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, H_2 stable; not He_2.

2. **Why atoms form molecules in definite proportions and why there is saturation of valency.** For example, CH_4 is a stable molecule but not CH_3, 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 (MO) theory 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 (MO Theory)**

❖ **Learning Objectives**

1. Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals

2. Describe traits of bonding and antibonding molecular orbitals

3. Write molecular electron configurations for some homo- and hetero-nuclear diatomic molecules

4. Relate these electron configurations to the molecules' stabilities and magnetic properties

5. Applications of MOT to AX_2 and AX_3 molecules

6. MOT and shapes of molecules

7. Applications of MOT to delocalized pi-bonding systems

8. Applications of MOT to solids (ionic and metallic)

❑ **Molecular Orbital Theory (MO Theory)**

❑ **Conceptual Development of Molecular Orbitals**

➢ The formalism that applies to the molecular orbital method will be illustrated by considering a hydrogen molecule (but a more detailed description of both H_2^+ and H_2 will be given in the next sections).

➢ 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, there is an attraction between them that gets greater as the distance between them becomes shorter.

➢ Eventually, the atoms reach a distance of separation that represents the most favorable (minimum energy) distance, the bond length in the H_2 molecule (74 pm).

- ❑ **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.

H atom   Large separation   H atom

No interaction

(a)

Constructive interference begins

(b)

H_2 at equilibrium bond length

(c)

FIGURE 6.2 The probability density for finding an electron in the 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)
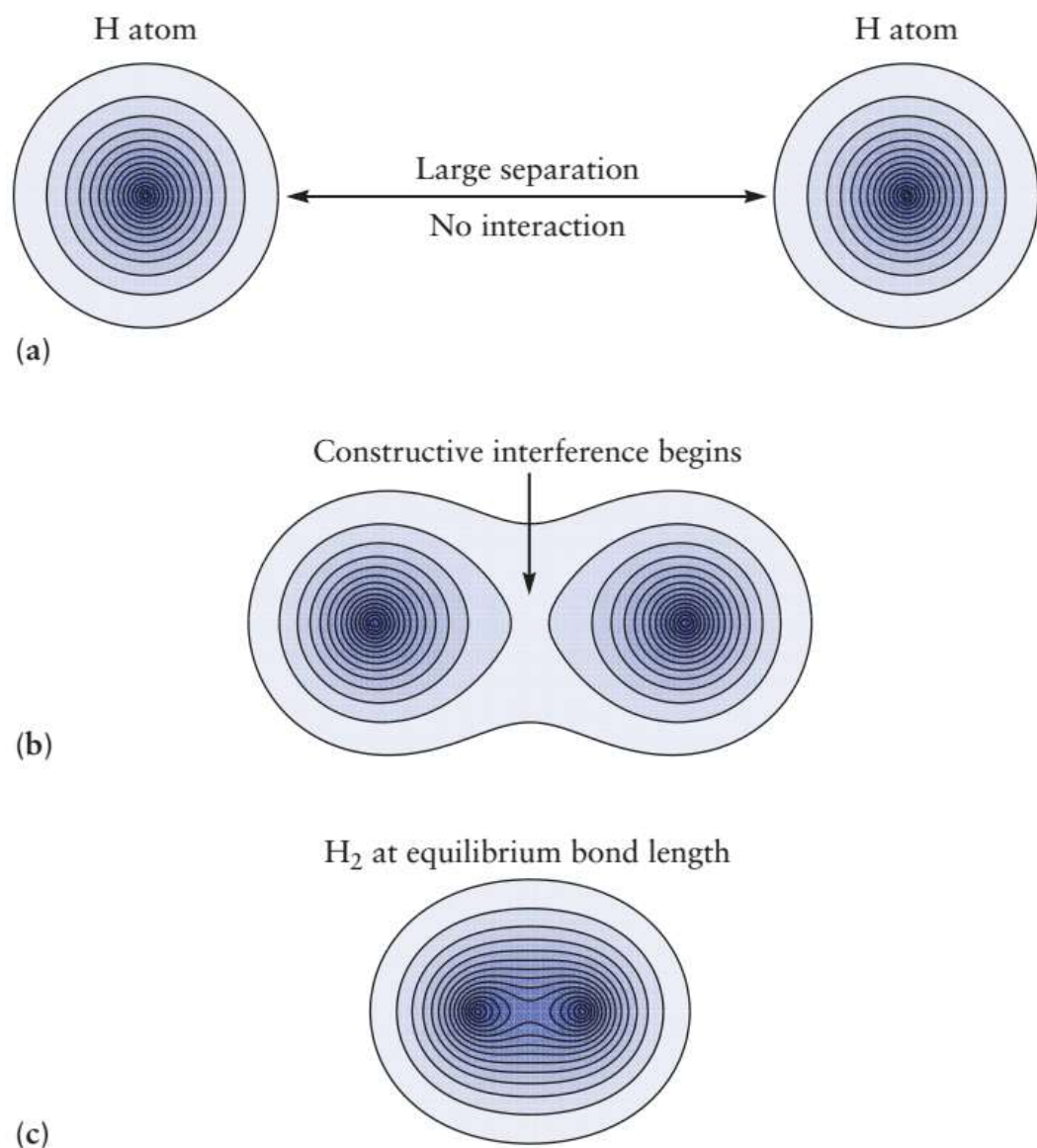
➤ The sequence of events traced in Figure 6.2 shows us that as the two atoms draw near, their electron densities interpenetrate and form a new electron density characteristic of the molecule. Because electrons behave like waves, the two atomic electronic wave functions can interfere either constructively 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 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 aJ, which is the energy required to dissociate the H_2 molecule into two separate hydrogen atoms.
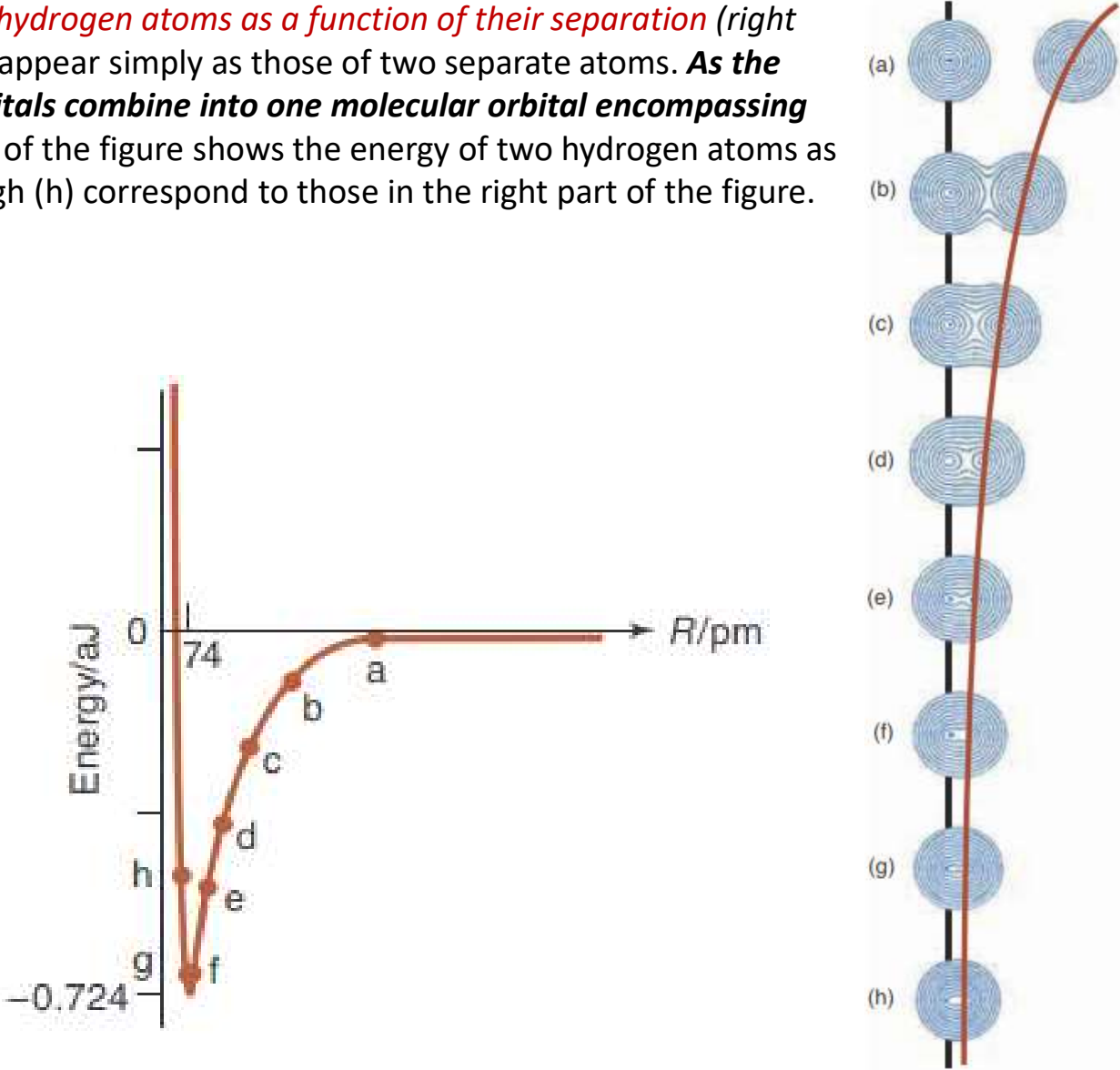
➤ Let's track progress by plotting the potential energy of the atoms as the distance between them R_{AB} decreases (Figure 6.1).
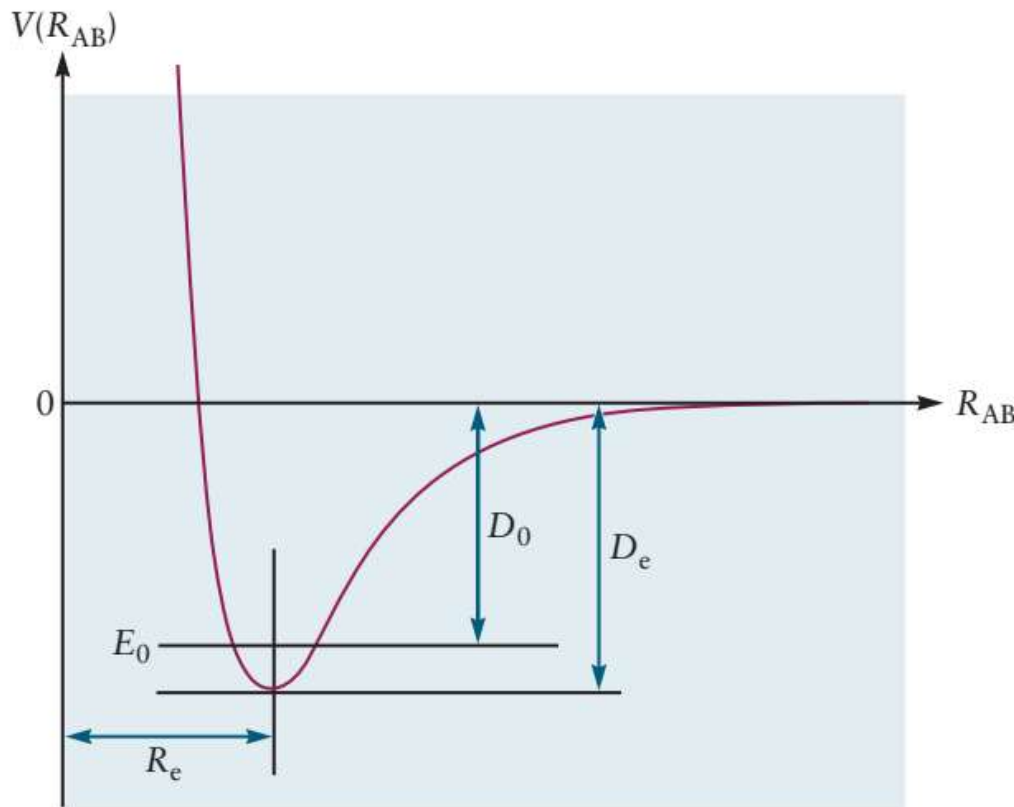

