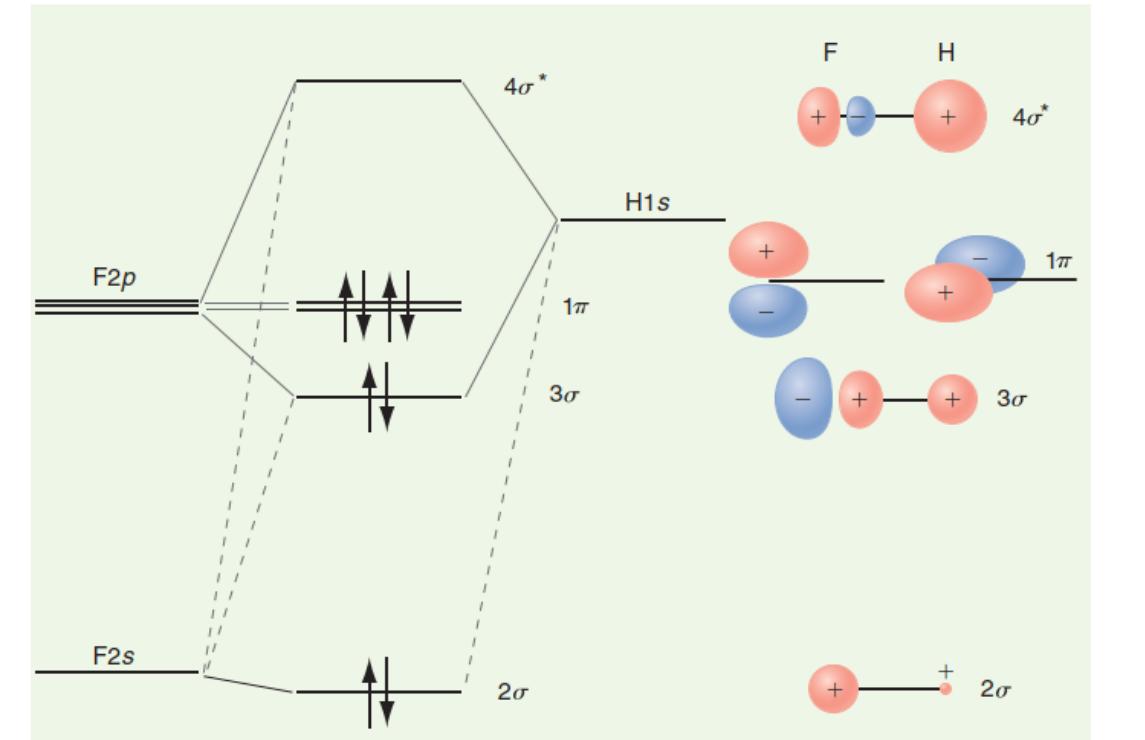


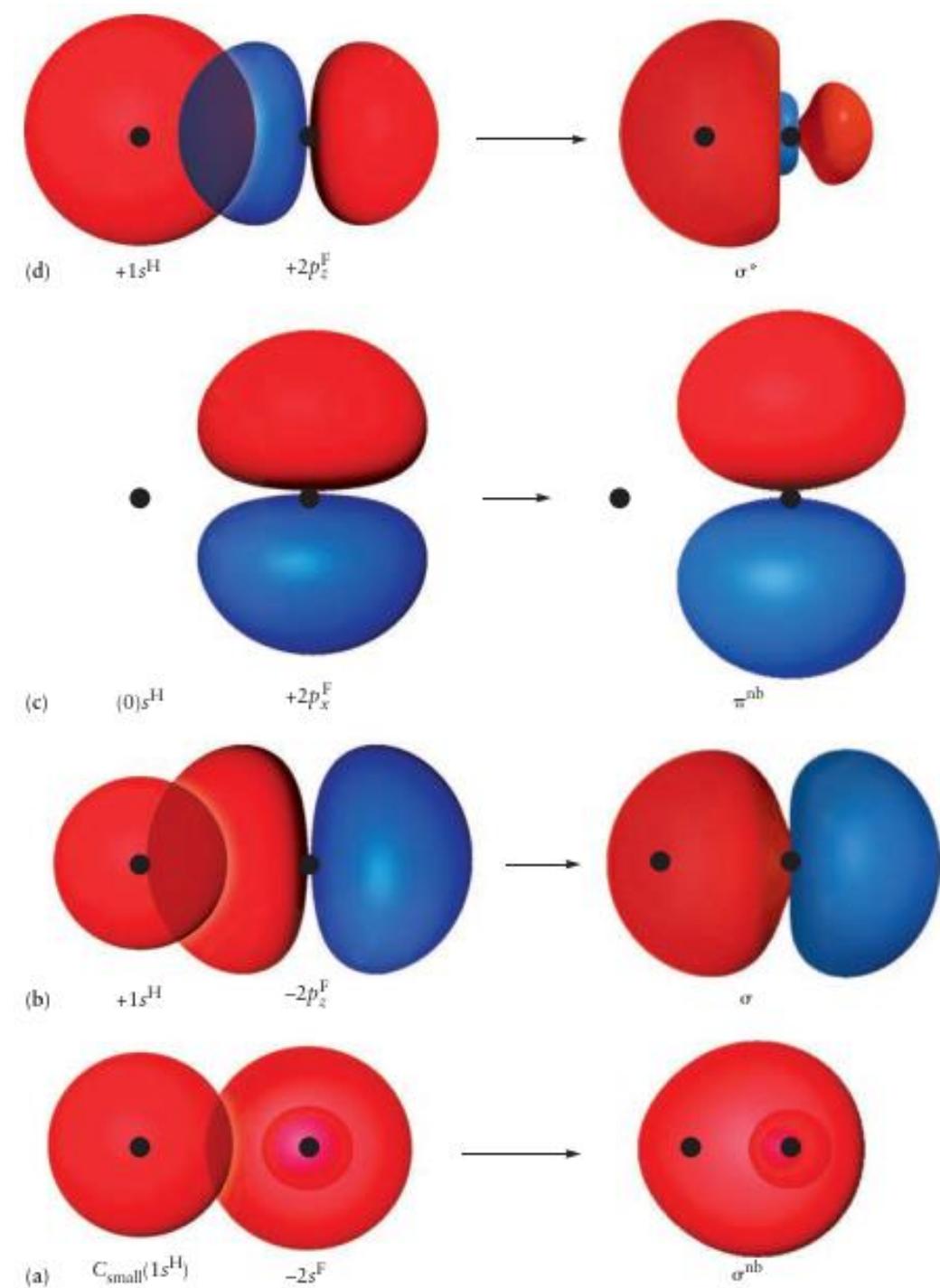
FIGURE 12.22 Schematic energy diagram (Correlation diagram) showing the relationship between the atomic and molecular orbital energy levels for the valence electrons in HF. The degenerate p and  $\pi$  orbitals are shown slightly offset in energy. The dominant atomic orbital contributions to the MOs are shown as solid lines. Lesser contributions are shown as dashed lines. The MOs are depicted to the right of the figure. We assign the 1s electrons on F to the  $1\sigma$  MO, which is localized on the F atom.

The  $2s$ ,  $2p_x$ , and  $2p_y$  atomic orbitals of fluorine do not mix with the 1s atomic orbital of hydrogen, and therefore remain *nonbonding*.

FIGURE 6.23 Overlap of atomic orbitals in HF.  
(Note: in the correlation diagram in Figure 6.24 it is assumed that lowest energy orbital is a nonbonding one that looks identical to a 2s orbital on the F atom, with no contribution from the H 1s orbital.)

In the graphical depiction of this orbital in (a) in this figure, a small coefficient multiplies the H 1s orbital in this linear combination; the overlap is negligible.)

(Courtesy of Mr. Hatem Helal and Professor William A. Goddard III, California Institute of Technology, and Dr. Kelly P. Gaither, University of Texas at Austin.)



- ✓ As expected, in the  $\sigma$  bonding orbital the electron density is much greater on the more electronegative fluorine than on the hydrogen.
- ✓ However, in the  $\sigma^*$  antibonding orbital, this **polarity is reversed**. *The estimated dipole moment is smaller in the excited state than in the ground state.*

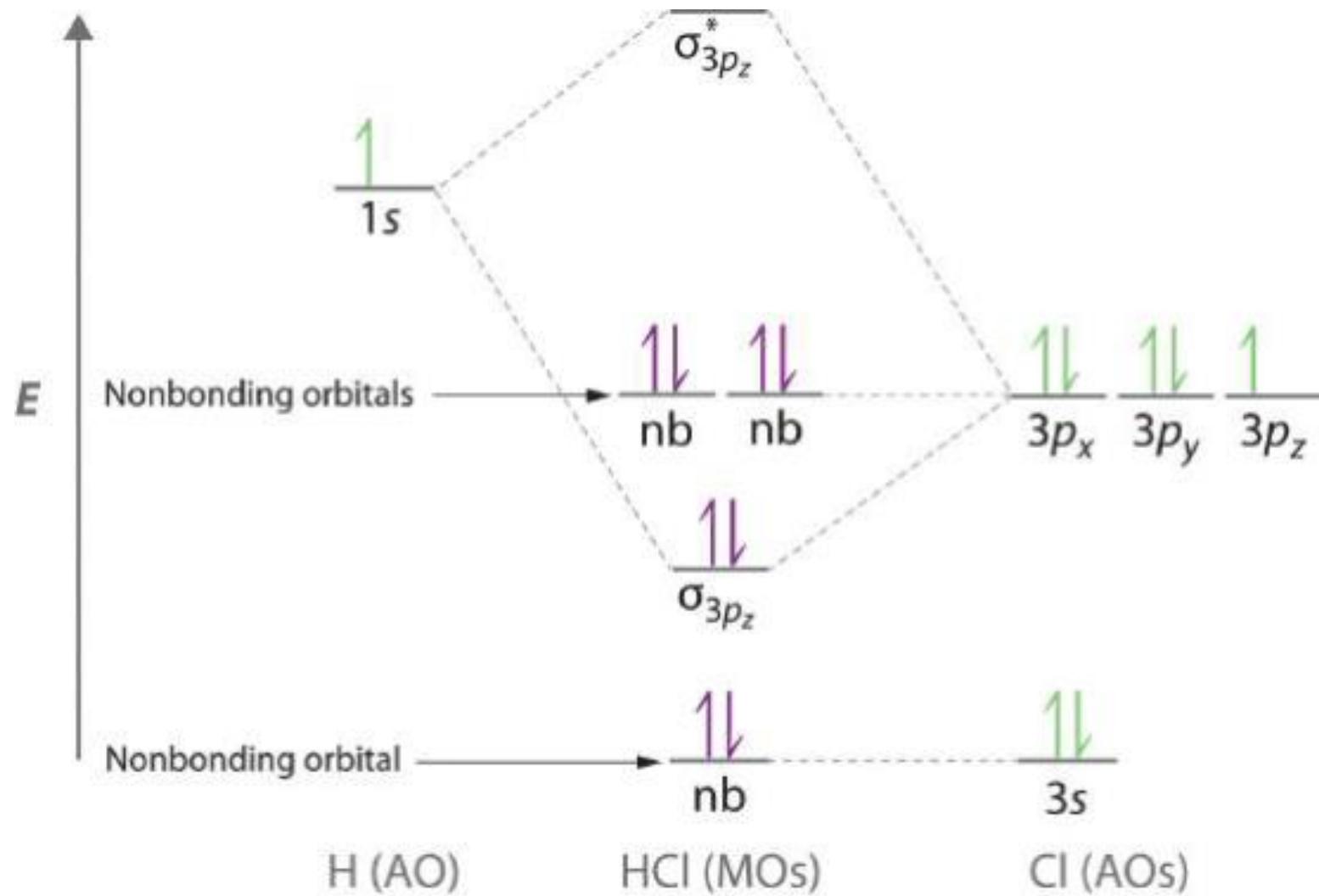
#### **Nonbonding Molecular Orbitals: Unshared or Lone pairs of electrons**

- Molecular orbital theory is also able to explain *the presence of lone pairs of electrons*.
- Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom.
- Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 10.8.6 that the 1s orbital of atomic hydrogen is closest in energy to the 3p orbitals of chlorine.

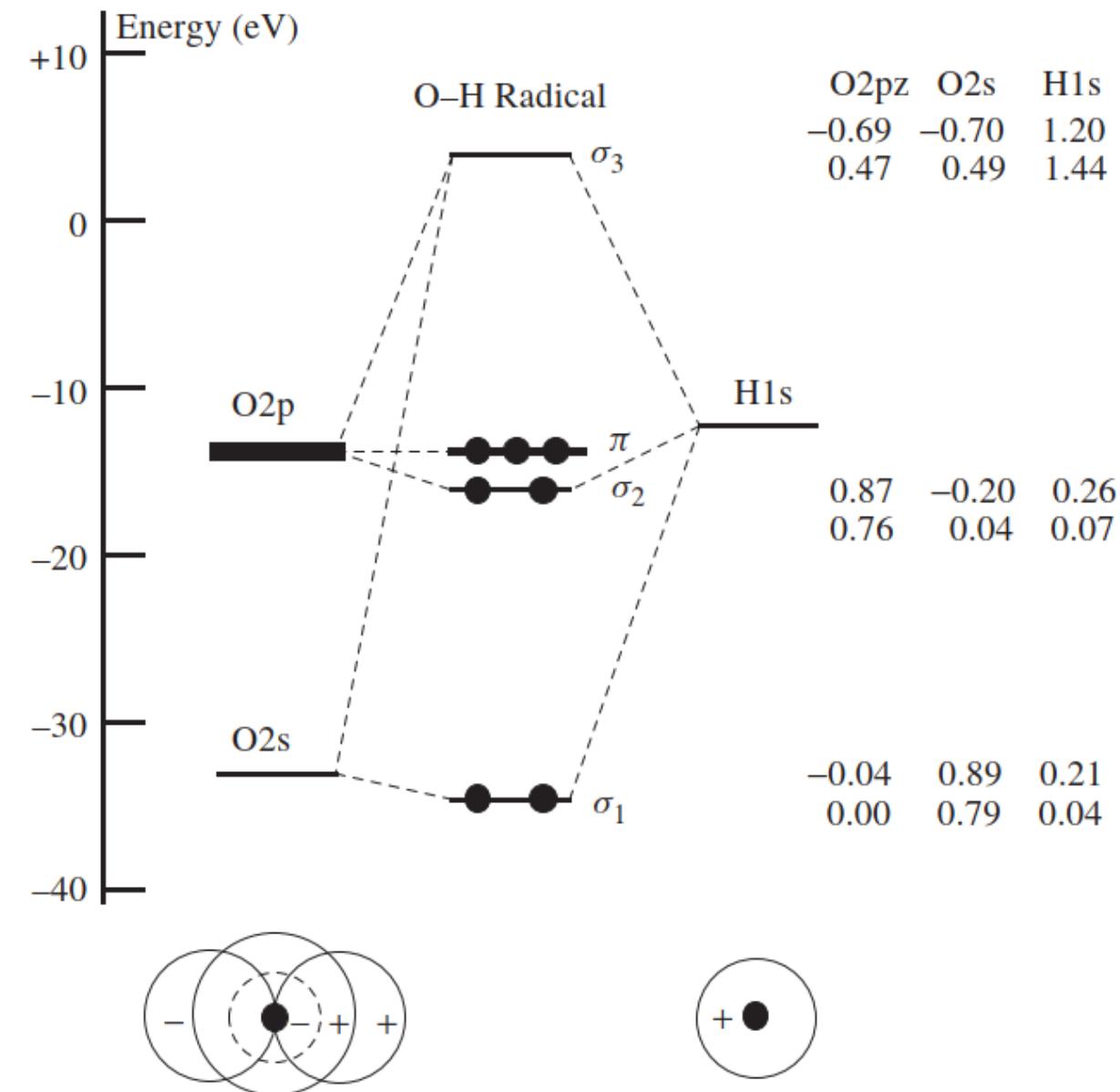
- Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3p orbitals. Of the three p orbitals, only one, designated as  $3p_z$ , can interact with the H 1s orbital.
- The  $3p_x$  and  $3p_y$  atomic orbitals have ***no net overlap*** with the 1s orbital on hydrogen, so they are *not involved in bonding*.
- Because the energies of the Cl 3s,  $3p_x$ , and  $3p_y$  orbitals do not change (significantly) when HCl forms, they are called ***nonbonding molecular orbitals***.
- A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons.
- By definition, electrons in ***nonbonding orbitals have no effect on bond order***, so they are not counted in the calculation of bond order.
- Thus, the predicted bond order of HCl is  $(2 - 0) \div 2 = 1$ .

- Because the  $\sigma$  bonding molecular orbital is closer in energy to the Cl 3p than to the H 1s atomic orbital, the electrons in the  $\sigma$  orbital are concentrated closer to the chlorine atom than to hydrogen. A **molecular orbital approach** to bonding can therefore be used to **describe the polarization of the H–Cl bond** to give  $\text{H}^{\delta+}\text{—Cl}^{\delta-}$ .

Figure 10.8.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the 3p orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding  $\sigma$  orbital is occupied by electrons, giving a bond order of 1.

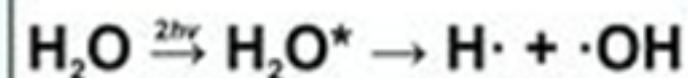


- An **energy-level diagram for O–H radical** calculated for the experimentally observed O–H bond length of 97.0 pm is shown in Figure 6.10.
- On the far right of the figure, the *coefficients of the AOs, i.e.,  $C_1$ ,  $C_2$  and  $C_3$ , for each  $\sigma$  MO are shown*. They tell us how each AO contributes to each MO and the signs also show the bonding or antibonding nature of the MO.
- *Immediately beneath each coefficient its square is entered* because it is the square of the wave function which gives the electron density and the second row of figures therefore reveals how the electrons are distributed in that particular MO; if it contains any.



**Figure 6.10** A molecular orbital energy-level scheme for the OH radical.

## ❖ Energy-level diagram for O–H Radical



- The positive lobe of the oxygen  $2p_z$  orbital is directed towards the hydrogen atom.
- On the right of the diagram the 1s AO of hydrogen is shown at an energy of  $-13.60$  eV. On the left of the diagram, the 2s and 2p AOs of the oxygen atom are plotted at  $-32.30$  eV and  $-14.80$  eV respectively.
- The oxygen 1s AO is not involved in the bonding and does not feature in the diagram.
- In the center of the figure, the calculated energy levels of O–H are shown at  $-33.39$  eV,  $-15.85$  eV,  $-14.80$  eV (doubly degenerate) and  $+6.62$  eV.
- The dots indicate the filling of the available MOs with electrons.

- On the far right of the figure, *the coefficients of the AOs, i.e.,  $C_1$ ,  $C_2$  and  $C_3$ , for each  $\sigma$  MO are shown.* They tell us how each AO contributes to each MO and the signs also show the bonding or antibonding nature of the MO.
- *Immediately beneath each coefficient its square is entered* because it is the square of the wave function which gives the electron density and the second row of figures therefore reveals how the electrons are distributed in that particular MO; if it contains any.
- Let us first consider the MO of lowest energy;  $\sigma_1$ ,  $E = -33.39$  eV. The major contributor with a coefficient of +0.889 is the oxygen 2s AO and hydrogen 1s also plays a part with a coefficient of +0.212. The contribution of oxygen 2p<sub>z</sub> is too small to concern us. Note that ***the orbital is bonding, because the two AO contributors overlap in phase, and of  $\sigma$  type.***
- ✓ We place ***two of our seven electrons in this MO.***

- The MO next in energy ( $\sigma_2$ ,  $E = -15.85$  eV) involves the same three AOs but the oxygen  $2p_z$  now plays by far the most important role.
- Note that the oxygen  $2s$  – hydrogen  $1s$  overlap is antibonding while the oxygen  $2p_z$  – hydrogen  $1s$  overlap is bonding. The last is by far the greater and dominates so that the MO is bonding *in total*.
- ✓ It is important to observe that, *where many AOs are involved, both bonding and antibonding interactions can be found within the same MO.*
- The next two MOs, the degenerate pair of  $\pi$  symmetry at  $E = -14.80$  eV, are ***non-bonding MOs***.
- ✓ The  $\pi$ -type oxygen  $2p_x$  and oxygen  $2p_y$  AOs have zero overlap with the  $\sigma$ -type hydrogen  $1s$  AO and there is no interaction between them. Consequently, these two oxygen  $2p$  AOs are found in the molecule with an unchanged energy of  $-14.80$  eV. *Their AO coefficients are each 1.0.*

- Since seven electrons are available to fill the MOs of O–H (the oxygen 1s electrons being omitted from the diagram), the last three electrons must be placed in these two orbitals, of which one will be only half-full.
- ***The unpaired electron makes the O–H radical paramagnetic and very reactive.***
- ***The highest MO ( $\sigma_3$ ) is very high in energy ( $E = +6.62$  eV) and strongly antibonding in all its overlaps. If electrons find their way into this MO, by absorbing light, for example, the molecule becomes even more reactive.***

- The molecular orbital energy-level diagrams of **heteronuclear** diatomic molecules are ***much harder to predict qualitatively***, and ***we have to calculate each one explicitly because the atomic orbitals contribute differently to each one.***
- Because ***CO is isoelectronic with N<sub>2</sub>***, which undergoes ***orbital mixing, it is likely that the MO diagram for CO will also exhibit mixing***. This result is borne out by the PES (photoelectron spectroscopy) data for CO.
- Because of the relative energies of the C and O AOs, a CO bonding MO, closer in energy to O, has a greater contribution from the O AO, while a CO *antibonding MO, closer in energy to C*, has a greater contribution from the C AO.
- MO diagram of NO molecule is also like that of CO.
- Write the configuration of the ground state of the **cyanide ion, CN<sup>-</sup>**, assuming that its molecular orbital energy-level diagram is the same as that for CO.
- ✓ Calculate the bond order.
- ✓ Could you suggest whether the negative charge is on C or N....??

## MO Diagram of CO

**Key points:** The HOMO of a carbon monoxide molecule is an almost nonbonding  $\sigma$  orbital largely localized on C; the LUMO is an antibonding  $\pi$  orbital.

- ***Why so many compounds are known in which CO is bonded to a d-metal?***
- The molecular orbital energy-level diagram for carbon monoxide is a somewhat more complicated example than HF because both atoms have 2s and 2p orbitals that can participate in the formation of  $\sigma$  and  $\pi$  orbitals. The energy-level diagram is shown in Figs. 2.22 and 2.23.
- *Using the periodic trend that the energies of the 2s and 2p orbitals decrease across the second period, the relative energies of the C and O AOs can be placed on the extreme left and right of the one-electron MO diagram. The C AOs lie at higher energies than those of the O AOs.*

## □ MO Diagram of CO

**Key points:** The HOMO of a carbon monoxide molecule is an almost nonbonding  $\sigma$  orbital largely localized on C; the LUMO is an antibonding  $\pi$  orbital.

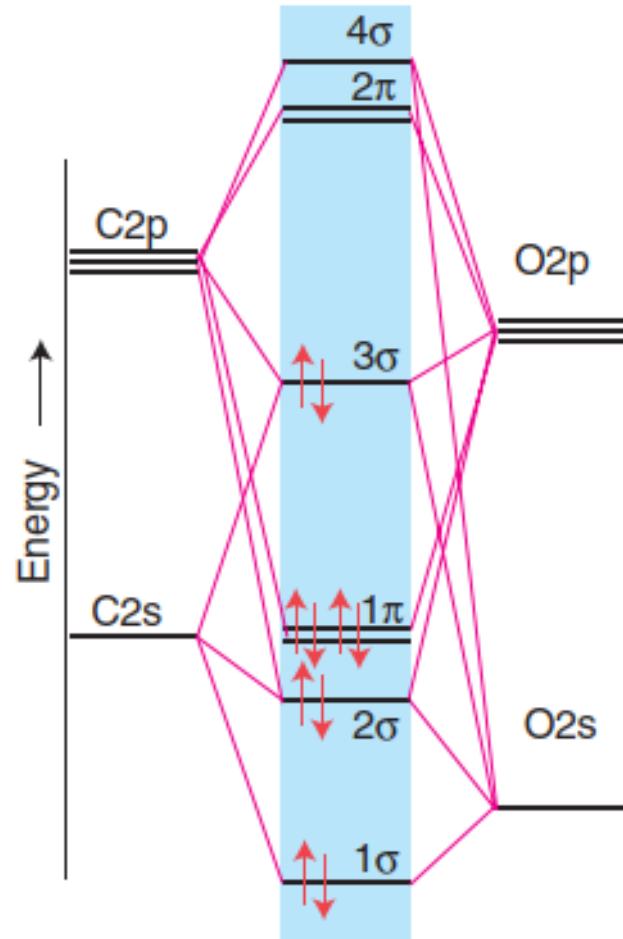


Figure 2.22\* The molecular orbital energy-level diagram for CO.

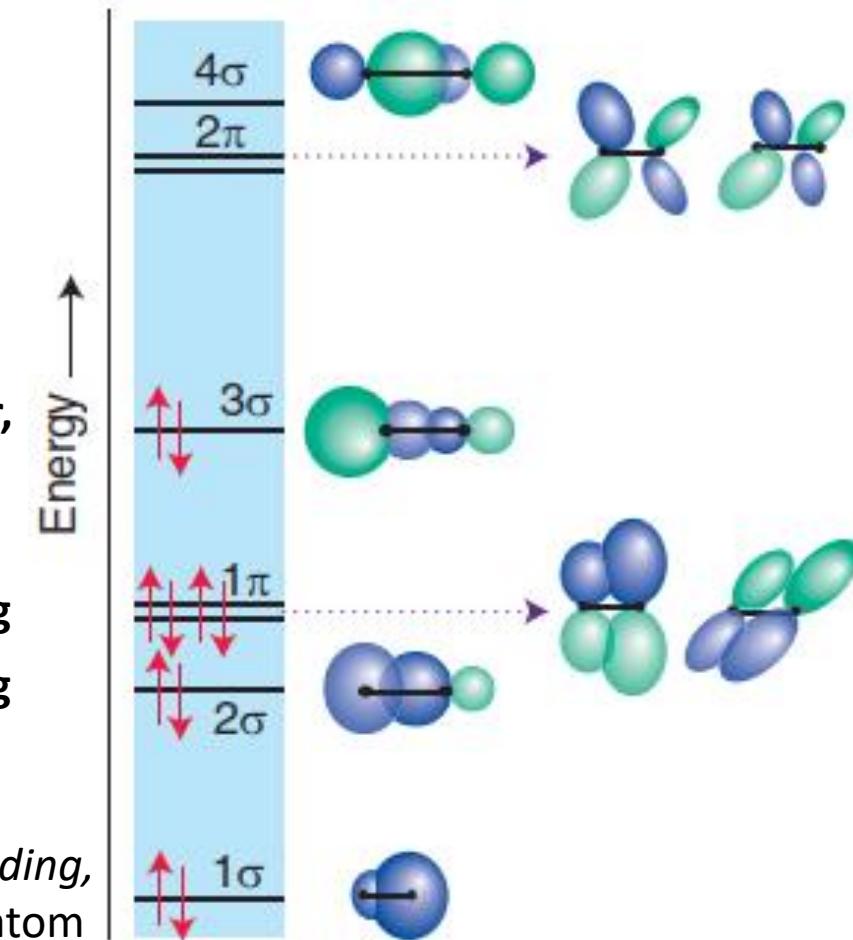
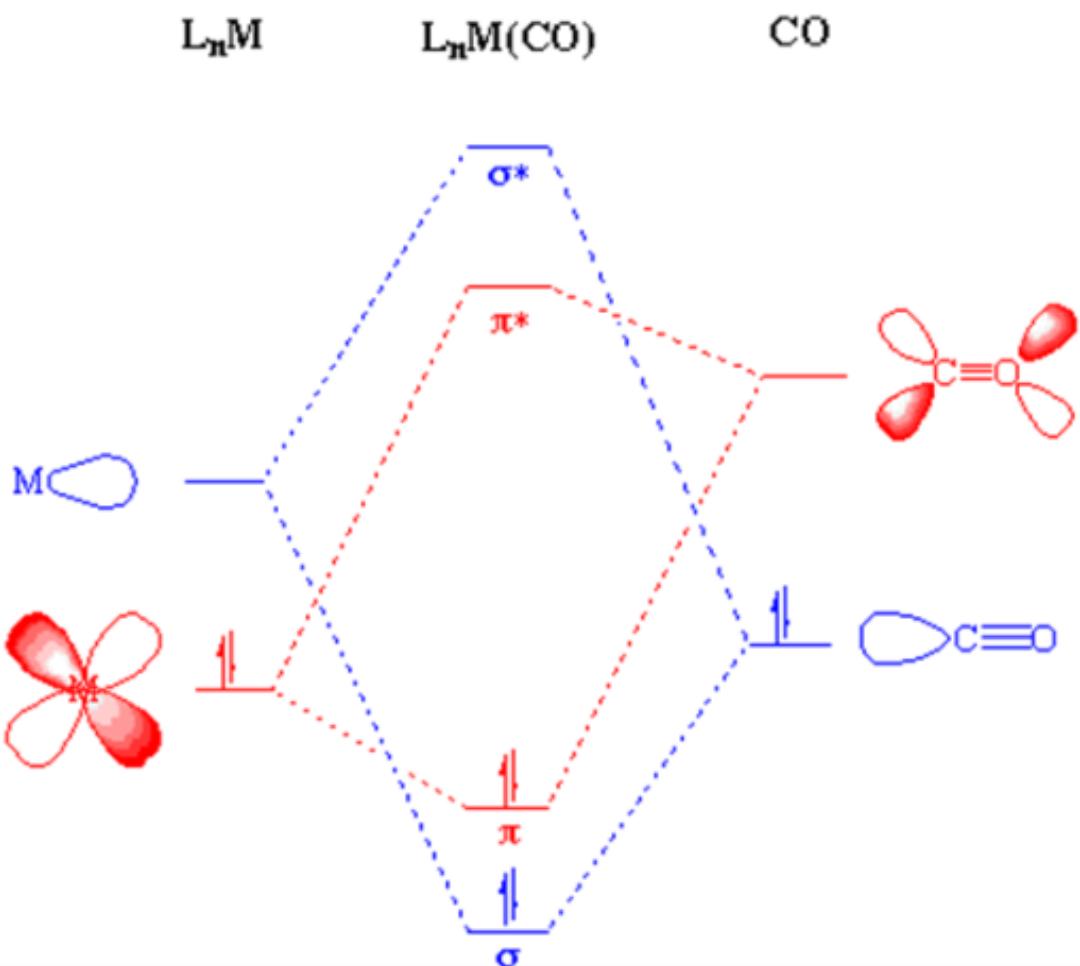
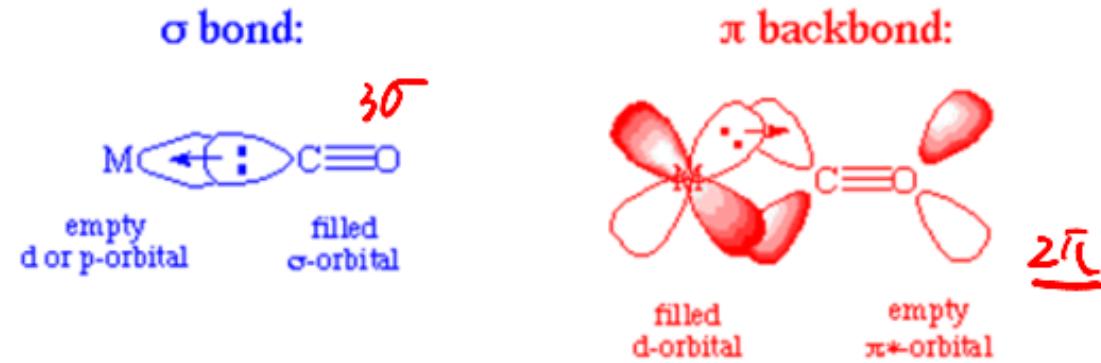


Figure 2.23 A schematic illustration of the molecular orbitals of CO, with the size of the atomic orbital indicating the magnitude of its contribution to the molecular orbital.

- The ground-state configuration is CO:  $1\sigma^2 2\sigma^2 \mathbf{1\pi^4} 3\sigma^2$
- The  $1\sigma$  orbital is localized mostly on the O atom and therefore essentially *nonbonding or weakly bonding*. The  **$2\sigma$  orbital is bonding**. The  $1\pi$  orbitals constitute the doubly degenerate pair of **bonding  $\pi$  orbitals**, with *mainly C $2p$  orbital character*.
- The **HOMO in CO is  $3\sigma$** , which is predominantly C $2p_z$  in character, largely *nonbonding*, and *located on the C atom*.
- The **LUMO is the doubly degenerate pair of antibonding  $\pi$  orbitals**, with mainly C $2p$  orbital character (Fig. 2.23).
- This combination of frontier orbitals—**a full  $\sigma$  orbital largely localized on C and a pair of empty  $\pi$  orbitals**—is one reason **why so many compounds are known in which CO is bonded to a d-metal**. In the so-called d-metal carbonyls, the HOMO lone pair orbital of CO participates in the formation of a  $\sigma$  bond and the LUMO antibonding  $\pi$  orbital participates in the formation of  $\pi$  bonds to the metal atom.

- The HOMO lone pair orbital ( $\sigma$  orbital largely localized on C) of CO participates in the formation of a  $\sigma$  bond.
  - The LUMO antibonding  $\pi$  orbital participates in the formation of  $\pi$  bonds to the metal atom.
  - —reasons *why so many compounds are known in which CO is bonded to a d-metal forming* the so-called d-metal carbonyls.



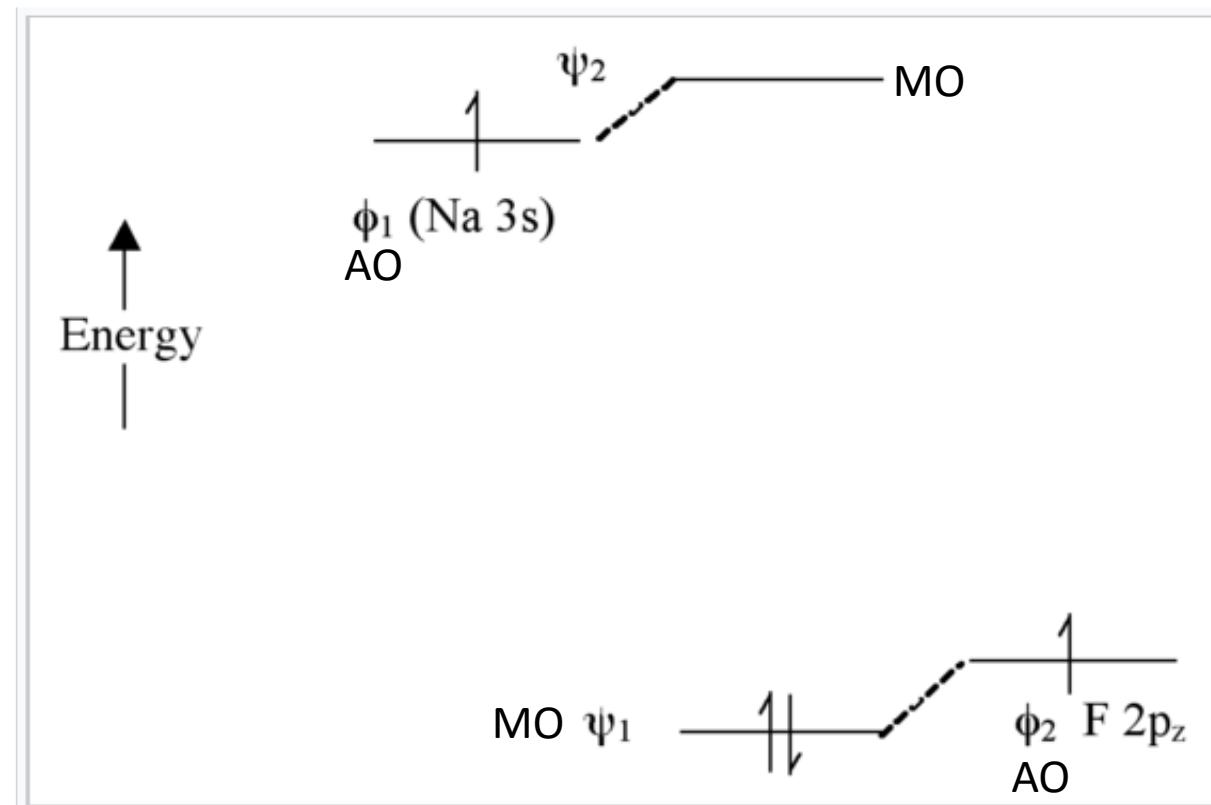
- ***Nonbonding MOs are not counted in the determination of the bond order.*** Thus, ***the overall bond order for CO is 3, consistent with its Lewis structure.***
- It is also consistent with the the **Lewis structure** of CO that has a lone pair of electrons on C and a second lone pair on O.
- Although ***the difference in electronegativity between C and O is large,*** the experimental ***value of the electric dipole moment of the CO molecule (0.1 D,*** where D is a unit of dipole moment, the debye) ***is small.*** Moreover, the ***negative end of the dipole is on the C atom despite that being the less electronegative atom.*** This odd situation stems from the fact that the lone pairs and bonding pairs have a complex distribution. It is wrong to conclude that, because the bonding electrons are mainly on the O atom, O is the negative end of the dipole, as this ignores the balancing effect of the lone pair on the C atom.
- The inference of polarity from electronegativity is particularly unreliable when antibonding orbitals are occupied.

## Extreme case - Ionic bonding (NaF):

In this case, there is not much mixing between the AO's because their energies are far apart (Fig. 2.2.8). ***The two bonding electrons are localized on the F atom*** so that we can write the molecule as  $\text{Na}^+\text{F}^-$ .

Note that if we were to ***excite an electron*** from  $\psi_1$  MO to  $\psi_2$  MO using light, the resulting electronic configuration would be  $(\psi^1\psi^1)$  and we would be  $\text{Na}^0\text{F}^0$ . ***This is called a charge transfer transition.***

**Figure 2.2.8 :** Molecular orbital energy diagram illustrating ionic bonding in the NaF molecule



- In NaCl, the **sodium 3s orbital** (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals.
- The chlorine 3s and 3p<sub>z</sub> orbitals *have compatible symmetry*, yet only the **3p<sub>z</sub>** orbital (-13.8 eV) is **close enough** in energy to interact with the Na 3s; still, the *energy difference is large enough to make bonding weak*.
- The Na 3s orbital combines with Cl 3p<sub>z</sub> to form the molecular orbitals labeled 4σ and 4σ\* in Figure 5.3.2.1. The **4σ orbital is weakly bonding but is very close** in energy to the **Cl 3p<sub>z</sub> orbital** and is **mostly Cl-like in character**.
- Notice that ***all σ orbitals look very much like either s or p orbitals centered on the Cl atom***, while the 4σ\* orbital is **centered almost entirely on Na**.
- The ***lack of molecular orbitals that are distributed over both atoms at once is consistent with a lack of significant covalent bond character*** in NaCl.
- The **bonding here is characterized by the transfer of one electron from Na to Cl and is almost entirely electrostatic**.
- Bonding that is mostly electrostatic in character is non-directional, unlike true covalent bonding.