FIGURE 6.1 Schematic representation of the potential energy of two hydrogen atoms as a function of the distance between them. As distance decreases, the potential energy reaches a minimum value of -458 kJ mol^{-1} at a distance of 0.74 Å. The value of D_0 for H_2 is 432 kJ mol^{-1} or 4.48 eV molecule^{-1}.
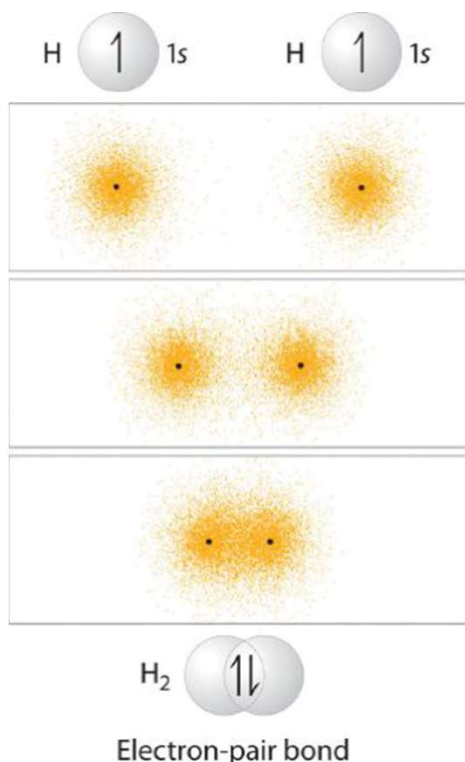
Figure: Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in H_2.
The formation of H_2 from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.
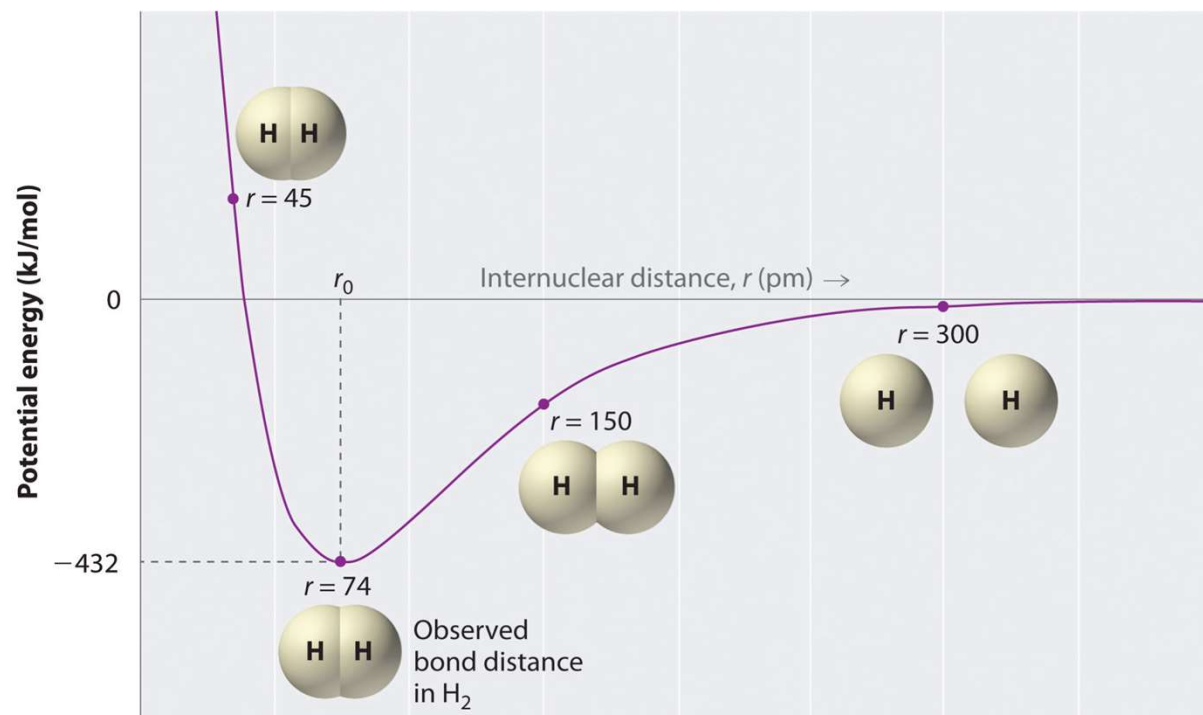

Figure: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.
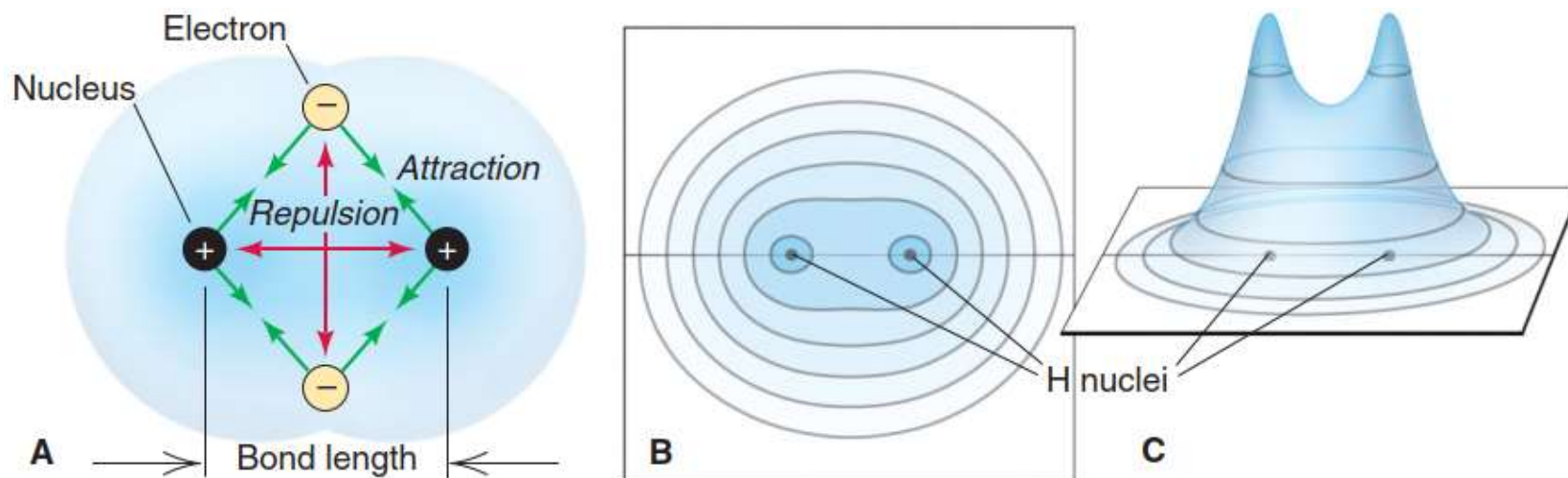
Figure 9.11 Distribution of electron density in H_2.
(A): At some **distance (bond length), attractions balance repulsions**. *Electron density (blue shading) is high around and between the nuclei*.
(B): Electron density doubles with each concentric curve.
(C): The highest regions of electron density are shown as peaks.

➢ At very large separation we define the energy of interaction to be zero.
➢ As the atoms come closer together, the potential energy decreases (becomes negative) due to attractive forces between the atoms.
➢ At very close distances the potential energy becomes positive due to repulsive forces between the atoms.
➢ At some intermediate but small distance between the atoms the attractive interactions dominate the repulsion, and the potential energy is negative; it reaches a minimum value where the attractive and repulsive forces balance exactly. This minimum is the signature of chemical bond formation.
➢ The value of the potential energy at this minimum measures the extent to which the bond is more stable than the separated atoms. The difference between this minimum and the value for the separated atoms is the amount of energy that must be invested to break the bond and liberate the free atoms. This is a positive number called the bond dissociation energy and denoted either D_e or ΔE_d.

➢ The distance R_e at which the minimum occurs is the equilibrium length of the bond. For H_2, the bond dissociation energy D_e is 458 kJ mol^{-1}, or 4.75 eV molecule^{-1}, and experimental measurements show that the bond length is 0.74 Å.

➢ The total energy of the molecule is quantized, so we can visualize a set of energy levels superposed on the potential energy curve. Just as shown for the particle-in-a-box model, the uncertainty principle requires that there is a **zero-point energy** for the molecule. This is the ***lowest allowed value of the total energy*** and is represented by the line E_0.

➢ Because the zero-point energy can never be removed from the molecule, it provides a reference point for the amount of energy required to dissociate the molecule. Relative to the zero-point energy, the ***bond dissociation energy*** is defined as D_0. Although both D_0 and D_e are called dissociation energies, only the ***former is measurable experimentally*** as the energy needed to dissociate the molecule. D_e is useful as a parameter to construct model potentials and optimize geometry in calculations.

➢ The bond dissociation energy D_0 for H_2 is 432 kJ mol^{-1} (measured experimentally and calculated with quantum theory); it is smaller than D_e by the zero-point energy of H_2 as shown in Figure 6.1. (If a polyatomic molecule dissociates, D_0 is measured from the lowest quantum state of the reactants, called the zero-point level, to the zero-point level of the products, so again equals the experimentally measured bond dissociation energy at 0 K.)

➢ The meaning of this curve is considerably more subtle than the simple description we gave to introduce it. Each atom contains one proton and one electron. Each of these four particles interacts with each of the others by a force described by Coulomb's law (see Fig. 3.1), and all these contributions must be included in the potential energy of the two atoms. However, the coordinates in Figure 6.1 track only the distance between the two protons, and do not describe the electrons at all.

➢ In fact, the curve in Figure 6.1 plots the effective potential energy function for the two protons in the molecule, against the distance between the protons. This effective potential energy function includes several contributions: (a) Coulomb repulsion between the protons; (b) Coulomb repulsion between the electrons; (c) Coulomb attractions of both electrons to both protons; (d) kinetic energies of the electrons. The contributions from the electrons have been averaged out in some sense, and their coordinates do not appear in the effective potential energy curve. The effective potential energy function governs the formation of the molecule (it gives the depth of the potential well relative to the isolated atoms), the structure of the molecule (by defining the equilibrium bond length), and the vibrations of the molecule (by defining the force that determines the relative motions of the nuclei). If we can find a way to predict the effective potential energy curve as a function of the distance between the nuclei, we will know all the structural properties of the molecule.

➢ The only justification for the effective potential energy curve for a molecule is provided by the quantum description of the chemical bond.

➢ Not only does this theory define the concept of the effective potential energy curve, it also provides an explicit procedure for calculating the curve.

➢ The quantum description of the chemical bond therefore has enormous predictive power. It can determine whether a particular molecule will exist, and if it does exist what will be its structure and properties.

➢ The definition of the effective potential energy curve for a molecule, and the method for calculating it, arise naturally within the Born–Oppenheimer approximation, which is the foundation of molecular calculations in quantum mechanics.

➢ Now let's see how to obtain the effective potential energy curve and how to use it.

❑ **Exact Molecular Orbitals for the Simplest Molecule: 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, H_2^+, which contains only one electron.

➢ Schrödinger's equation for the motion of the electron in 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 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 $(-\hbar^2/2\mu)\nabla^2\psi + V\psi = E\psi$.

➤ *Ψ 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**: H_2^+ Is the Prototypical Species

➤ For the case where the protons in 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.
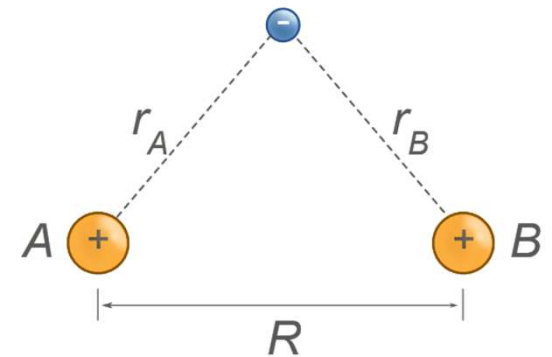

Figure 9.2.1 : Hydrogen molecular ion H_2^+ with fixed nuclei A and B, internuclear distance R.

❑ Molecular-Orbital Theory: 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 ψ 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 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 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 kJ·mol^{-1} ($0.103E_h$).

➤ Because H_2^+ is a one-electron species, **the Schrodinger equation for 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 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 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 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 H_2^+, there are two possible outcomes*: an electron may be found either in an atomic orbital φ_A centred on A or in an atomic orbital φ_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

$$\Psi_\pm = c_A \varphi_A \pm c_B \varphi_B$$

where c_A and c_B are numerical coefficients.

➢ The AOs are the **basis functions** for the MO.

➢ In this case the **basis set**, *the atomic orbitals φ_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.
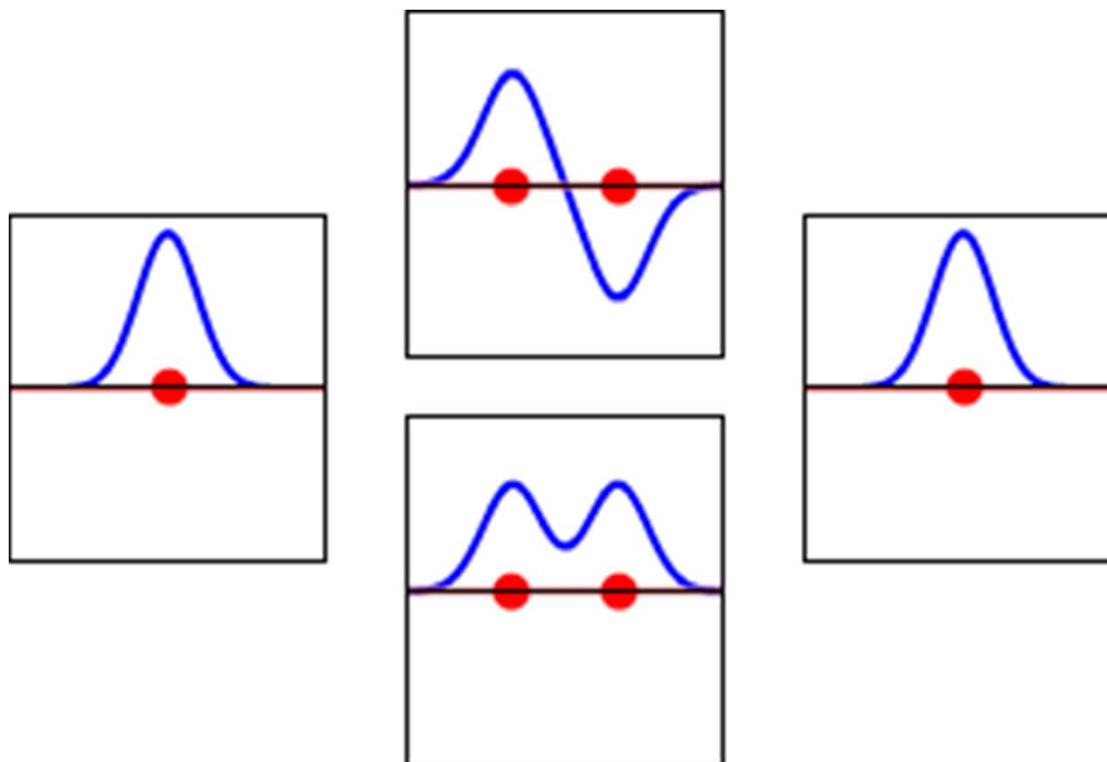
Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots 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, ψ is the molecular wave function, ϕ 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 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 H_2, O_2, or 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 calculation 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 α***, it is necessary to make use of the relationship

$$\langle a \rangle = \frac{\int \psi^* \alpha \psi \, d\tau}{\int \psi^* \psi \, d\tau} \tag{3.3}$$

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

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \tag{3.4}$$

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

➤ The expression shown in Eq. (3.2) is substituted for ψ in the equation above which gives

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

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

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

➤ In writing this equation, it was assumed that

$$\int \phi_1^*\,\widehat{H}\,\phi_2\,d\tau = \int \phi_2^*\,\widehat{H}\,\phi_1\,d\tau \qquad (3.7)$$

➤ and that

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

➤ These assumptions are valid for a diatomic molecule composed of identical atoms (homo-nuclear diatomic) because ϕ_1 and ϕ_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:

$$H_{11} = \int \phi_1^* \widehat{H} \phi_1 \, d\tau \qquad (3.9)$$

$$H_{12} = \int \phi_1^* \widehat{H} \phi_2 \, d\tau \qquad (3.10)$$

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

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

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

➢ 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

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

➢ On the other hand, the integrals of the type

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

➤ *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.
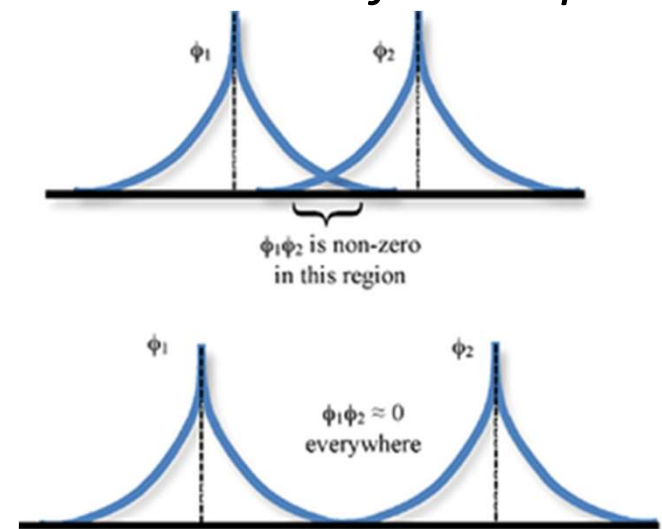
➢ *If the two atoms are **separated by a large distance**, the **overlap integral approaches 0** (Figure 9.3.1: bottom).*

➢ 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 $S > 0$*.
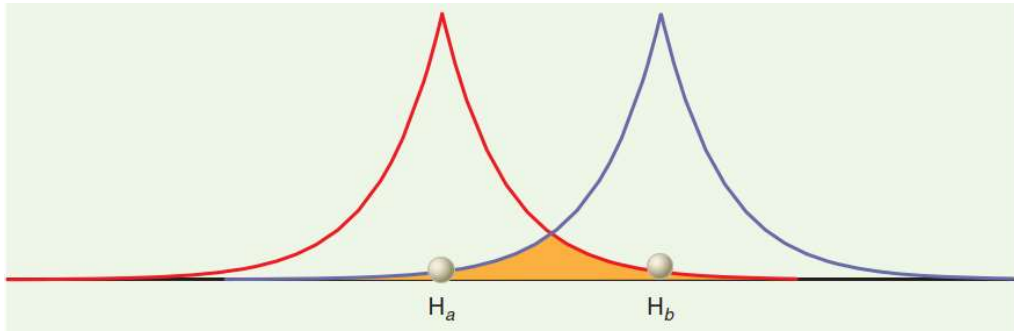
➢ Thus, we see that $0 \leq S(R) \leq 1$.

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.
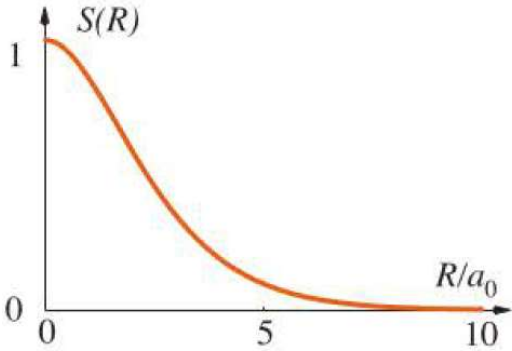
FIGURE 10.10
The overlap integral $S(R)$, for two hydrogen-atom 1s orbitals, plotted versus the internuclear separation in atomic units.