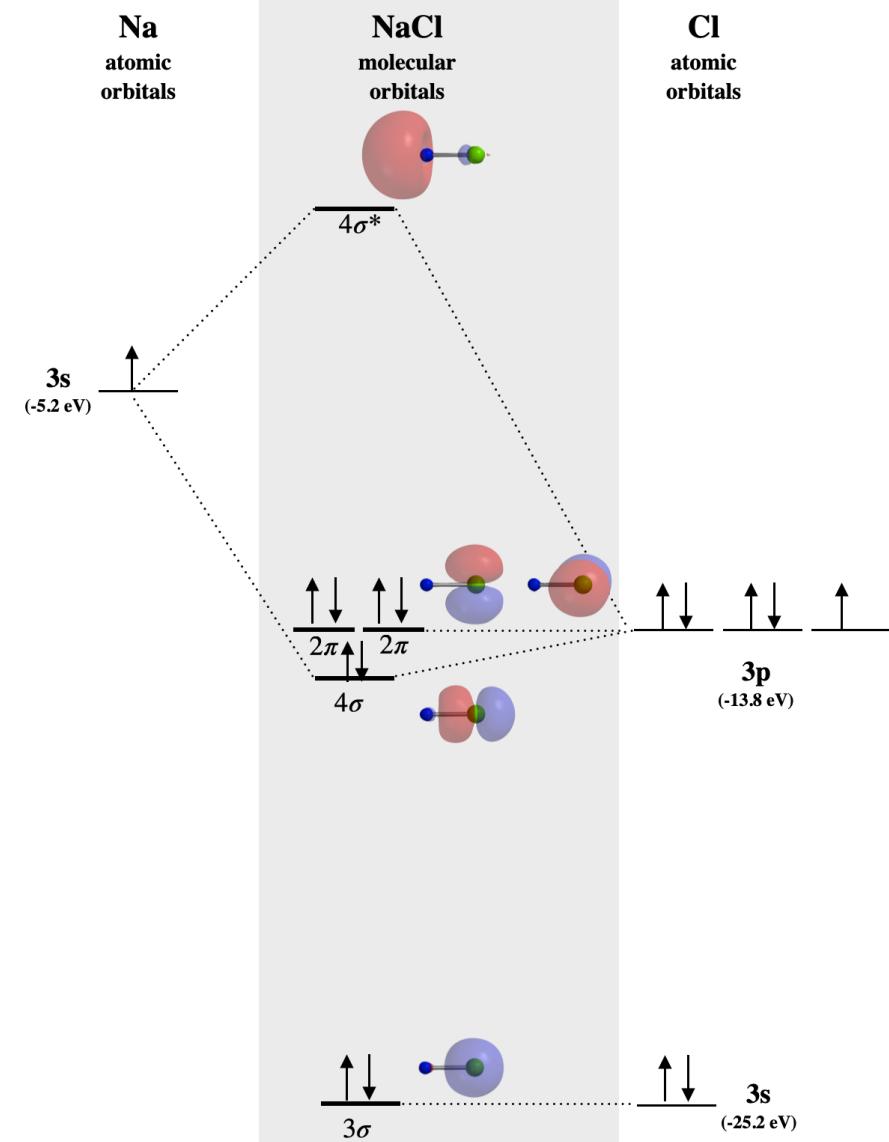


Figure 5.3.2.1: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding.

## Dipole Moment

- The considerations earlier assumed that the linear combination of atomic orbitals occurs between two atoms of the same element, which results in formation of homonuclear diatomic molecules. This manifests itself in the fact that the two interacting atomic orbitals possess the same energy. Moreover, at the level of the quantum mechanical wave function, this results in equality of the two coefficients  $c_1$  and  $c_2$  (Eq. 11.12) or  $\lambda = \pm 1$  (Eq. 11.13).
  - $\Psi = c_1 \Psi_1 + c_2 \Psi_2$  (Eqn. 11:12)
  - This approach is called the linear combination of atomic orbitals (LCAO) and can alternatively be formulated as:
  - $\Psi = \Psi_1 + \lambda \Psi_2$ , (Eqn. 11:13)
  - where  $\lambda$  is a measure of the polarity of the molecular orbital.

- Whereas the same methodology can be applied to hetero-nuclear diatomic molecules, we appreciate that the two atoms no longer belong to the same element, hence the energies of the interacting atomic orbitals are no longer equal.
- Similarly, the weighting coefficients  $c_1$  and  $c_2$  are not the same, and  $\lambda \neq \pm 1$ .
- As mentioned in Sect. 11.3.2, the coefficient  $\lambda$  is a measure of the polarity of the molecular orbital, and if its value deviates from 1, the bond possesses a ***permanent electric dipole momentum*** (i.e., a bond moment).
- This is a result of one atom in the molecule attracting electrons more strongly than the other, leading to a formal partial negative charge on one atom and a formal positive charge on the other.
- In general, a dipole moment  $\mu$  arises from a charge separation in space, and is thus defined as

$$\mu = Q \cdot r, \quad (11.15)$$

- where Q is the separated charge (e.g.,  $1 \text{ e} = 1.602 \times 10^{-19} \text{ C}$ ) and  $r$  the distance between the positive and negative centers.
- Since such separations happen at the scale of a chemical bond, the dipole moment is measured in multiples of  $3.338 \times 10^{-30} \text{ C m}$  which is called the *debye*:

$$[\mu] = 3.338 \cdot 10^{-30} \text{ C m} = 1 \text{ D}$$

- and leads to the dipole moment for the charge separation due to one electron displaced by  $1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$  of

$$\mu = 1.602 \cdot 10^{-19} \text{ C} \cdot 10^{-10} \text{ m} = 1.602 \cdot 10^{-29} \text{ C m} = 4.8 \text{ D.}$$

- When assessing the ***overall dipole moment*** of a molecule, one considers the individual bond moments as vectors (i.e. they have a value/length and a direction) and estimates the overall dipole moment by vector addition.

- Every polar covalent bond contains an ionic character due to the displacement of shared electron clouds towards the atom with high electronegativity.
  - The percentage of ionic character in a covalent bond is obtained using the formula,
- % ionic character = ( $\mu$ (observed) /  $\mu$ (theoretical)) \*100**
- where,  $\mu$  = Dipole moment in Debye.
  - ❖ Calculate the percentage ionic and covalent character in HF molecules having bond distance = 0.92 $\text{\AA}$  and dipole moment=1.78D?

Ans: Given,  $\mu$ (observed) = 1.78D =  $1.78 \times 10^{-18}$  esu.cm      (1D =  $10^{-18}$  esu.cm)  
 $r = 0.92\text{\AA} = 0.92 \times 10^{-8}$  cm

We know,      % ionic character = ( $\mu$ (observed)/ $\mu$ (theoretical))\*100

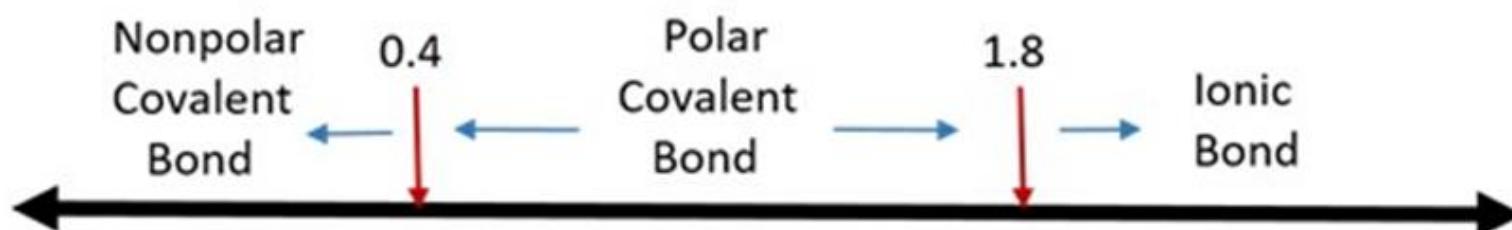
Also,  $\mu$ (theoretical) = Q\*r =  $4.8 \times 10^{-10}$  esu\* $0.92 \times 10^{-8}$  cm, (where Q= charge of electron).

Now,    % ionic character =  $(1.78 \times 10^{-18}\text{esu.cm}) / (4.8 \times 10^{-10}\text{esu} \times 0.92 \times 10^{-8}\text{cm}) = 0.403 = 40.3\%$

Ionic character = 40.3%

Hence, Covalent character =  $100 - 40.3 = 59.7\%$ .

## Electronegativity Difference



Examples:



$$2.5 - 2.1 = 0.4$$

$$3.5 - 2.5 = 1.0$$

$$3.0 - 0.9 = 2.1$$

## Dipole Moment of Ionic Compounds

The electronegativity difference between Na and Cl of 2.1 suggests that NaCl forms an ionic bond. If the bonding in crystalline NaCl was 100% ionic, the charge on the sodium atom was  $+1\text{-}e$ , and the charge on the chlorine  $-1\text{-}e$ . With an inter-nuclear distance of 2.36 Å, this results in a dipole moment of  $\mu = 11.34 \text{ D}$ . The experimental value of the dipole moment can be obtained by microwave spectroscopy and yields  $\mu = 9.001 \text{ D}$ . The ratio of the experimental and theoretical dipole moments

$$\frac{\mu_{\text{exp}}}{\mu_{\text{theor}}} = \frac{9.001 \text{ D}}{11.34 \text{ D}} = 0.794$$

indicates that the bonding between sodium and chlorine in the ionic solid is ~80% ionic.

## Larger Polyatomic Molecules: MOT

- Molecular orbital theory can be used to discuss in a uniform manner the electronic structures of triatomic molecules, finite groups of atoms, and the almost infinite arrays of atoms in solids.
- In each case the molecular orbitals resemble those of diatomic molecules, the only important difference being that the orbitals are built from a more extensive basis set of atomic orbitals.
- As remarked earlier, a key point to bear in mind is that from *N* atomic orbitals it is possible to construct *N* molecular orbitals.
- We have seen that the general structure of molecular orbital energy-level diagrams can be derived by grouping the orbitals into different sets, the  $\sigma$  and  $\pi$  orbitals, according to their shapes.
- The same procedure is used in the discussion of the molecular orbitals of polyatomic molecules. However, because their shapes are more complex than diatomic molecules, we need a more powerful approach.
- The discussion of polyatomic molecules are therefore carried out in two stages. First, we use intuitive ideas about molecular shape to construct molecular orbitals, as is done here. Also, one discusses the shapes of molecules and the use of their symmetry characteristics to construct molecular orbitals and account for other properties.

## (a) Polyatomic molecular orbitals

**Key points:** Molecular orbitals are formed from linear combinations of atomic orbitals of the *same symmetry*; their energies can be determined experimentally from gas-phase photoelectron spectra and interpreted in terms of the pattern of orbital overlap.

- The features that have been introduced in connection with diatomic molecules are present in all polyatomic molecules. In each case, we write the molecular orbital of a given symmetry (such as the  $\sigma$  orbitals of a linear molecule) as a *sum of all the atomic orbitals that can overlap to form orbitals of that symmetry*:

$$\Psi = \sum_i c_i \chi_i \quad (2.8)$$

In this linear combination, the  $\chi_i$  are atomic orbitals (usually the valence orbitals of each atom in the molecule) and the index  $i$  runs over all the atomic orbitals that have the appropriate symmetry.

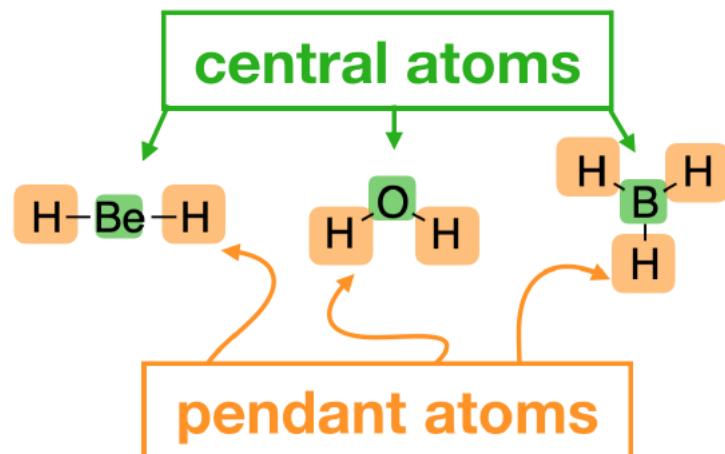
➤ From  $N$  atomic orbitals we can construct  $N$  molecular orbitals. Then,

- *The greater the number of nodes in a molecular orbital, the greater the antibonding character and the higher the orbital energy.*
- *Orbitals constructed from lower energy atomic orbitals lie lower in energy* (so atomic s orbitals typically produce lower energy molecular orbitals than atomic p orbitals of the same shell).
- Interactions between nonnearest-neighbor atoms are weakly bonding (lower the energy slightly) if the orbital lobes on these atoms have the same sign (and interfere constructively). They are weakly antibonding if the signs are opposite (and interfere destructively).

➤ To combine several different atoms in a molecular orbital diagram, we will ***group orbitals from different atoms into sets that match the symmetry of a central atom***. These **group orbitals** are also referred to as **symmetry adapted linear combinations (SALCs)**. We'll use a stepwise approach to do this as summarized below.

❖ **Symmetry adapted linear combinations (SALCs)**

➤ We need SALCs (aka ***ligand group orbitals***) to draw molecular orbital (MO) diagrams of **polyatomic molecules**. SALCs are groups of orbitals on **pendant atoms**. *These groups of orbitals must match the symmetry of valence orbitals on the central atom in order to create a productive interaction.* When ***we combine SALCs with the atomic orbitals on the central atom***, we can generate a MO diagram that gives us information about the molecule's bonding and electronic states.



## MO Diagrams for Linear Triatomic ( $XA_2$ ) Molecules: A-X-A

### ❖ Construction of molecular orbitals

- First, we combine the AOs of the outer atoms (here A) into sensible combinations, then we see how these combinations interact with the AOs on the central atom. Don't forget about **net overlap**, which is important for deciding how the orbitals interact. If they don't have net overlap, they can't interact.
- The application of symmetry concepts and group theory greatly simplifies the construction of molecular orbitals. For example, it can be shown that the combination of two hydrogen 1s wave functions  $\phi_{1s}(1) + \phi_{1s}(2)$  transforms as  $A_1$  (usually written as  $a_1$  when molecular orbitals are considered) and the combination  $\phi_{1s}(1) - \phi_{1s}(2)$  transforms as  $B_1$  (sometimes written as  $b_1$ ).
- According to the description of species in the character tables, we see that the  $A_1$  combination is a singly degenerate state that is symmetric about the internuclear axis. Also, the  $B_1$  combination represents a singly degenerate state that is antisymmetric about the internuclear axis.

- Therefore, the states described by the combinations  $(\phi_{1s}(1) + \phi_{1s}(2))$  and  $(\phi_{1s}(1) - \phi_{1s}(2))$  describe the bonding ( $a_1$ ) and antibonding ( $b_1$ ) molecular orbitals, respectively, as shown in the  $\text{H}_2$  molecule.
- The linear combinations of H1s orbitals  $\phi_1$  and  $\phi_2$  are illustrated in Fig. 2.36. ‘Symmetry adapted’ combinations such as these will figure extensively in later discussions.

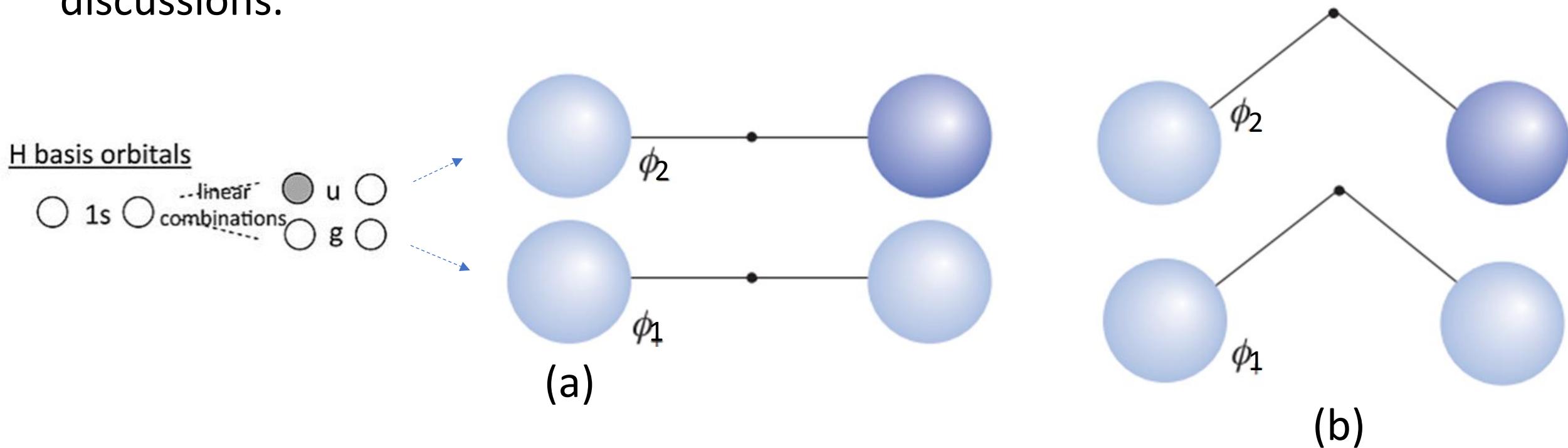


Fig. 2.36 The combination of H1s orbitals that are used to construct molecular orbitals in (a) *linear* and (b) *angular*  $\text{XH}_2$ .

- As shown earlier, the orbital combinations  $\phi_{1s}(1) + \phi_{1s}(2)$  and  $\phi_{1s}(1) - \phi_{1s}(2)$  represent the bonding and antibonding molecular orbitals for the  $H_2$  molecule. Therefore, the qualitative molecular orbital diagram for the  $H_2$  molecule can be constructed as shown in Fig. 5.4.
- The combinations of hydrogen orbitals are known as group orbitals (GO).

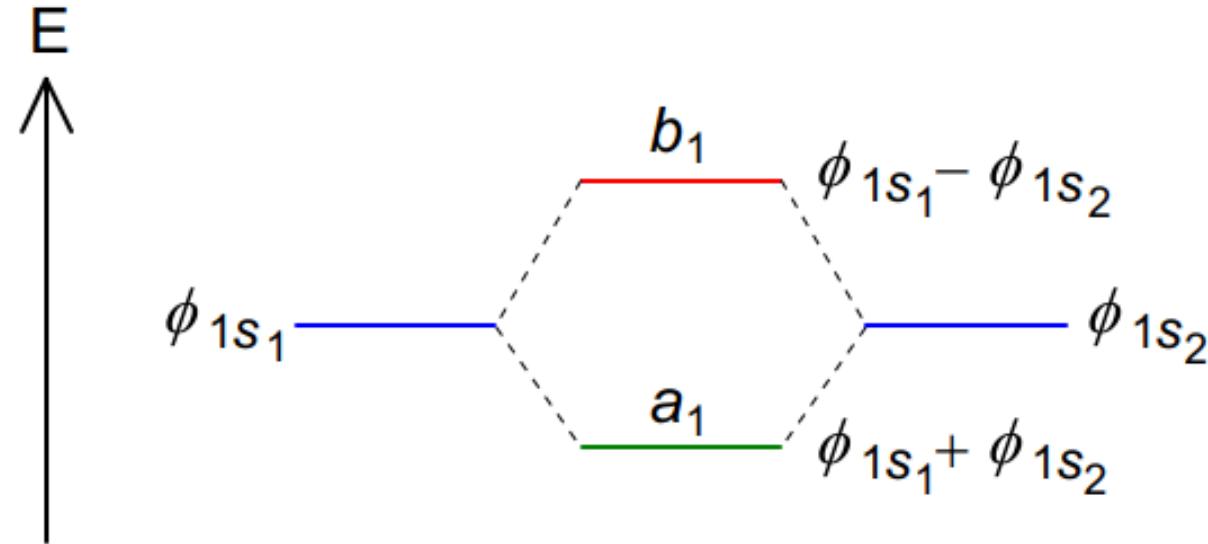


FIGURE 5.4 Two combinations of 1s wave functions that give different symmetry.

➤ Because they are combined in such a way that they match the symmetry of the orbitals on the central atom, they are sometimes referred to *symmetry adapted linear combinations* (SALCs).

### ❖ Orbital symmetry

➤ It is not always strictly appropriate to use the notation  $\sigma$  and  $\pi$  in polyatomic molecules because these labels apply to a linear molecule. The correct procedure for labelling orbitals in polyatomic molecules according to their symmetry. For our present purposes all we need know of this more appropriate procedure is the following:

- $a, b$  denote a nondegenerate orbital
- $e$  denotes a doubly degenerate orbital (two orbitals of the same energy)
- $t$  denotes a triply degenerate orbital (three orbitals of the same energy).

➤ Subscripts and superscripts are sometimes added to these letters, as in  $a_1, b'', e_g$ , and  $t_2$  because it is sometimes necessary to distinguish different  $a, b, e$ , and  $t$  orbitals according to a more detailed analysis of their symmetries.

- $a$  ( $A$ ) denotes a nondegenerate orbital or state that is **symmetric around the principal axis**.
- $b$  ( $B$ ) denotes a nondegenerate orbital or state that is **antisymmetric around that axis**.
- Subscripts 1 and 2 indicate *symmetry* or *antisymmetry, respectively*, with respect to a *rotation axis (plane)* other than the *principal axis of symmetry*.
- For the linear form of the ion, the highest and lowest MO's are symmetric with respect to the inversion center in the molecule. Note that the central 1s orbital has g symmetry, so by symmetry, it has zero overlap with the u combination of the two 1s orbitals on the ends. This makes the  $\sigma$  orbital a nonbonding orbital.
- In the triangular form of the molecule, the orbitals that derive from  $\sigma$  and  $\sigma^*$  become degenerate (i.e., they have identically the same energy by symmetry).

- For a molecule that has a rotation axis other than the principal one, symmetry or antisymmetry with respect to that axis is indicated by subscripts 1 or 2, respectively.
- When no rotation axis other than the principal one is present, these subscripts are sometimes used to indicate symmetry or antisymmetry with respect to a vertical plane,  $\sigma_v$ .
- The marks ‘ and “ are sometimes used to indicate symmetry or antisymmetry with respect to a horizontal plane,  $\sigma_h$ . It should now be apparent how the species  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  arise.
- If an orbital possesses a center of symmetry, the subscript “g” indicates symmetry with respect to that center and the subscript “u” indicates antisymmetry with respect to that center of symmetry.
- Note that we drop the “g” and “u” for the triangular orbitals because a triangle does not have an inversion center.

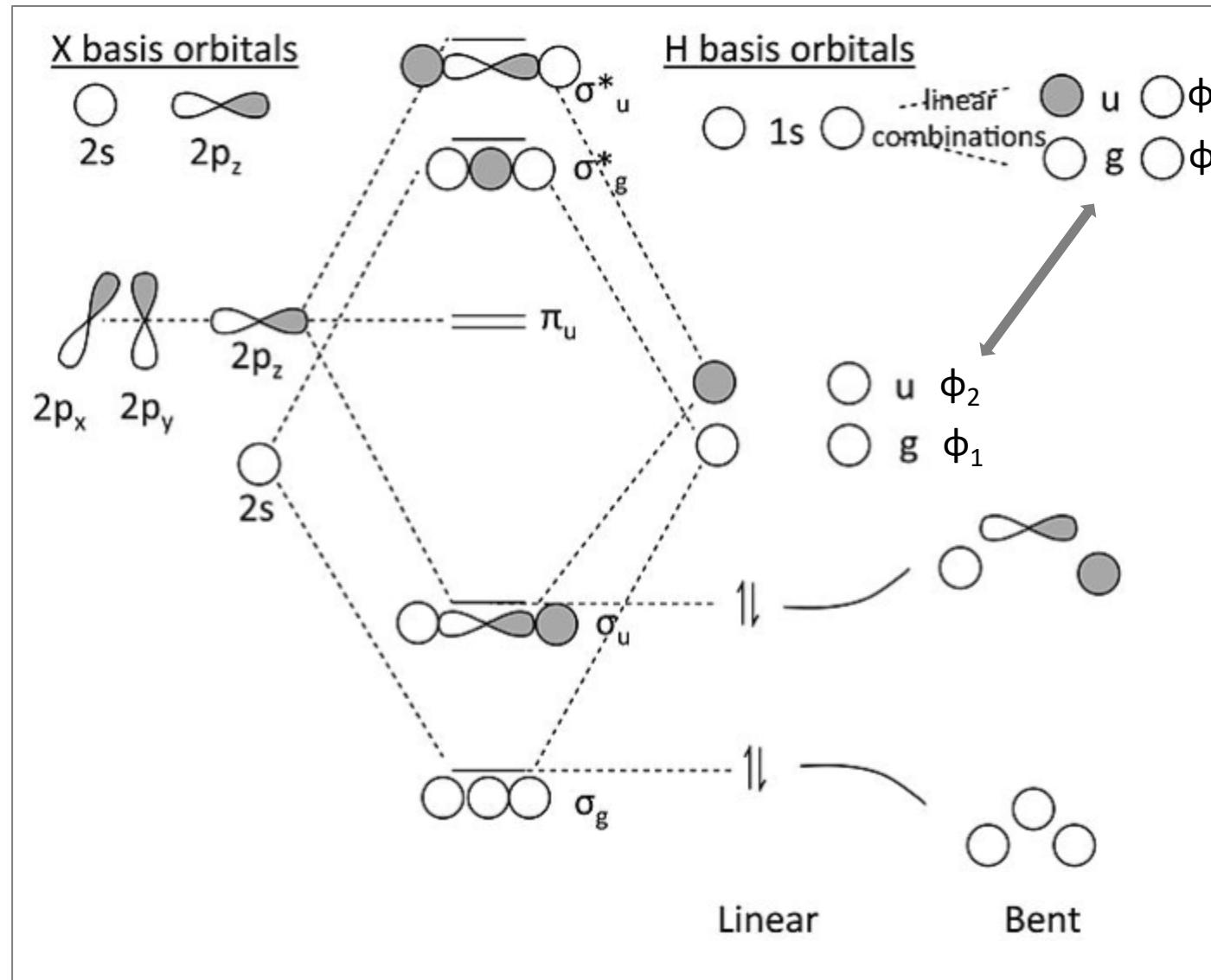
## MO diagram for $XH_2$ ( $X = Be, B, C\dots$ ):

In the **linear form** of the molecule, which has inversion symmetry, the 2s and 2p orbitals of the X atom factor into three symmetry classes:

$$2s = \sigma_g$$

$$2p_z = \sigma_u$$

$$2p_x, 2p_y = \pi_u$$



Two H 1s orbitals make two linear combinations, one with  $\sigma_g$  symmetry and one with  $\sigma_u$  symmetry. They look like the bonding and antibonding MO's of the  $H_2$  molecule.

► The  $\pi$  orbitals must be non-bonding because there is no combination of the H 1s orbitals that has  $\pi_u$  symmetry.

## ❖ Delocalized or multi-centred $\sigma$ orbitals: Construction of molecular orbitals

- Instead of constructing a set of two-center bonds we could describe a polyatomic species by constructing orbitals centered over all the atoms of the molecule. A full discussion is beyond our scope, but the general approach may be illustrated.
- Consider first a very simple example, the  $\text{BeH}_2$  monomer. The orbital combinations are shown in Fig. 4.17.
- $\text{BeH}_2$  might be hard to make, but it's very nice and simple as an example! Using the electron domain model, we predict that it will be linear.
- Be has 2s and 2p orbitals, and it is in the middle. H has 1s orbitals; there are 2 H atoms on the outside. We need to make combinations of the H AOs, and we'll use the same combinations we used to make  $\text{H}_2$ , except now they (viz.,  $\phi_1(g)$  and  $\phi_2(u)$ ) aren't touching. These combinations will match the 2s and 2p<sub>z</sub> on Be, as shown in the figure.

- The beryllium 2s orbital combines, *in phase*, with the  $\phi_1$  group orbitals obtained from 1s orbitals on hydrogens A and B to form the 3-centre orbital,  $\psi_1$ .
- The electron probability density in this orbital,  $\psi_1^2$ , will be concentrated in the regions of highest field between the nuclei, and will experience more attraction than in the isolated atoms. Thus,  $\psi_1$  is bonding.
- Similarly,  $\psi_2$ , formed by the combination  $\phi_2$  (GO) +  $p_z$  (on B), is bonding.
- The corresponding out-of-phase combinations  $\psi_1^*$  and  $\psi_2^*$  are clearly anti-bonding.
- Since both the  $p_x$  and  $p_y$  orbitals on beryllium have nodes in the plane of the two hydrogens, no combinations between these and the hydrogens group orbitals are possible.
- Thus, we can draw up a qualitative energy level diagram, Fig. 4.18.

- Notice, firstly, that six atomic orbitals (4 on Be and 1 on each H) give six  $\text{BeH}_2$  orbitals ( $\psi_1, \psi_1^*, \psi_2, \psi_2^*$  together with  $p_x$  and  $p_y$ ). Secondly, the four electrons are placed in the two bonding levels giving two bonds holding the three atoms together. This is equivalent to two Be—H single bonds, but the *bonding electrons are spread over all three atoms*.
- Finally, the energy separation of  $\psi_1$  and  $\psi_2$  reflects approximately the separation of the beryllium 2s and 2p atomic levels.

# Symmetry Adapted Linear Combinations

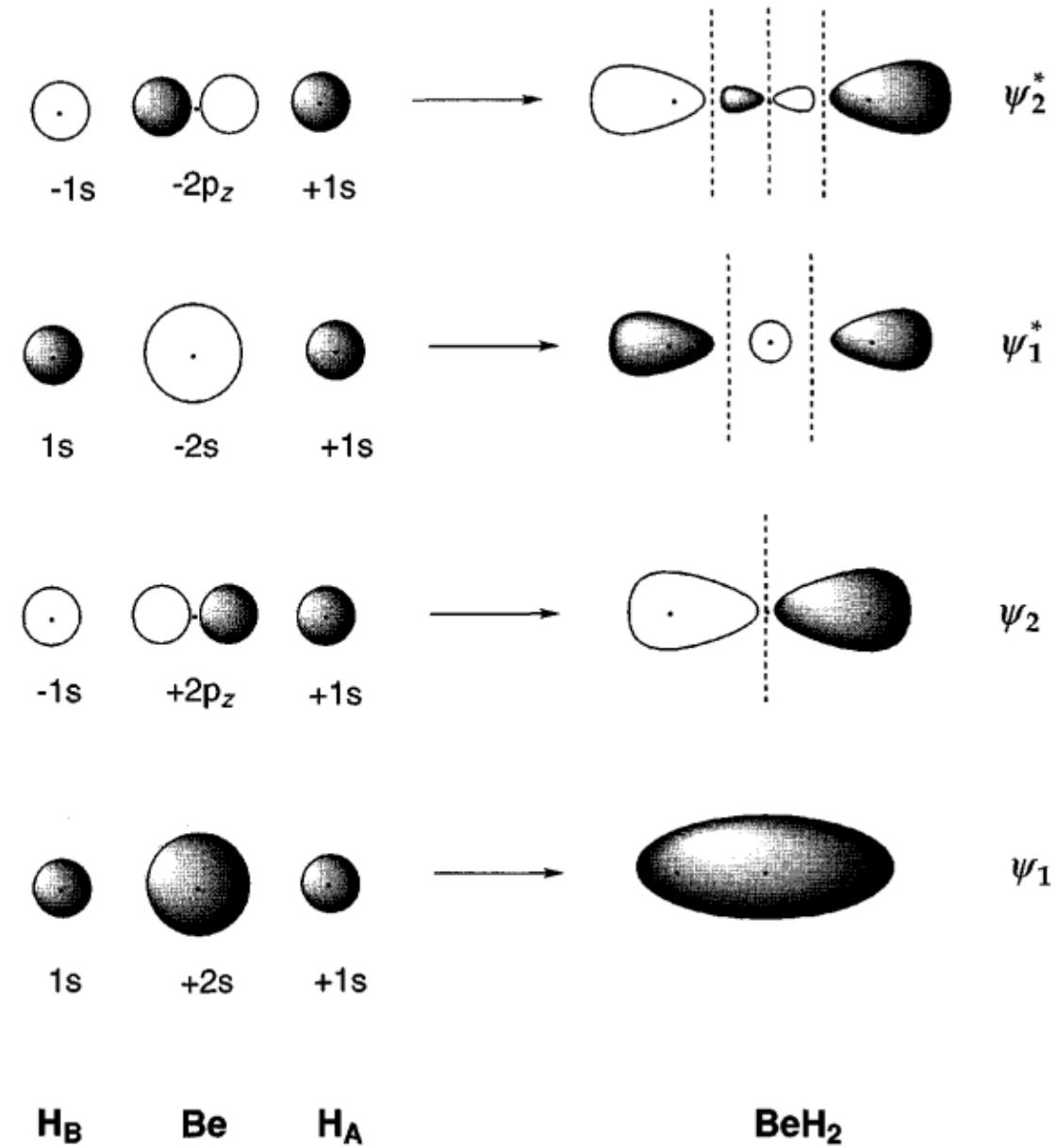


FIG. 4.17 Formation of molecular orbitals in  $\text{BeH}_2$  (schematic). Nodal planes are indicated by dotted lines