➢ The Overlap Integral Is a Quantitative Measure of the Overlap of Atomic Orbitals Situated on Different Atoms. For 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:

➢ $S(R) = \int 1s_A 1s_B \, d\tau = e^{-R/a_0}\left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right)$

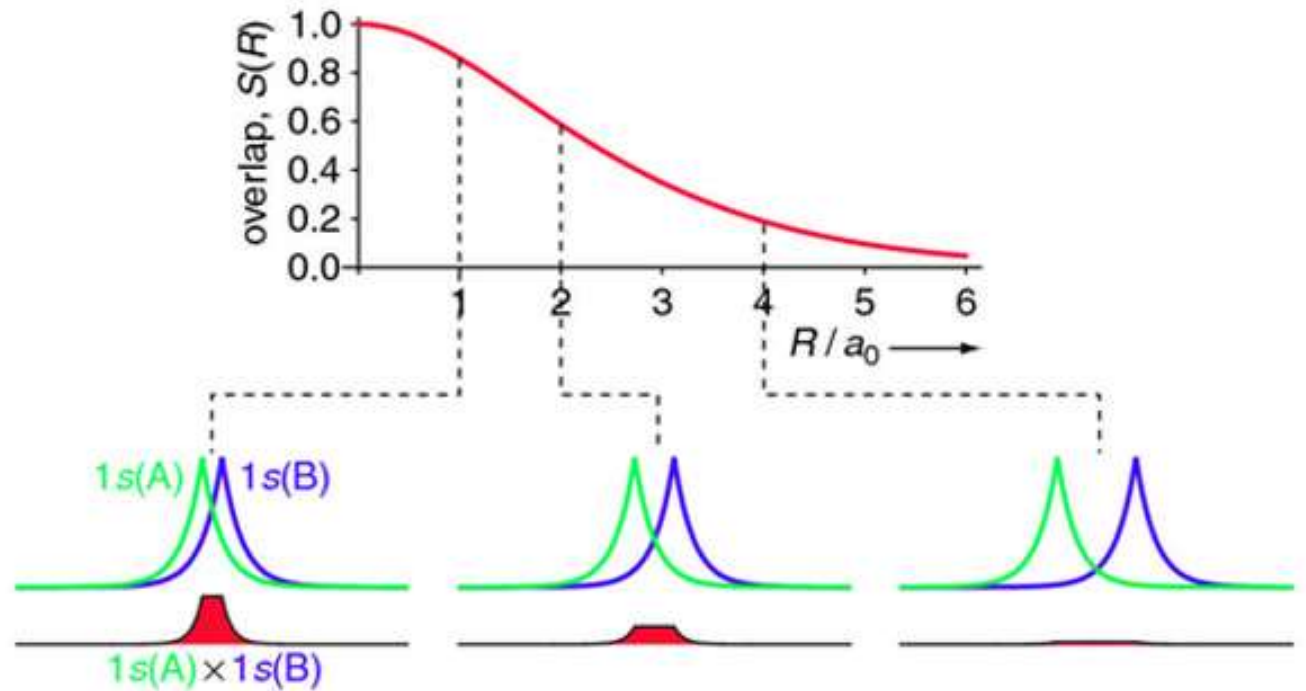➢ The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

Figure 9.3.2 : The overlap integral at different proton separations.

➢ For 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 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 ψ$_+$ and ψ$_-$ also should be reflected in the energy. If ψ$_+$ 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, $\int C_{\pm}(1s_A \pm 1s_B). C_{\pm}(1s_A \pm 1s_B)d\tau = 1$

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

Or, $|C_{\pm}|^2 [\int 1s_A 1s_A \, d\tau \pm \int 1s_B 1s_A \, d\tau \pm \int 1s_A 1s_B \, d\tau \pm \int 1s_B 1s_B \, d\tau] = 1$ ...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=∞ 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: $C_\pm = \dfrac{1}{\sqrt{2(1\pm S)}}$.

➢ Hence, the normalized molecular orbitals in Equations 9.3.1 and 9.3.2 are:

➢ $\psi_+ = \dfrac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B)$ ……..bonding molecular orbital ….(9.3.1)

➢ and $\psi_- = \dfrac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B)$ ………antibonding molecular orbital. ….(9.3.2)

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

➤ The probability density for 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 ψ_+^2 and ψ_-^2 is that the charge density for ψ_+ is enhanced between the two protons, whereas it is diminished for ψ_-.

➤ ψ_- has a node in the middle while ψ_+ 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 ψ_+ is called a ***bonding molecular orbital***.

➤ If the electron were described by ψ_-*, **the low charge density between the two protons*** would not balance the Coulomb repulsion of the protons, so ψ_- 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 ψ_+ is

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

Bonding probability density   (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:

- ψ_A^2, the probability density if the electron were confined to atom A;
- ψ_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.
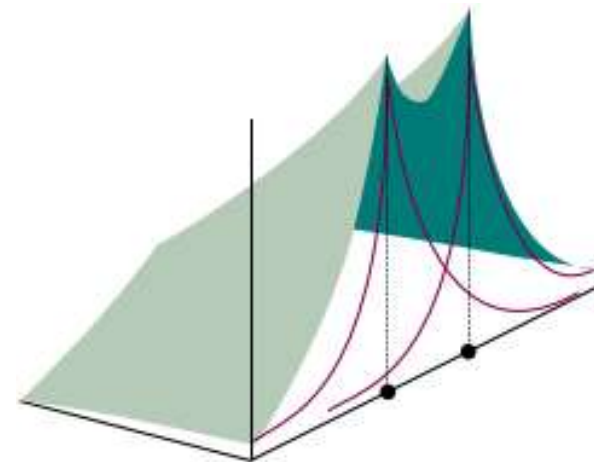
Figure 9B.4 The electron density calculated by forming the square of the wavefunction used to construct Fig. 9B.2. Note the accumulation of electron density in the internuclear region.

- ❑ 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.*

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

Region of constructive interference

Figure 9B.7 A representation of the constructive interference (blue line) that occurs when two H_{1s} orbitals overlap and form a bonding σ orbital.
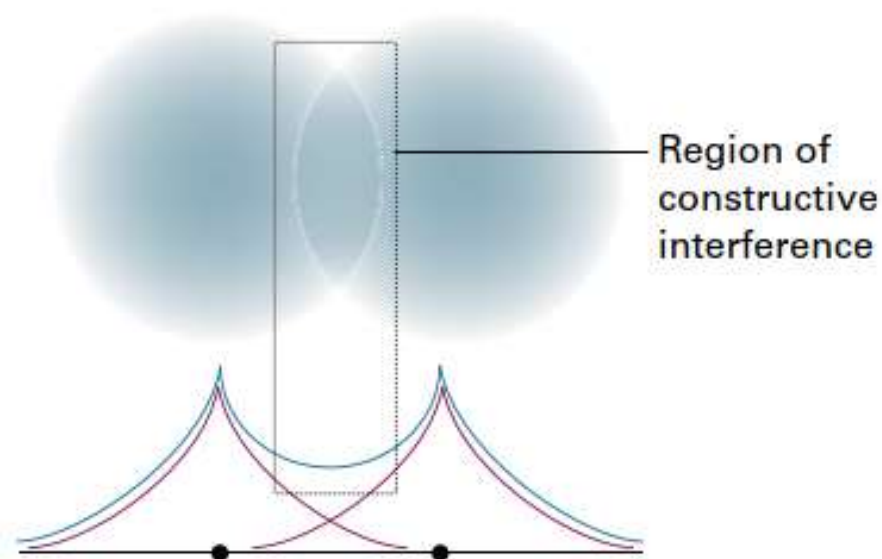
➢ The **conventional explanation** of this observation is based on the notion that *the accumulation of electron density between* the nuclei puts the electron in a position where it interacts strongly with both nuclei. Hence, *the energy of the molecule is lower than that of the separate atoms*, where 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 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 ψ_- has higher energy than ψ^+, and for now, it is labeled σ* because it is also a σ orbital. This orbital has a nodal plane perpendicular to the internuclear axis and passes through the mid-point of the bond where ψ_A and ψ_B cancel exactly (Figs. 9B.8 and 9B.9).

The probability density is

$$\psi_-^2 \propto \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B \qquad \text{Antibonding probability density} \qquad (9B.6)$$

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 σ* 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

Region of destructive interference
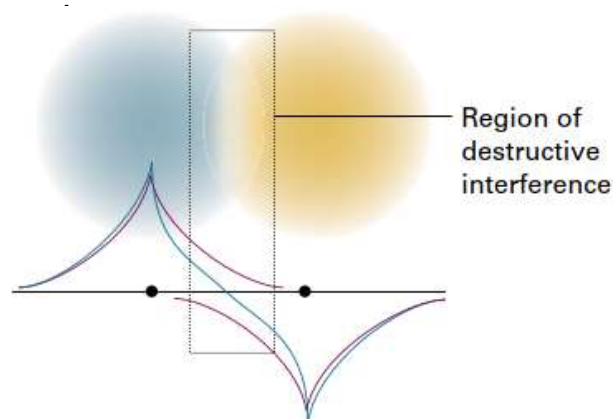
Figure 9B.8 A representation of the destructive interference that occurs when two H1s orbitals overlap and form an antibonding σ orbital.

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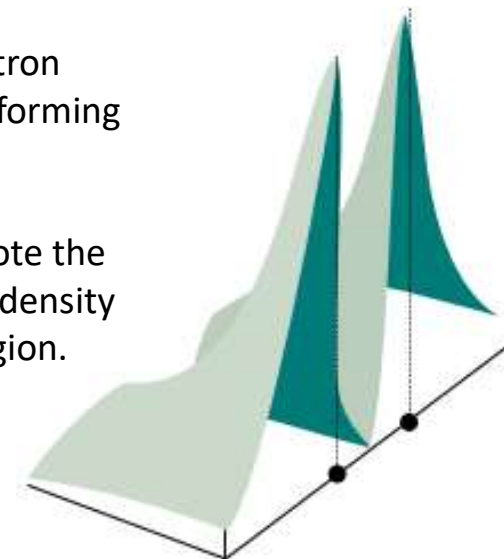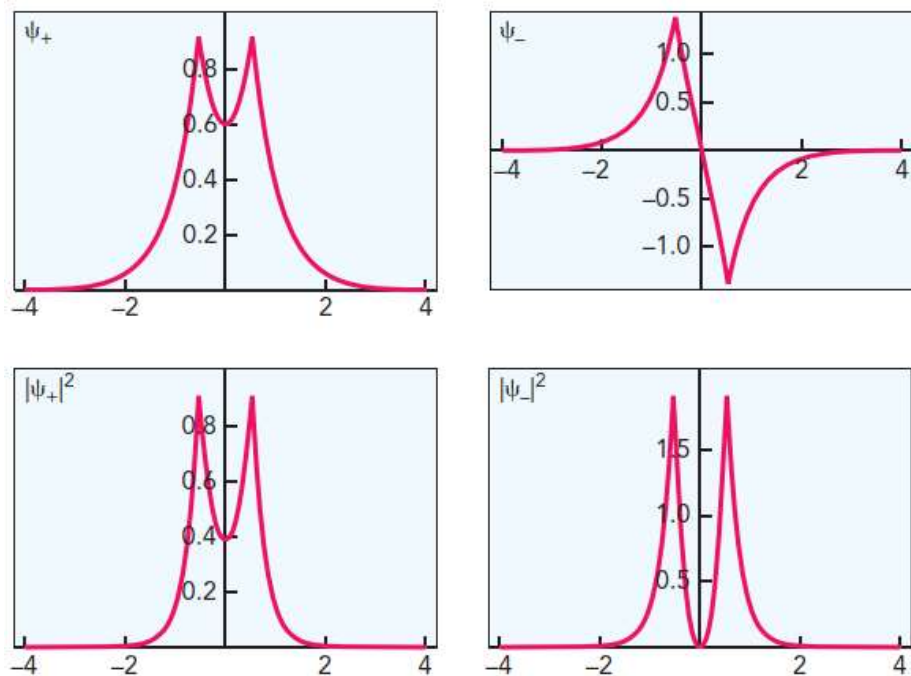
Figure 5.8. The ψ_+ and ψ_- wavefunctions and
probability densities, graphed as functions
of z.