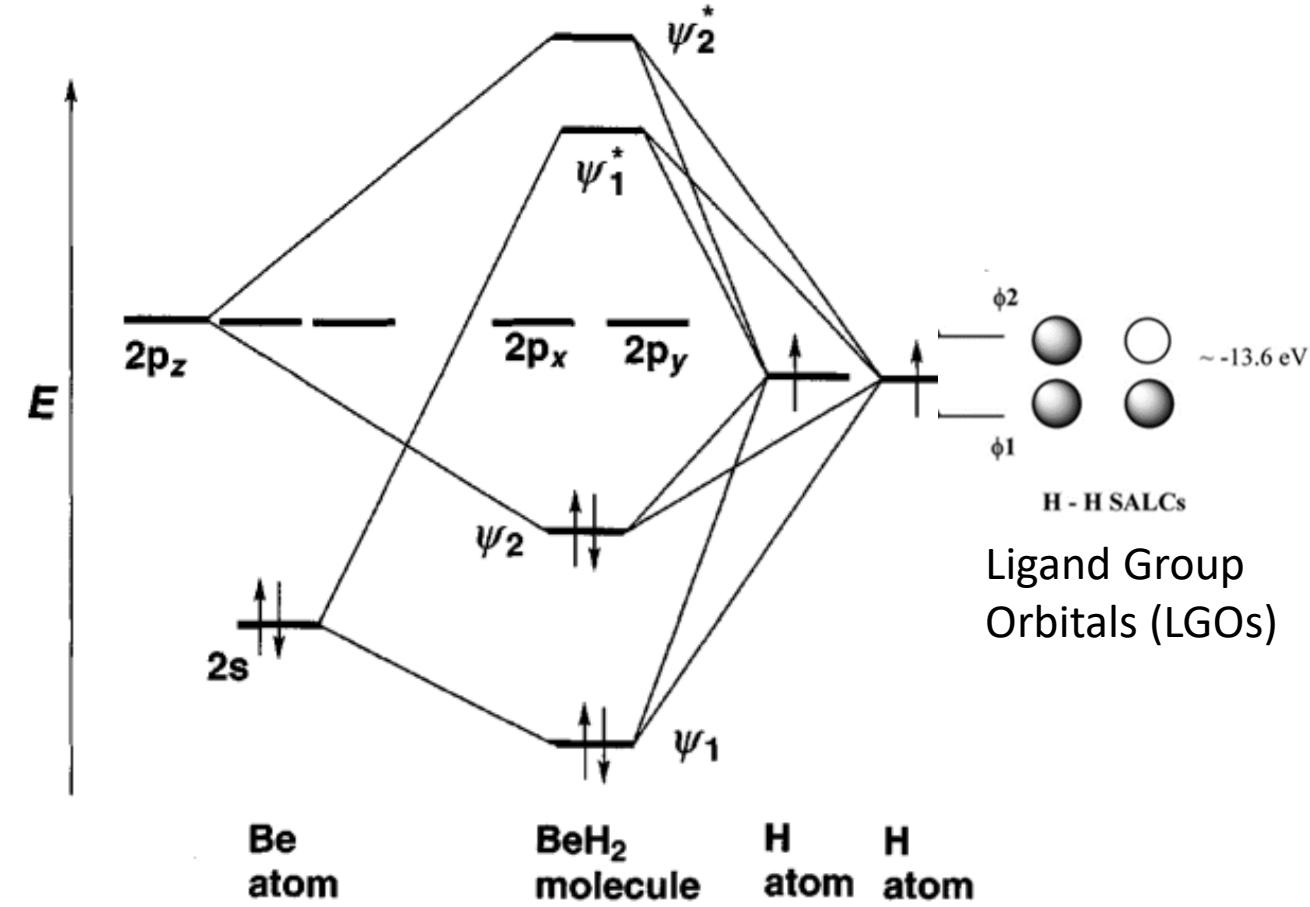
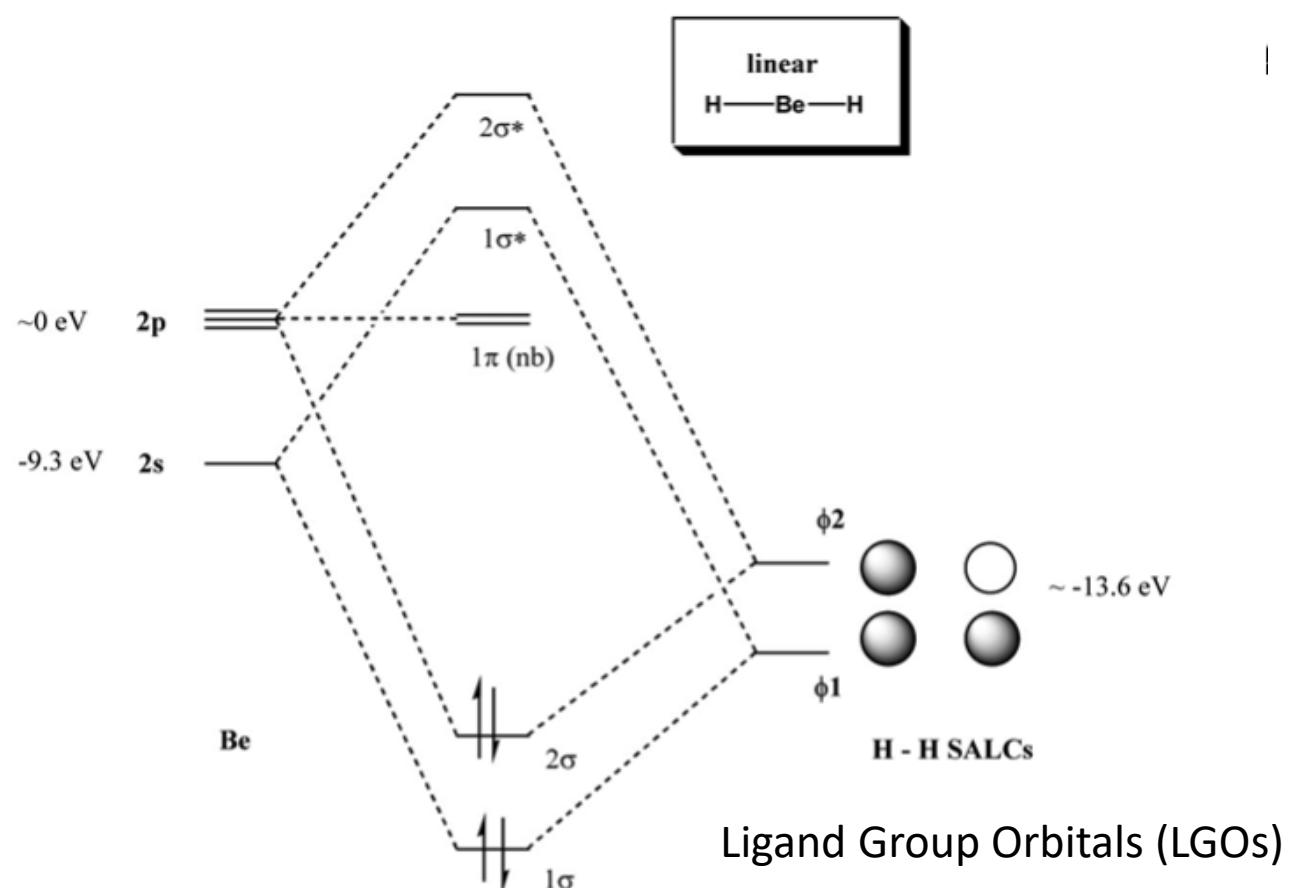
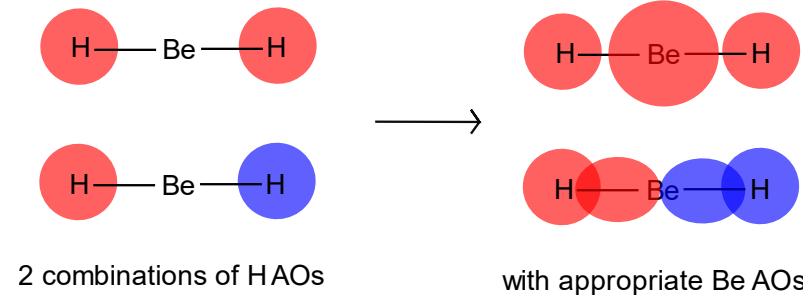
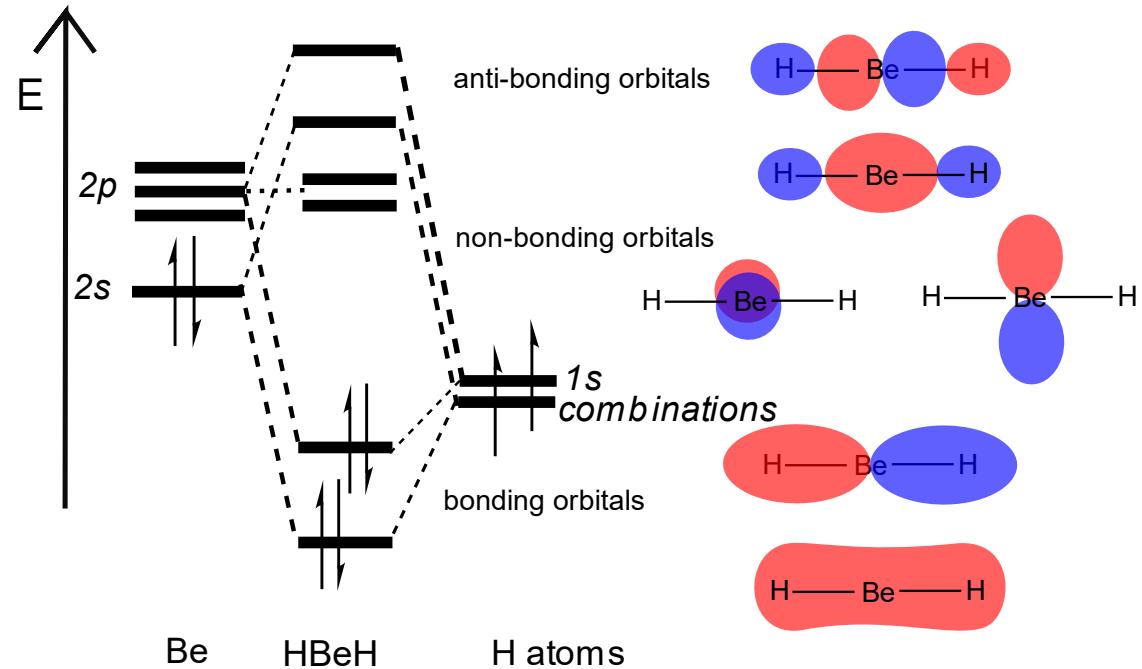


FIG. 4.18 Schematic energy level diagram for  $\text{BeH}_2$ . Note that the z axis is the H-Be-H axis (*linear molecule*). The  $p_x$  and  $p_y$  orbitals on Be are not involved in molecular orbital formation and are simply repeated in the  $\text{BeH}_2$  column of the diagram



allowed overlaps: Symmetry Adapted Linear Combinations

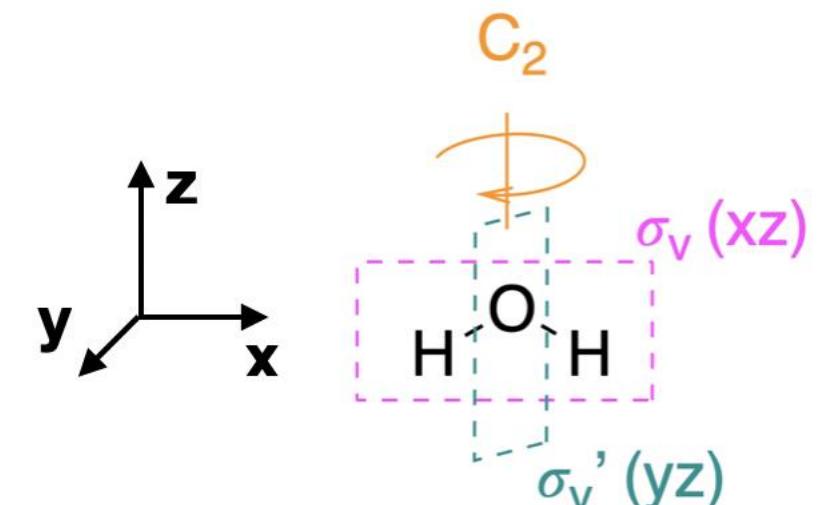


## Construct SALCs and the molecular orbital diagram for $\text{H}_2\text{O}$

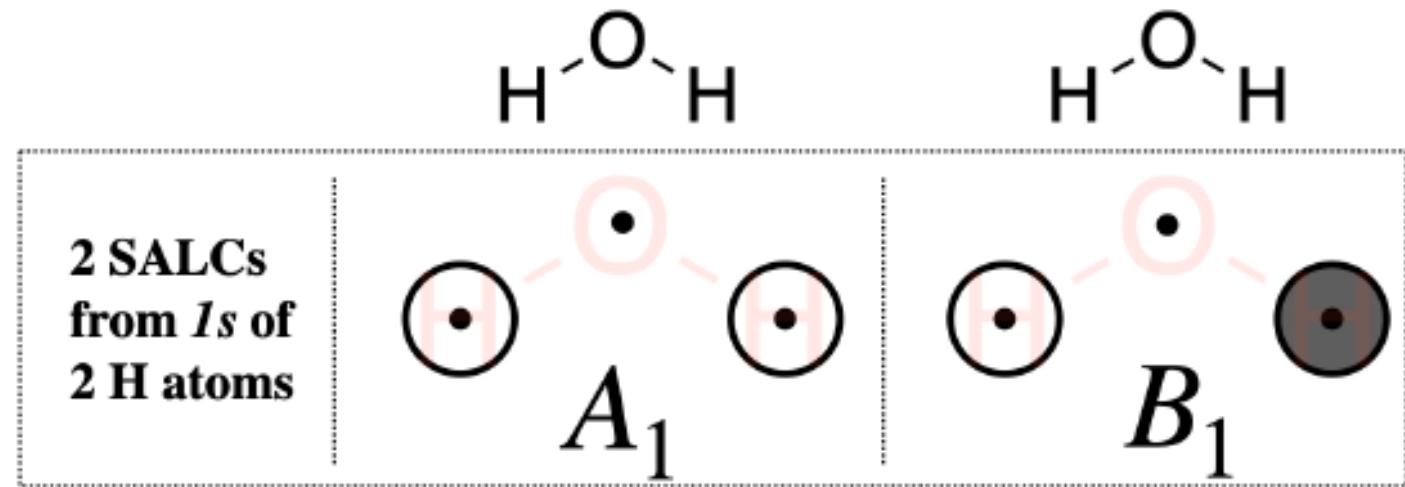
➤  $\text{H}_2\text{O}$  is a **bent molecule**, and so it is important to remember that interactions of pendant ligands are dependent on their positions in space. You should consider the positions of the three atoms in water to be essentially fixed in relation to each other. The process for constructing the molecular orbital diagram for a non-linear molecule, like water, is similar to the process for linear molecules. We will walk through the steps below to construct the molecular orbital diagram of water.

▪ **Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.**

➤ The  $\text{H}_2\text{O}$  molecule is bent and its point group is  $\text{C}_{2v}$ . The ***z axis is collinear with the principal axis, the  $\text{C}_2$  axis***. There is no need to simplify this problem, as we had done for previous examples. The  $\text{C}_{2v}$  point group is simple enough.



- Identify and count the pendant atoms' valence orbitals.
- Each of the two pendant hydrogen atoms has one valence orbital, the 1s. Thus, we can expect a total of two SALCs from these two atoms.
- Sketch the SALCs



The  $A_1$  SALC is singly degenerate and symmetric with respect to both the principal axis (z) and the inversion center (*i*) (based on its Mulliken Label). This would be the same symmetry as an s orbital on the central oxygen atom. From this information, we know that this SALC must have symmetry compatible with an s orbital on the central atom. We can also see that a p<sub>z</sub> orbital on oxygen, also possesses  $A_1$  symmetry. This tells us that in addition to being compatible with the oxygen s orbital, it should also be compatible with the oxygen p<sub>z</sub> orbital. From this information we can draw the  $A_1$  SALC shown in Figure 5.4.3.2.

- The Mulliken Label tells us that the  $B_1$  SALC is singly degenerate and antisymmetric with respect to both the principal axis and the inversion center.  $B_1$  has the same symmetry as a  $p_x$  orbital on the central oxygen atom. From this information, we know that this SALC should be compatible with a  $p_x$  orbital on the central atom, and we can draw the  $B_1$  SALCs shown in Figure 5.4.3.2.
- With knowledge of both orbital symmetries and energies, we can construct the molecular orbital diagram. The valence orbitals of oxygen go on one side of the diagram while the hydrogen group orbitals are drawn on the opposite side. Molecular orbitals are drawn in the center column of the diagram, as shown in Figure 5.4.3.3:

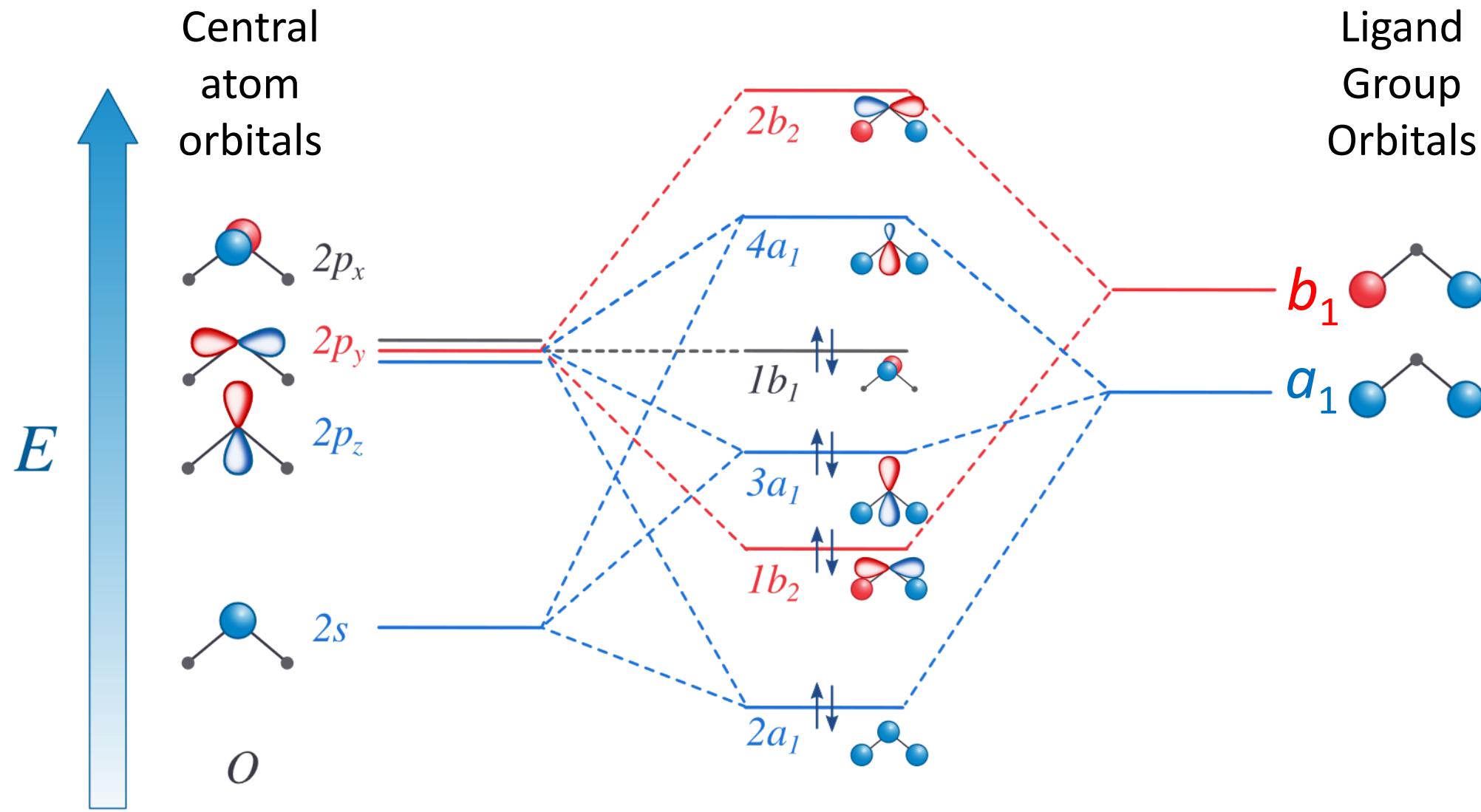
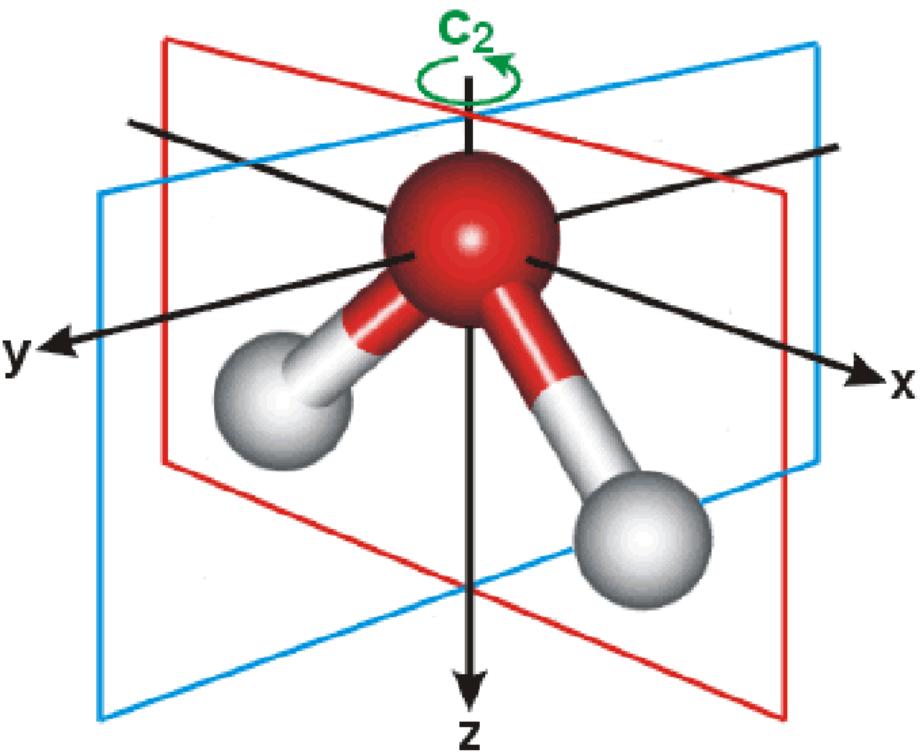


Figure 10.4.7 : MO diagram for water.



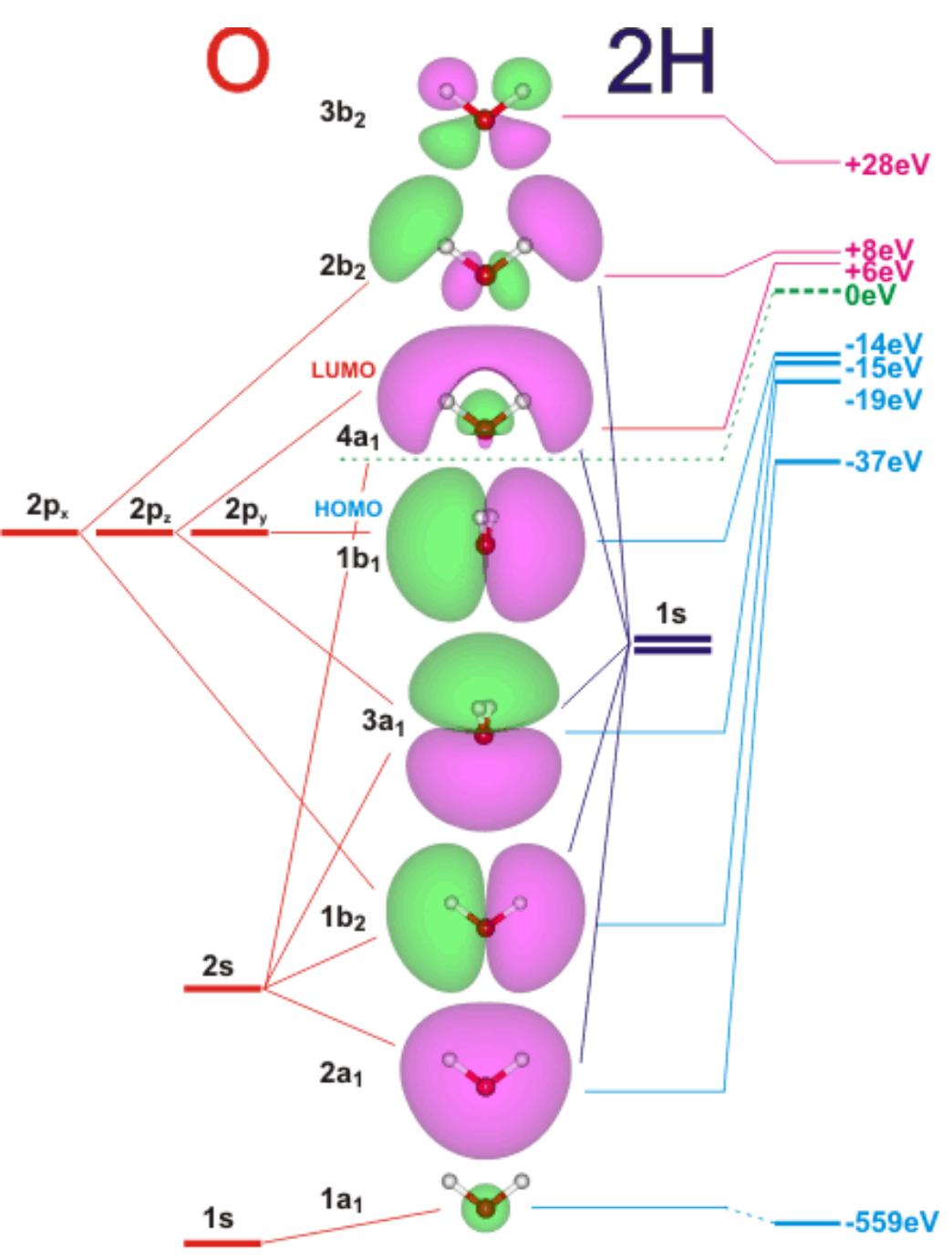
**NOTE:**

The nomenclature is based upon the symmetry of the orbitals. The figure right shows the planes of symmetry (xz and yz) and the two-fold axis of rotation ( $C_2$ , z-axis).

If the orbitals are **unchanged** (that is, symmetric) with respect to the planes of symmetry (xz and yz) and the two-fold axis of rotation ( $C_2$ ) then they are denoted as ' $a_1$ ' orbitals and numbered from the lowest energy (i.e.  $1a_1$  is the lowest energy  $a_1$  orbital)

If the sign of the orbital **changes** with respect to  $180^\circ$  rotation about  $C_2$  and reflection through the xz plane it is  $b_1$ , whereas if the sign of the orbital changes with respect to  $180^\circ$  rotation about  $C_2$  and reflection through the yz plane it is  $b_2$ .

An  $a_2$  orbital has **no change in sign with respect to  $180^\circ$  rotation** about  $C_2$  but **changes** sign on reflection through both xz and yz planes (for example, the 9<sup>th</sup> lowest unoccupied molecular orbital for H<sub>2</sub>O).



The five occupied and the lowest three unoccupied molecular orbitals of the isolated molecule  $(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2$  were calculated using the Restricted Hartree-Fock wave function (RHF) using the 6-31G\*\* basis set. They are set out with the lowest energy (that is, most negative energy) molecular orbitals at the bottom. They are all given in the  $xz$  plane ( $z$ -axis upwards) except  $1b_1$  and  $3a_1$ , which are in the  $yz$  plane ( $z$ -axis upwards). The two lowest energy orbitals  $1a_1$  and  $2a_1$  are contributed from the  $1s$  and  $2s$  (mostly) orbitals of the oxygen atom, respectively, and are consequentially approximately spherical. The three highest energy occupied orbitals ( $1b_2$ ,  $3a_1$ ,  $1b_1$ ) are orthogonal around the oxygen atom and without obvious  $sp^3$  hybridization characteristics.

The highest occupied molecular orbital (HOMO),  $1b_1$ , is predominantly  $2p_z$  in character with no contribution from the hydrogen  $1s$  orbital and mainly contributes to the "lone pair" effects. The  $2a_1$ ,  $1b_2$  and  $3a_1$  all contribute to the O-H bonds. The two lowest unoccupied molecular orbitals  $4a_1$  (LUMO) and  $2b_2$  are O-H antibonding orbitals, seen in X-ray spectroscopy. They have greatest electron densities around the O-atom whereas orbital  $3b_2$  has greatest electron density around the H-atoms. The experimental binding energy of the  $1a_1$  orbital in the gas phase is 539.9 eV. These orbitals are appreciably changed in ice and water; the experimental electron binding energies in liquid water being  $2a_1$  30.90 eV,  $1b_2$  17.34 eV,  $3a_1$  13.50 eV,  $1b_1$  11.16 eV. The experimental binding energy of the  $1a_1$  orbital in the liquid phase consists of a broad energy distribution centered about 538.1 eV plus a smaller contribution at 536.6 eV within the tetrahedrally hydrogen bonded bulk. The  $1b_2$  and  $3a_1$  orbitals are largely responsible for the donation of hydrogen bonding with the  $3a_1$  orbital shown experimentally to contribute the most. Also, the  $4a_1$  and  $2b_2$  antibonding orbitals are reported to be partially occupied in hydrogen bond formation, receiving electron density from donor  $1b_1$  orbitals.

- Water contains ***two lone pairs*** in its Lewis structure. Let us compare the predictions about water's lone pairs of electrons and its reactivity based on (1) the combination of elementary models (Lewis, Valence Bond, and Hybridized Orbital theories) and (2) Molecular Orbital theory. Specifically let us address and explain how the elementary models differ from molecular orbital theory in the following respects:
  1. Where are the lone pairs in water?
  2. Are the two lone pairs equivalent or are they different?
  3. Where are sites on the molecule that will undergo reaction with electrophiles and nucleophiles?
- **A) Elementary models:** The Lewis structure predicts that two lone pairs are (a) localized on the oxygen atom of water and that (b) both lone pairs are equivalent. The Lewis structure, combined with Valence Bond Theory, would predict that lone pairs occupy two equivalent hybridized  $sp^3$  atomic orbitals on oxygen. (c) Lewis theory would predict that the oxygen lone pairs are nucleophiles; thus, an electrophile would react with the oxygen atom lone pairs. The polarized O-H bond leaves the H atoms as the most electrophilic locations on the water molecule; thus, nucleophiles would react at the H atoms of water.

- B) Molecular orbital theory: The molecular orbitals predict that
- ✓ (a) the two lone pairs of water ***are not equivalent***, and that
  - ✓ (b) each is ***distributed over the entire molecule***.
  - ✓ ***One lone pair*** is in the ***truly non-bonding***  $1b_1$  orbital, which is also the HOMO.
  - ✓ There is ***not another truly non-bonding orbital*** in the molecule, but the lowest-energy  $2a_1$  orbital could be considered ***bonding and slightly non-bonding due to the large energy difference between it and other valence orbitals***.
  - ✓ (c) Although the  $2a_1$  orbital can be considered mostly non-bonding, we ***cannot expect the electrons in  $2a_1$  to react readily***, as they are *in the lowest-energy molecular orbital*. Molecular orbital theory predicts that ***reactions occur at the HOMO and LUMO orbitals***. The **HOMO** reacts with electrophiles, and in this case, the ***HOMO is distributed over the top and bottom faces of the molecule*** and is centered on the oxygen atom. The LUMO would react with nucleophiles. The **LUMO** is the orbital labeled  $4a_1$  and ***has a major lobe that is distributed more heavily over the H atoms***, and from this ***we should predict H atoms to be the preferred site of reaction for nucleophiles***.

## MO Theory and Molecular Geometry

❖ **Key point:** In the Walsh model, the shape of a molecule is predicted on the basis of the occupation of molecular orbitals that, in a correlation diagram, show a strong dependence on bond angle. The Walsh Diagram predicts the geometry of a molecule by assigning its valence electrons to the appropriate energy levels. **In general, the lowest energy configuration is preferred.**

- One of the strengths of VSEPR theory was that it could correctly predict the geometries of most small molecules. We now show how **MO theory** is also capable of **predicting molecular geometry**. In MO theory, the electrons responsible for bonding are delocalized over the entire molecule. Current ab initio and semiempirical molecular orbital calculations, which are easily carried out with software, are able to predict the shapes of even quite complicated molecules with high reliability. Nevertheless, there is still a need to understand the qualitative factors that contribute to the shape of a molecule within the framework of MO theory.
- In 1953, A. D. Walsh made a plot of the “**orbital binding energies**” as a function of the bond angle. The total energy for a molecule will then be the sum of its orbital binding energies. **Whichever configuration has the lowest overall energy will dictate the molecule’s geometry.** The **molecular geometry will therefore depend on which orbitals are occupied.**

- Let us begin this process by considering the class of molecules having the formula  $\text{AH}_2$ , where A can represent any element. There are ***two limiting geometries having this molecular formula: linear ( $D_{\infty h}$ ) and bent ( $C_{2v}$ ).***
- The one-electron MO diagrams for these two limiting cases were shown in Figure 10.29 and Example 10-7.
- The Walsh diagram for  $\text{AH}_2$  is nothing more than a correlation diagram, where each MO in the  $D_{\infty h}$  point group has a corresponding MO in the  $C_{2v}$  point group.
- For each pair of corresponding MOs, a consideration of ***the degree of orbital overlap can be used to determine if the energy of that orbital is lower in the linear or in the bent geometry.***
- Thus, ***a plot of the relative orbital energies can be made as a function of the bond angle.***
- Whether the geometry of a molecule is linear or bent (at a particular angle) depends on which structure is lowest in energy, which can be determined using the ***Walsh correlation diagram.***
- A plot of the energy of a molecular orbital as a function of a systematic change in molecular geometry is called a ***Walsh correlation diagram.***

- The molecular orbitals for a bent triatomic molecule will be represented by different linear combinations of the atomic orbitals from those found for a linear structure.
- By solving for the energy as a function of all bond angles between a linear geometry and a 90° geometry, we can determine how the molecular orbitals for the linear molecule evolve into those characteristics of the 90° geometry.
- Figure 10.12 (*Ref. McQuarrie's book*) shows the Walsh correlation diagram for a triatomic molecule, AH<sub>2</sub>, for which the energies of all six of the molecular orbitals are plotted as a function of bond angle.
- Note that the labels designating the orbitals for the 90° geometry are different from those used for the linear molecule.
- By their definitions, the σ and π designations can be used to describe only a linear molecule.
- The labels for a bent molecule, a<sub>1</sub>, b<sub>1</sub> and b<sub>2</sub>, reflect specific symmetry properties of the molecule.
- Here we will use them simply as a short-hand notation for the molecular orbitals of the bent molecule.

Figure 2.35 shows the Walsh diagram for an  $\text{XH}_2$  molecule. A Walsh diagram is a special case of a correlation diagram, a diagram that shows how one set of orbitals evolves into another as a parameter (such as a bond angle) is changed; we shall meet other examples later. A Walsh diagram adopts a simple pictorial approach to the task of analysing molecular shape in terms of delocalized molecular orbitals. Such diagrams play an important role in understanding the shapes, spectra, and reactions of polyatomic molecules. The  $\text{XH}_2$  diagram has been constructed by considering how the composition and energy of each molecular orbital changes as the bond angle is varied from  $90^\circ$  to  $180^\circ$ .

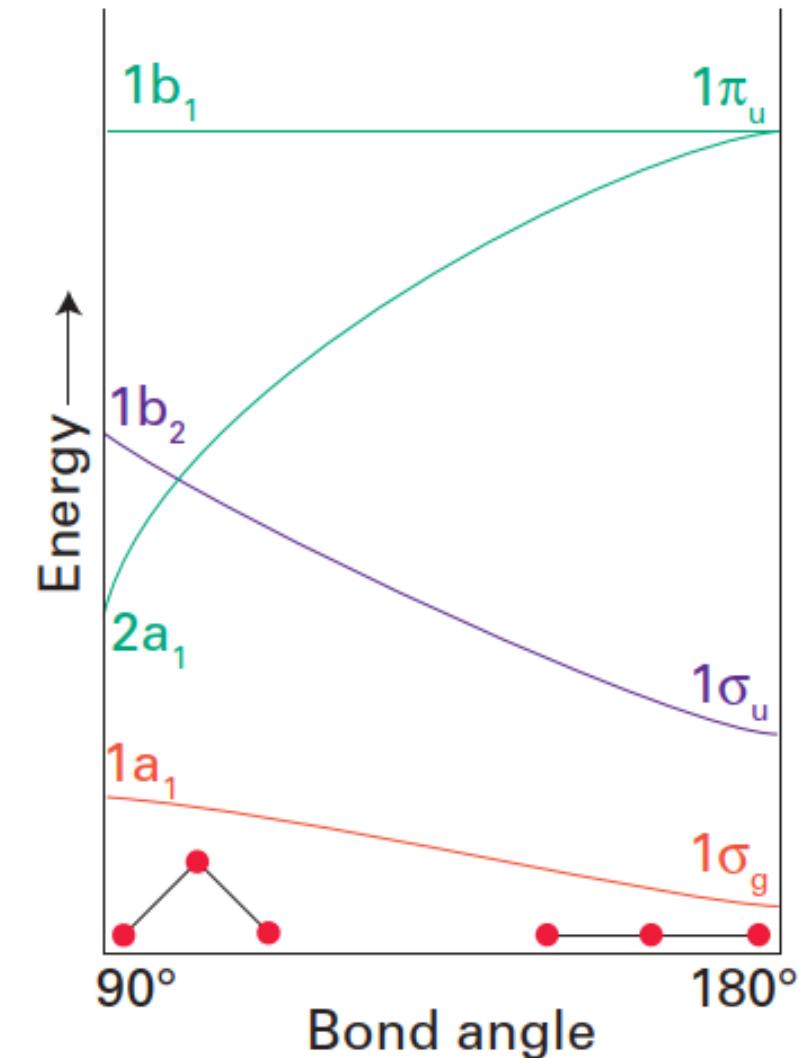
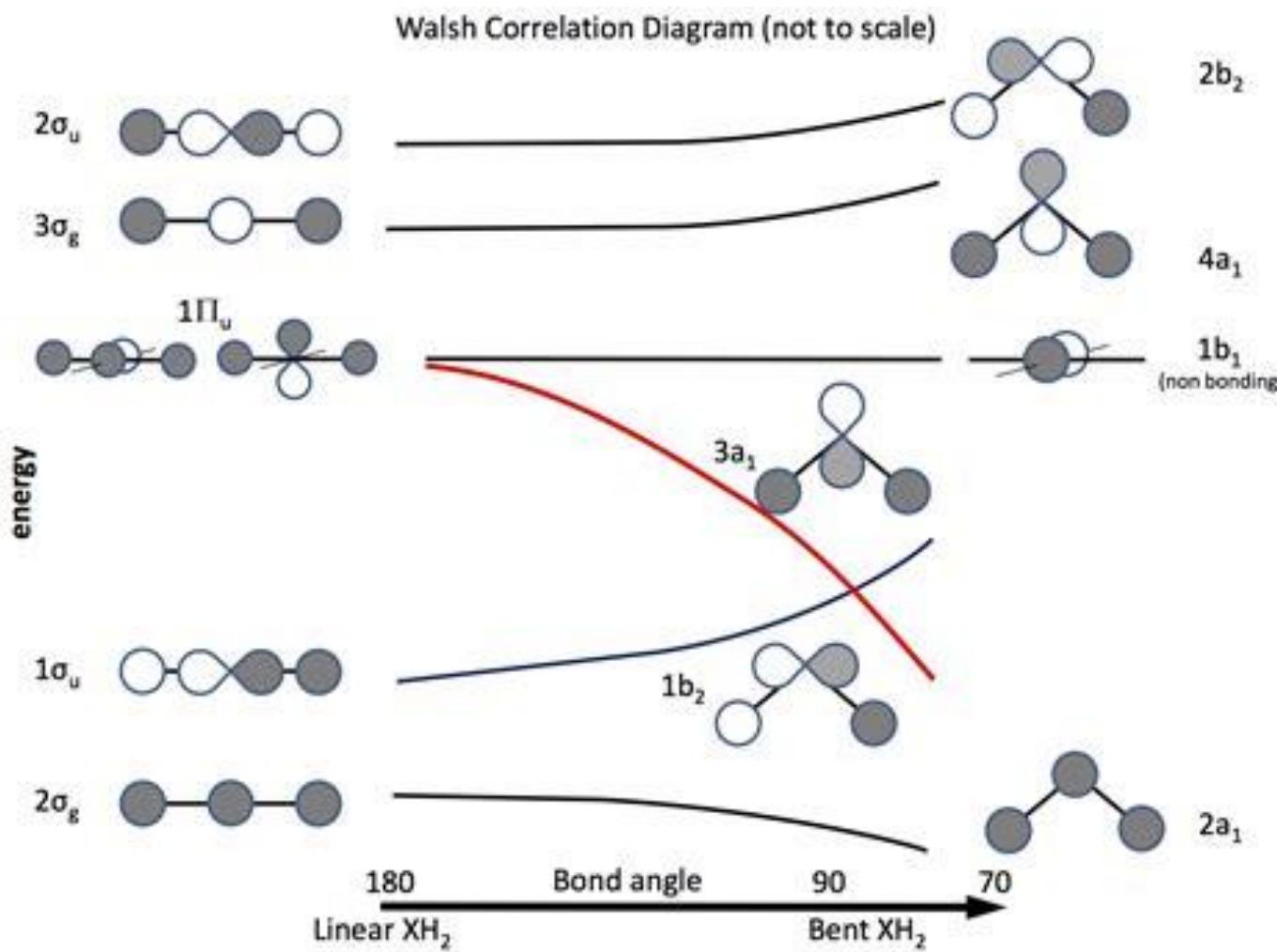


Fig. 2.35 The Walsh diagram for  $\text{XH}_2$  molecules. Only the bonding and nonbonding orbitals are shown.

- Each of the curves plotted on Fig. 2.35 will have a maximum or minimum on the 180° axis.
- The two lowest energy curves have a minimum on the 180° line. Therefore, we would expect  $\text{XH}_2$  molecules having four valence electrons to be linear.  $\text{XH}_2$  molecules with more than four valence electrons are expected to be angular because at least one electron is in the nonbonding  $2a_1$  orbital. **If the molecule is close to linear then the order of filling the molecular orbitals will be in the order of their increasing energy, which is  $1a_1 2a_1 1b_2 1b_1$ .**
- The simplest  $\text{XH}_2$  molecule in Period 2 is the transient gas-phase  $\text{BeH}_2$  molecule ( $\text{BeH}_2$  normally exists as a polymeric solid, with four-coordinate Be atoms). There are four valence electrons in a  $\text{BeH}_2$  molecule, which occupy the lowest two molecular orbitals. If the lowest energy is achieved with the molecule angular, then that will be its shape. We can decide whether or not the molecule is likely to be angular by accommodating the electrons in the two lowest-energy orbitals corresponding to an arbitrary bond angle in Fig. 2.35.
- We then note that the HOMO decreases in energy on going to the right of the diagram (in the direction of increasing bond angle) and that the lowest total energy is obtained when the molecule is linear. Hence,  $\text{BeH}_2$  is predicted to be linear and to have the configuration  $1\sigma^2 2\sigma^2$ .
- In  $\text{CH}_2$ , which has two more electrons than  $\text{BeH}_2$ , three of the molecular orbitals must be occupied. In this case, **the lowest energy is achieved if the molecule is angular and has configuration  $1a_1^2 2a_1^2 1b_2^2$ .**

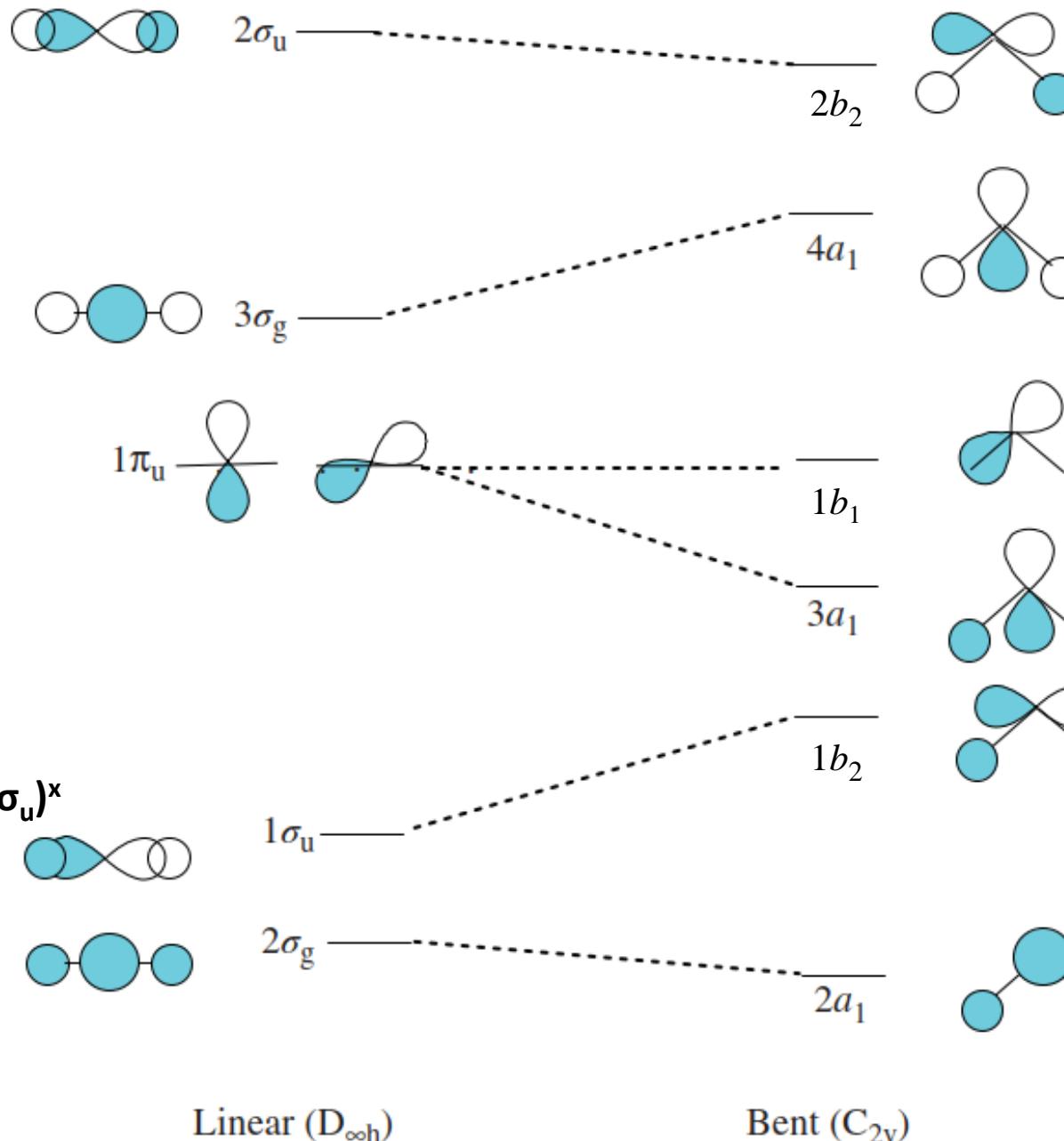
- In general, any  $XH_2$  molecule with from five to eight valence electrons is predicted to be angular. The observed bond angles are:
  - $BeH_2$     $BH_2$     $CH_2$     $NH_2$     $OH_2$
  - $180^\circ$     $131^\circ$     $136^\circ$     $103^\circ$     $105^\circ$
- These experimental observations are qualitatively in line with Walsh's approach, but for quantitative predictions we have to turn to detailed molecular orbital calculations.
- Walsh applied his approach to molecules other than compounds of hydrogen, but the correlation diagrams soon become very complicated. His approach represents a valuable model because it traces the influences on molecular shapes of the occupation of orbitals spreading over the entire molecule. Correlation diagrams like those introduced by Walsh are frequently encountered in contemporary discussions of the shapes of complex molecules. They illustrate how inorganic chemists can sometimes identify and weigh competing influences by considering two extreme cases (such as linear and  $90^\circ$   $XH_2$  molecules), and then rationalize the fact that the state of a molecule is a compromise intermediate between the two extremes.



**FIGURE 10.12** The Walsh correlation diagram for the *valence electrons* of an  $\text{AH}_2$  molecule. The left side of the diagram gives the energy ordering of the molecular orbitals for an H-A-H bond angle of  $180^\circ$  (linear). The right side gives the energy ordering of the molecular orbitals for an H-A-H bond angle of  $90^\circ$ . The solid lines tell us how the energies of the molecular orbitals depend upon H-A-H bond angles between  $90^\circ$  and  $180^\circ$  (linear).

- Bending lifts the degeneracy of the  $1\Pi_u$  orbitals in the linear structure, stabilizing the  $3a_1$  (see Figure 10.12), and not affecting the energy of the  $1b_1$  orbital. For large bending angles, the energy of the  $3a_1$  orbital drops below that of the  $1b_2$  orbital.

➤ The MOs for the Walsh diagram for  $\text{AH}_2$  molecules are shown in Figure 10.30.



➤ note a combination of first and second order Jahn-Teller effects

$$(2a_1)^2 (1b_2)^2 (3a_1)^2 1b_1^x$$

$$(2a_1)^2 (1b_2)^2 (3a_1)^x$$

$\text{BH}_2$ : bond angle of  $131^\circ$   
 $\text{BeH}_2$ ...shape?  
 $\text{H}_2\text{O}$ ...?

- The  $2a_1$  MO in the bent configuration is lower in energy than the corresponding  $2\sigma_g$  MO in the linear geometry because of the increased orbital overlap between the ligands as the bond angle decreases from  $180^\circ$ .
- Thus, any  $AH_2$  molecule having 1–2 valence electrons will prefer to populate the  $2a_1$  MO in the bent molecular geometry.
- ✓ The  $H_3^+$  ion, whose structure has been determined to form an equilateral triangle, is an example of a two-electron  $AH_2$  molecule.
- A consideration of the next highest level of MOs in each geometry shows that there is considerably more overlap in the  $1\sigma_u$  MO of the linear geometry (where the  $2p_z$  orbital interacts directly with the 2H SALC (symmetry-adapted linear combination)) than in the  $1b_2$  MO of the bent geometry (where the  $2p_z$  orbital and the SALC are at an angle to one another).
- ✓ Thus, any  $AH_2$  molecule having 3–4 valence electrons will prefer the linear molecular geometry.
- ✓ We have already encountered one such example in  $\text{BeH}_2$ , which has four valence electrons. Lithium dihydride (which has three valence electrons) is another example.

- Moving up the MO diagram to the third set of corresponding MOs, the  $1\pi_{ux}$  MO in  $D_{\infty h}$  is nonbonding, while the corresponding  $3a_1$  MO in  $C_{2v}$  is bonding.
- ✓ Thus, any *AH<sub>2</sub> molecule having 5–6 valence electrons will favor the bent* molecular geometry, as is the case for BH<sub>2</sub>, which has five valence electrons and an equilibrium bond angle of 131°.
- Moving up to the fourth energy level, the  $1\pi_{uy}$  MO in  $D_{\infty h}$  is nonbonding, while the corresponding  $1b_1$  MO in  $C_{2v}$  is also nonbonding. Thus, these two orbitals have the same energy. Any AH<sub>2</sub> molecule having **7–8 total valence** electrons will prefer the **bent molecular geometry**, because it is the **overall orbital energy that matters**.
- ✓ The **water molecule**, which has eight valence electrons, has a **bent molecular geometry** (104.5°).
- Continuing up the MO diagram to the fifth energy level, the  $3\sigma_g$  MO in  $D_{\infty h}$  is less antibonding than the  $4a_1$  MO in  $C_{2v}$ .
- ✓ Thus, any AH<sub>2</sub> species containing 9–10 valence electrons will prefer a linear geometry.
- Finally, the  $2\sigma_u$  MO in  $D_{\infty h}$  is more antibonding than the  $2b_2$  MO in  $C_{2v}$ , so that 11- to 12-electron AH<sub>2</sub> molecules would prefer to be bent. Because of the population of antibonding MOs at these higher levels, very few such species actually exist.

- ✓ For a linear structure, this would correspond to the electron configuration of  $(2\sigma_g)^2 (1\sigma_u)^2$ .
  - ✓ A bent structure would have an electron configuration of  $(2a_1)^2 (1b_2)^2$  or  $(2a_1)^2 (3a_1)^2$ , depending on the bond angle.
  - ✓ Because bending destabilizes the energy of the lowest two molecular orbitals, the electron configuration  $(2\sigma_g)^2 (1\sigma_u)^2$  is lower in energy than either  $(2a_1)^2 (1b_2)^2$  or  $(2a_1)^2 (3a_1)^2$ .
  - ✓ The Walsh correlation diagram correctly predicts that BeH<sub>2</sub> is linear.
- 
- ❖ Recall: a molecule adopts the structure that best stabilizes the HOMO.
- ✓ If the HOMO is unperturbed by the structural change under consideration, then the occupied MO lying closest to it governs the geometric preference.

- Walsh diagrams are extremely accurate in the prediction of molecular geometries. A summary of the results for  $\text{AH}_2$  molecules is provided in Table 10.9.

### Walsh's Rules:

- An  $\text{AH}_2$  molecule will be Linear if it contains 3 or 4 valence electrons. e.g.  $\text{BeH}_2$ ,  $\text{BH}_2^+$ .
- Bent if it contains 1,2, or 5-8 **valence** electrons. e.g.  $\text{BH}_2$ ,  $\text{CH}_2$ ,  $\text{NH}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ .

**TABLE 10.9 Predicted molecular geometries of  $\text{AH}_2$  molecules using Walsh diagrams as a function of the total number of valence electrons in the molecule.**

Number of Valence $e^-$	Predicted Geometry
1–2	Bent
3–4	Linear
5–8	Bent
9–10	Linear
11–12	Bent

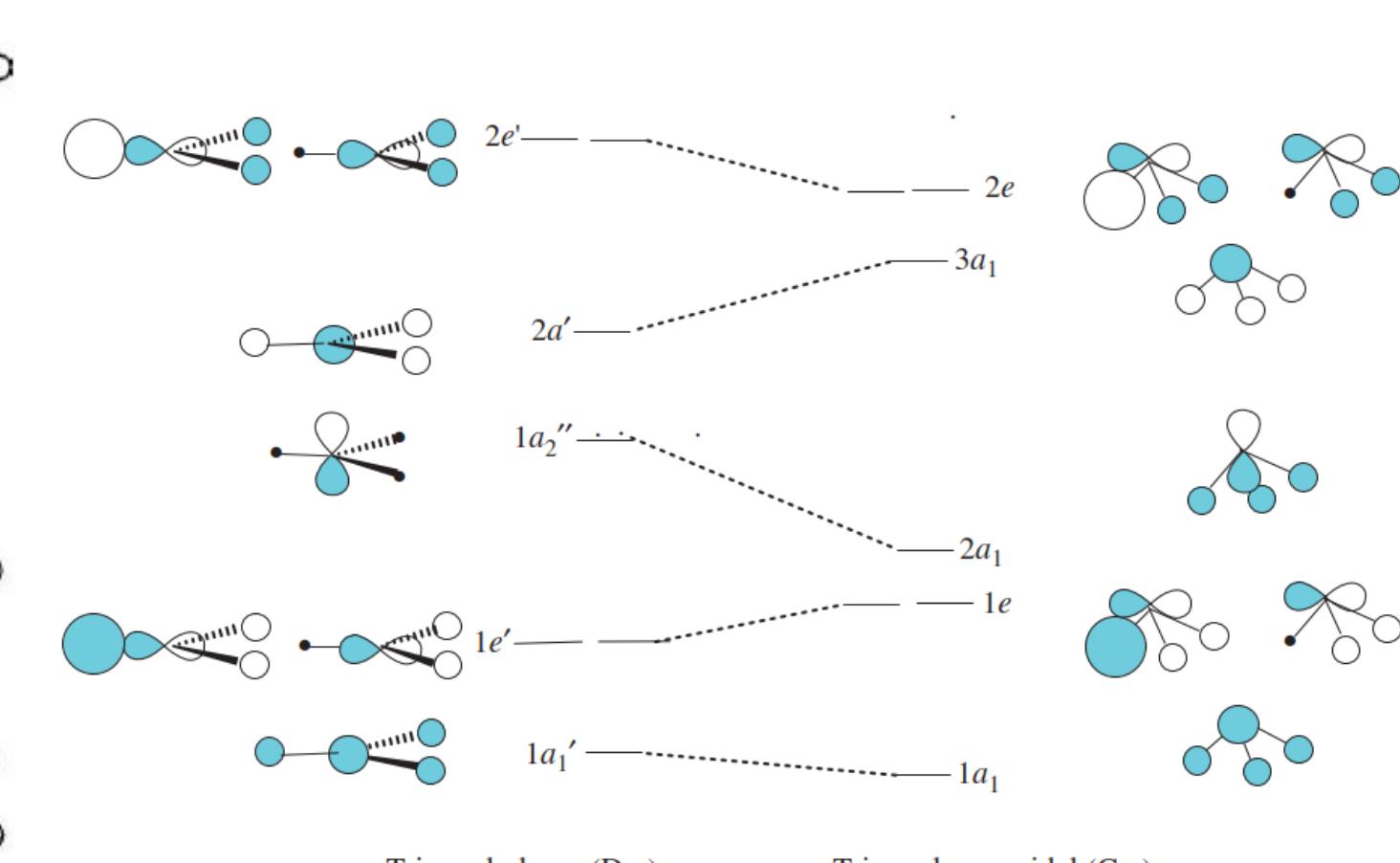
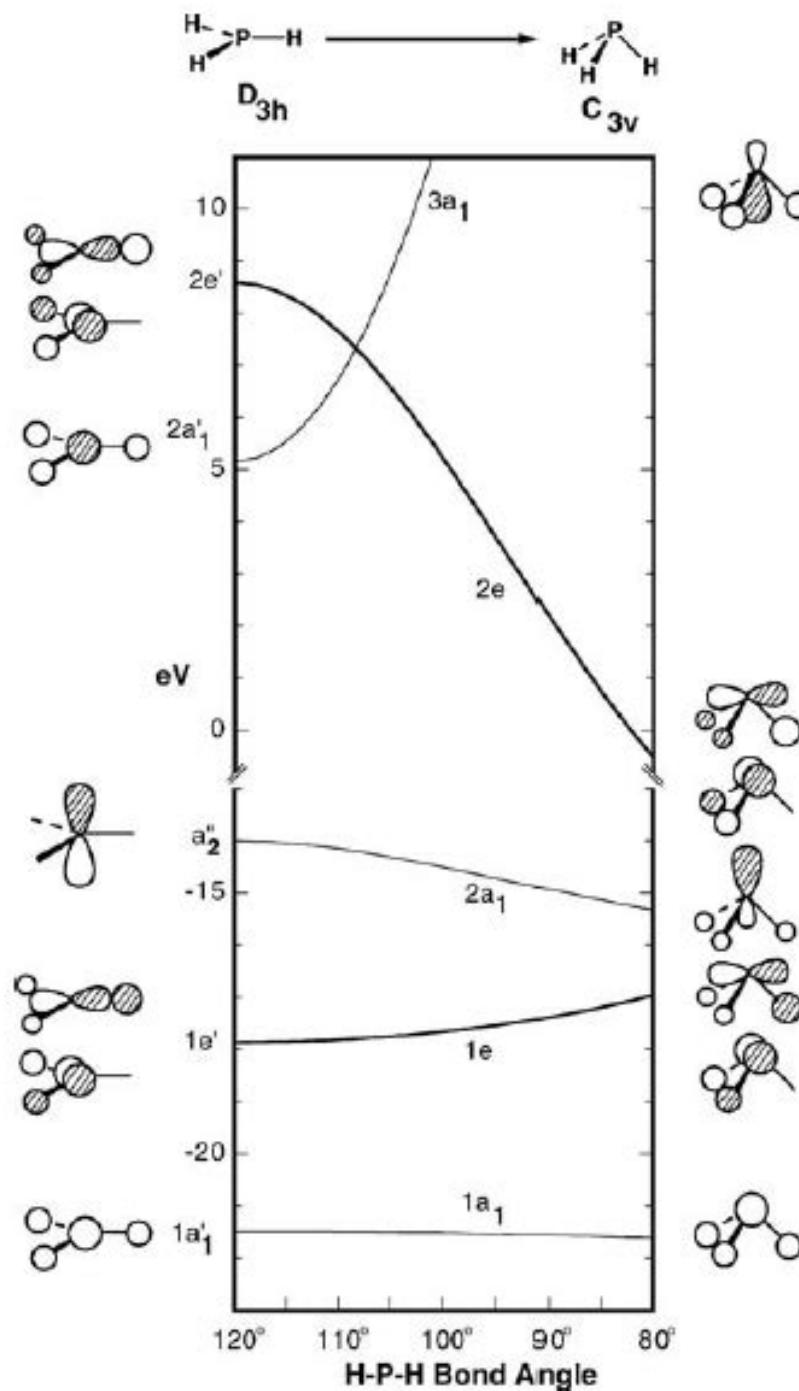


FIGURE 10.31 Walsh diagram for  $\text{AH}_3$  molecules.

**TABLE 10.10** Predicted molecular geometries of  $\text{AH}_3$  molecules using Walsh diagrams as a function of the total number of valence electrons in the molecule.

Number of Valence $e^-$	Predicted Geometry
1–2	Trigonal pyramidal
3–6	Trigonal planar
7–8	Trigonal pyramidal
9–10	Trigonal planar
11–14	Trigonal pyramidal

### Walsh's Rules:

- An  $\text{AH}_3$  molecule will be *pyramidal* if it contains 1, 2, 7 or 8 valence electrons. e.g.,  $\text{NH}_3$ .
- *planar* if it contains 3–6 valence electrons. e.g.  $\text{BH}_3$ ,  $\text{NH}_3^{2+}$ .

## ❖ Lewis acidic character of $\text{BF}_3$ and $\text{CH}_3^+$ :

- Six electron  $\text{AH}_3$  molecules should have a planar conformation.
- It can be seen that the HOMO,  $1e'$ , of planar  $\text{AH}_3$  is destabilized upon bending of the A-H bonds to form a pyramid shape, due to disruption of bonding.
- The LUMO, which is concentrated on one atomic center, is a good electron acceptor and explains the Lewis acid character of  $\text{BH}_3$  and  $\text{CH}_3^+$ .
- Walsh correlation diagrams can also be used to predict relative molecular orbital energy levels. The distortion of the hydrogen atoms from the planar  $\text{CH}_3^+$  to the tetrahedral  $\text{CH}_3\text{-Nu}$  causes a stabilization of the C-Nu bonding orbital,  $\sigma$ .
- Note that  $\text{CH}_3\text{-Nu}$  has a total of 8 valence electrons favoring trigonal pyramidal geometry.

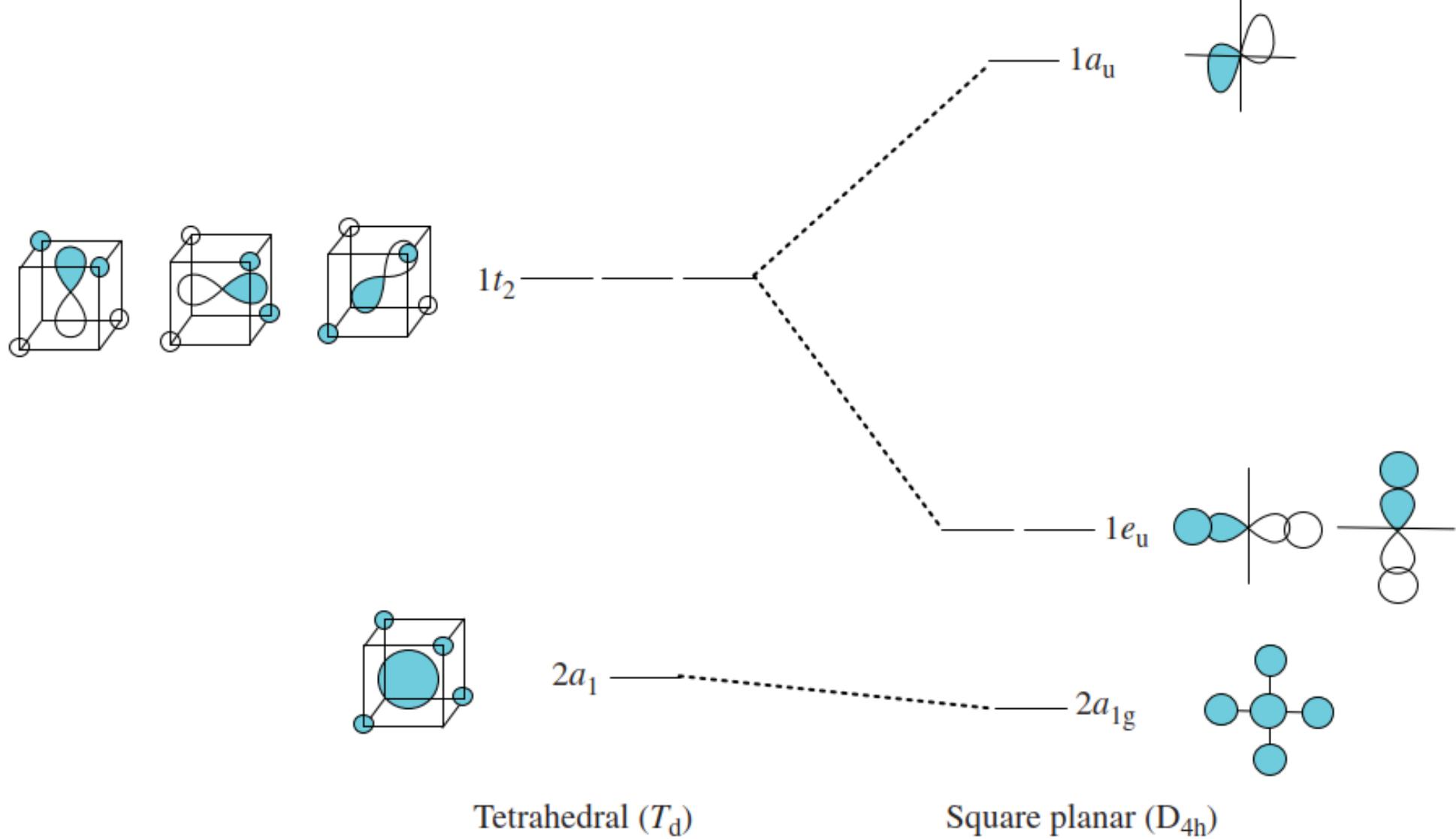


FIGURE 10.35 Partial Walsh diagram for  $\text{AH}_4$  molecules.

**TABLE 10.12** Predicted molecular geometries of  $\text{AH}_4$  molecules as a function of the total number of valence electrons in the molecule using the partial Walsh diagram shown in Figure 10.34.

Number of Valence $e^-$	Predicted Geometry
1–6	Square planar
7–8	Tetrahedral

A qualitative Walsh diagram for  $\text{AH}_4$  molecules is shown in Figure 10.35. Only the lower energy MOs in the  $T_d \rightarrow D_{4h}$  transition are shown in the figure. Table 10.12 lists the predicted molecular geometries for  $\text{AH}_4$  molecules as a function of the total number of valence electrons. Thus, the **eight-electron species**  $\text{BH}_4^-$ ,  $\text{CH}_4$ , and  $\text{NH}_4^+$  are **tetrahedral**, while the **six-electron species**  $\text{LiH}_4^-$ ,  $\text{BeH}_4$ , and  $\text{BH}_4^+$  are **square planar**.

## The pi-Electron Approximation of Conjugation

**Learning Objectives:** Demonstrate how Hückel's theory approximates the full molecular orbital picture of molecules *by treating the  $\sigma$ -bonding and  $\pi$ -bonding networks independently.*

- ❖ A ***conjugated system*** has a region of overlapping p-orbitals, bridging the interjacent single bonds, that allow a ***delocalization of  $\pi$ -electrons*** across all the adjacent aligned p-orbitals.  
*These electrons do not belong to a single bond or atom, but rather to a group of atoms.*
- Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing ***chains of carbon atoms with alternating single and double bonds***.
- An ***approximation introduced by Hückel*** in 1931 considers ***only the delocalized p electrons moving in a framework of  $\pi$ -bonds***. This is, in fact, a more sophisticated version of a free-electron model.

- The Hückel approximation is used to determine the energies and shapes of the molecular orbitals in conjugated systems.
- Within the Hückel approximation, the covalent bonding in these hydrocarbons can be separated into two independent "frameworks": the  $\sigma$ -bonding framework and the  $\pi$ -bonding framework.
- The wavefunctions used to describe the bonding orbitals in each framework results from different combinations of atomic orbitals. The method limits itself to addressing conjugated hydrocarbons and specifically only electron molecular orbitals are included because these determine the general properties of these molecules; the sigma electrons are ignored. This is referred to as sigma-pi separability and is justified by the orthogonality of  $\sigma$  and  $\pi$  orbitals in planar molecules. For this reason, the Hückel method is limited to planar systems. Hückel approximation assumes that the electrons in the bonds “feel” an electrostatic potential due to the entire  $\sigma$ -bonding framework in the molecule (i.e. it focuses only on the formation of bonds, given that the bonding framework has already been formed).

## Ethylene

- Before considering the Hückel treatment for ethylene, it is beneficial to review the general bonding picture of the molecule. Bonding in ethylene involves the  $sp^2$  hybridization of the 2s,  $2p_x$ , and  $2p_y$  atomic orbitals on each carbon atom; leaving the  $2p_z$  orbitals untouched (Figure 10.5.2).
- The use of hybrid orbitals in the molecular orbital approach described here is merely a convenience and not invoking valence bond theory (directly). An identical description can be extracted using exclusively atomic orbitals on carbon, but the interpretation of the resulting wavefunctions is less intuitive.

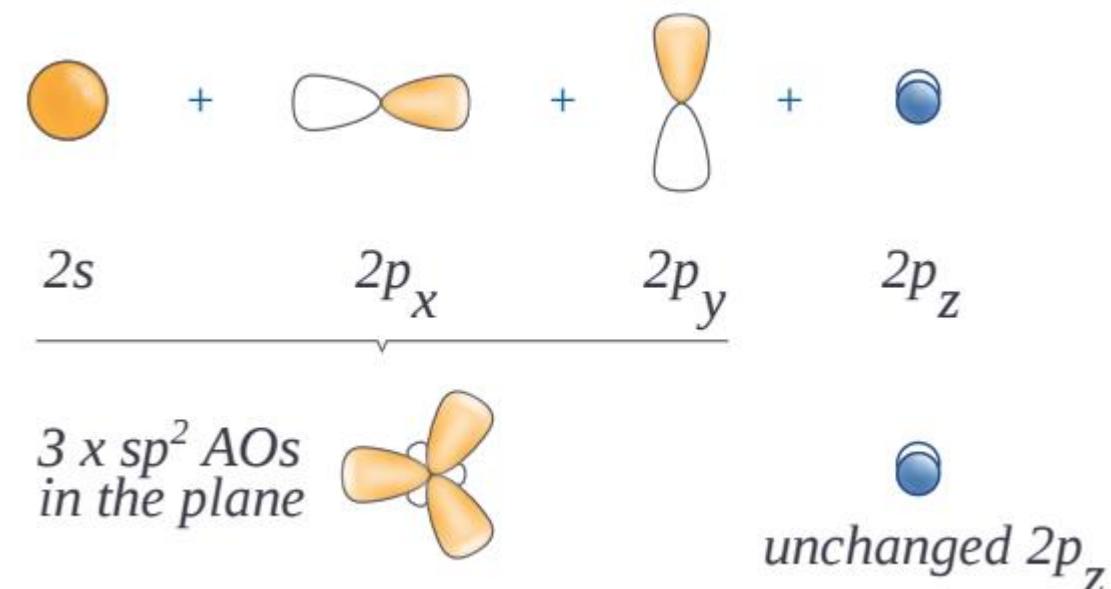
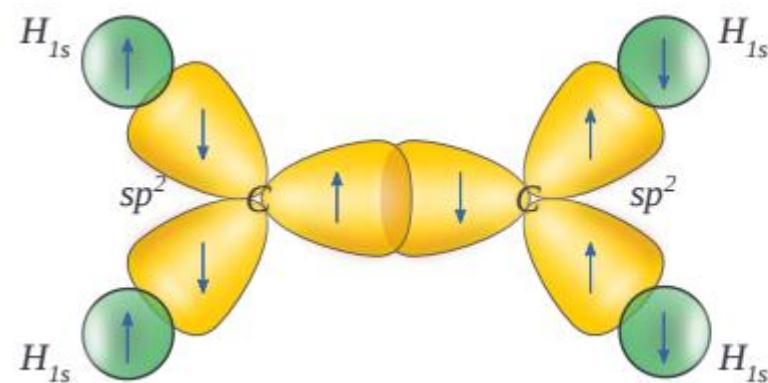
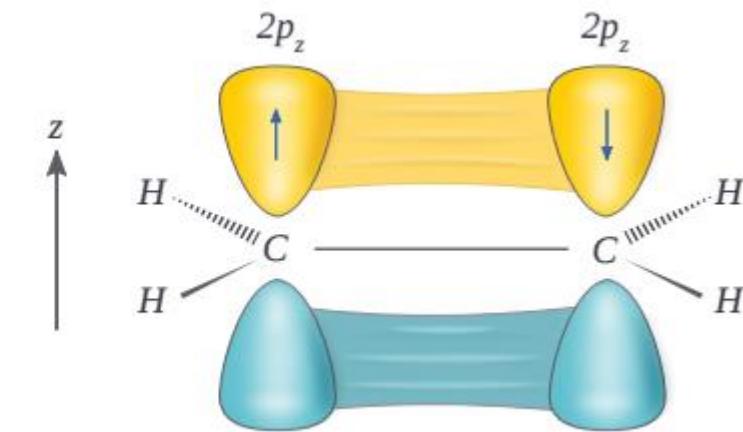


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give hybrid orbitals for bonding to hydrogen atoms in ethylene

➤ The simplest hydrocarbon to consider that exhibits bonding is ethylene (ethene), which is made up of four hydrogen atoms and two carbon atoms. Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately  $120^\circ$ . This angle suggests that the carbon atoms are  $sp^2$  hybridized, which means that a singly occupied  $sp^2$  orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied  $sp^2$  lobe on the other C. Thus, each carbon forms a set of three bonds: *two* C–H ( $sp^2 + s$ ) and *one* C–C ( $sp^2 + sp^2$ ) (part (a) of Figure 10.5.1 ).



(a)  $C_2H_4$   $\sigma$ -bonded framework



(b)  $C_2H_4$   $\pi$  bonding

Figure 10.5.1 : (a) The  $\sigma$ -bonded framework is formed by the overlap of two sets of singly occupied carbon  $sp^2$  hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five bonds (four C–H bonds and one C–C bond).

(b) ***One singly occupied unhybridized 2p orbital remains*** on each carbon atom ***to form a carbon–carbon bond.*** (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the z-axis.)

➤ The bonding occurs via the mixing of the electrons in the hybrid orbitals on carbon and the electrons in the atomic orbitals of the four hydrogen atoms (Figure 10.5.1; left) resulting in the  $\sigma$ -bonding framework. ***The  $\pi$ -bonding framework results from the unhybridized orbitals*** (Figure 10.5.2; right). ***The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram*** in Figure 10.5.3. Hückel theory is concerned only with describing the molecular orbitals and energies of the  $\pi$ -bonding framework.

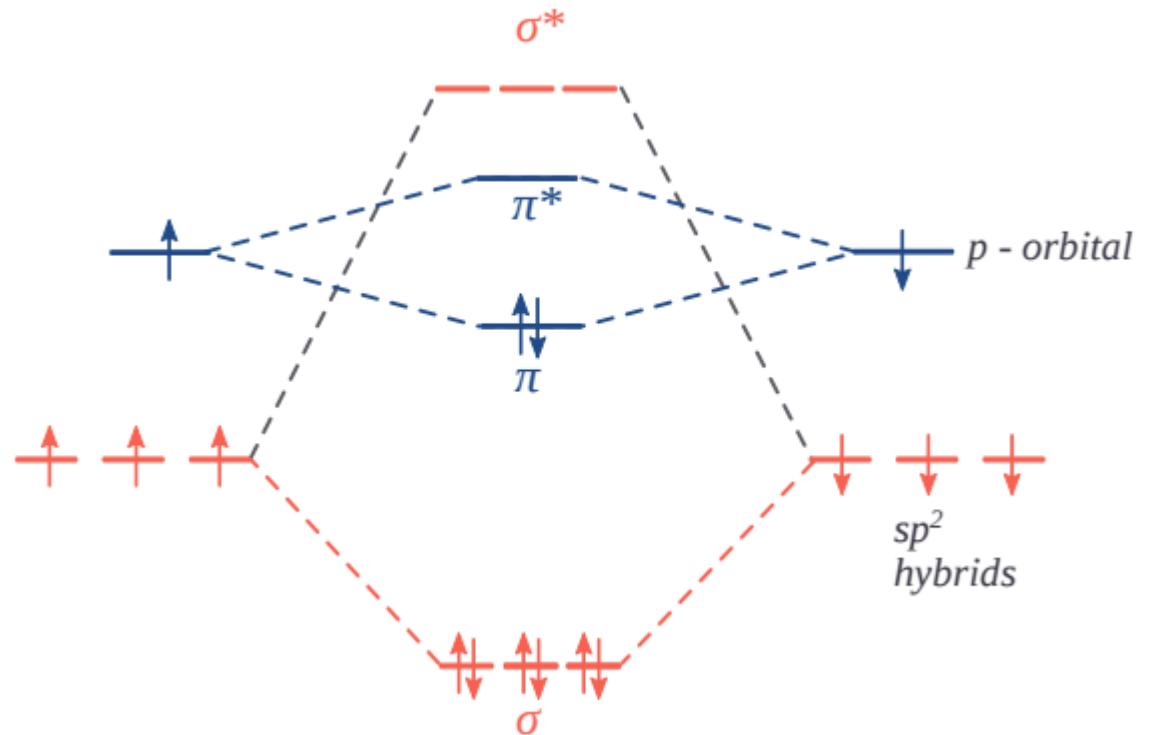


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the  $\pi$ -bonding framework (blue) and the  $\sigma$ -bonding frameworks (red) of ethylene.

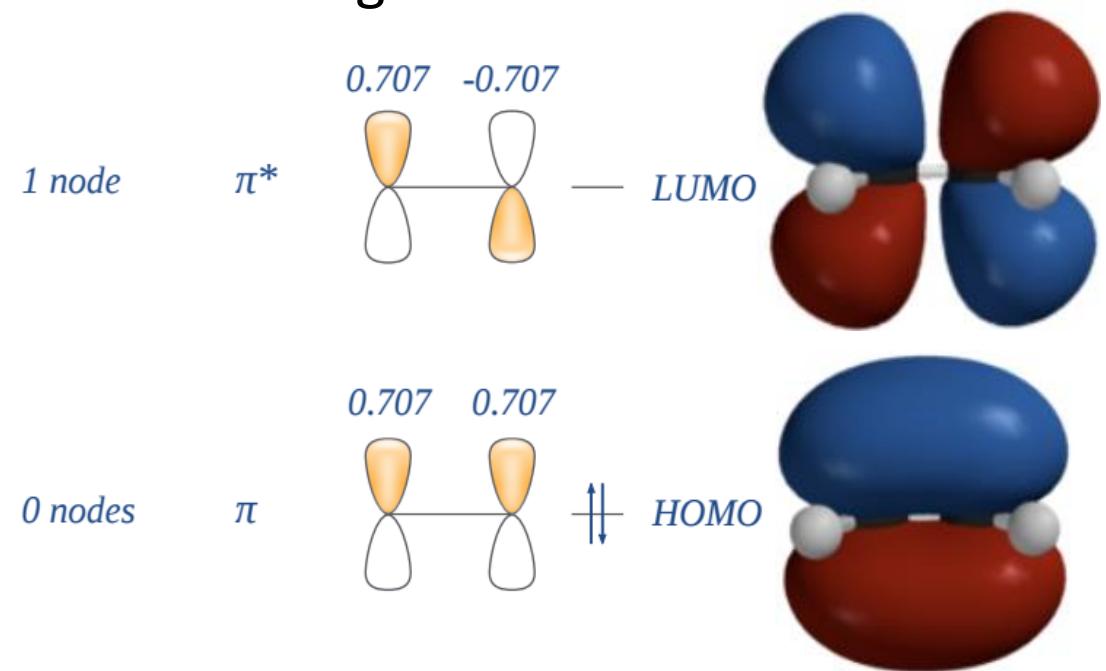


Figure 10.5.5 : Schematic representation of the  $\pi$  molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy.

- The above Figure shows that the ***energy difference between  $\pi$  bonding and  $\pi$  antibonding orbitals is less than the difference between  $\sigma$  bonding and  $\sigma$  antibonding orbitals***, suggesting that ***unsaturated hydrocarbons such as ethene should absorb light at longer wavelengths (less energy) than do saturated hydrocarbons***. Ethene, for example, turns out to have an ultraviolet absorption peak at  $58\ 500\ \text{cm}^{-1}$ , whereas ethane (with no  $\pi$  orbitals) does not begin to absorb strongly until  $62\ 500\ \text{cm}^{-1}$
- Therefore, we can develop a simplified molecular-orbital treatment of unsaturated hydrocarbons that includes only the  $\pi$  orbitals. In this approximation, the relatively complicated energy-level diagrams can be simplified.