The key feature for us here is that in the ψ_- 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.
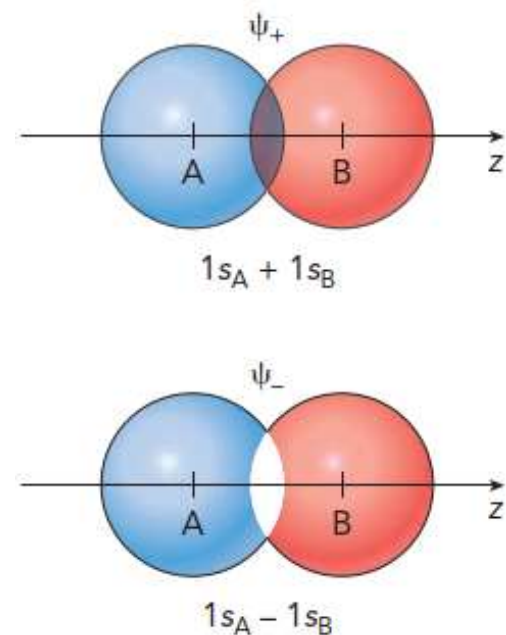
Figure 5.7 The ψ_+ and ψ_-
MOs. We combine the two
spherically symmetric 1s
orbitals on nuclei A and B to
get the simplest molecular
orbitals.

➢ 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

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

➢ (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.

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

➤ 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

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

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

➤ 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

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

➤ 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

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

➢ 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

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

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

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

➢ 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:

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

➤ 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.
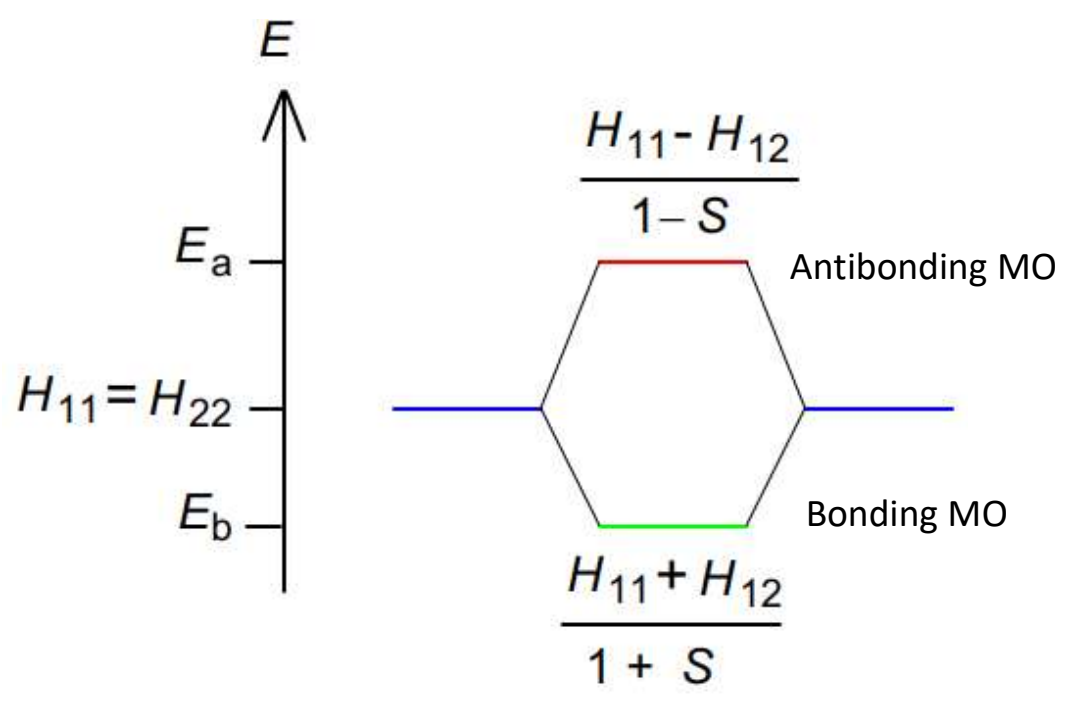

FIGURE 3.3 Combination of two *s* orbitals to produce *bonding* and *antibonding* orbitals.

➢ As shown previously, we can construct two molecular orbitals for the 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 ϕ_1 and ϕ_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: H_2^+ and H_2**

➤ As a ***first step*** in *setting up the Schrödinger equation for H_2^+ and 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, H_2. The Schrödinger equation for a 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 H_2 and therefore are called **molecular orbitals (MOs)**.

➢ The **Hamiltonian operator for a hydrogen molecule (H$_2$)** is given by

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0 r_{1A}} - \frac{e^2}{4\pi\varepsilon_0 r_{1B}}$$

$$- \frac{e^2}{4\pi\varepsilon_0 r_{2A}} - \frac{e^2}{4\pi\varepsilon_0 r_{2B}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 R} \qquad (9.1)$$

➢ 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*.
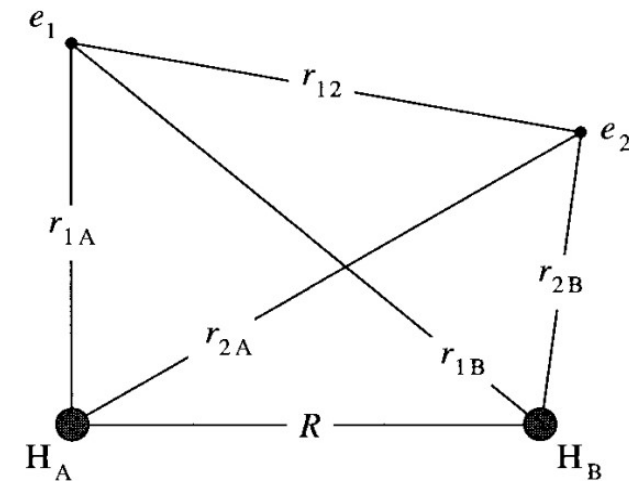
➤ In these expressions e is the magnitude of the charge on the protons and the electrons, m_e and M are the masses of the electron and proton respectively and ε_0 is the vacuum permittivity.

➤ The symbol ∇^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.*

➢ 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.*

➢ 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 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**.*

➢ 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

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0 r_{1A}} - \frac{e^2}{4\pi\varepsilon_0 r_{1B}}$$

$$-\frac{e^2}{4\pi\varepsilon_0 r_{2A}} - \frac{e^2}{4\pi\varepsilon_0 r_{2B}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 R} \tag{9.1}$$

➤ **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:

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0 r_{1A}} - \frac{e^2}{4\pi\varepsilon_0 r_{1B}} - \frac{e^2}{4\pi\varepsilon_0 r_{2A}} - \frac{e^2}{4\pi\varepsilon_0 r_{2B}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 R}$$

$$(9.2)$$

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

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

➤ *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 stationery atoms.*

➢ Similar considerations apply to **polyatomic molecules,** where **bond angles** *may be varied* as well as *bond lengths.*
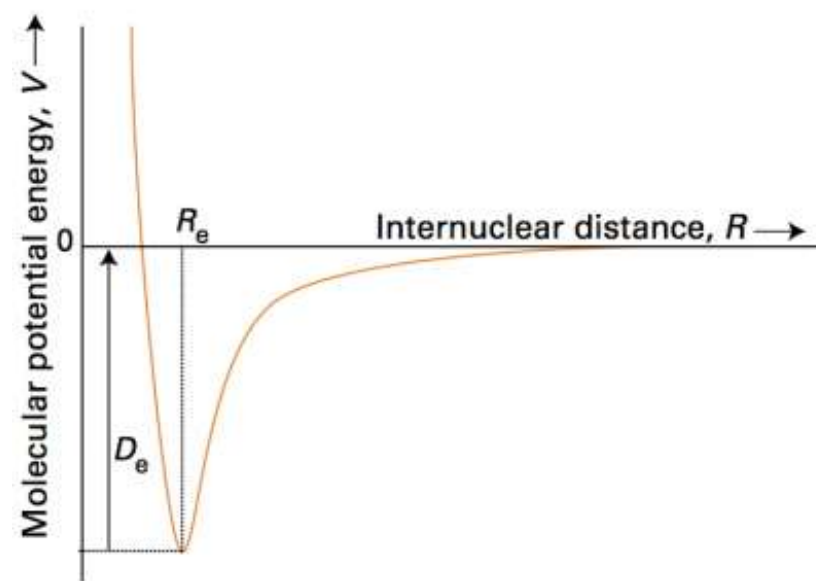
Fig. 1 A molecular potential energy curve. The equilibrium bond length R_e, corresponds to the energy minimum D_e.

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 × 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.
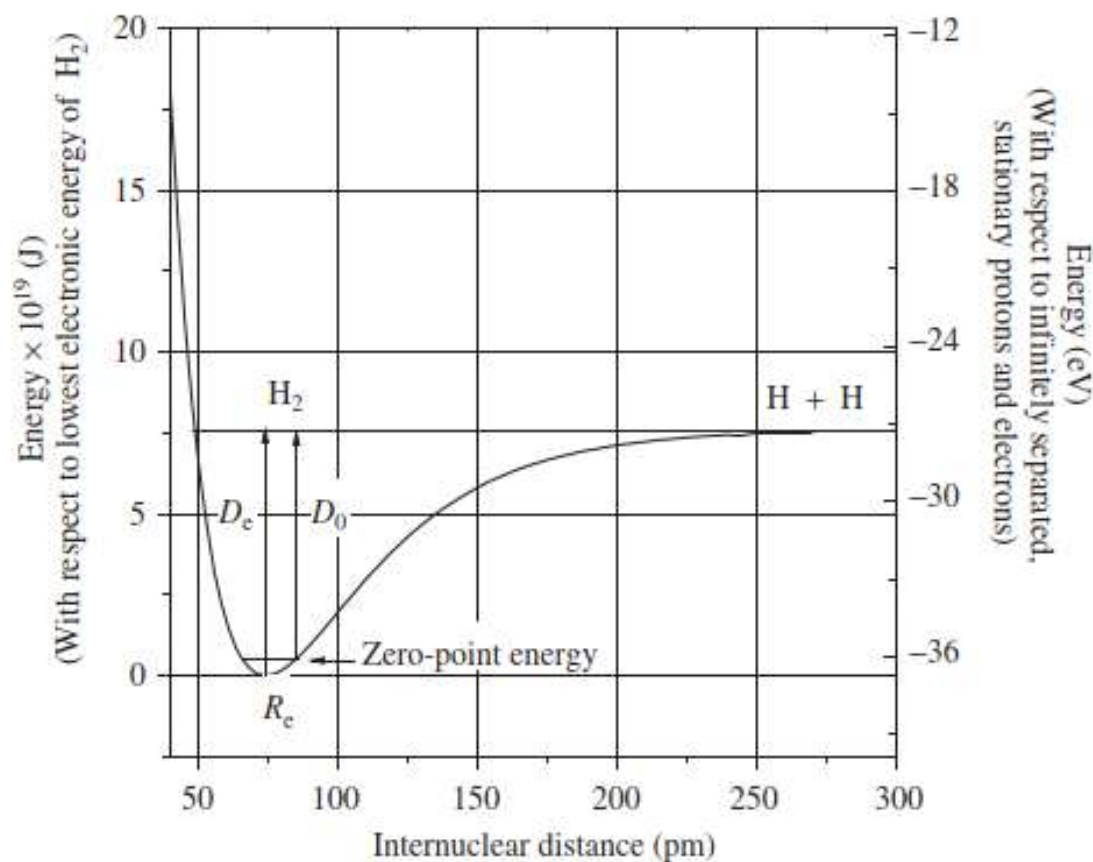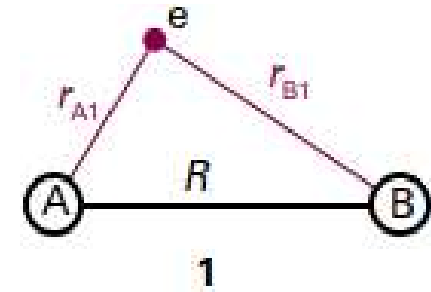

Figure 6.3 The hydrogen molecule: energy versus internuclear distance

❖ **The Case of the Simplest Diatomic Species: Hydrogen Molecular Ion H_2^+ (one-electron system)**

The Hamiltonian for the single electron in 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 H_2^+ (one-electron system)

A one-electron system that applies to homonuclear diatomic molecules is the hydrogen molecular ion, H_2^+, which consists of two protons and one electron. The H_2^+ ion can be produced experimentally by using $H_2(g)$ 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 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 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 H_2^+ molecular orbitals to build up the electronic structures of more complicated diatomic molecules.