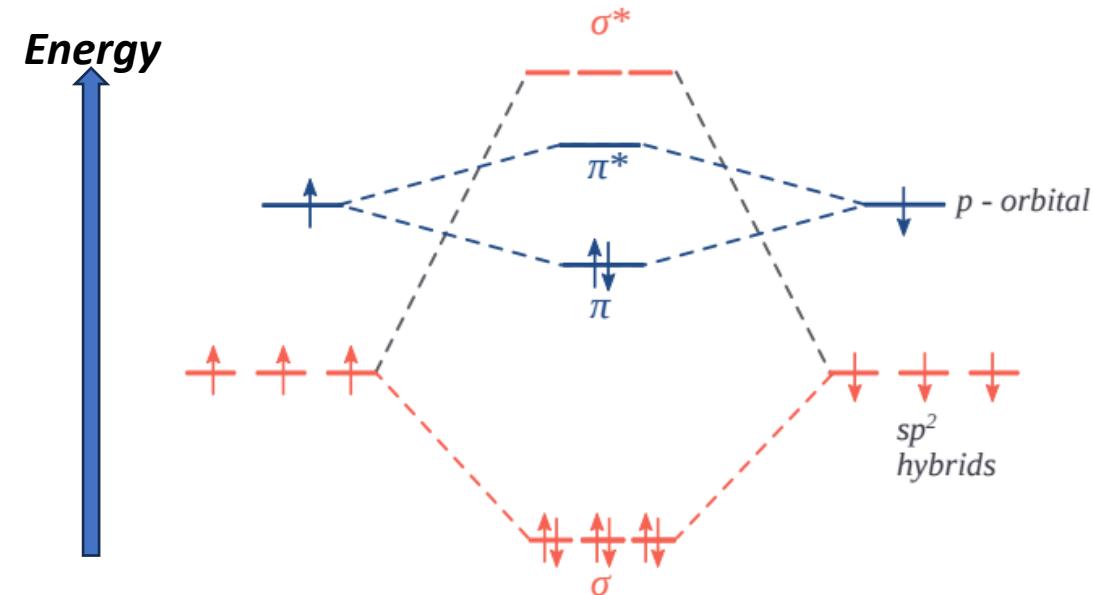
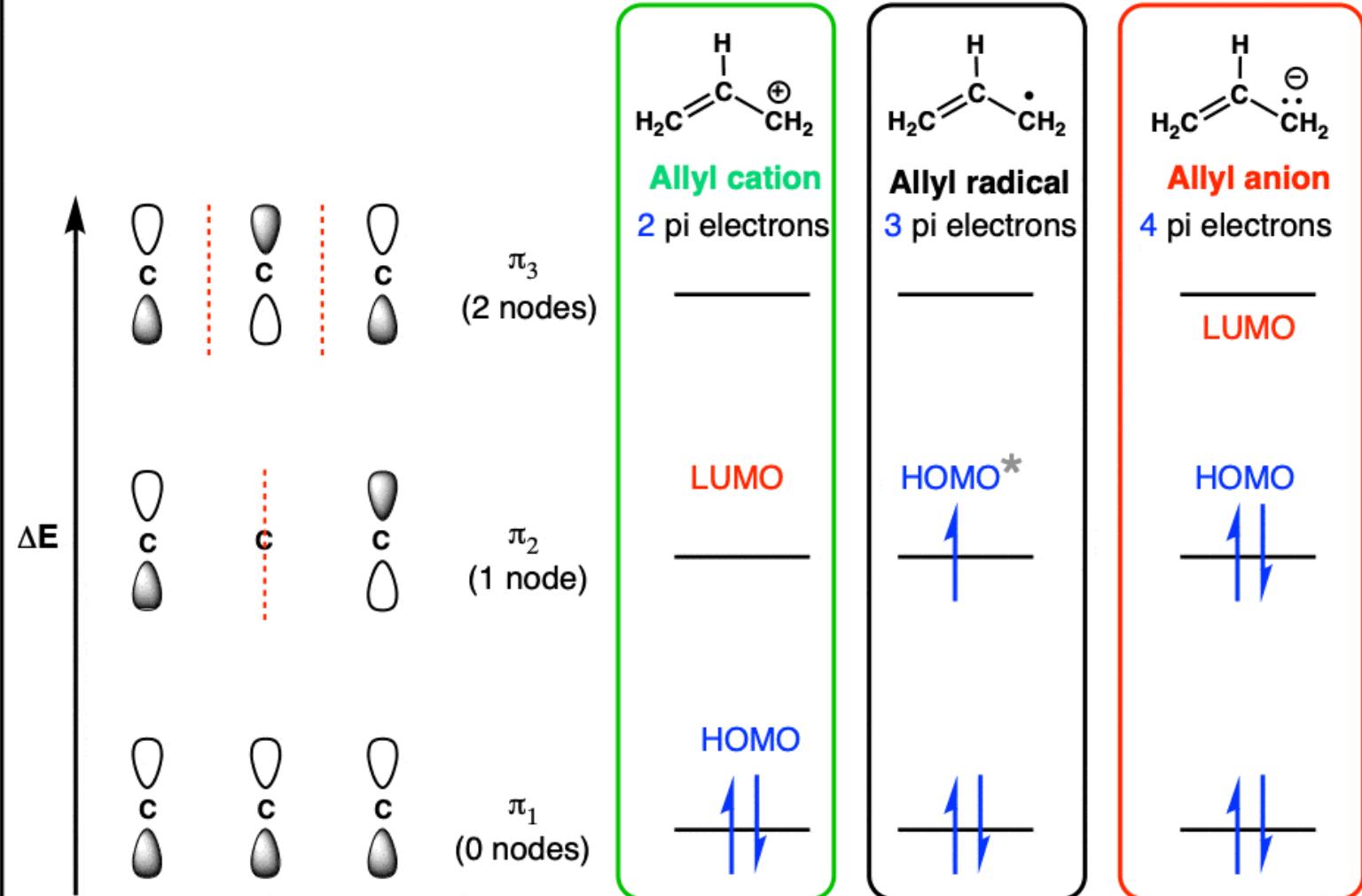


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the  $\pi$ -bonding framework (blue) and the  $\sigma$ -bonding frameworks (red) of ethylene.

## Molecular Orbitals of pi-Congugated System: The Allyl Cation, Allyl Radical And Allyl Anion

- ❖ Drawing out the molecular orbitals of each of these systems can be done in a stepwise manner.
- ❖ Here, on three carbon atoms, we have 3 p-orbitals. 3 p-orbitals combine to form 3 MOs.
- ❖ The **lowest-energy** molecular orbital ( $\pi_1$ ) will have all three p-orbitals aligned with the *same phase* and zero **nodes**.
- ❖ The **highest-energy** molecular orbital ( $\pi_3$ ) will have all three p-orbitals with **opposite phases** and **two nodes**.
- ❖ The intermediate energy molecular orbital has **one** node that is on the central atom.
- ❖ The next step is to fill it with pi-electrons: **two** for the allyl cation, **three** for the allyl radical, and **four** for the allyl anion.

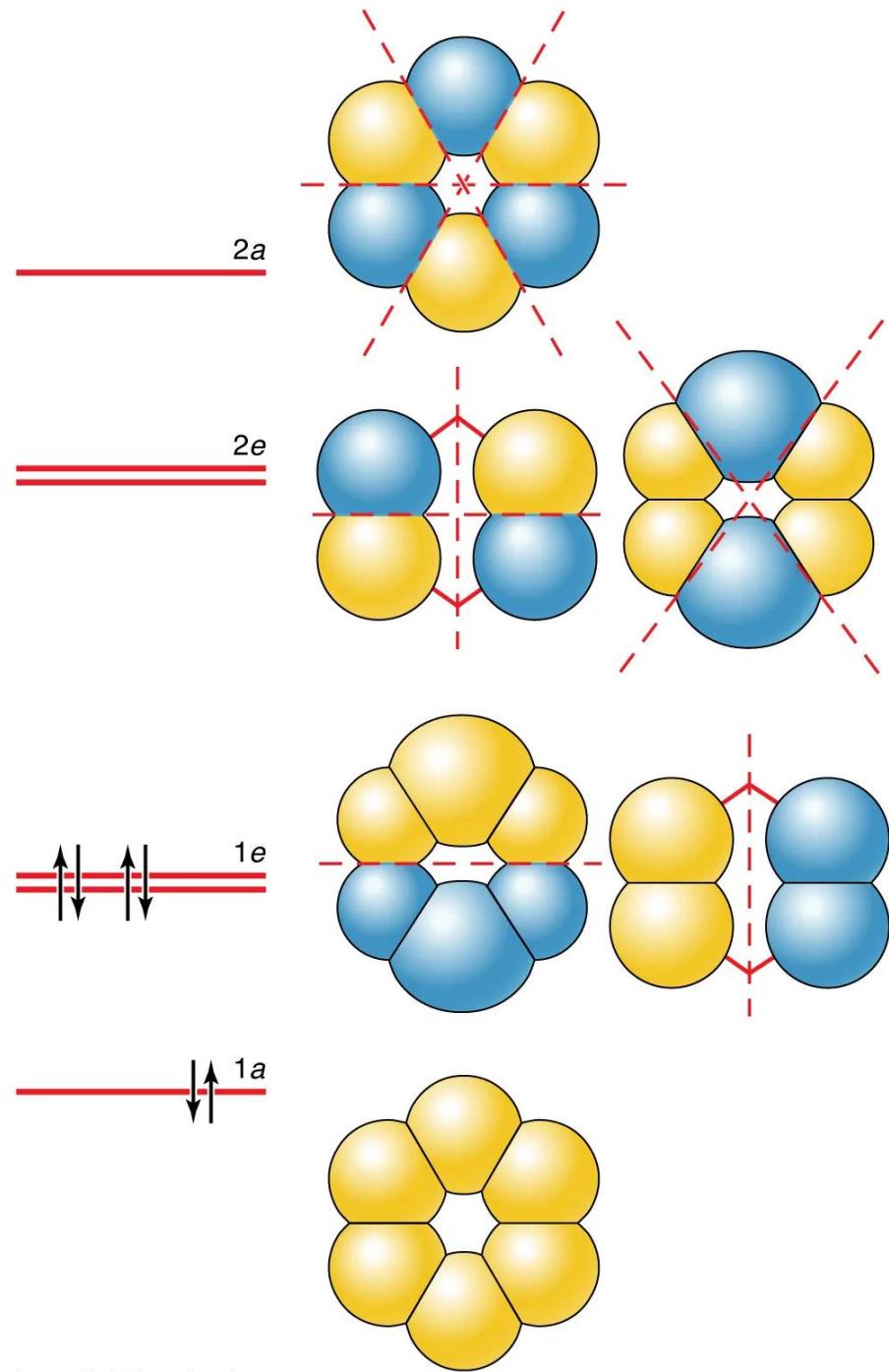
## Summary: Molecular Orbitals For The “Allyl” System (3 p-orbitals)



**LUMO** lowest unoccupied molecular orbital

**HOMO** highest occupied molecular orbital

\*sometimes called "singly occupied molecular orbital", or SOMO



## Benzene

Figure 15: The six  $\pi$  molecular orbitals of a benzene molecule and their relative energies. Only the three lowest-energy orbitals are occupied in benzene. The bonding and antibonding character of these orbitals is distributed around the ring of carbon atoms. The dashed lines represent nodal planes, and the shading reflects the two possible phases of the orbitals. Constructive interference, resulting in an area of high electron density, occurs between like phases; destructive interference, resulting in a nodal plane, occurs between unlike phases.

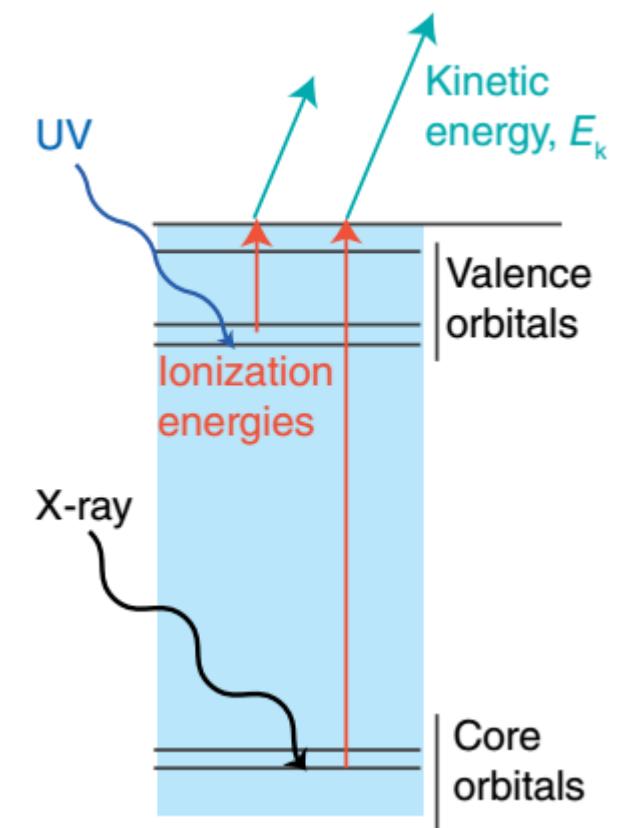
## EXPERIMENTAL TECHNIQUES FOR AOs, MOs, AND BOND INFORMATION

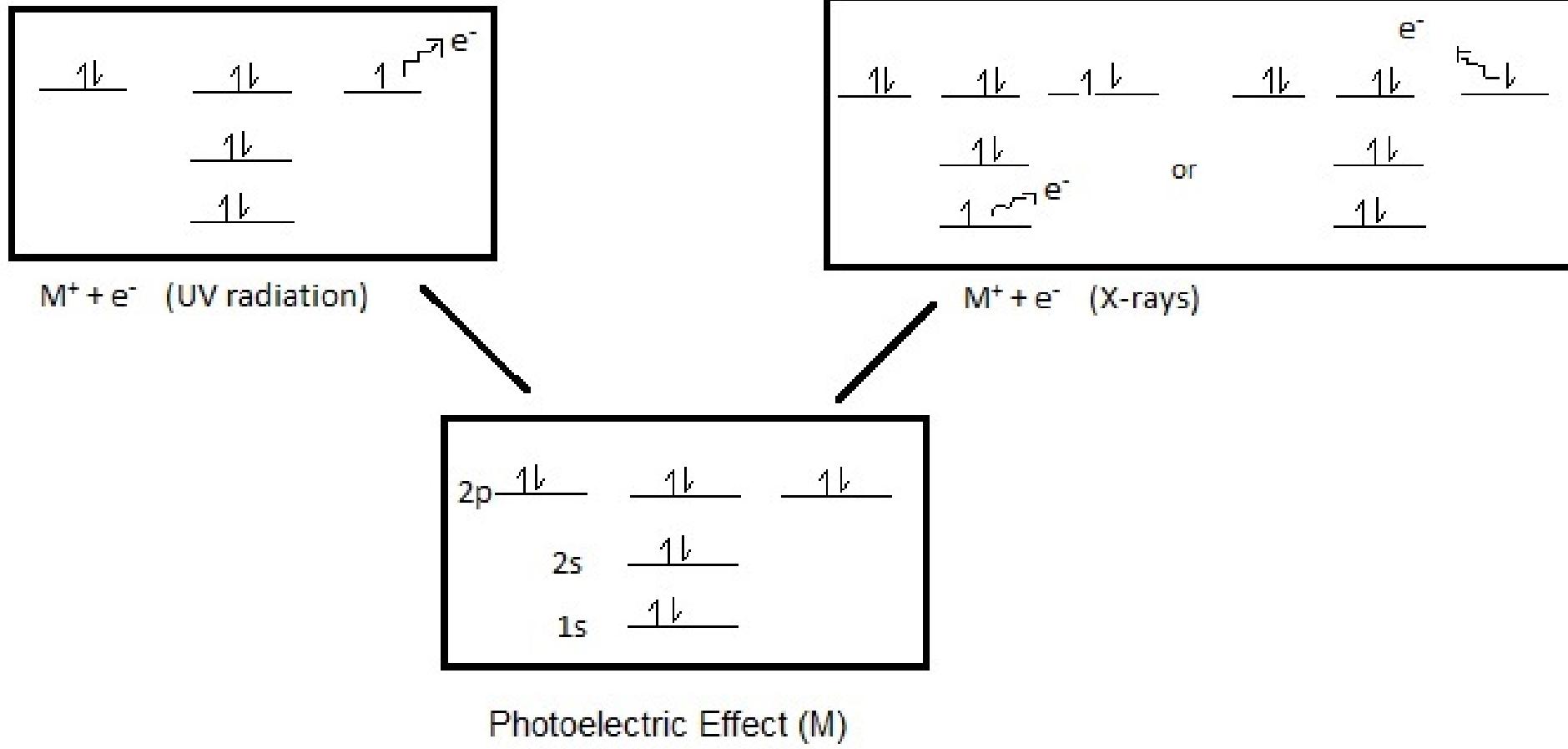
- Most of what we know about the structure of atoms and molecules has been obtained *by studying the interaction of electromagnetic radiation with matter.*
- **Line spectra reveal the existence of shells of different energy where electrons are held in atoms.**
- From the study of molecules by means of ***infrared*** and ***microwave*** spectroscopies we obtain information about vibrational and rotational states of molecules. The ***types of bonds*** present, the ***geometry of the molecule***, and even ***bond lengths*** may be determined in specific cases.

## Photoelectron Spectra (PES) Support the Existence of Molecular Orbitals

- ❖ **Photoelectron spectroscopy** (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.
  - **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.
  - **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels. The idea of atomic orbitals and molecular orbitals is rather abstract and sometimes appears far removed from reality.
- The energies of orbitals are calculated today by solving the Schrödinger equation with computer software. The commercial software available is now so sophisticated that this approach can be as easy as typing in the name of the molecule or drawing it on screen. But these values are theoretical. How do we determine orbital energies experimentally?
- It so happens, however, that the electron configurations of molecules can be demonstrated experimentally. The approach used is very similar to the photoelectric effect.
- The spectroscopic technique known as ***photoelectron spectroscopy (PES) has been of enormous importance in determining how electrons are bound in molecules.*** This technique ***provides direct information on the energies of molecular orbitals in molecules.***

- Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:  $E = h\nu$  (10.4.1)
- where  $h$  is Planck constant and  $\nu$  is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the present topic.
- Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy).
- In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. *the number of emitted photoelectrons as a function of their kinetic energy*) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.





**Figure 1.** Scheme for UPS and XPS. Illustrates the ejection of electrons from respectively the valence electrons and core electrons.

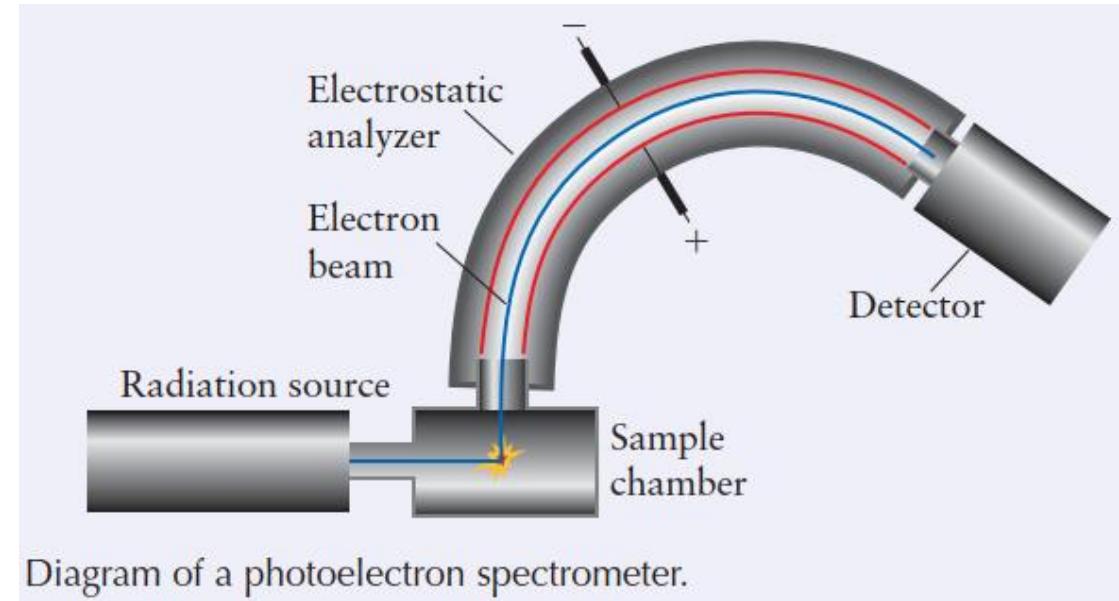
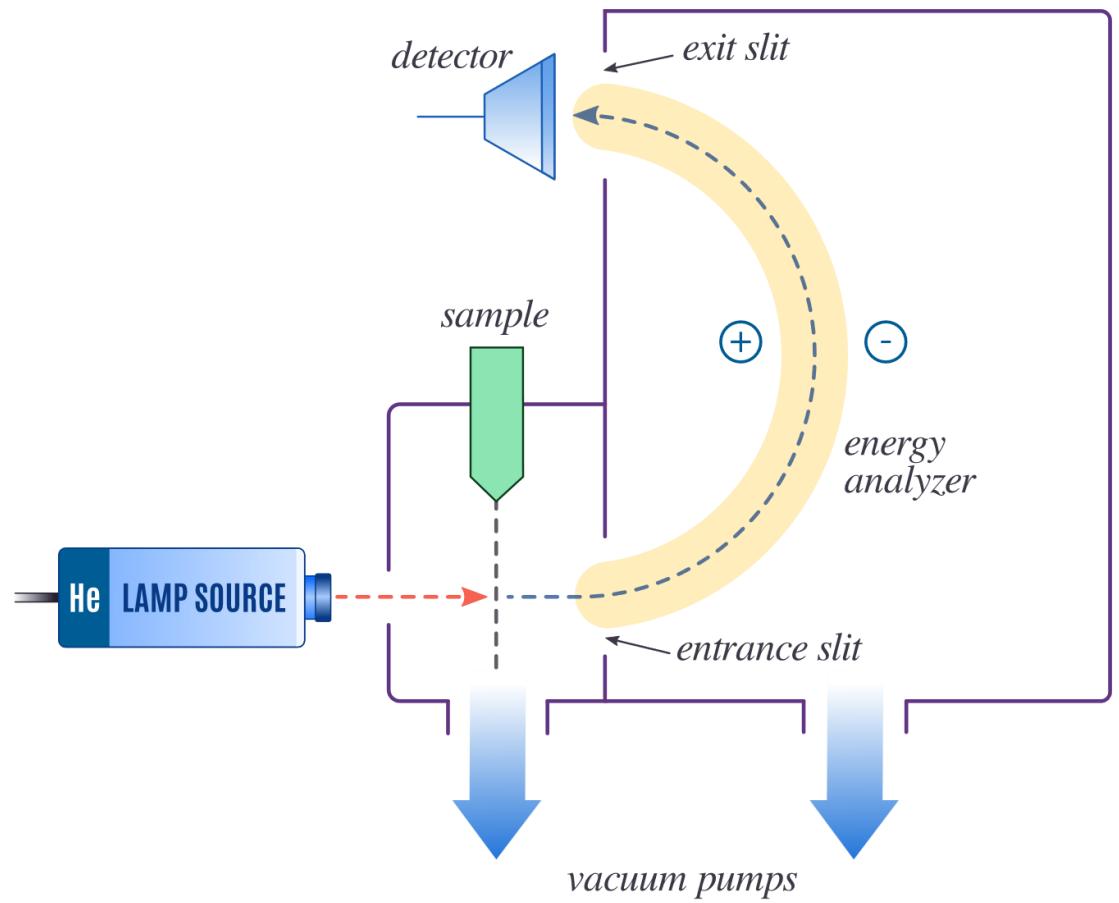


Diagram of a photoelectron spectrometer.

Figure 10.4.1 : Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit.

- A photoelectron spectrometer contains a source of high-frequency, short-wavelength radiation.
- ***Ultraviolet radiation is used (for PES) most often for molecules***, but
- ***x-rays are used (for ESCA) to explore orbitals buried deeply inside solids***.

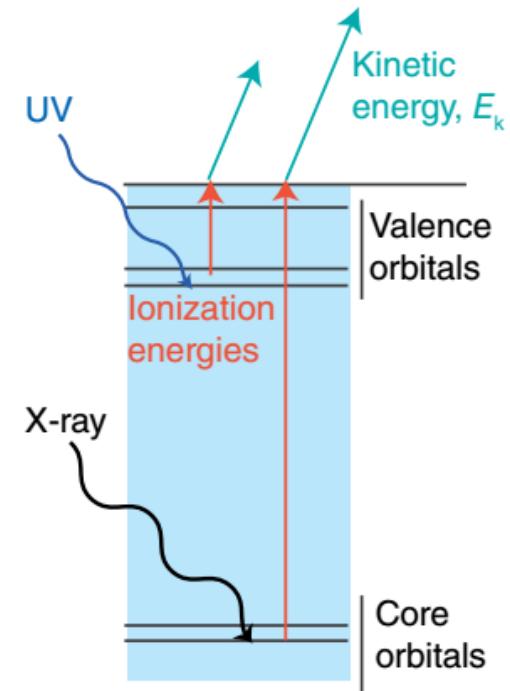
Photons in both frequency ranges have so much energy that they can eject electrons from the molecular orbitals they occupy. Photoelectron spectroscopy may be used to study ***orbital energies of either core or valence electrons***.

Applying a source that produces x-rays (the source is high energy X-rays: 1000-1500 eV), the photon energy suffices to remove electrons from inner shells of atoms. **Electron spectroscopy for chemical analysis** (ESCA) or **X-PES** (or, even shorter, **XPS**) is an analytical technique founded on this process. As the ***energy of inner shell electrons is almost independent from the molecular surroundings***, X-PES spectra ***contain information on the elements present*** in a sample; a feature that led to the name "... for chemical analysis".

If ultraviolet radiation is used, we speak of **UV-PES** (or simply **UPS** which uses the energy of ultraviolet rays <41 eV). Here, the photon represents an energy quantum that allows the removal or ***ionization of valence electrons (which are responsible for bonding in molecules)*** from a ***valence shell or molecular orbitals***. Therefore, from UV-PES spectra, information on the energy of such orbitals is gained.

- Helium gas is the most common UV radiation source used for the ***photoelectron spectroscopy*** of molecules. The photon source that is frequently employed is the **He(I) source** that emits photons having an energy of 21.22 eV as the excited state  $2s^1\ 2p^1$  relaxes to the  $1s^2$  ground state. (When electronically excited, He atoms emit nearly monochromatic (single wavelength) radiation at a wavelength of 58.4 nm.) The ionization potential for the hydrogen atom is 13.6 eV, and the first ionization potential for many molecules is of comparable magnitude. The energy of these photons is above the threshold required to eject electrons from many valence shell molecular orbitals.
- If **high-energy electromagnetic radiation** is directed into a gas, electrons are ejected from the molecules in the gas.
- The **energy required to eject an electron from a molecule**, called the **ionization energy**, is a direct measure of how strongly bound the electron is within the molecule.

- The ionization energy of an electron within a molecule depends upon the molecular orbital the electron occupies; ***the lower the energy of the molecular orbital, the more energy needed to remove, or ionize, an electron from that molecular orbital.***
- *The measurement of the energies of the electrons ejected by radiation incident on gaseous molecules is called photoelectron spectroscopy (PES).*
- **Photoelectron Spectra (PES) Support the Existence of Atomic and Molecular Orbitals.**



## Photoelectron Spectra (PES) Support the Existence of Molecular Orbitals

Photoelectron spectroscopy is an instrumental technique that enables the measurement of **orbital energies** in atoms and molecules. In this technique gas phase atoms or molecules are ionized by high-energy radiation. For a molecule ( $M$ ), the process is as follows:



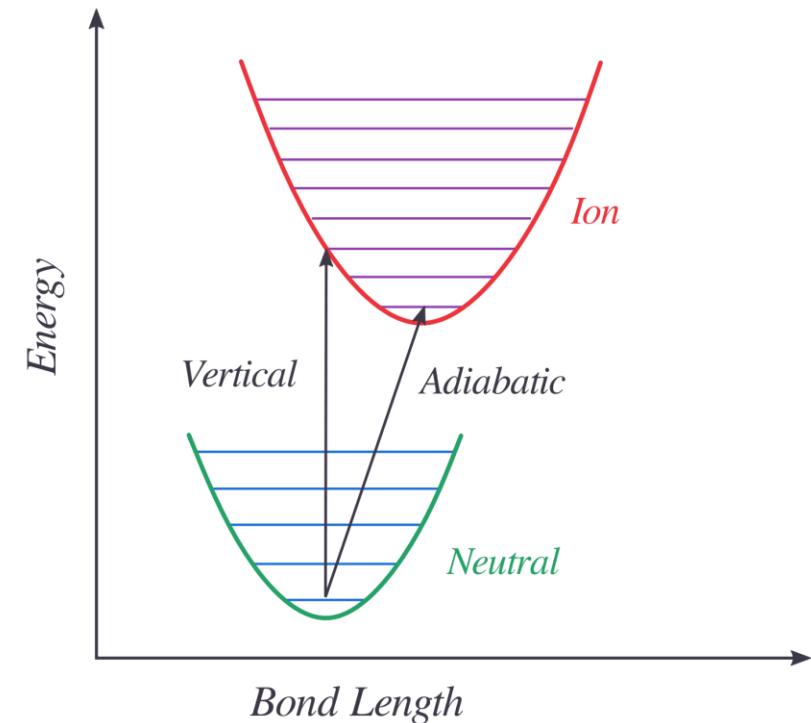
A photon with sufficient energy ( $h\nu$ ) can cause an electron to be ejected from the atom or molecule. If the photon has energy that is above the threshold required for ionization, the excess energy is imparted as kinetic energy to the ejected electron. The ionization energy (**orbital energy**), the energy of the absorbed photon, and the kinetic energy of the ejected electron are related by the equation.

$$IE = h\nu - KE(\text{electron})$$

We know  $\nu$ , the frequency of the radiation being used to bombard the molecules; so, if we could measure the kinetic energy of the ejected electron,  $KE$ , we could solve this expression to find the orbital energy.

The kinetic energy of an ejected electron depends on its speed,  $V$ , because  $KE = mV^2/2$ . A photoelectron spectrometer acts like a mass spectrometer in that it measures  $V$  for electrons just as a mass spectrometer can measure  $V$  for ions. In this method, the electrons pass through a region of electric or magnetic field, which deflects their path. As the strength of the field is changed, the paths of the electrons change, too, until they fall on a detector and generate a signal. From the strength of the field required to obtain a signal, we can work out the speed (and hence the kinetic energy) of electrons ejected from a given orbital and so obtain the energy of the orbital from which they came.

- Electrons that are ejected are passed through an analyzer and by means of a variable voltage, electrons having different energies can be detected. *The number of electrons having specific energies is counted, and a spectrum showing the number of electrons emitted (intensity) versus energy is produced.*
- In most cases, when an electron is removed during ionization, most molecules are in their lowest vibrational state. Spectra for diatomic molecules show a series of closely spaced peaks that correspond to ionization that leads to ions that are in excited vibrational states.
- If ionization takes place with the ***molecule in its lowest vibrational state to produce the ion in its lowest vibrational state***, the transition is known as ***adiabatic ionization***.
- When a diatomic molecule is ionized, the ***most intense absorption corresponds to ionization with the molecule and the resulting ion has the same bond length***. This is known as ***vertical ionization***, and it leads to ***the ion being produced in excited vibrational states***.
- The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.
- The vertical ionization energy is ***always greater than the adiabatic ionization energy***.
- In general, the ***molecule and the ion have nearly identical bond lengths when the electron is ejected from a nonbonding orbital***.



- The vertical ionization leads to the ion being produced in excited vibrational states. In general, the molecule and the ion have nearly identical bond lengths when the electron is ejected from a nonbonding orbital.
- Photoejection commonly results in cations that are excited vibrationally. Because different energies are needed to excite different vibrational states of the ion, the photoelectrons appear with different kinetic energies. The result is ***vibrational fine structure***, a ***progression of lines with a spacing in energy that corresponds to the vibrational frequency*** of the molecular ion.

In photoelectron spectroscopy (PES), we illuminate a sample with high-frequency radiation (ultraviolet or X-ray) and measure the kinetic energy of the photoelectrons emitted from the sample.

We used PES to confirm the shell structure of the atom predicted by quantum mechanics. For molecules, PES confirms the MO description of bonding and measures the energy,  $\varepsilon$ , for individual MOs. ***The bridge between PES results and MO theory is Koopmans's approximation.*** These three tools are used together to study the electronic structure of molecules in all branches of chemistry.

As a concrete example, suppose we illuminate a diatomic gaseous sample with He(I) radiation, which has energy of 21.22 eV and a wavelength of 58.43 nm, and we measure the kinetic energy of the emitted photoelectrons with an energy analyzer. The resulting PES spectrum shows a series of peaks, each of which we label with an index  $i$ . We subtract the measured kinetic energy from the photon energy, which is fixed in our experiment. Thus, by conservation of energy, we are measuring the *ionization energy*,  $IE_i$ , required to liberate those electrons that contribute to peak  $i$ . **Koopmans's theorem states that the measured ionization energy is the negative of the energy of the orbital from which the photoelectrons were emitted:  $IE_i = -\varepsilon_i$ .** (Recall that  $IE_i$  is positive because it must be provided to the system, and that  $\varepsilon_i$  is negative because it measures the amount by which the molecular orbital is stabilized relative to the cation plus a free electron.) Koopmans's theorem is only an approximation because it assumes that the ion produced during photoemission has the same orbital energies as the parent neutral molecule. In addition to the relaxation of the resulting ion, as observed for atoms, *some of the energy provided by the photon can be used to excite vibrational states in the molecular ion*, which requires an amount of energy,  $E_i^{(vib)}$ . Now the energy conservation equation is

$$h\nu_{\text{photon}} - \frac{1}{2} m_e v^2 = -\varepsilon_i + E_i^{(vib)} = IE_i$$

***As a result of the vibrational excitation, peak  $i$  in the spectrum is actually a series of narrower peaks; the separation between adjacent peaks depends on the vibrational frequency of the diatomic ion.*** The result illustrated in Figure C6.1 shows the PES of hydrogen.

The peak near 15.5 eV corresponds to the ionization energy for removing electrons with no vibrational excitation of the resulting molecular ion. As the energy increases along the axis toward 18 eV, the amount of vibrational excitation of the  $\text{H}_2^+$  ion increases, and *the spacing between vibrational levels becomes smaller. The  $\text{H}_2^+$  ion is approaching its dissociation limit.*

- These vibrational “**fine-structure**” peaks on the PES data at first appear to be a nuisance, but in fact, they greatly aid in relating experimental data to particular MOs. **The connection is made through the concept of bond order.**
- **Case A:** If the photoelectron is removed from a bonding MO, the bond order of the positive ion will be smaller than the bond order of the parent molecule. Consequently, **the bond in the molecular ion will be less stiff**, and **its vibrational frequency** (determined directly from the PES fine structure) will be **lower than that of the parent molecule** (determined by vibrational spectroscopy). The spectrum in *Case A will show several vibrational fine structure peaks* because the removal of a bonding electron is a major disturbance that starts many vibrations of the bond.
- **Case B:** If the photoelectron is emitted from an antibonding orbital, the bond order of the positive ion will be larger than the bond order of the parent molecule. The bond in the diatomic molecular ion will be **stiffer** and will show a **higher vibrational frequency**. *Case B is intermediate between case A and C, with fewer vibrational subpeaks*, because removing an antibonding electron disturbs the bond, but less so than in Case A.
- **Case C:** If the photoelectron is emitted from a **nonbonding orbital, there is no change in the bond order, and consequently little or no change** in the vibrational frequency. *In case C, the PES spectrum for the orbital will show few vibrational peaks because the disturbance to the bond during photoemission is quite small.*

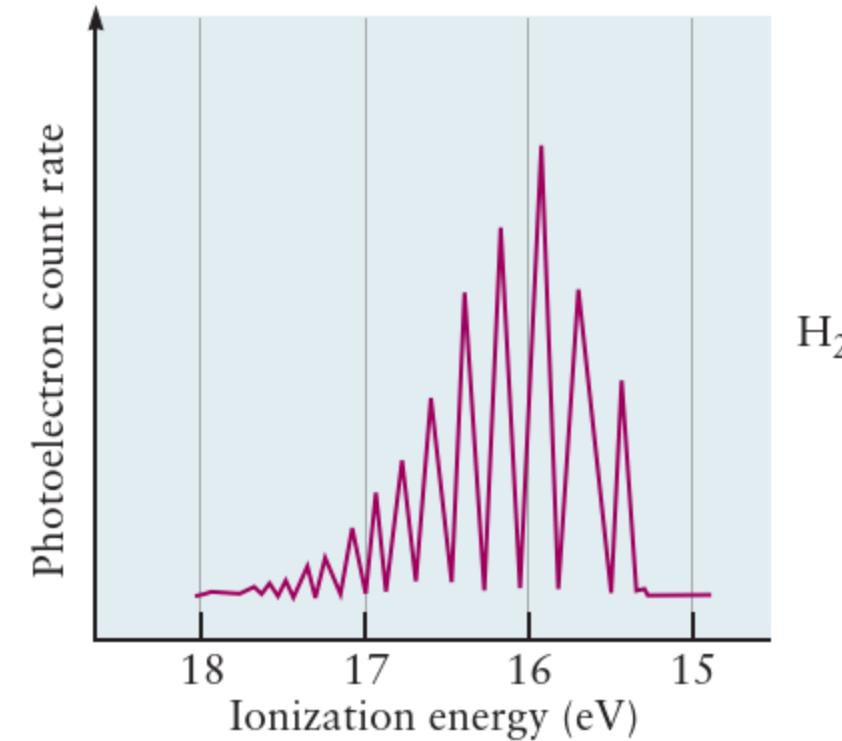


Figure c6.1 The photoelectron spectrum of  $\text{H}_2$  shows a series of peaks corresponding to the vibrational excitation of  $\text{H}_2^+$ .

TABLE 7. 2 Vibrational structure of photoelectron bands

<i>Orbital from which electron is ionized</i>	<i>Vibrational frequency in <math>M^+</math> compared with <math>M</math></i>	<i>Number of vibrational components</i>	<i>Most intense vibrational components</i>
Bonding	Markedly smaller	Large	Near centre
Nonbonding	Similar	Small	First
Antibonding	Similar or larger	Medium	Near centre
<i>Example NO: stretching frequency <math>1890\text{ cm}^{-1}</math></i>			
Bonding $\pi$	1200	8	4th
Nonbonding $\sigma$	1610	3	1st
Antibonding $\pi^*$	2260	5	2nd

## Steps to Relate the Relationship between the Photoelectron Spectrum and the Electron Configuration of the Species

- A photoelectron count vs. binding energy graph is called a PES spectrum.
- The ***ionization energy defines the position of each peak***, whereas ***the height identifies the ratio of electrons in each level or orbital***.
- ***PES peaks represent electrons in various subshells*** of an atom.

**Step 1:** Write the electron configuration of the element or ion provided in the question.

**Step 2:** The number of subshells should equal the number of peaks provided in the PES.

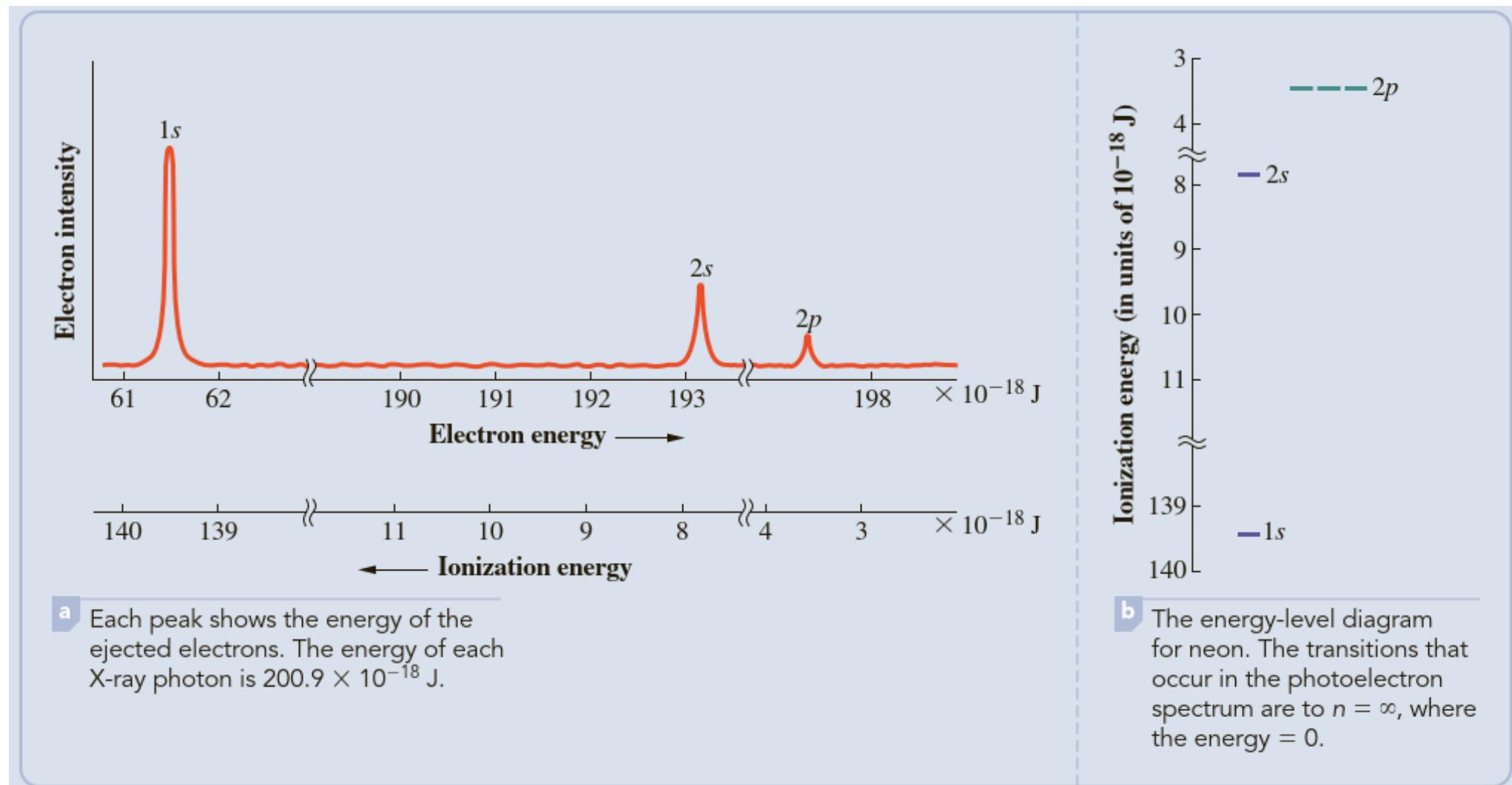
Molecules get ***vibrational fine structure*** (with multiplets) if the orbital has any ***bonding or antibonding character*** overall, although **atoms do NOT**.

**Step 3:** Assign each subshell with an individual peak from the photoelectron spectrum. The graph is constructed to have the highest binding energy closest to the left and the lowest binding energy to the right, so ***the lowest subshell is assigned to the leftmost peak***, followed by each subsequent subshell.

**Step 4:** Determine the number of electrons associated with each peak. ***The height (area) of each peak provides the relative number of electrons***, and ***the height (area) ratio provides how many electrons***.

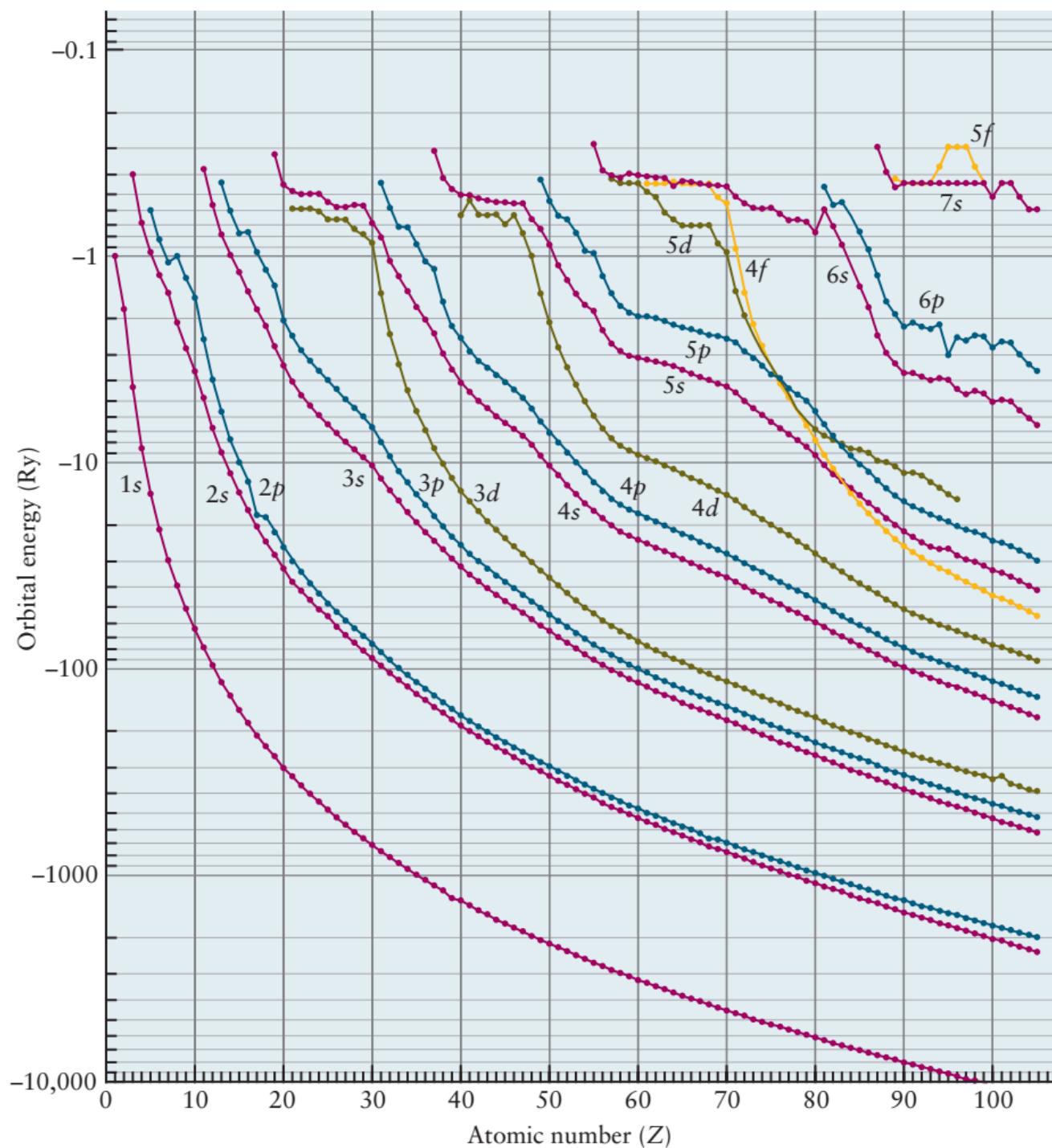
If you look at the electrons ejected from neon, you find that they have kinetic energies related to the ionization energies from all possible orbitals (1s, 2s, and 2p) in the atom. When you scan the various kinetic energies of ejected electrons, you see a spectrum with peaks corresponding to the different occupied orbitals (see Figure 8.11a). These ionization energies are approximately equal to the positive values of the orbital energies (Figure 8.11b), so this spectrum provides direct experimental verification of the discrete energy levels associated with the electrons of the atom/molecule.

Figure 8.11. X-ray photoelectron spectrum of neon

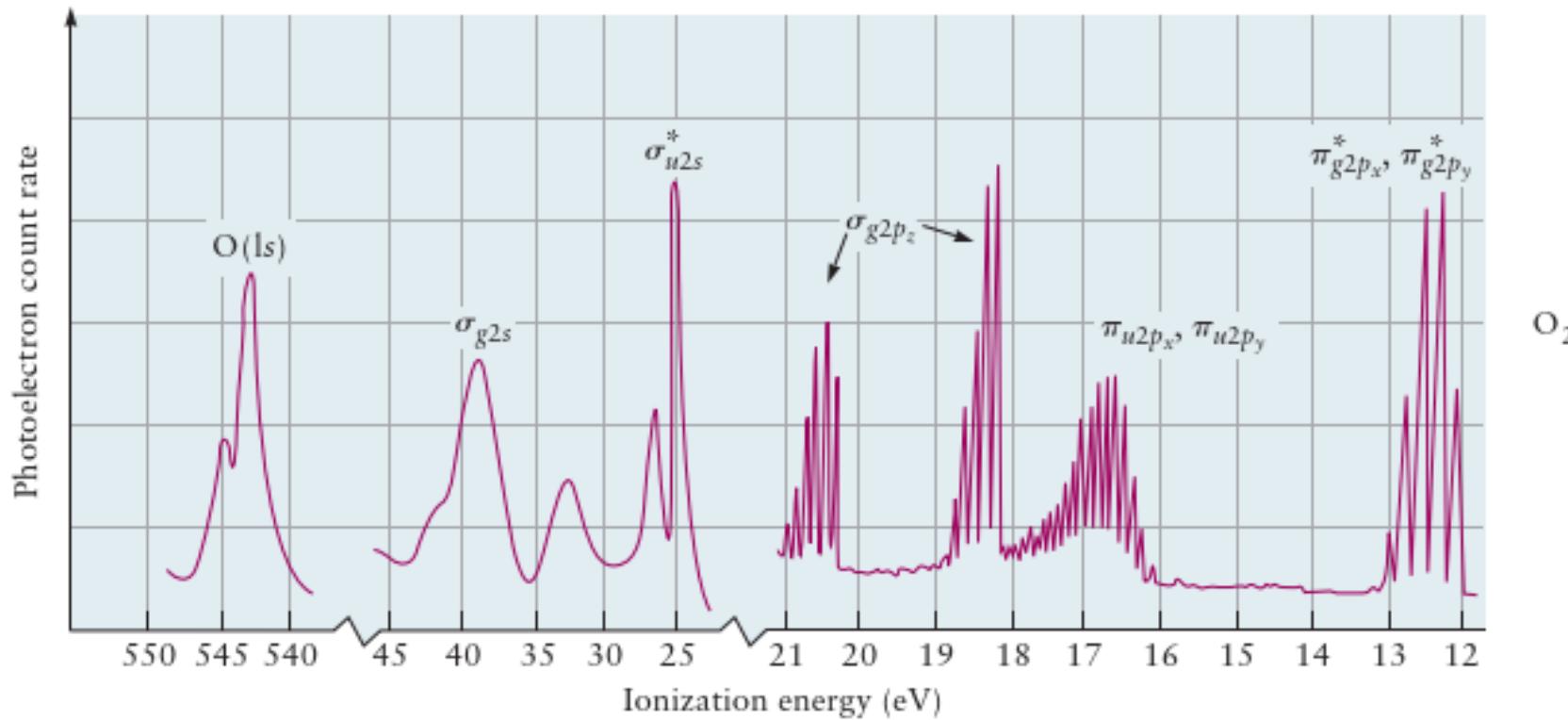


- These experimental results for neon are consistent with the electron configuration Ne:  $1s^2 2s^2 2p^6$  predicted by the aufbau principle. Ionization energies measured in this way are used to construct the energy-level diagram for atoms and to show explicitly the value of the ground-state energy.
- This method has been used to determine the energy levels for orbitals in most neutral atoms (Fig. 5.26). The energies are reported in units of rydbergs and plotted on a logarithmic scale. These data confirm the existence of sub-shells, which are grouped into shells having similar energies. However, there are significant exceptions. The 3d subshell for elements 21 through 29 (scandium through copper) lies substantially higher than 3s and 3p and only slightly lower than 4s. This is consistent with the chemical observation that the 3d electrons are valence electrons in these transition metals. As Z goes above 30, the energy of the 3d subshell decreases rapidly, so the 3d electrons are not valence electrons for zinc and higher elements. The 4d, 5d, 4f, and 5f subshells all behave similarly, so electrons in filled d and f subshells are not valence electrons. We can develop an approximate criterion for distinguishing valence and core electrons by examining the noble gases (elements 2, 10, 18, 36, 54, and 86), which participate poorly or not at all in chemical bonding. The highest-energy subshell for each of them lies below -1 rydberg. Therefore, -1 rydberg is a reasonable approximate boundary for the difference between valence and core electrons.

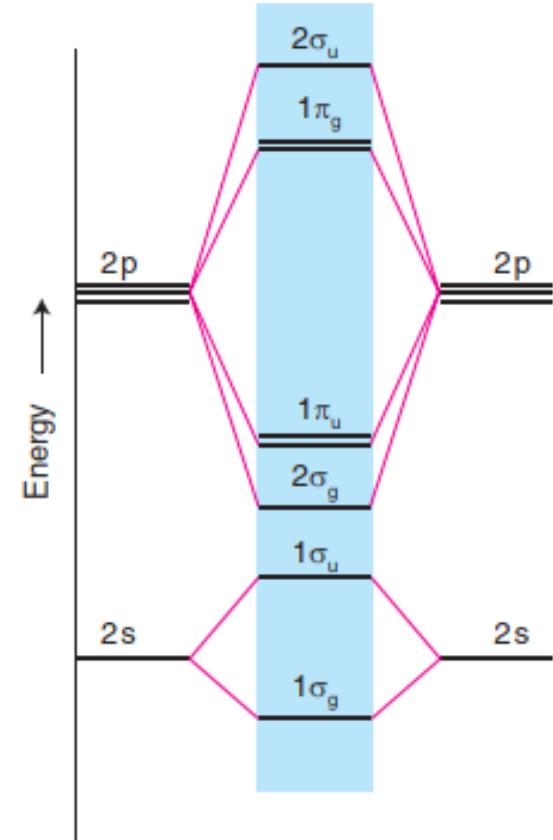
Figure 5.26 The energies of different subshells in the first 97 elements, as determined by photoelectron spectroscopy. Negative values on the vertical axis correspond to the bound state orbital energies. Subshells having the same principal quantum number  $n$ , such as  $2s$  and  $2p$ , have similar energies and are well separated from orbitals of different  $n$ . Significant exceptions do exist, as explained in the text. Note the logarithmic energy scale. One rydberg is  $2.18 \times 10^{-18}$  J.



- The photoelectron spectrum for  $O_2$  is shown in Figures C6.3. The experimental peaks have been assigned to orbitals by slightly more complex versions of the arguments used previously.



$O_2$



MO energy-level diagram for  $O_2$  and  $F_2$ .

FIGURE c6.3 The photoelectron spectrum for  $O_2$  shows valence electrons in the occupied molecular orbitals and the  $O(1s)$  core electrons.

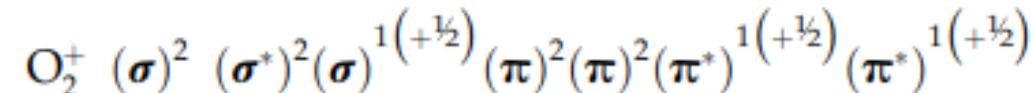
***Applications of the PES technique to molecules have yielded an enormous amount of information regarding molecular orbital energy levels.***

For example, ***PES has shown that the bonding  $\pi$  orbitals in oxygen are higher in energy than the  $\sigma$  orbital arising from the combination of the 2p wave functions.***

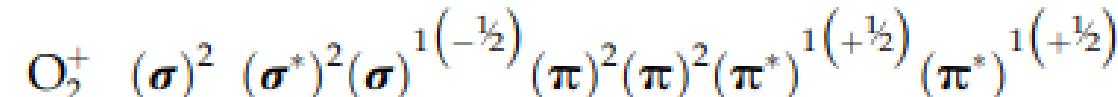
**For nitrogen, the reverse order of orbitals is found.**

When electrons are ejected from the bonding  $\pi_{2p}$  orbital of  $O_2$ , two absorption bands are observed. There are two electrons populating that orbital, one with a spin of  $+ \frac{1}{2}$  and the other with a spin of  $- \frac{1}{2}$ . If the electron removed has a spin of  $- \frac{1}{2}$ , the electron having a spin of  $+ \frac{1}{2}$  remains, and it can interact with the two electrons in the  $\pi^*$  orbitals that have spins of  $+ \frac{1}{2}$ .

This can be shown as follows where  $(\sigma)^{1(+\frac{1}{2})}$  means that there is one electron having a spin of  $+ \frac{1}{2}$  in the  $\sigma$  orbital, etc.:



If the electron removed from the  $\sigma$  orbital has a spin of  $+ \frac{1}{2}$ , the resulting  $O_2^+$  ion is



These two  $O_2^+$  ions have slightly different energies as is exhibited by their photoelectron spectra.

Studies such as these have contributed greatly to our understanding of molecular orbital energy diagrams.

The photoelectron spectrum for  $\text{N}_2$  is shown in Figures C6.2. The experimental peaks have been assigned to orbitals by the arguments as given later. Note that for  $\text{N}_2$ , the energy for the  $\sigma_{g2p_z}$  MO is lower than that for  $\pi_{u2p_x}$  and  $\pi_{u2p_y}$  whereas the order is switched for  $\text{O}_2$ , as indicated in Figure 6.17, Table 6.3, and the related text. This switch is due to interaction between the 2s and 2p AOs.

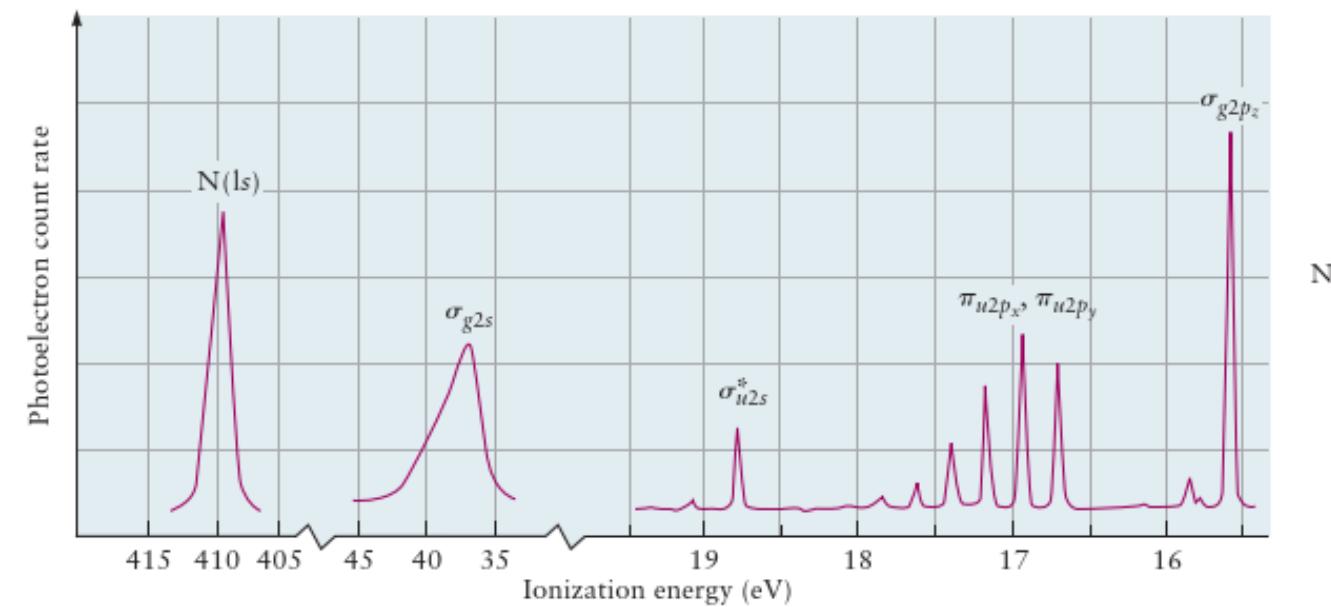
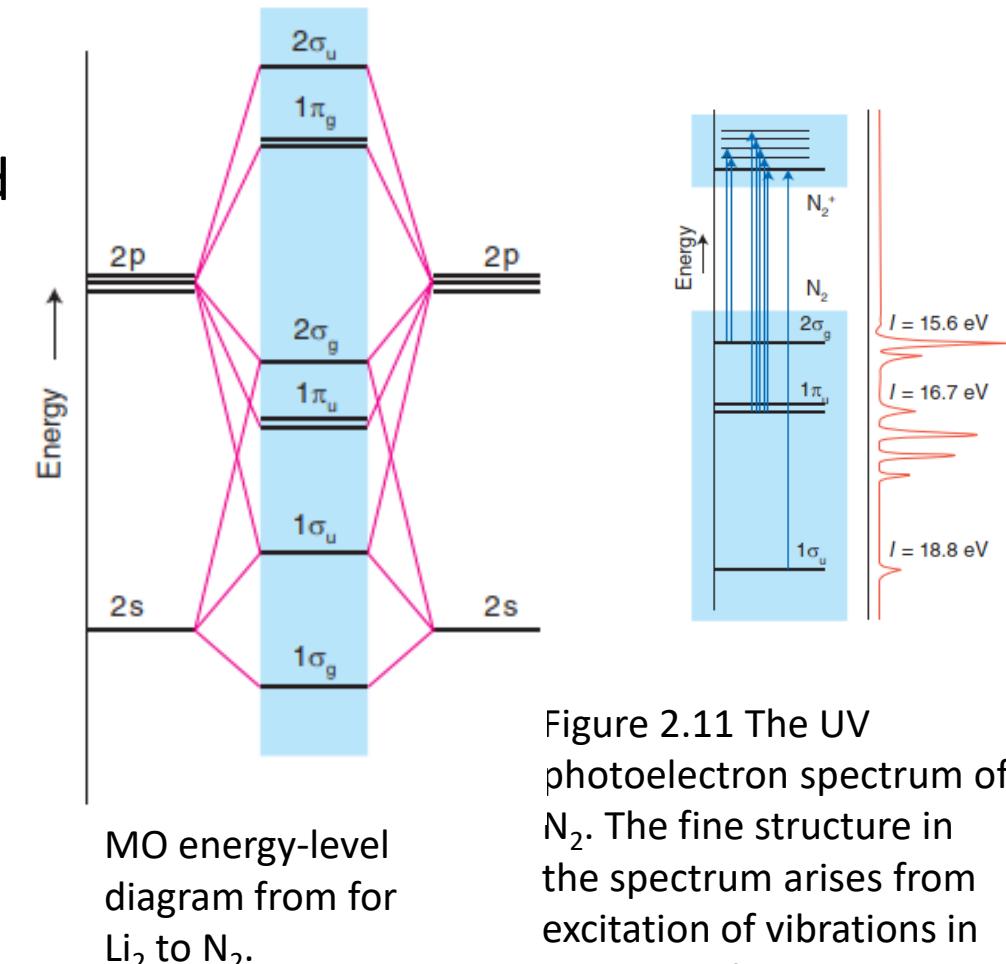


FIGURE c6.2 The photoelectron spectrum for  $\text{N}_2$  shows the valence electrons in the occupied molecular orbitals and the  $\text{N}(1s)$  core electrons.



MO energy-level diagram from for  $\text{Li}_2$  to  $\text{N}_2$ .

Figure 2.11 The UV photoelectron spectrum of  $\text{N}_2$ . The fine structure in the spectrum arises from excitation of vibrations in the cation formed by photoejection of an electron.

## Photoelectron spectrum of dinitrogen

Diatomically nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Five molecular orbitals are occupied; two of them are degenerate. Three bands in the photoelectron spectrum correspond to ionization of an electron in  $\sigma_g(2p)$ ,  $\pi_u(2p)$  and  $\sigma_{g^*}(2s)$  molecular orbitals. Ionization of the fourth type of orbital,  $\sigma_g(2s)$ , does not appear in Figure 5.2.4.2 because it is either off scale or because the incident light  $h\nu$  used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital. Note that ***extensive vibrational structure for the  $\pi_u(2p)$  band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.***

From the photoelectron spectrum of dinitrogen, we can see that the electrons in the  $\sigma_g(2p)$  orbital can be ionized using less energy than required to ionize electrons in the  $\pi_u(2p)$  orbital. This is evidence for  $\sigma_g(2p)$  existing at a higher energy than the  $\pi_u(2p)$  orbitals.

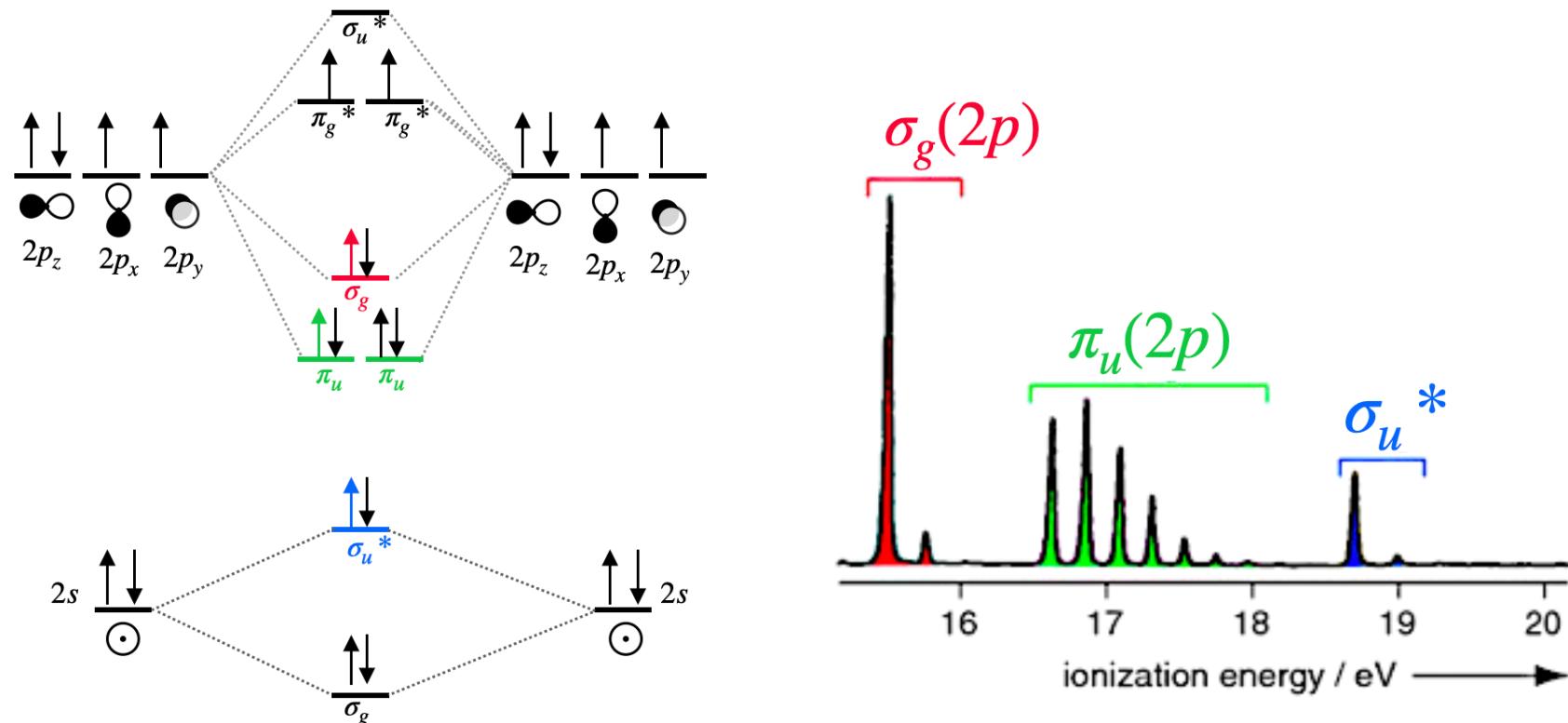


Figure 5.2.4.2: The molecular orbital diagram and photoelectron spectrum of dinitrogen (N<sub>2</sub>).

The figure shows the valence shell photoelectron spectrum for  $\text{N}_2$  molecules. The molecular orbital diagram indicates that  $\text{N}_2$  has four types of filled orbitals:  $\sigma_{2s}$ ,  $\sigma^*_{2s}$ ,  $\pi_{2p}$ , and  $\sigma_{2p}$ . The photoelectron spectrum detects three groupings of ejected electrons with average ionization energies of 15.6 eV, 16.7 eV, and 18.6 eV (where **1 electron volt =  $1.60218 \times 10^{-19} \text{ J}$** ). These electrons are ejected from the  $\sigma^*_{2s}$ ,  $\pi_{2p}$ , and  $\sigma_{2p}$  orbitals, respectively. A fourth peak is not seen because the energy required to remove an electron from the  $\sigma_{2s}$  orbital is higher than that of the photons emitted by the excited helium atoms.

The extra peaks, most obvious around 17–18 eV, are associated with ionization from the  $\pi$  orbital. They result from coupling of the ionization energy and the energy resulting from molecular vibrations.

If we turn to nitrogen,  $N_2$ , we find that we are forced to consider mixing among the sigma states, as in Fig. 3.19b.

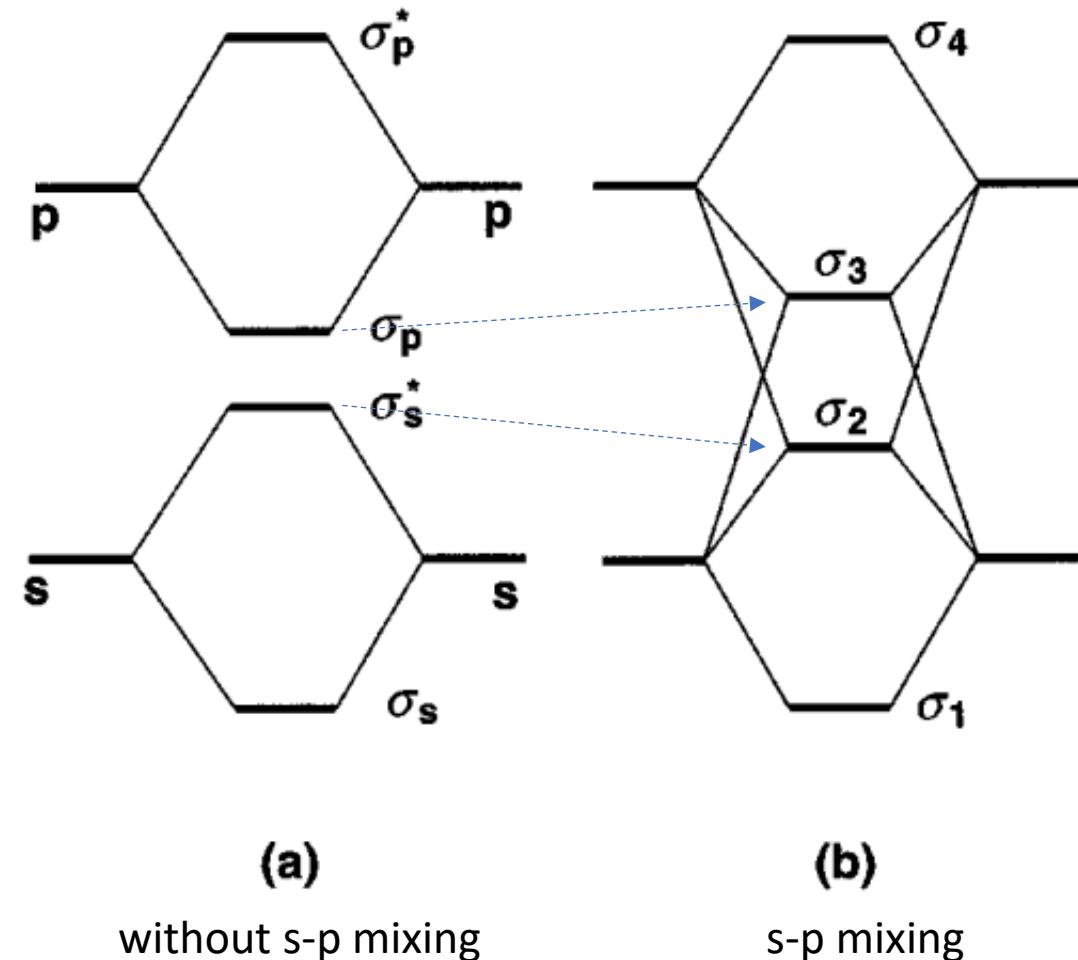


FIG. 3.19 (a) combinations without s-p mixing, (b)  $\sigma$  combinations with s mixed with p. This shows the relation between the  $\sigma_s$ ,  $\sigma_s^*$ ,  $\sigma_p$  and  $\sigma_p^*$  levels (a) and the levels  $\sigma_1$  to  $\sigma_4$  (b) which result when s and p contributions are allowed to mix. The main effect is to stabilize  $\sigma_2$  relative to  $\sigma_s^*$  and to destabilize  $\sigma_3$  relative to  $\sigma_p$ .

- The He (I) photoelectron spectrum of  $N_2$  is shown in Fig. 3.22 listed in Table 3.4. It is immediately obvious that the ***15.6 eV ionization is from an orbital that is only weakly bonding and cannot therefore be from the  $\pi$  level.*** Further, we expect the  $N_2 \pi$  level to be similar in energy to the  $O_2 \pi$  level which is 17.0 eV. Thus ***the 16.69 eV level in  $N_2$  has the expected attributes of the bonding  $\pi$  level.*** This leads to the conclusion that the ***weakly bonding level at 15.57 eV and the weakly antibonding level at 18.75 eV arise from the two higher sigma orbitals,*** and ***the least stable of these lies above the  $\pi$  level.***
- This can only happen if  $\sigma_s$  and of  $\sigma_s^*$ , and  $\sigma_p$  and  $\sigma_p^*$ , interact with each other, as discussed earlier in this section. The net effect of this s-p mixing is to (a) raise  $\sigma_3$  and lower  $\sigma_2$ , and (b) *average out their bonding and antibonding character to give relatively nonbonding combinations.* It must be emphasized, however, that *the  $\pi$  levels are unaffected by this s-p mixing since they are orthogonal to the molecular axis.* Thus the energy level diagram for  $N_2$  has the  $\pi$  bonding level lying between  $\sigma_2$  and  $\sigma_3$  of Fig. 3.19b. The electronic structure of  $N_2$  is therefore given as in Fig. 3.23.

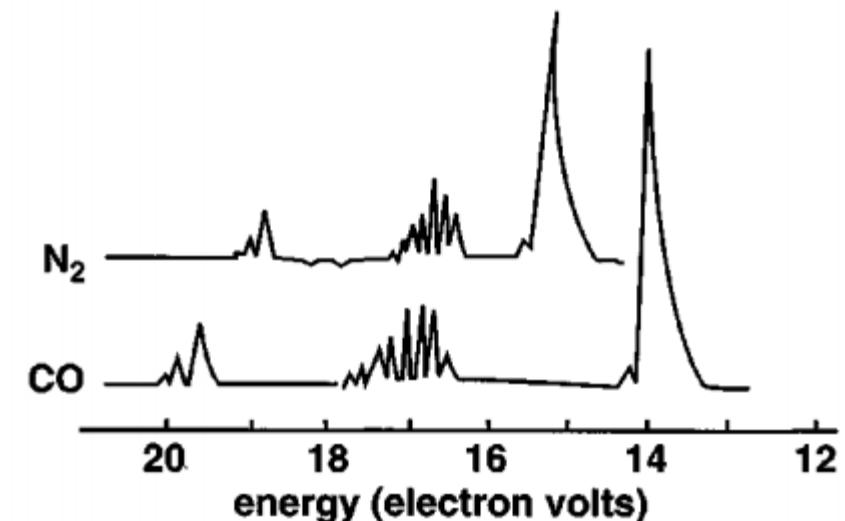


FIG. 3.22 Photoelectron spectra of  $N_2$  and CO

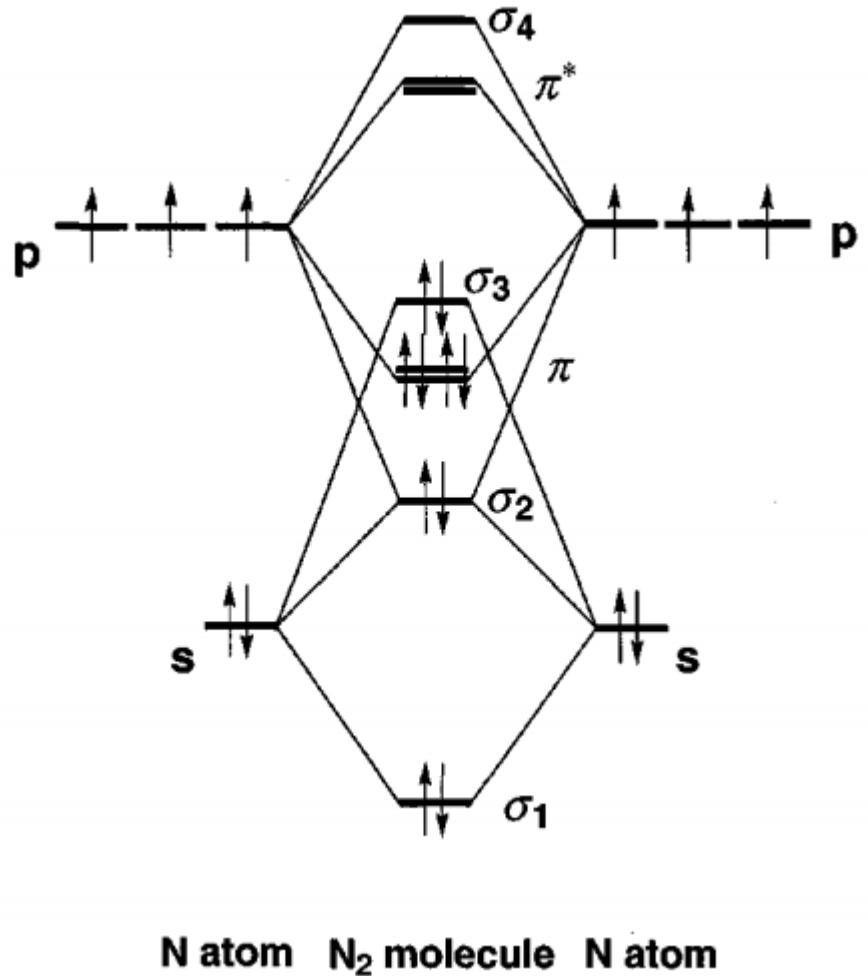
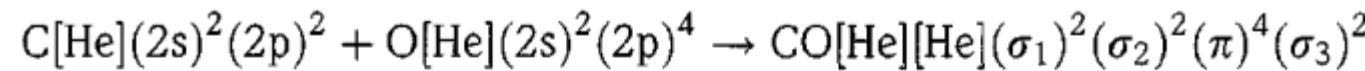


FIG. 3.23(a) The electronic structure of  $N_2$ . In the structure of  $N_2$ , the bonding  $\pi$  levels lie below  $\sigma_3$ . The bonding and antibonding contributions of  $\sigma_2$  and  $\sigma_3$  cancel, leaving  $\sigma_1$ , and the two  $\pi$  levels to make up a total bond order of three.