The Hamiltonian for the single electron in H_2^+ is

$$\hat{H}=-\frac{\hbar^2}{2m_e}\nabla_1^2+V \qquad V=-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}}+\frac{1}{r_{B1}}-\frac{1}{R}\right)$$
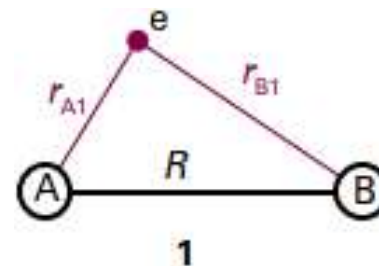
where r_{A1} and r_{B1} are the distances of the electron from the two nuclei A and B and R is the distance between the two nuclei. In the expression for V, the first two terms in parentheses are the attractive contribution from the interaction between the electron and the nuclei; the remaining term is the repulsive interaction between the nuclei. The collection of fundamental constant $e^2/4\pi\varepsilon_0$ 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_{22}) and H_{12} (or H_{21}) integrals after inserting the Hamiltonian operator for H_2^+ (single electron). The electronic Hamiltonian for H_2^+ is:

- ➤ $\widehat{H}_{elec}(r,R) = -\dfrac{\hbar^2}{2m_e}\nabla^2 - \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r_{A1}} - \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r_{B1}} + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}$ (where r gives the

  coordinates of the electron, and R is the distance between the two protons.)

- ➤ $H_{11} = \int 1s_A \left(-\dfrac{\hbar^2}{2m_e}\nabla^2 - \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r_{A1}} - \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r_{B1}} + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}\right) 1s_A \, \delta\tau$

- ➤ $= \int 1s_A \left(-\dfrac{\hbar^2}{2m_e}\nabla^2 - \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r_{A1}}\right) 1s_A \, \delta\tau - \int 1s_A \left(\dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r_{B1}}\right) 1s_A \, \delta\tau + \int 1s_A \left(\dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}\right) 1s_A \, \delta\tau$

- ➤ 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. 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.

➢ $H_{11} = E_H + J_{AB} + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}$

➤ Now consider H_{12} (H_{AB}):

➤ $H_{12} = \int 1s_A \left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{A1}} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{B1}} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} \right) 1s_B \ \delta\tau$

➤ $= \int 1s_A \left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{B1}} \right) 1s_B \ \delta\tau - \int 1s_A \left(\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{A1}} \right) 1s_B \ \delta\tau$

$+ \int 1s_A \left(\frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} \right) 1s_B \ \delta\tau$

➤ 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_HS**.

➤ 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.

- ➤ $H_{12} = E_H S + K_{AB} + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}S$

- ➤ Then: $H_{11} + H_{12} = E_H + J_{AB} + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R} + E_H S + K_{AB} + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}S$

- ➤ $= E_H(1 + S) + (J_{AB} + K_{AB}) + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}(1 + S)$

- ➤ $= (1 + S)\left(E_H + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}\right) + (J_{AB} + K_{AB})$

➢ We know: $E_b = \dfrac{H_{11}+H_{12}}{1+S}$ and $E_a = \dfrac{H_{11}-H_{12}}{1-S}$

➢ $E_b = \dfrac{(1+S)\left(E_H+\frac{e^2}{4\pi\varepsilon_0 R}\frac{1}{}\right)+ (J_{AB}+ KAB)}{1+S}$ and $E_a = \dfrac{(1-S)\left(E_H+\frac{e^2}{4\pi\varepsilon_0 R}\frac{1}{}\right)+ (J_{AB}-K_{AB})}{1-S}$

➢ $E_b = E_H + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}+\dfrac{(J_{AB}+ K_{AB})}{1+S}$ and $E_a = E_H + \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{R}+\dfrac{(J_{AB}-K_{AB})}{1-S}$

➢ 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

➢ $\dfrac{(J_{AB} \pm K_{AB})}{1\pm S}$.

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

➢ $\Delta E_\pm = E_\pm - E_H = \dfrac{e^2}{4\pi\varepsilon_0 R} + \dfrac{(J_{AB} \pm K_{AB})}{1 \pm S}.$ .....(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., $\dfrac{(J_{AB} \pm K_{AB})}{1 \pm S}$ must be *sufficiently negative* to *overcome the positive repulsive energy* of the two protons $\dfrac{e^2}{4\pi\varepsilon_0 R}$ 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 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 for zero to one**, and

✓ *J and K become increasingly negative*.
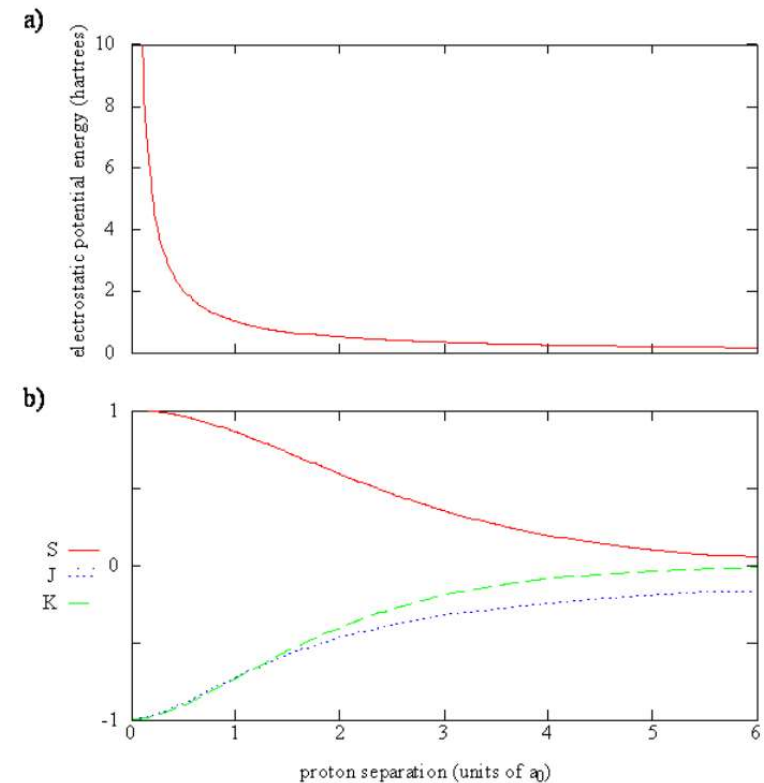
Figure 9.4.2
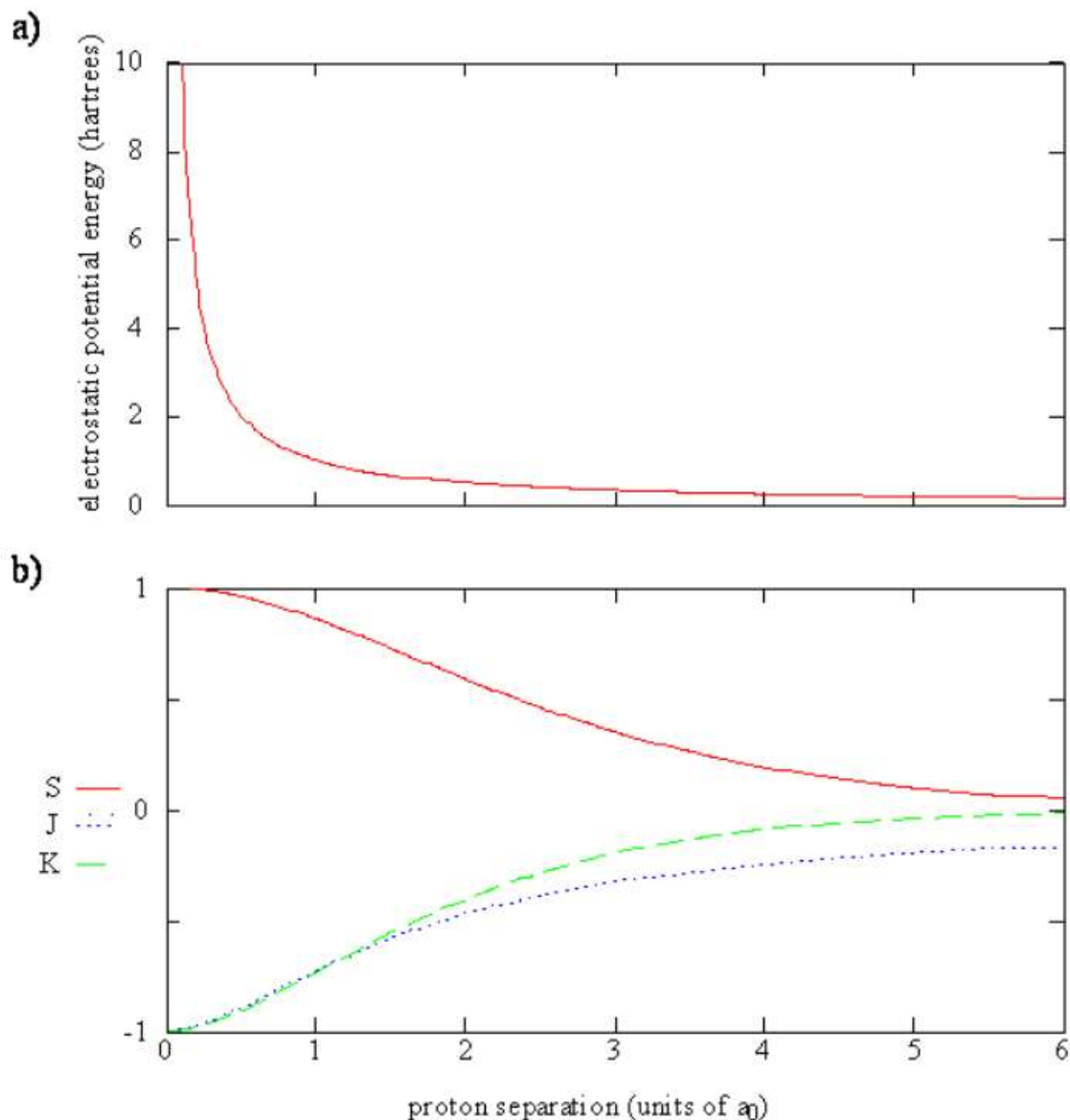
Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance *R* in units of the Bohr radius (52.92 pm).
(b) The overlap (*S*), Coulomb (*J*), and exchange (*K*) integrals at different proton separations. The units for *J* and *K* are hartrees; *S* has no units.
(CC BY-SA-NC; David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski via ChemEdDL)

➢ 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 ψ_+ 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 ψ_- is even lower than that given by the atomic orbitals.

➢ Figure 9.4.3 shows the energy of 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 ψ_- orbital, the energy of the molecule, $E_{el}(R)$, always is greater than the energy of the separated atom and proton.
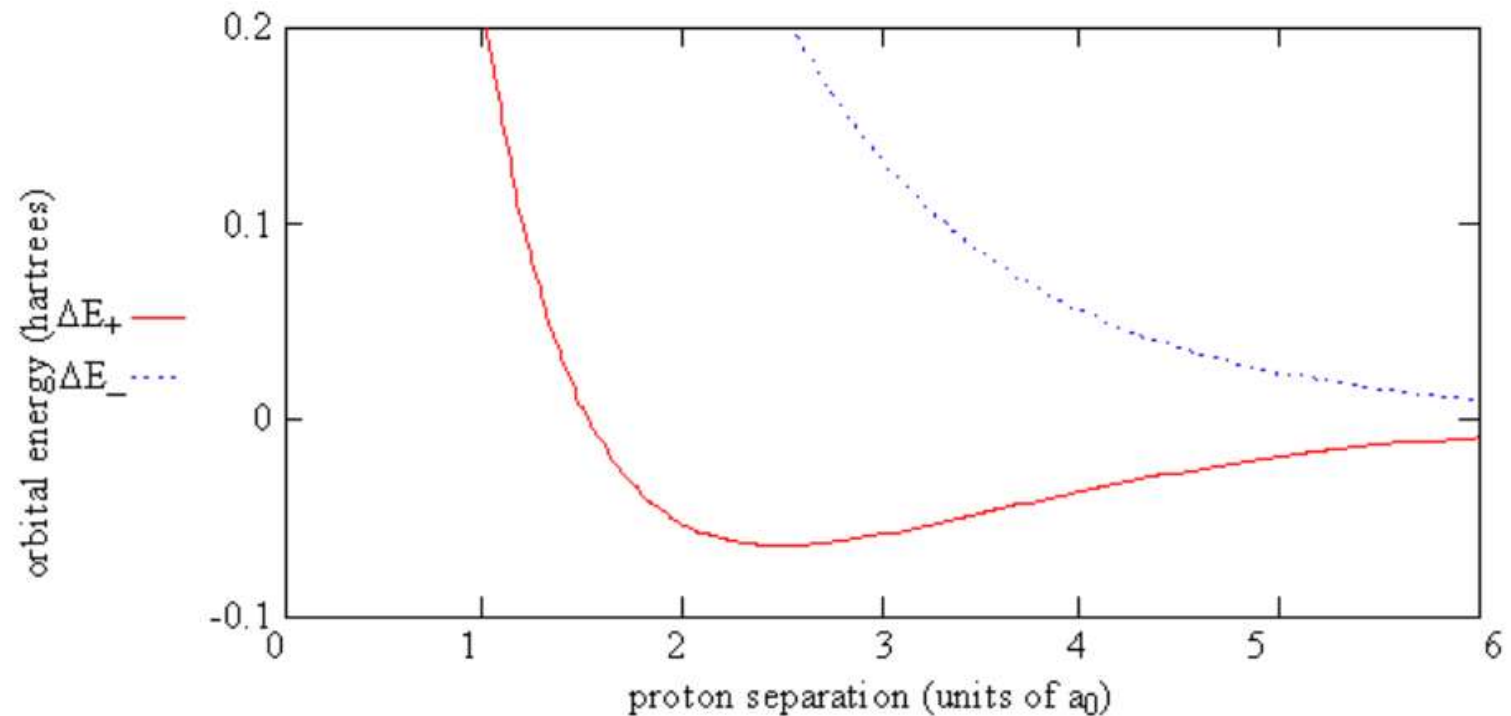
Figure 9.4.3 : Energy of the H_2^+ bonding molecular orbital ΔE_+ and the antibonding molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.
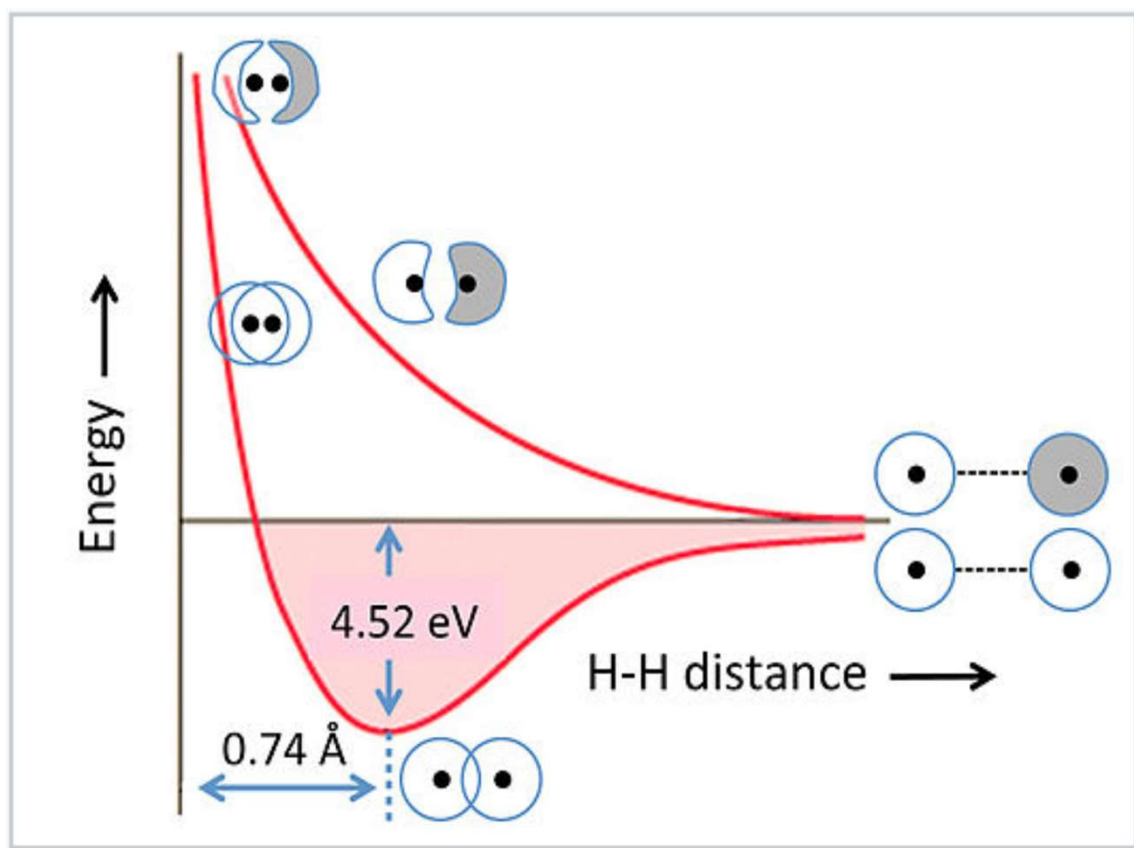
Figure 2.2.5 : Energy *as a function of internuclear distance* for the bonding and antibonding orbitals of the H_2 molecule

Figure 12.2 *summarizes* the following results of this discussion *pictorially* in a molecular orbital energy diagram using 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 ε_2 is raised relative to the AO energy more than ε_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 $\hat{H}$.
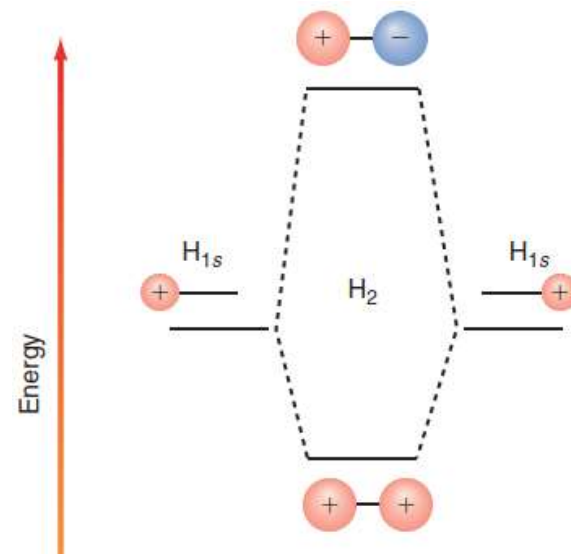
FIGURE 12.2

Molecular orbital energy diagram for a qualitative description of bonding in 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 kJ mol^{-1} because the ionization potential is 1312 kJ mol^{-1} (13.6 eV). Note also that the bonding molecular orbital has an energy of -1528 kJ mol^{-1}, which is lower than that of the 1s atomic state.
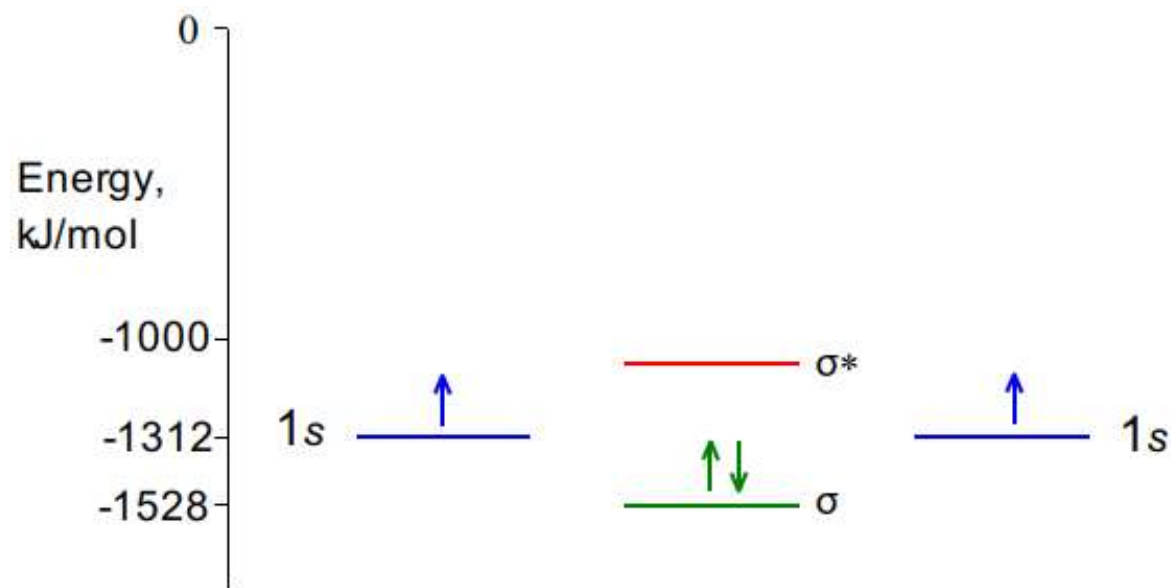

FIGURE 3.4 The energy level diagram for the H_2 molecule.