The bonding character added to  $\sigma_2$  relative to  $\sigma_p$  of exactly equals the loss of bonding character in  $\sigma_3$  relative to  $\sigma_p$  and there is no net bonding effect when  $\sigma_2$  and  $\sigma_3$  are both filled. Thus  $N_2$  has six more bonding than antibonding electrons ( $\sigma_1^2 \pi^4$ ) making a triple bond.

➤ In carbon monoxide and in the cyanide ion, the  $\sigma_3$  level also lies above the bonding  $\pi$  orbitals. The species are triply bonded and the formation equations may be written:



and

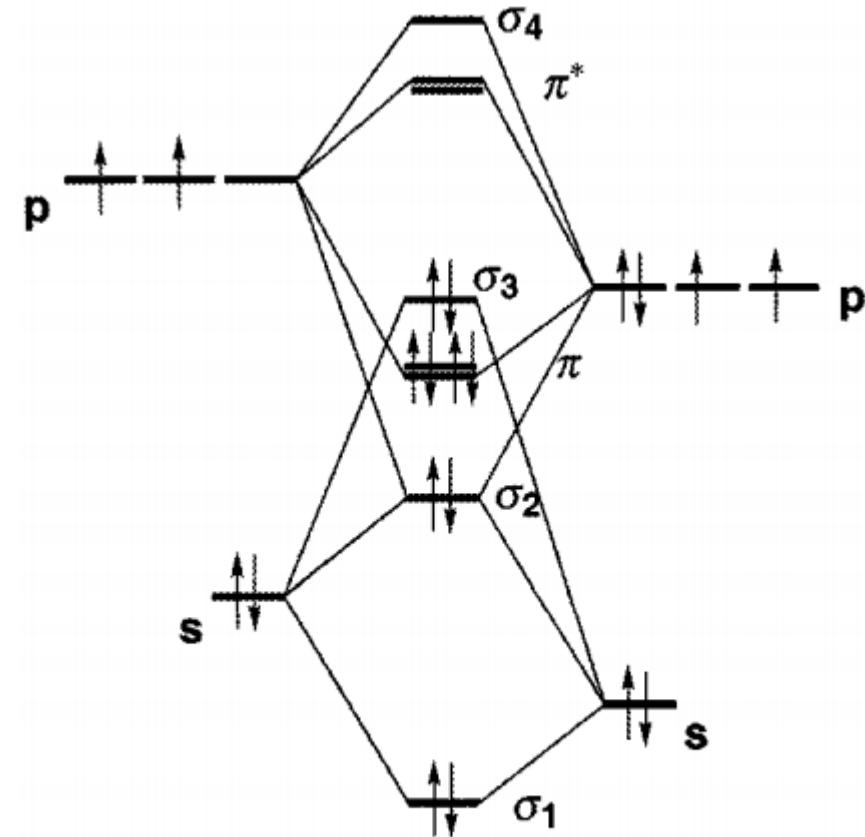
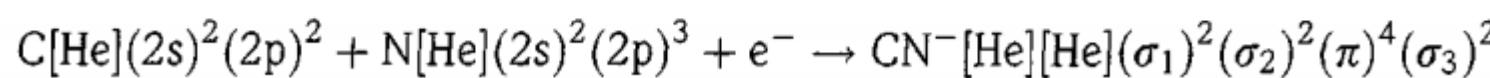


FIG. 3.23(b) The electronic structure of CO

C atom   CO molecule   O atom

- This interpretation is supported by the data for CO, Table 3.4. Carbon monoxide has the same number of valency electrons as  $N_2$  (such species are termed isoelectronic) but its energy level diagram is a skew one, reflecting the unequal atomic levels, Fig. 3.23b.
- We see that the  $\pi$  level of CO is of almost exactly the same stability as for  $N_2$ , but the electrons in  $\sigma_3$  are less tightly bound (reflecting the greater contribution from C2p<sub>z</sub> in  $\sigma_3$ ) while those in  $\sigma_2$  are more tightly bound (O contribution greater) than in the respective orbitals of  $N_2$ .

**TABLE 3.4** Photoionization of  $N_2$  and CO. (Stretching frequency of  $N_2$  = 2345 cm<sup>-1</sup>, CO = 2157 cm<sup>-1</sup>)

		Photoelectron energy (eV)	Vibrational separation (cm <sup>-1</sup> )	Assignment of lost electron
For $N_2^+$	(1) 15.57	2150		weakly bonding
	(2) 16.69	1810		strongly bonding
	(3) 18.75	2390		weakly antibonding
	(4) 37.3			strongly bonding
	(5) 410			1s electron
For CO <sup>+</sup>	(1) 14.01	2160		non-bonding
	(2) 16.53	1610		bonding
	(3) 19.68	1690		bonding
	(4) 38.3			strongly bonding
	(5) 293			C 1s electron
	(6) 542			O 1s electron

- The photoelectron spectrum for NO is shown in Figure C6.4. The orbital assignments are based on the arguments summarized above. Note that the 1s core levels for both N and O appear at the same orbital energies as they do in their respective elemental gases, N<sub>2</sub> and O<sub>2</sub>.
- This experimental result demonstrates clearly that the ***core levels do not participate in chemical bond formation*** and can be neglected in the MO analysis of bond formation.
- These examples show that photoelectron spectroscopy is useful in testing theoretical models for bonding because it directly measures ionization energies that can be correlated with theoretical orbital energies through Koopmans's theorem. These methods are readily extended to polyatomic molecules

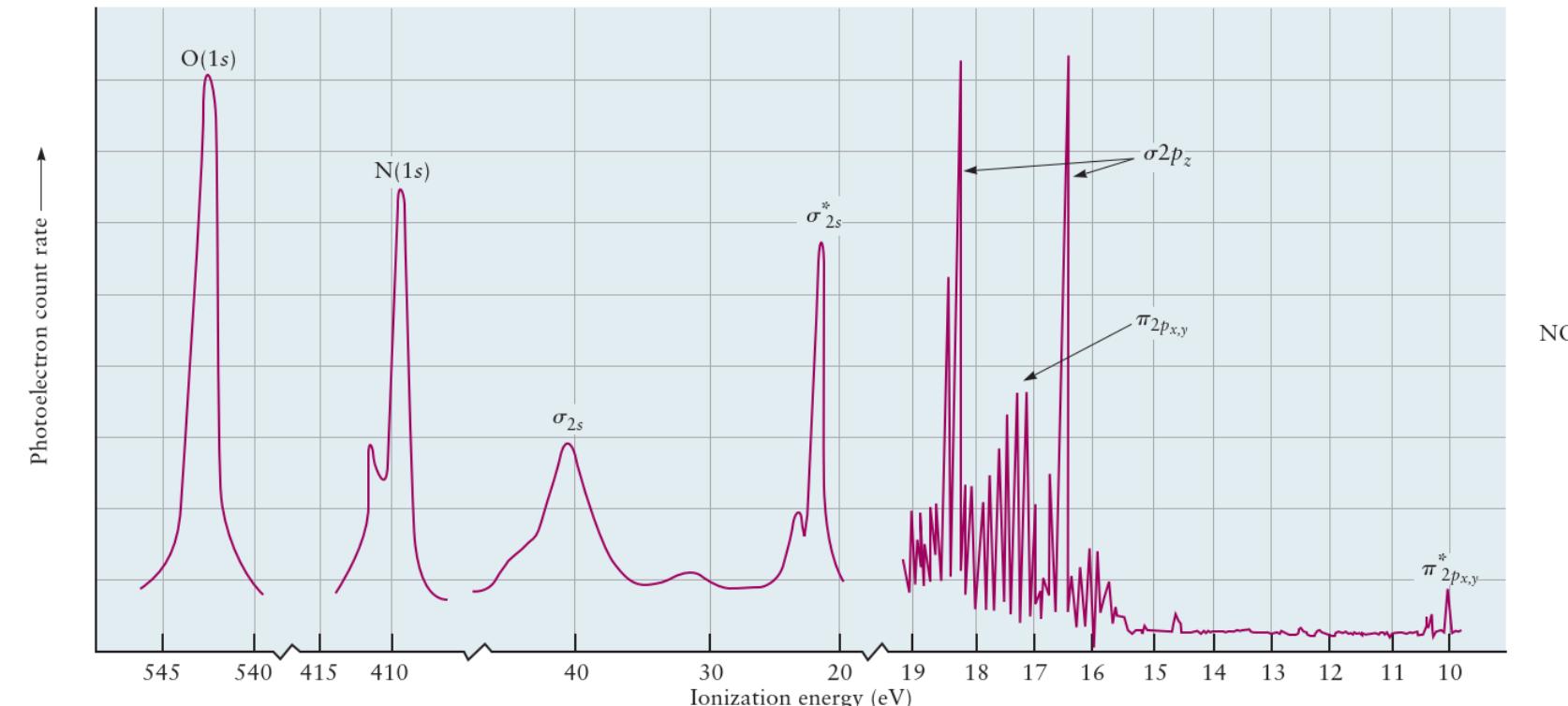
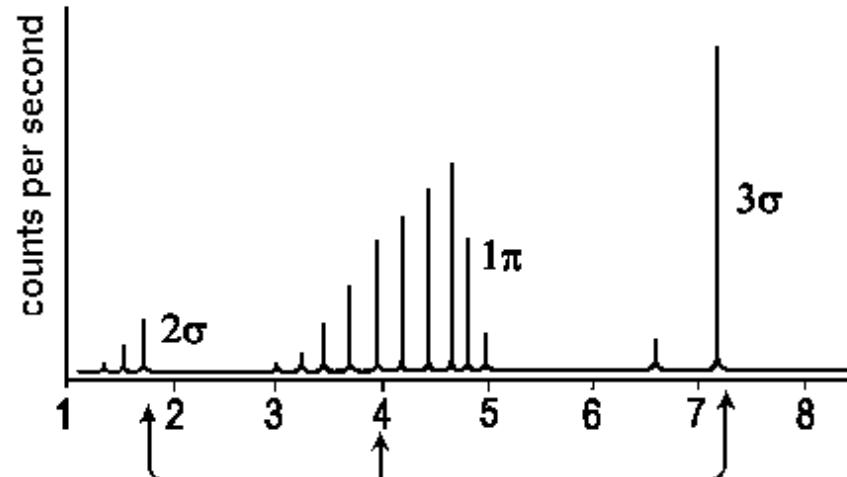


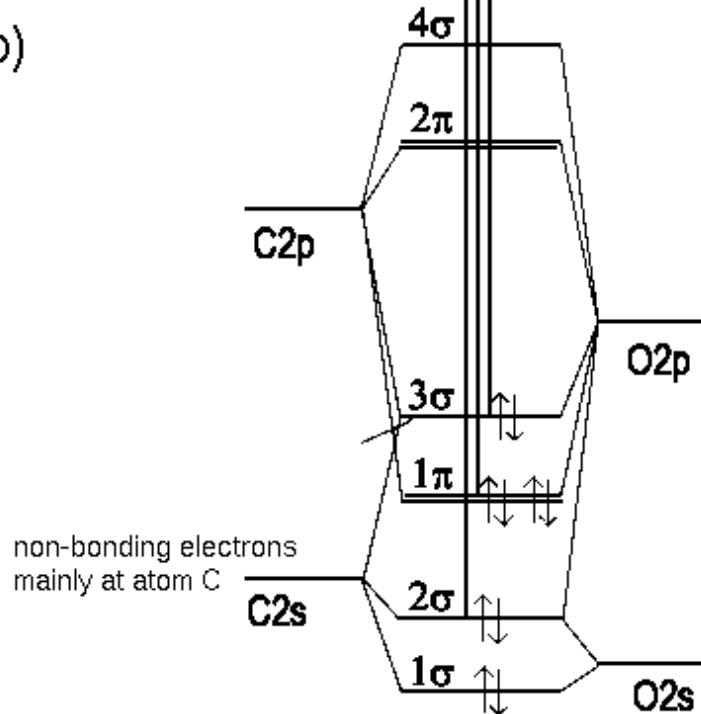
FIGURE C6.4 The photoelectron spectrum for NO.

FIGURE C6.4 The photoelectron spectrum for NO.

a)

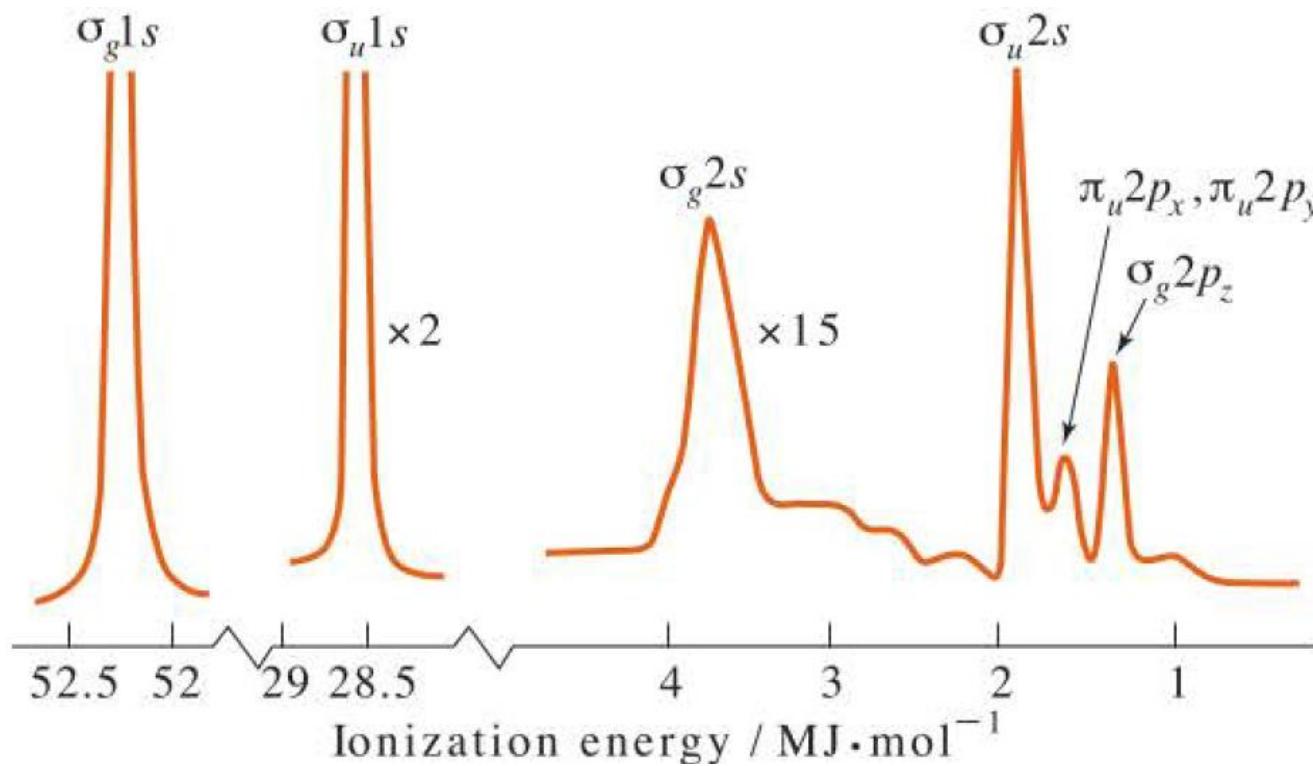


b)



Removal of an electron from a valence orbital produces a cationic molecule in a nonequilibrium state, i.e. a molecules that instantly transforms potential energy in vibrational energy. Note that the kinetic energy of the photoelectron corresponds with the final vibrational state. Therefore, the energy distribution of photoelectrons, i.e. a spectrum received by photoelectron spectroscopy, displays a fine structure which can be interpreted in terms of the reached vibrational state, or, of a major or minor contribution of the removed electron to the initial molecular bonding. ***A long progression of lines indicates that the removed electron had been important for the molecular bonds.*** In contrast, electrons removed from ***nonbonding orbitals have no pronounced effect*** on the position of nuclei and appear without or with inferior progression.

Figure 9.17 presents the photoelectron spectrum of CO. The energies of the molecular orbitals are revealed nicely by these data. In addition, the photoelectron spectrum exhibits peaks characteristic of the atomic 1s orbitals on carbon and oxygen. Notice the high binding energy of the 1s atomic orbitals. This energy is a result of their being close to the nuclei and these data further verify that the 1s electrons do not play a significant role in the bonding of these molecules.



**FIGURE 9.17**  
The photoelectron spectrum of CO. The energies associated with various molecular orbitals are identified. The  $\sigma 1s$  and  $\sigma 1s^*$  orbitals are essentially the 1s electrons of the oxygen and carbon atoms, respectively. The relatively large ionization energies of these electrons indicate that they are held tightly by the nuclei and play no role in bonding.

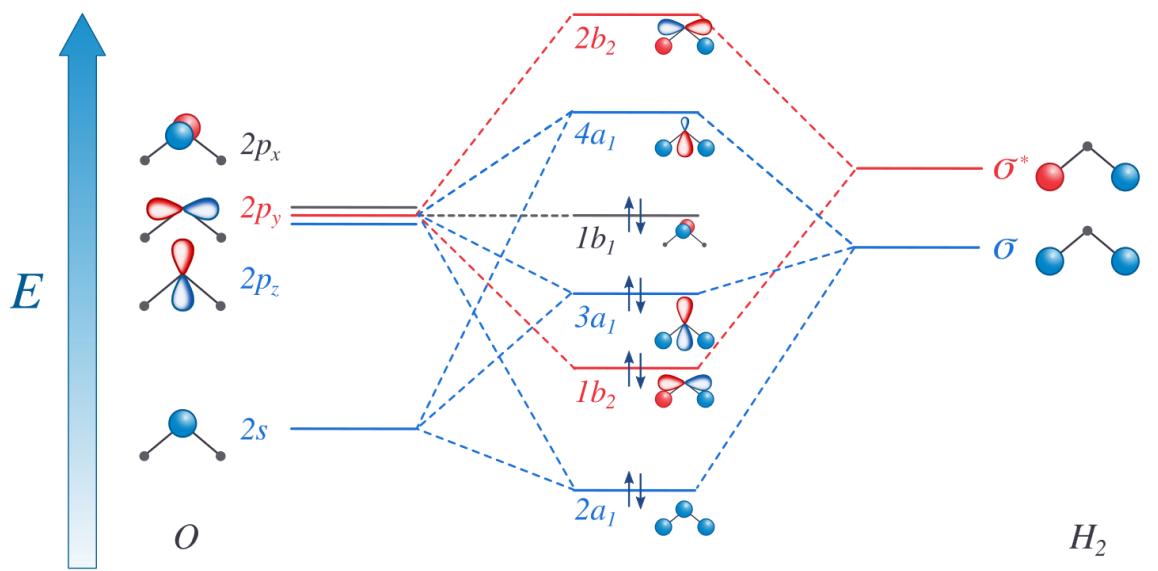


Figure 10.4.7: MO diagram for water.

#### Molecular orbital      Experimental Ionization Energies (eV)

$2a_1$                           32.2

$1b_2$                           18.5

$3a_1$                           14.7

$1b_1$                           12.6

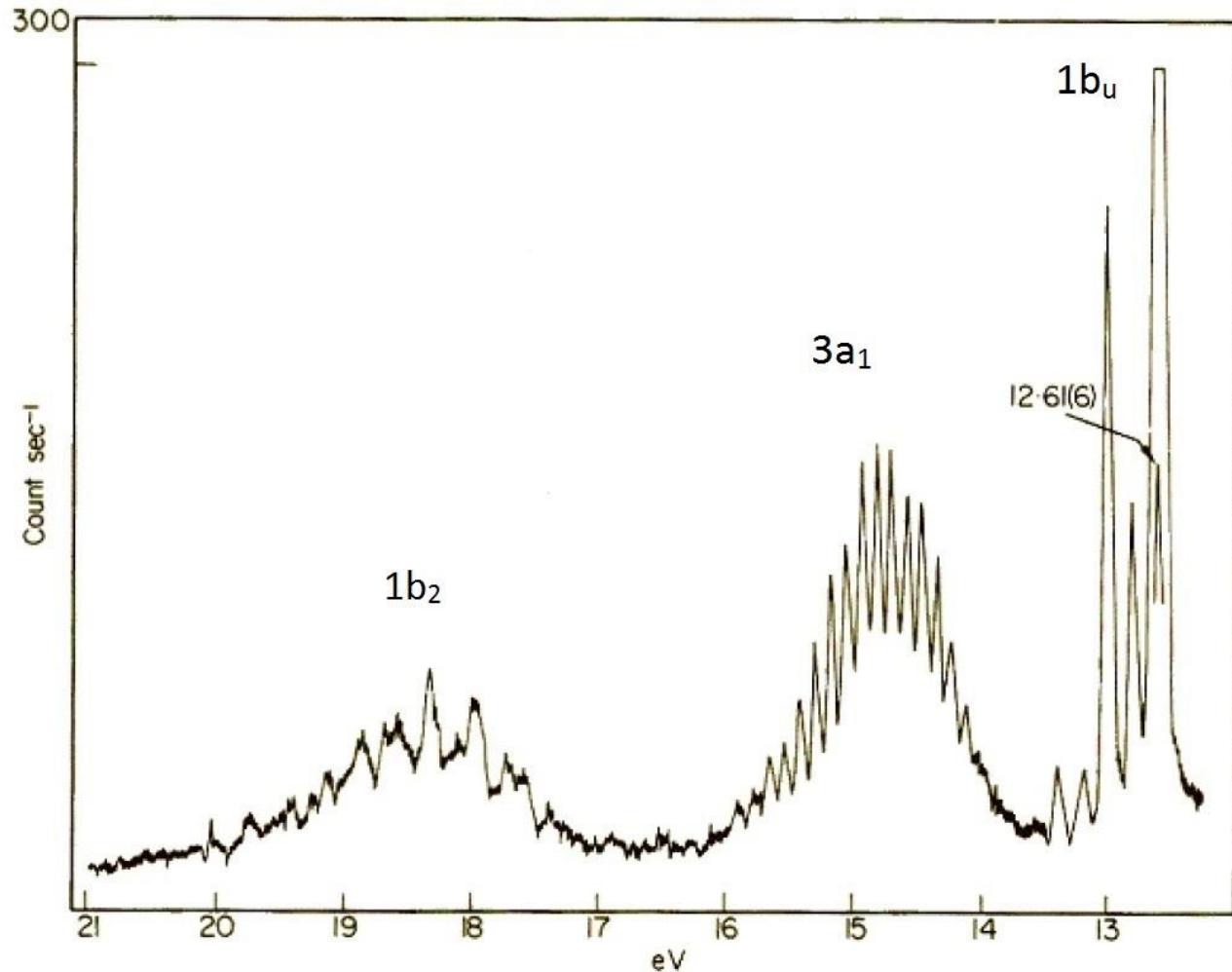


Figure 10.4.8 : Photoelectron spectrum of water. This spectrum does not go to high enough energy to show the deep  $2a_1$  molecular orbital.

- The molecular orbital perspective has the lone pair in different orbitals (*one in a non-bonding orbital* ( $1b_2$ ) and *one in the bonding (partially non-bonding) orbital*). We turn to ***the photoelectron spectroscopy to help identify which theory is more accurate*** (i.e., describes reality better).
- If water formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 ***would have two peaks, one for the two bonds and one for the two lone pairs.***
- The photoelectron spectrum of water in Figure 10.4.8 ***clearly shows three peaks*** with some fine structure arises from vibrational energy changes as expected for the molecular orbitals in Figure 10.4.7. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.
- If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the  $2a_1$ ,  $1b_1$  and  $3a_1$  molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality.

**QUESTIONS:**

1. Photoelectron spectroscopy is similar to the photoelectric effect. However, in the photoelectric effect, electrons are ejected when light strikes the surface of a(n) .....
2. Using the accompanying figure regarding N<sub>2</sub>, state which molecular orbital ( $\sigma^*2s$ ,  $\pi2p$ , or  $\sigma2p$ ) has an ionization energy of 15.6 eV.
3. The N<sub>2</sub><sup>+</sup> ions that are formed when electrons with ionization energies of 15.6 eV and 16.7 eV are ejected have longer bond lengths than the ion when an electron with an ionization energy of 18.6 eV is created. Why?

**Bond length.** A covalent bond has a bond length, the distance between the nuclei of two bonded atoms. The bond length is the distance between the nuclei at the point of minimum energy (bottom of the well). Like bond energies, these values are average bond lengths for a bond in different substances. Bond length is related to the sum of the radii of the bonded atoms. In fact, most atomic radii are calculated from measured bond lengths. Bond lengths for a series of similar bonds, as in the halogens, increase with atomic size (Figure 9.12).

**The order, energy, and length of a covalent bond are interrelated.** Two nuclei are more strongly attracted to two shared pairs than to one, so double-bonded atoms are drawn closer together and are more difficult to pull apart than single-bonded atoms: **for a given pair of atoms, a higher bond order results in a shorter bond length and a higher bond energy.** Thus, as Table 9.3 shows, for a given pair of atoms, a shorter bond is a stronger bond.

**Table 9.3** The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C=O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C=C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N=N	2	122	418
N≡N	3	110	945

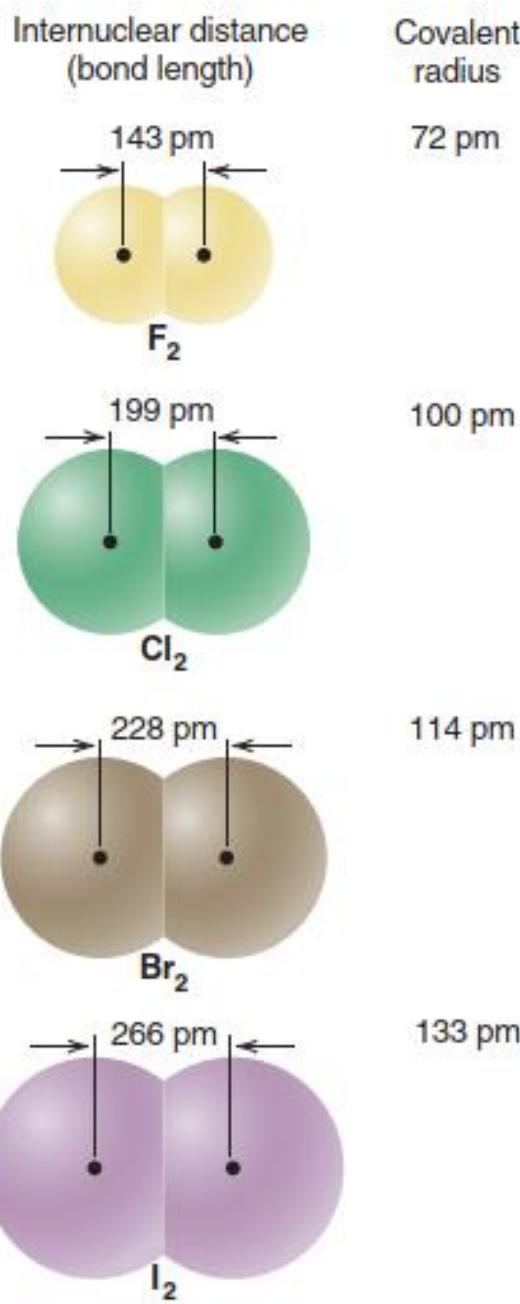


Figure 9.12 Bond length and covalent radius.

In some cases, we can see a ***relation among atomic size, bond length, and bond energy*** by varying one of the atoms in a single bond while holding the other constant:

- ***Variation within a group.*** The trend in carbon-halogen single bond lengths, C—I > C—Br > C—Cl, parallels the trend in atomic size, I > Br > Cl, and is opposite to the trend in bond energy, C—Cl > C—Br > C—I.
- ***Variation within a period.*** Looking again at single bonds involving carbon, the trend in bond lengths, C—N > C—O > C—F, is opposite to the trend in bond energy, C—F > C—O > C—N.

## HOW DO WE KNOW . . . THE LENGTH OF A CHEMICAL BOND?

Why do you need to know?

*Rotational spectroscopy* **provides** very precise details of **bond lengths** and **bond angles** of molecules in the gas phase. Transitions between rotational levels also contribute to vibrational and electronic spectra and are used in the investigation of gas-phase reactions such as those taking place in the atmosphere.

- Analysis of rotational spectra yields the bond lengths and bond angles of molecules in the gas phase.

Very little energy is needed to change the state of rotation of a molecule, so the electromagnetic radiation emitted or absorbed lies in the microwave region, with wavelengths of the order of 0.1-1 cm and frequencies close to 10 GHz. The *rotational spectroscopy* of gas-phase samples is therefore also known as *microwave spectroscopy*. Gaseous samples are essential for rotational (microwave) spectroscopy, for in that phase molecules rotate freely.

### The rotational energy levels of molecules:

The rotational states of molecules are based on a model system called a *rigid rotor*, a body that is not distorted by the stress of rotation. The simplest type of rigid rotor is called a linear rotor, and corresponds to a linear molecule, such as HCl, CO<sub>2</sub>, or HCCH, that is supposed not to be able to bend or stretch under the stress of rotation. As shown in the following Justification, the energies of a linear rotor are

$$E_J = \hbar B J(J + 1)$$
$$J = 0, 1, 2, \dots$$

Rotational energy levels  
[linear rotor] (1)

where  $J$  is the rotational quantum number. The constant  $B$  (a frequency, with the units hertz, Hz, with 1 Hz denoting 1 cycle per second; expressed as a wavenumber, with  $B/c$ , where  $c$  is the speed of light) is called the rotational constant of the molecule, and is defined as

$$B = \frac{\hbar}{4\pi I}$$

Rotational constant (2)

where  $I$  is the moment of inertia of the molecule.

The moment of inertia of a molecule is the mass of each atom multiplied by the square of its perpendicular distance from the axis of rotation (Fig. 1):

$$I = \sum_i m_i r_i^2$$

Moment of inertia (3)

#### Moments of inertia\*

##### 1. Diatomic molecules



$$I = \mu R^2 \quad \mu = \frac{m_A m_B}{m}$$

Here  $R$  is the bond length.

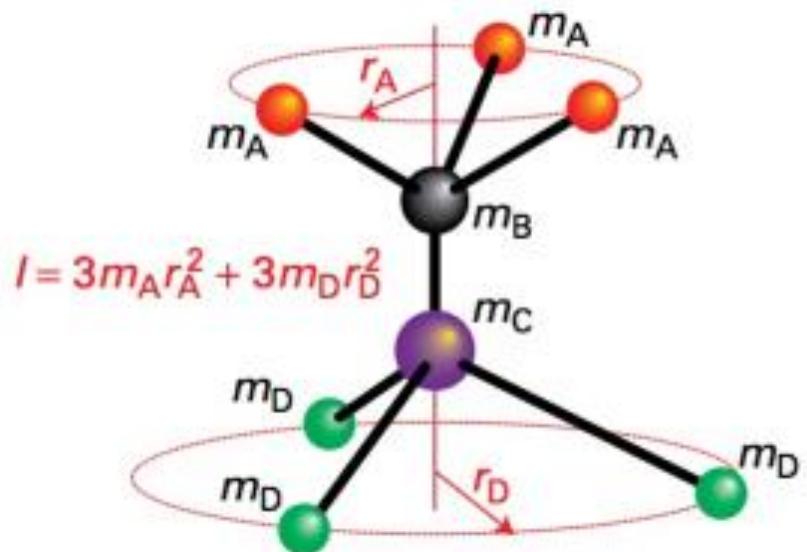


Fig. 1 The definition of moment of inertia. In this molecule there are three identical atoms attached to the B atom and three different but mutually identical atoms attached to the C atom. In this example, the center of mass lies on an axis passing through the Band C atoms, and the perpendicular distances are measured from this axis.

# BOND STRENGTH: Using IR Spectroscopy to Study Covalent Compounds

## *Infrared spectroscopy and Vibrations of Chemical Bonds:*

Chemists often study the types of covalent bonds in a molecule using a technique called infrared (IR) spectroscopy. The bonds in all molecules, whether in a gas, a liquid, or a solid, undergo continual vibrations. We can think of any covalent bond between two atoms, say, the C—C bond in ethane ( $\text{H}_3\text{C}—\text{CH}_3$ ), as a spring that is continually stretching, twisting, and bending.

***Each motion occurs at a particular frequency, which depends on the “stiffness” of the spring (the bond energy), the type of motion, and the masses of the atoms. The frequencies of these vibrational motions correspond to the wavelengths of photons that lie within the IR region of the electromagnetic spectrum.*** Thus, the energies of these motions are quantized. And, just as an atom can absorb a photon of a particular energy and attain a different electron energy level, a molecule can absorb an IR photon of a particular energy and attain a different vibrational energy level.

Each kind of bond (C—C, C=C, C—O, etc.) absorbs a characteristic range of IR wavelengths and quantity of radiation, which depends on the molecule’s overall structure. The absorptions by all the bonds in a given molecule create a unique pattern that appears as downward pointing peaks of varying depth and sharpness. Thus, each compound has a characteristic IR spectrum that can be used to identify it, much like a fingerprint is used to identify a person. As an example, consider the compounds 2-butanol and diethyl ether. These compounds have the same molecular formula ( $\text{C}_4\text{H}_{10}\text{O}$ ) but different structural formulas and, therefore, are constitutional (structural) isomers. Figure 9.15 shows that they have very different IR spectra.

The stiffness of a bond is measured by its force constant,  $k$ .

This constant is the same as that in Hooke's law for the restoring force of a spring: Hooke observed that the restoring force is proportional to the displacement of the spring from its resting position, and wrote

$$\text{Force} = -k \cdot \text{displacement}$$

$$\text{Force} = -k \times \text{displacement}$$

A stiff bond (like a stiff spring) experiences a strong restoring

force, even for quite small displacements, and so in this case  $k$  is large. A loose bond (like a weak spring) experiences only a weak restoring force, even for quite large displacements, so its associated  $k$  is small. In general, the force constant is larger for stretching displacements of molecules than for bending motions. The stiffness of a bond should not be confused with its strength, which is the energy required to break the bond. Typically, though, the stiffness of a bond increases with the strength of the bond (Fig. 1).

The vibrational frequency, ( $\nu$ ), of a bond between two atoms A and B of masses  $m_A$  and  $m_B$  is given by the expression

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

The quantity ( $\mu$ ) is called the effective mass of the molecular vibration (some people call it the "reduced mass"). As we anticipated, the frequency is higher for stiff bonds (large  $k$ ) and low atomic masses (low  $\mu$ ). We see that by measuring the vibrational frequency of a molecule, which involves measuring the frequency (or wavelength) at which it absorbs infrared radiation, we can measure the stiffness of its bond.

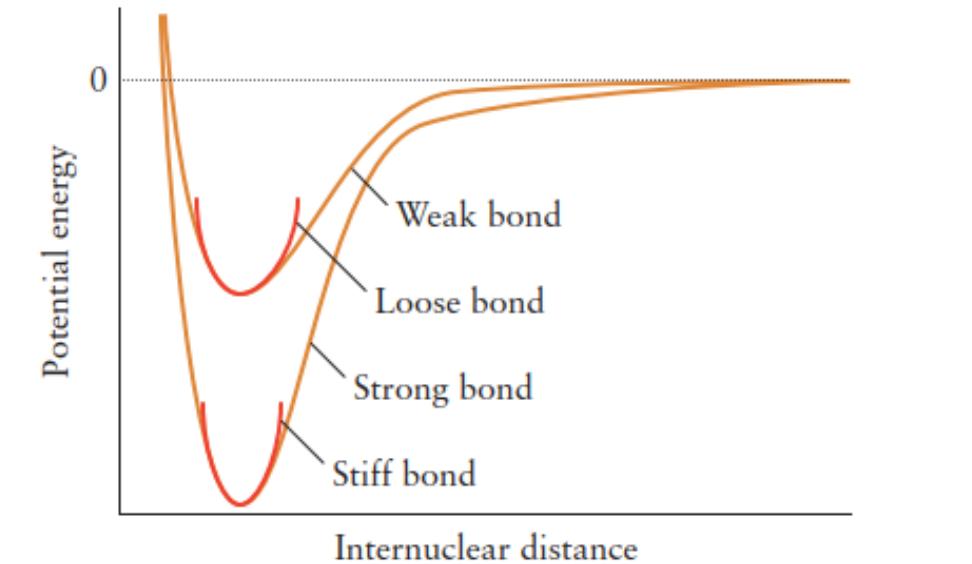


FIGURE 1 The strength of a bond is a measure of the depth of the well in the potential energy curve; the stiffness—which governs the vibrational frequency—is determined by the steepness with which the potential energy rises as the bond is stretched or compressed.

Although it might seem natural to assume that the vibrations in molecules involve completely random gyrations of all the atoms in the molecule, the actual vibrational motions of the atoms are always a superposition (or linear combination) of certain fundamental vibrations known as the normal modes of vibration. As mentioned previously, there are a total of  $3N-6$  (or  $3N-5$  if the molecule is linear) normal modes of vibration, and it is the different types and symmetries of these normal modes with which we shall be concerned. Each normal mode of vibration occurs at one of the natural frequencies of the molecule in much the same way as a tuning fork vibrates at a natural frequency. A more rigorous definition is that a normal mode of vibration is one in which “each atom is displaced from its equilibrium position by an amount that corresponds to its maximum amplitude and that when they are allowed to relax they will all undergo a motion at the same frequency so that they will simultaneously pass through the equilibrium configuration.”

A diatomic molecule will have only a single vibrational mode and it will be a stretching mode that lies along the internuclear axis, as shown in Figure 9.23. One can consider the two nuclei in the A-X bond to be attached by an imaginary spring that allows them to simultaneously stretch to their maximum amplitude, pass back through their equilibrium bond length, and then contract to some minimum distance in sync with one another.

The vibrational quantum number can take only nonnegative, integral values:  $v = 0, 1, 2, \dots$

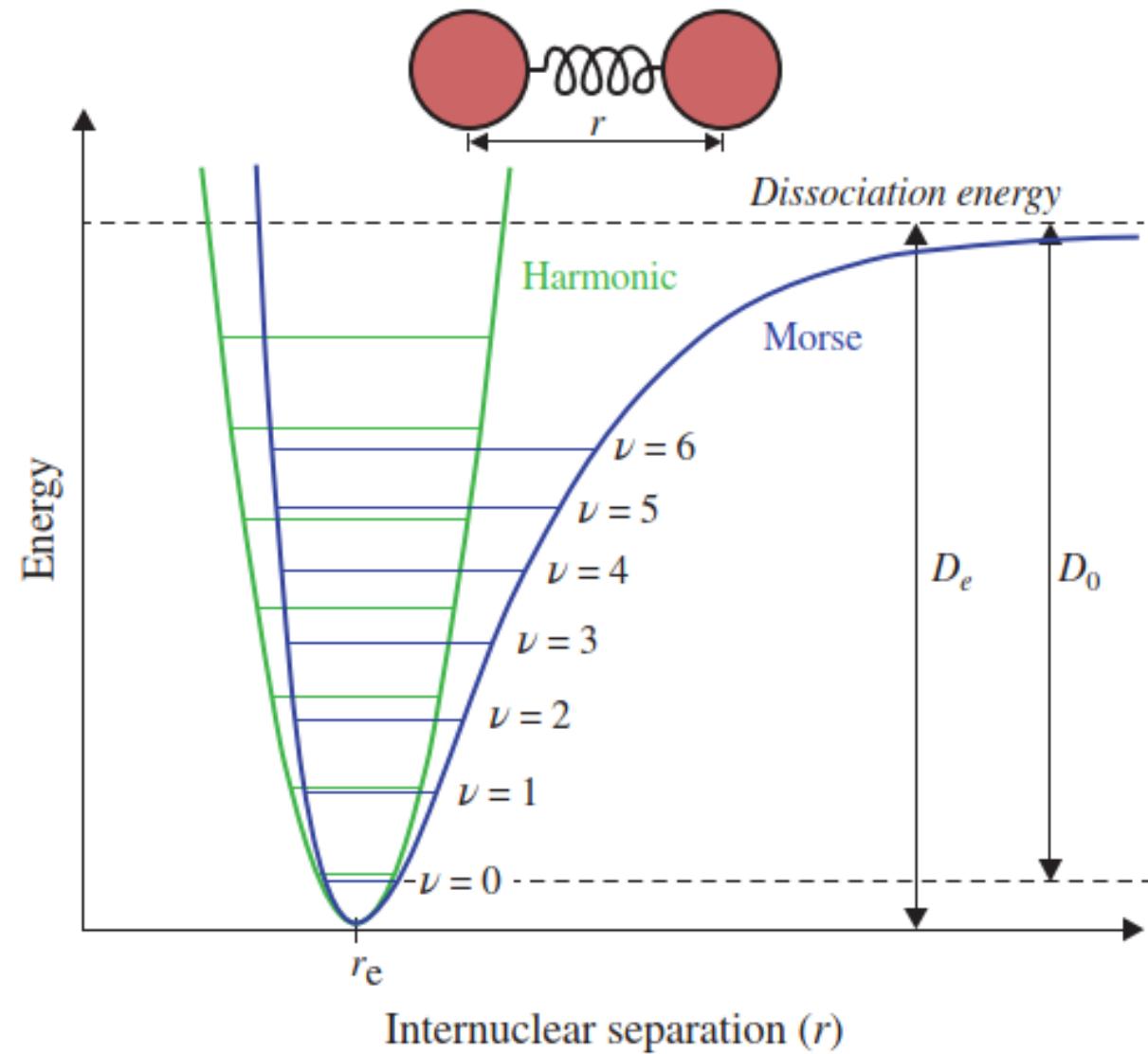
Notice that the molecule has a zero-point energy even at 0 K and that the vibrational levels are evenly spaced for a harmonic oscillator. The transition from the  $v = 0$  level to the  $v = 1$  level is known as the *fundamental frequency*, whereas transitions from  $v = 0$  to higher levels are known as the *overtones*.

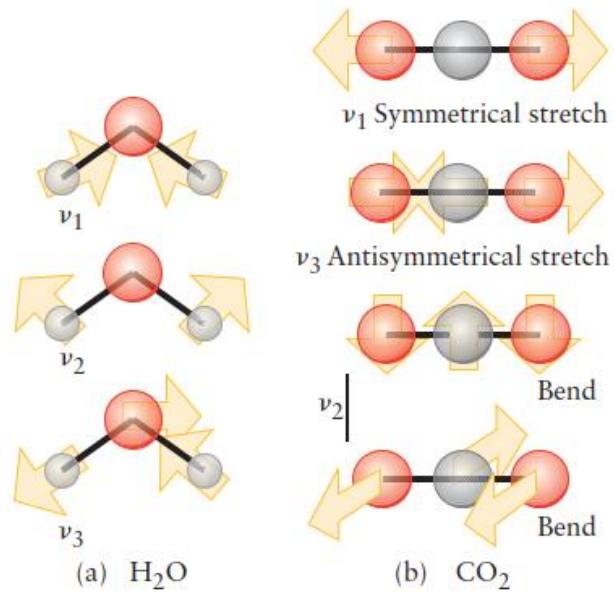
$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \quad (9.5)$$

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (9.6)$$

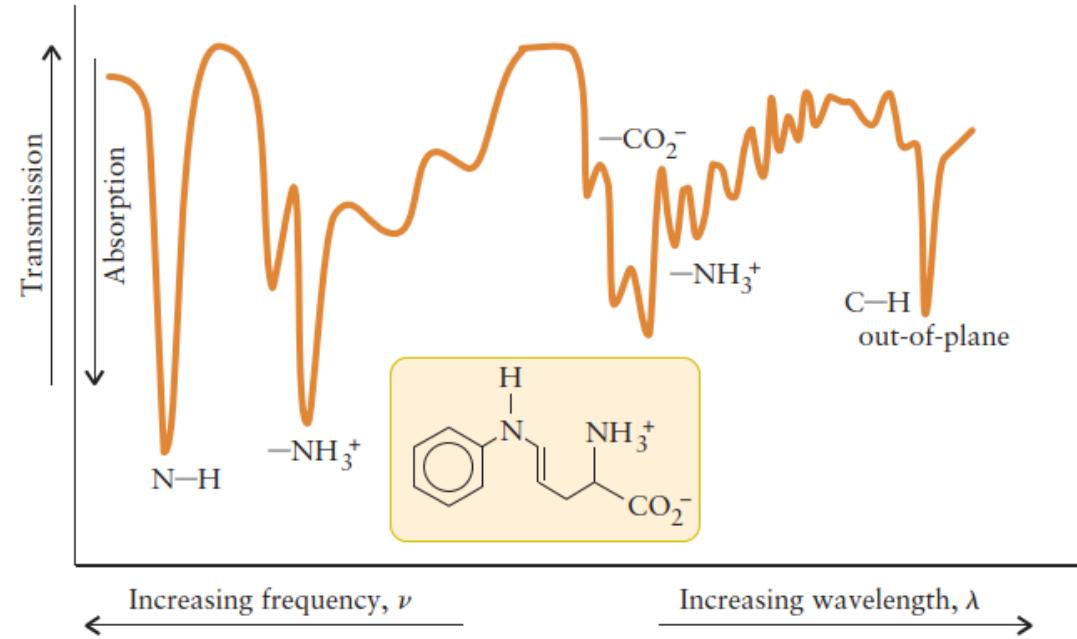
$$\mu = \frac{m(A) m(X)}{m(A) + m(X)} \quad (9.7)$$

**FIGURE 9.5**  
A comparison of the Morse potential (blue) and the harmonic oscillator potential (green), showing the effects of anharmonicity of the potential energy curve, where  $D_e$  is the depth of the well. [© Mark M Samoza/CCC-BY-SA\_3.0/GFDL /Wikimedia Commons; reproduced from [http://en.wikipedia.org/wiki/Morse\\_potential.](http://en.wikipedia.org/wiki/Morse_potential.)]





**FIGURE 2** (a) The three normal vibrational modes of  $\text{H}_2\text{O}$ . Two of these modes are principally stretching motions of the bonds, but mode 2 is primarily bending. (b) The four normal vibrational modes of  $\text{CO}_2$ . The first two are symmetrical and antisymmetrical stretching motions, and the last two are perpendicular bending motions.



**FIGURE 3** The infrared spectrum of an amino acid, with the groups contributing to some of the peaks identified.

## Infrared spectroscopy and Vibrations of Chemical Bonds:

A chemical bond acts like a stiff spring connecting nuclei. As a result, the nuclei in a molecule vibrate, rather than maintaining fixed positions relative to each other.

Nuclear vibration is depicted in Figure 9.23, which shows a spring model of HCl.

This vibration of molecules is revealed in their absorption of infrared radiation. (An instrument for observing the absorption of infrared radiation is shown in Figure 9.24.)

The frequency of radiation absorbed equals the frequencies of nuclear vibrations. For example, the H-Cl bond vibrates at a frequency of  $8.652 \times 10^{13}$  vibrations per second.

If radiation of this frequency falls on the molecule, it absorbs the radiation, which is in the infrared region, and begins vibrating more strongly.

The infrared absorption spectrum of a molecule of even moderate size can have a rather complicated appearance. Figure 9.25 shows the infrared (IR) spectrum of ethyl butyrate, a compound present in pineapple flavor. The complicated appearance of the IR spectrum is actually an advantage. Two different compounds are unlikely to have exactly the same IR spectrum. Therefore, the IR spectrum can act as a compound's "fingerprint."

The IR spectrum of a compound can also yield structural information. Suppose you would like to obtain the structural formula of ethyl butyrate. The molecular formula, determined from combustion analysis, is  $C_6H_{12}O_2$ . Important information about this structure can be obtained from Figure 9.25.

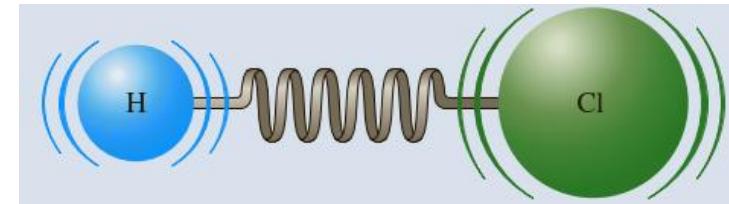
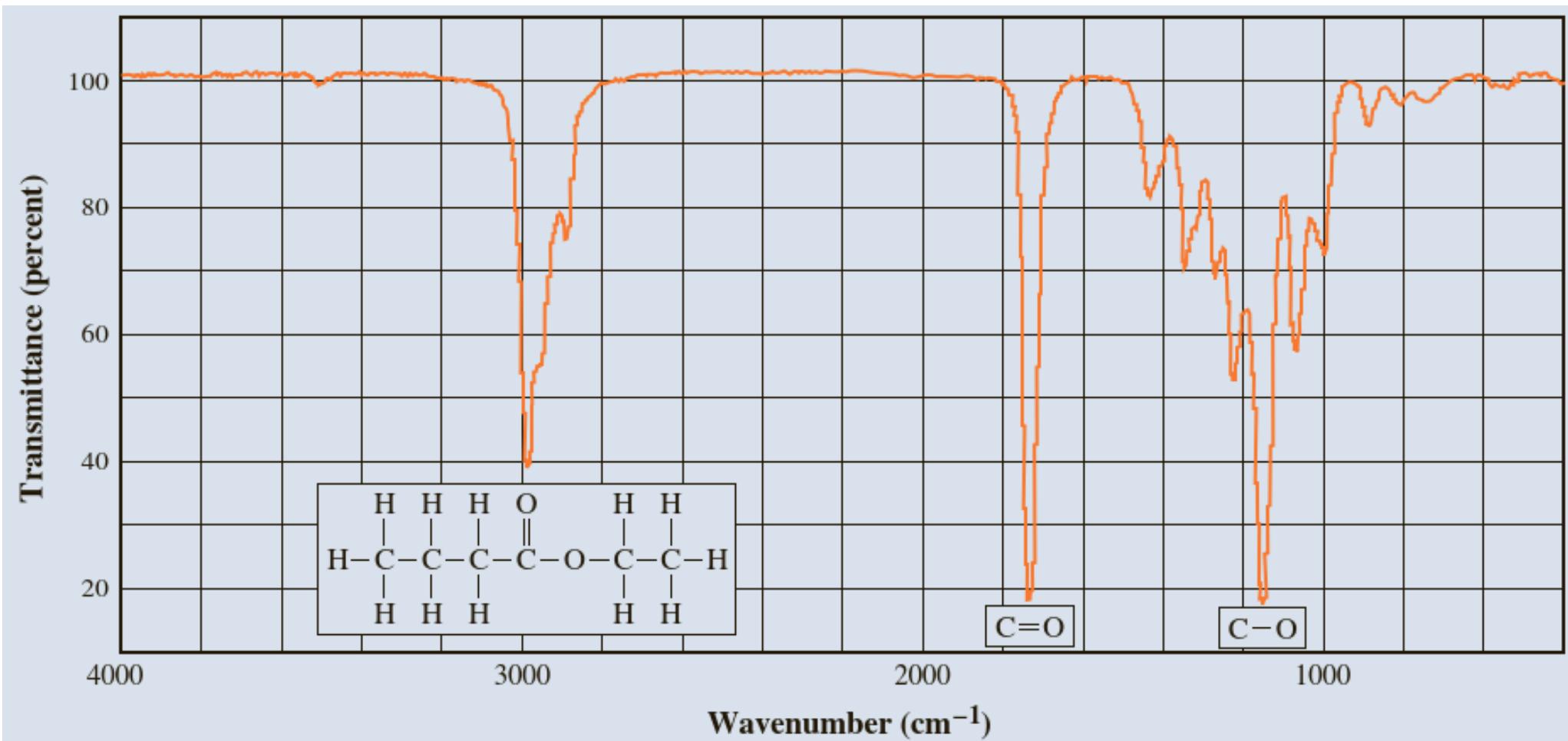


Figure 9.23. Vibration of the HCl molecule The vibrating molecule is represented here by a spring model. The atoms in the molecule vibrate; that is, they move constantly back and forth.



Courtesy of Thermoscientific

Figure 9.24. A Fourier transform infrared (FTIR) spectrometer A Fourier transform instrument collects data over a broad range simultaneously, using Fourier transform mathematics to obtain an infrared spectrum. The instrument shown is a Nicolet iS 50 FT-IR Spectrometer.



**Figure 9.25 ▲**

**Infrared spectrum of ethyl butyrate (gas phase)** Note the peaks corresponding to vibrations of C=O and C—O bonds. The molecular structure is shown at the bottom left. (From NIST Mass Spec Data Center, S.E. Stein, director, “IR and Mass Spectra” in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, Eds. W.G. Mallard and P.J. Linstrom, February 2000, National Institute of Standards and Technology, Gaithersburg, MD, 20899 [<http://webbook.nist.gov>]. © 1991, 1994, 1996, 1997, 1998, 1999, 2000. Copyright by the U.S. Secretary of Commerce on behalf of the United States of America. All rights reserved.)

You first need to be able to read such a spectrum. Instead of plotting an IR spectrum in frequency units (since the frequencies are very large), you usually would give the frequencies in wavenumbers, which are proportional to frequency. To get the wavenumber, you divide the frequency by the speed of light expressed in centimeters per second. For example, HCl absorbs at  $(8.652 \times 10^{13} \text{ s}^{-1})/(2.998 \times 10^{10} \text{ cm/s}) = 2886 \text{ cm}^{-1}$  (wavenumbers).

Wavenumber, or sometimes wavelength, is plotted along the horizontal axis.

*Percent transmittance* – that is, the percent of radiation that passes through a sample – is plotted on the vertical axis. When a molecule absorbs radiation of a given frequency or wavenumber, this is seen in the spectrum as an inverted spike (peak) at that wavenumber. Certain structural features of molecules appear as absorption peaks in definite regions of the infrared spectrum. For example, the absorption peak at  $1730 \text{ cm}^{-1}$  is characteristic of the C=O bond. With some knowledge of where various bonds absorb, one can identify other peaks, including that of C – O at  $1180 \text{ cm}^{-1}$ . (Generally, the IR peak for an A–B bond occurs at lower wavenumber than for an A=B bond.) The IR spectrum does not reveal the complete structure, but it provides important clues. Data from other instruments, such as the mass spectrometer, give additional clues.

Vibrational spectroscopy confines itself to that narrow region of the electromagnetic spectrum where the absorption of a photon has sufficient energy to cause the nuclei of the excited molecule to vibrate. For all practical purposes, this implies a wavelength in the range 2.5–50  $\mu\text{m}$  (or 200–4000  $\text{cm}^{-1}$  in wavenumbers) with corresponding energies of 2.4–48 kJ/mol.

The only circumstances under which IR transition will be allowed are when the absorption of IR radiation causes a change in the molecule's permanent dipole moment.

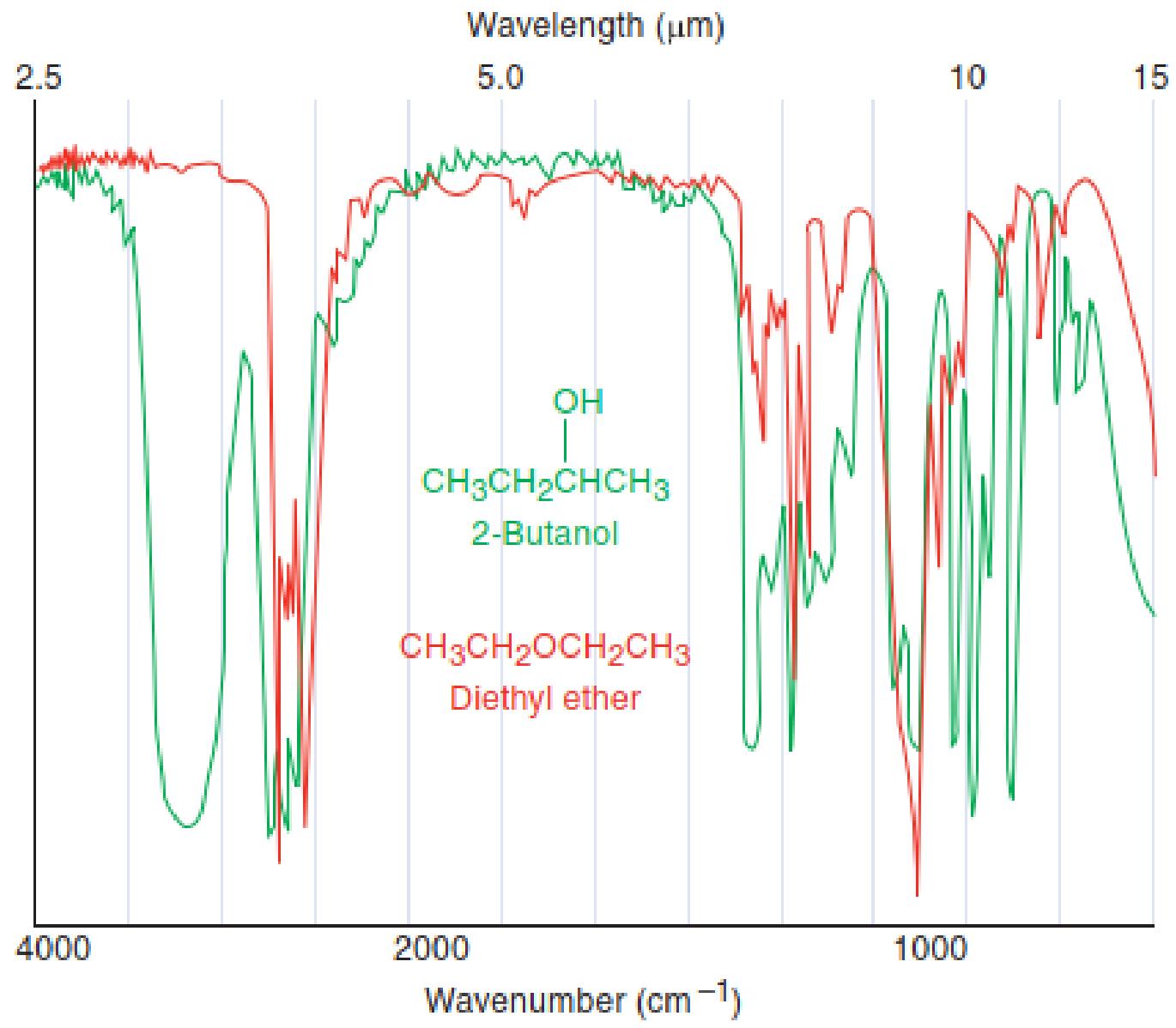


Figure 9.15 The infrared spectra of 2-butanol (green) and diethyl ether (red).

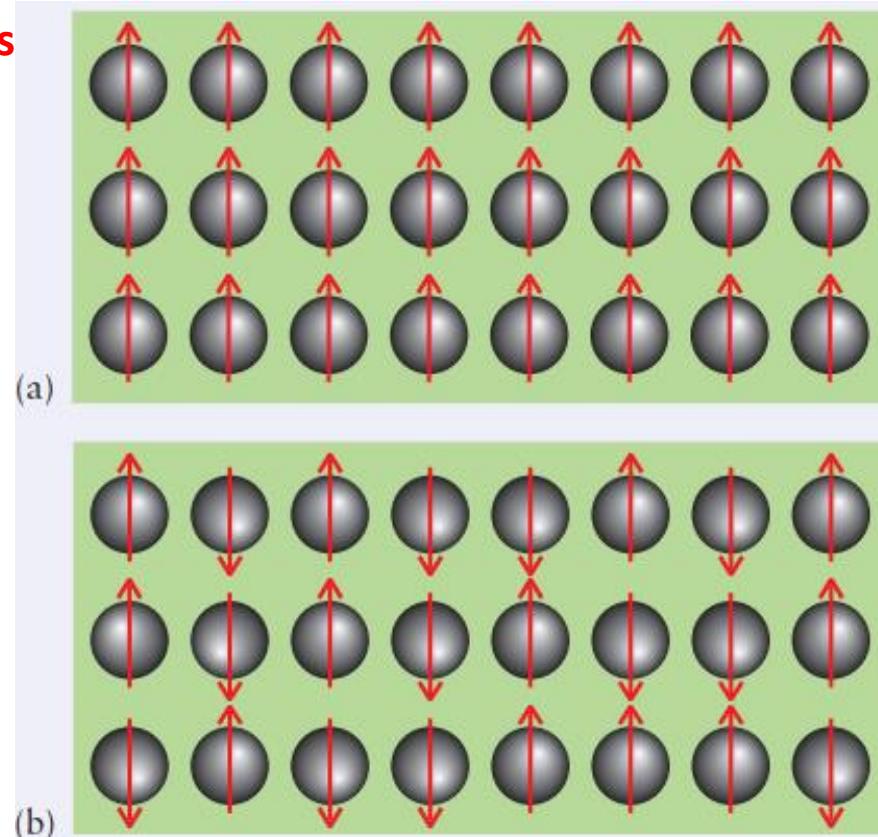
## HOW DO WE KNOW . . . THAT ELECTRONS ARE NOT PAIRED? **Magnetic Moments**

*Compounds with unpaired electrons are paramagnetic.* They tend to move into a magnetic field and can be identified because they seem to weigh more in a Gouy balance when a magnetic field is applied than when it is absent. **Paramagnetism arises from the electron spins,** which behave like tiny bar magnets that tend to line up with the applied field. The more that can line up in this way, the greater the lowering of energy and the heavier the sample appears to weigh.

Oxygen is a paramagnetic substance because it has two unpaired electrons: this property is used to detect the concentration of oxygen in incubators. *All radicals are paramagnetic.*

Many compounds of the d-block elements are paramagnetic because they have various numbers of unpaired d-electrons.

The modern approach to measuring magnetic properties is to use a *superconducting quantum interference device (a SQUID)*, which is highly sensitive to small magnetic fields and can make very precise measurements on small samples.

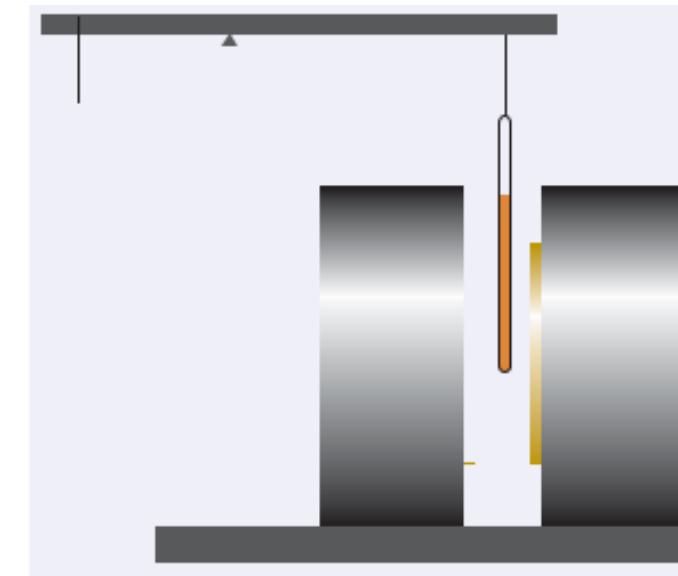


(a) In a magnetic field, the spins of electrons in both paramagnetic and ferromagnetic substances are aligned. (b) The spins of electrons in a paramagnetic substance return to a random orientation after an applied magnetic field is removed. However, the spins of electrons in a ferromagnetic substance remain aligned after a magnetic field is removed.

## HOW DO WE KNOW . . . THAT ELECTRONS ARE NOT PAIRED? **Magnetic Moments**

Most common materials are diamagnetic. The tendency of a diamagnetic substance to move out of a magnetic field can be detected by hanging a long, thin sample from the pan of a balance and letting it lie between the poles of an electromagnet.

This arrangement, which was once the primary technique used to measure the magnetic properties of samples, is called a **Gouy balance**. When the electromagnet is turned on, a diamagnetic sample tends to move upward, out of the field, so it appears to weigh less than in the absence of the field. The diamagnetism arises from the effect of the magnetic field on the electrons in the molecule: the field forces the electrons to circulate through the nuclear framework. Because electrons are charged particles, this circulation corresponds to an electric current circulating within the molecule. That current gives rise to its own magnetic field, which opposes the applied field. The sample tends to move out of the field so as to minimize this opposing field.



A Gouy balance is used to observe the magnetic character of a sample by detecting the extent to which it is drawn into (paramagnetic substances) or driven out of (diamagnetic substances) a magnetic field.

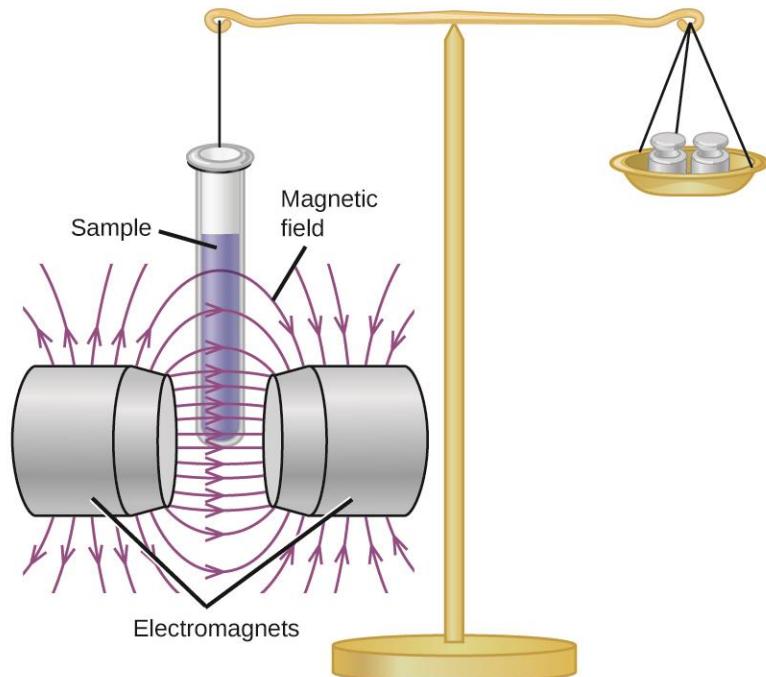
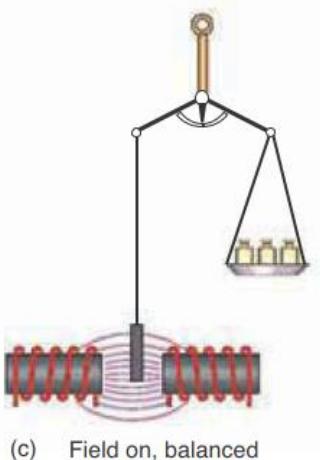
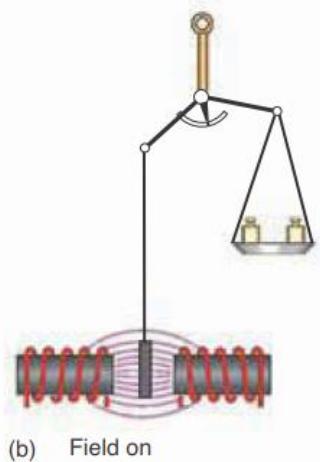
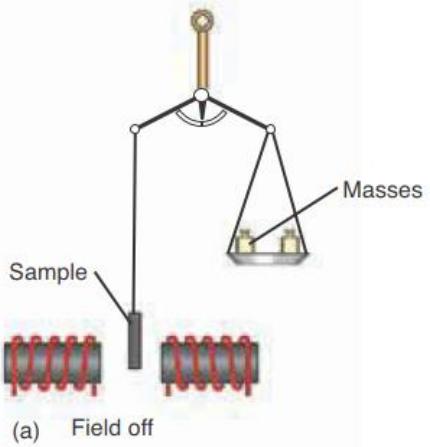
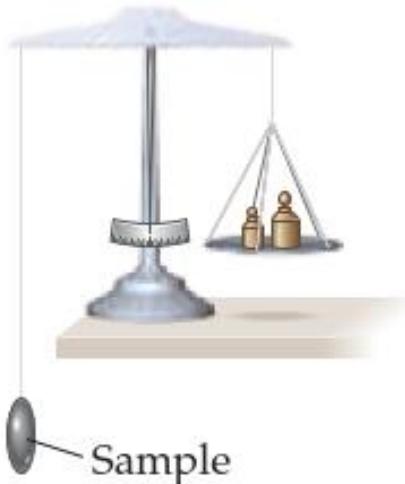


Figure 8.4.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

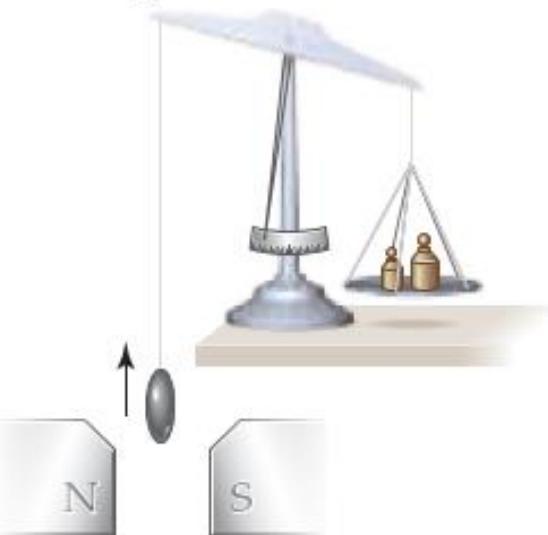


**Figure 6.7** One method for determining the electronic configuration of transition metal ions is to use a magnetic field. Because unpaired electrons act like tiny magnets, the number of unpaired electrons in a transition metal ion can be determined by weighing the sample in a magnetic field. If the sample contains unpaired electrons, the magnetic attractive force on the sample makes it appear heavier. The number of unpaired electrons in the sample and the electron configuration can be calculated from the apparent mass gain when the field is on. Masses are added to the balance pan until balance is restored with the field on.

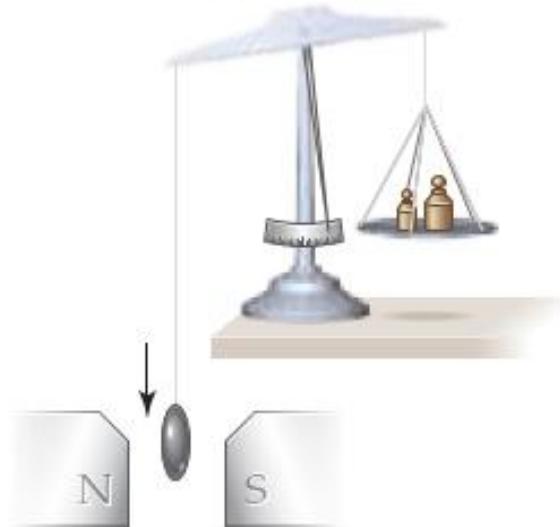
Weigh sample in absence  
of a magnetic field



A diamagnetic sample  
appears to weigh less in  
magnetic field (weak effect)



A paramagnetic sample  
appears to weigh more  
in magnetic field



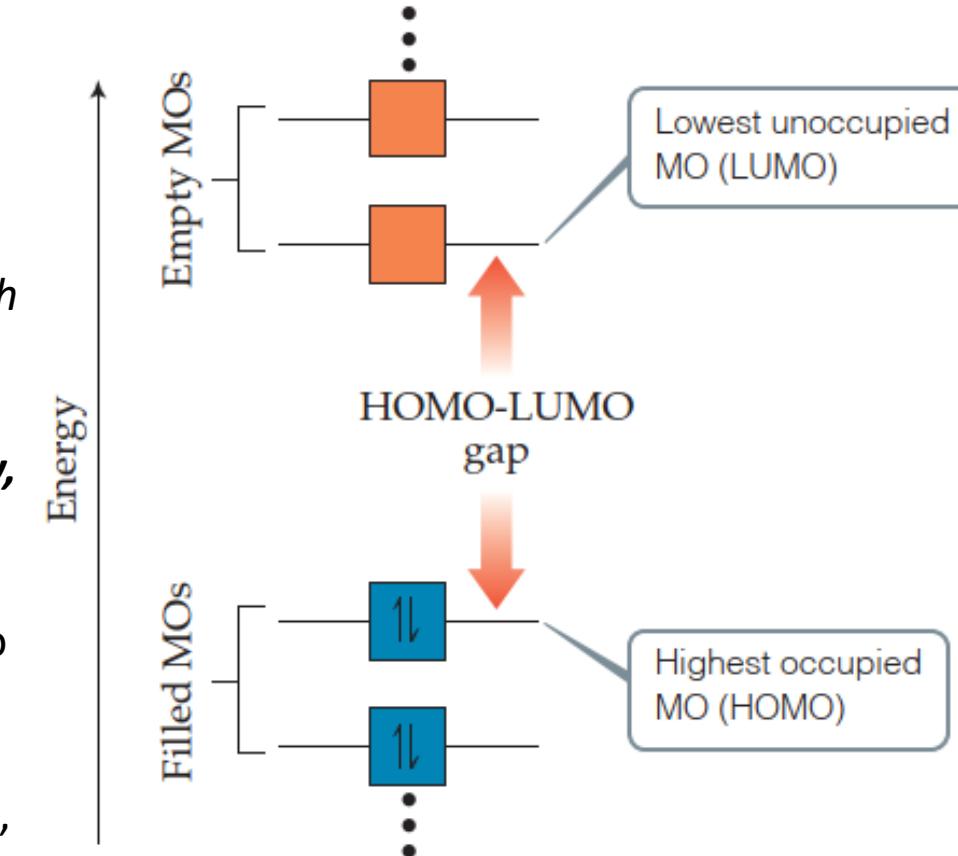
**Figure 9.44** Determining the magnetic properties of a sample.

## ❖CHEMISTRY PUT TO WORK: Orbitals and Energy

- Asked to identify the **major technological challenge for the twenty-first century, you might say “energy,”** reasoning that development of sustainable energy sources is crucial to meet the needs of future generations of people on our planet. *One of the most remarkable sources of clean energy is the Sun, which sends enough energy to power the world for millions of years.* Our challenge is to capture enough of this energy in a form that allows us to use it as needed.
- **Photovoltaic solar cells convert the light from the Sun into usable electricity,** and the development of more efficient solar cells is one way to address Earth’s future energy needs.

**How does solar energy conversion work?** Fundamentally, we need to be able to use photons from the Sun, especially from the visible portion of the spectrum, to excite electrons in molecules and materials to different energy levels. The brilliant colors around you—those of your clothes, the photographs in this book, the foods you eat—are due to the selective absorption of visible light by chemicals. It is helpful to think of this process in the context of molecular orbital theory: **Light excites an electron from a filled molecular orbital to an empty one at higher energy.** Because MOs have definite energies, only light of the proper wavelengths can excite electrons.

In discussing light absorption by molecules, we can focus on the two **frontier MOs** shown in Figure 9.47. The highest occupied molecular orbital (**HOMO**) is the MO of the highest energy that has electrons in it. The lowest unoccupied molecular orbital (**LUMO**) is the MO of the lowest energy that does not have electrons in it.



▲ Figure 9.47 Definitions of the highest occupied and lowest unoccupied molecular orbitals. The energy difference between these is the HOMO-LUMO gap.

- The energy difference between the HOMO and the LUMO—known as the HOMO–LUMO gap—is related to the **minimum energy needed to excite an electron in the molecule**.
- *Colorless or white substances usually have such a large HOMO–LUMO gap that visible light is not energetic enough to excite an electron to a higher level.*
- The minimum energy needed to excite an electron from the HOMO to the LUMO in N<sub>2</sub> corresponds to light with a wavelength of less than 200 nm, which is far into the ultraviolet part of the spectrum. As a result, *N<sub>2</sub> cannot absorb visible light and is therefore colorless*.
- The magnitude of the ***energy gap between filled and empty electronic states*** is critical for ***solar energy conversion***. Ideally, we want a substance that absorbs as many solar photons as possible and then converts the energy of those photons into a useful form of energy.
- Titanium dioxide is a readily available material that can be reasonably efficient at converting light directly into electricity. However, TiO<sub>2</sub> is white and absorbs only a small amount of the Sun's radiant energy.
- *Scientists are working to make solar cells in which TiO<sub>2</sub> is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light to absorb more of the solar spectrum.* If the HOMO of these molecules is higher in energy than the HOMO of TiO<sub>2</sub>, the excited electrons will flow from the molecules into the TiO<sub>2</sub>, thereby generating electricity when the device is illuminated with light and connected to an external circuit.
- Efficient solar energy conversion promises to be one of the most interesting and important areas of both scientific and technological development in our future. Many of you may ultimately end up working in fields that have an impact on the world's energy portfolio.