➢ 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 kJ.mol^{-1}, the **bond energy** of the 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) 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

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

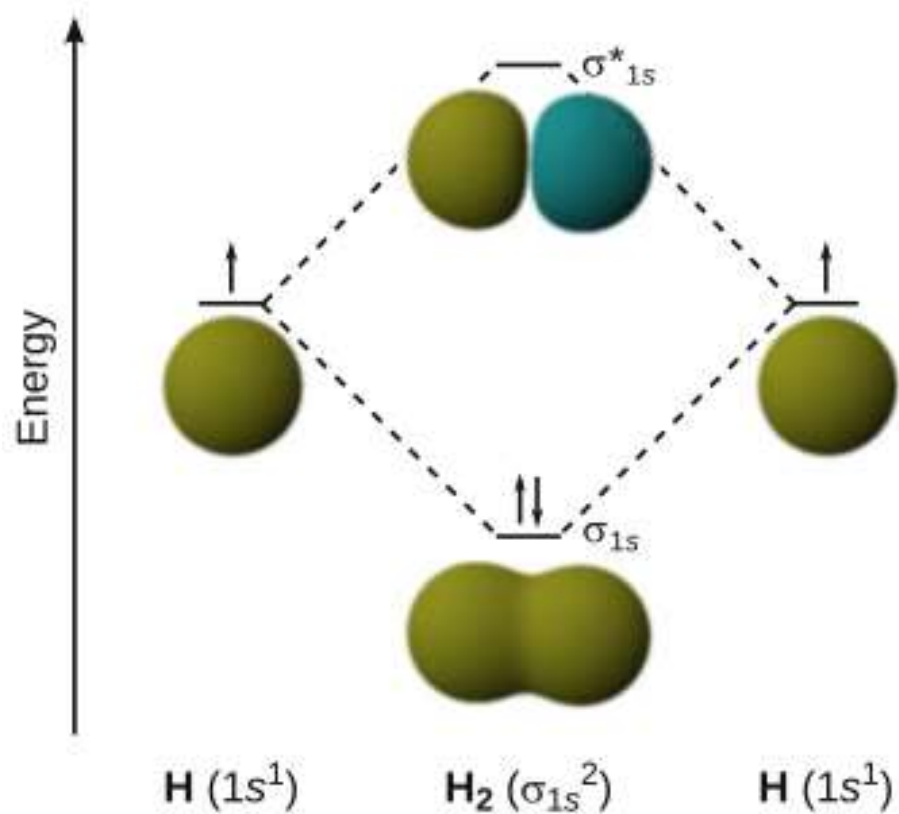$$\Delta E_\pm = E_\pm - E_H = \frac{e^2}{4\pi\varepsilon_0 R} + \frac{(J_{AB} \pm K_{AB})}{1 \pm S}.$$

$H_A\text{--}H_B{}^+$ molecule
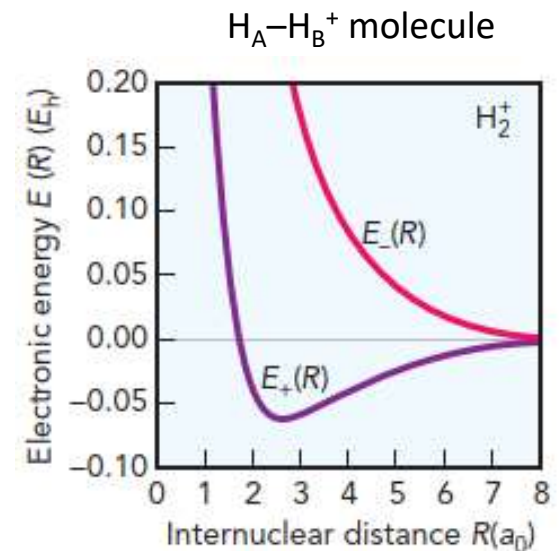
Figure 5.10 The electronic energy functions $E_+(R)$ and $E_-(R)$ for $H_2{}^+$.

Fig. 11.3 Linear combination of the two 1s orbitals in hydrogen leads to bonding and anti-bonding molecular orbitals of H_2

σ^*_{1s}

Energy

σ_{1s}

H $(1s^1)$ H_2 (σ_{1s}^2) H $(1s^1)$

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 **σ 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 σ orbital is called a σ electron*, and if that is the only electron present in the molecule (as in the ground state of H_2^+), then the configuration of the molecule is σ^1.

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

Figure 9.4 Potential energy of the σ_{1s} bonding molecular orbital and σ^*_{1s} antibonding molecular orbital for 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 σ^*_{1s} orbital (upper curve) is always above that of the separated atoms, making this an antibonding orbital.

Calculations on H_2^+ give R_e = 2.49a0 = 132 pm and hcD_e = 1.76 eV (171 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.
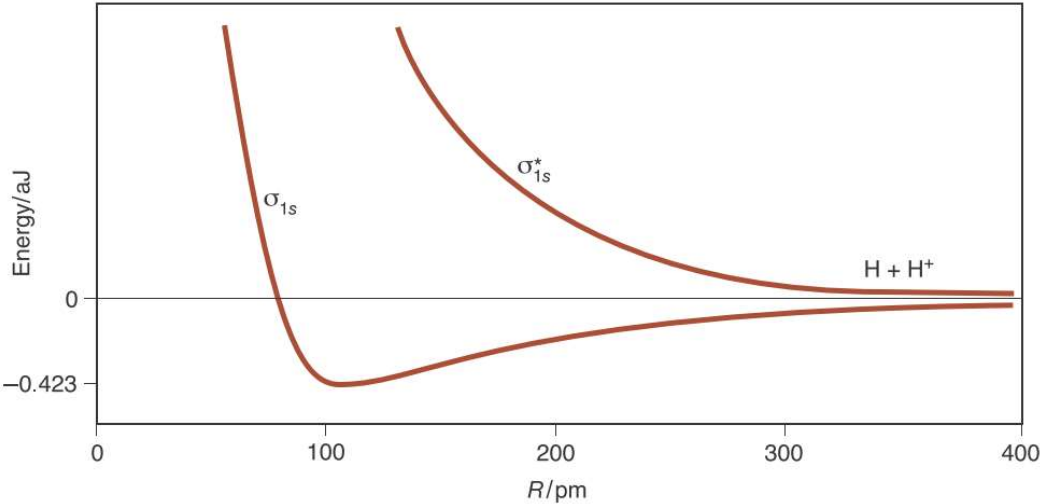
Orbital notation

For homonuclear diatomic molecules (molecules consisting of two atoms of the same element, such as N_2), 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 **σ$_g$**. The same procedure applied to the antibonding σ* 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 **σ$_u$**.

✓ 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.
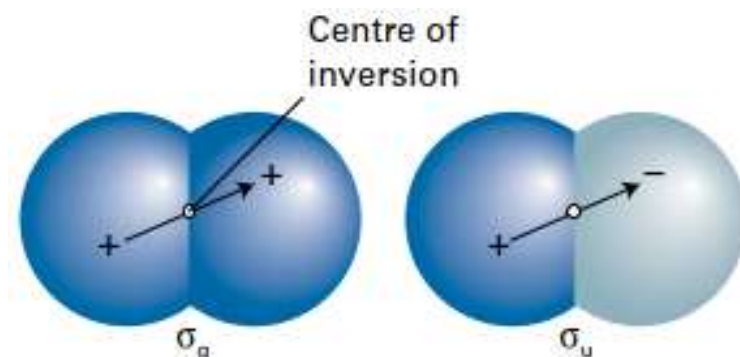

Figure 9B.12 The parity of an orbital is even (g) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (u) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g, u classification is irrelevant.

Although the subject of symmetry has not yet been discussed, it is true that σ 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 σ orbital is g, π 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

$$B_2 \; (\sigma_g)^2 (\sigma_u)^2 (\pi_u)^1 (\pi_u)^1$$
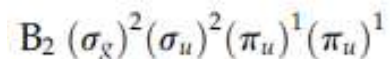
Molecular orbitals are sometimes given numerical prefixes to show the order in which the orbitals having those type and symmetry designations are encountered. When this is done, the order of filling the molecular orbitals for the second-row elements is shown as

$$1\sigma_g \; 1\sigma_u \; 2\sigma_g \; 1\pi_u \; 1\pi_u \; 1\pi_g \; 1\pi_g \; 2\sigma_u$$
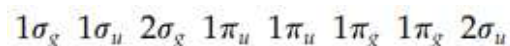
In this case, "1" indicates the first instance where an orbital of that type is encountered. A "2" indicates the second time an orbital having the designation following the number is encountered.

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 H_2^+ when the electron is in a σ_{g1s} (bonding) and $\sigma_{g1s}*$ (antibonding) molecular orbital, shown as a function of internuclear separation RAB in the LCAO approximation.
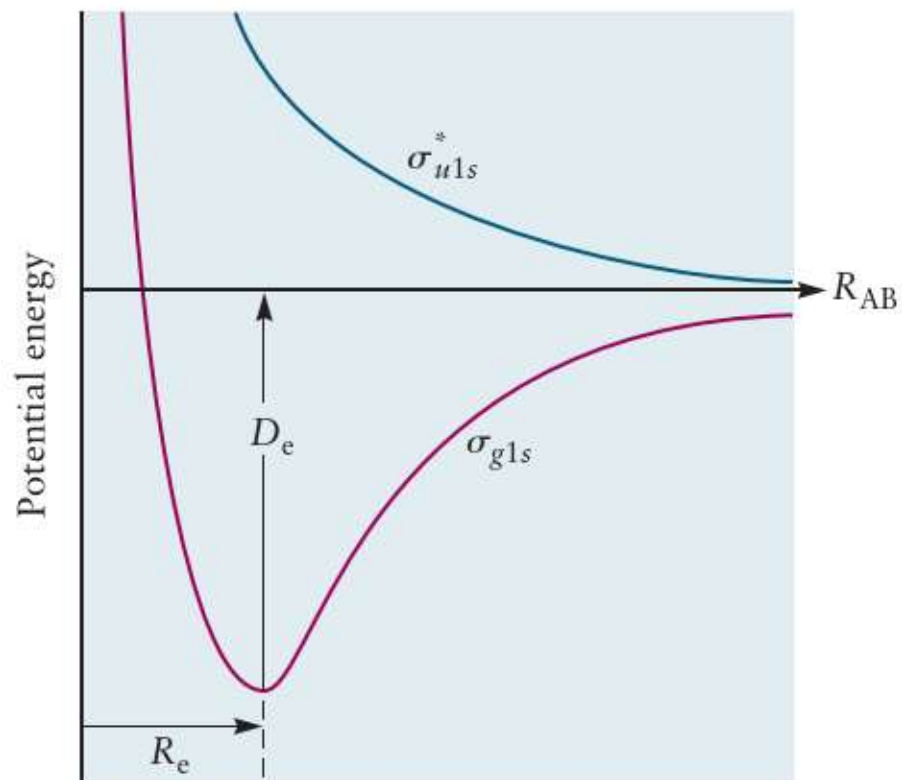
The energy-level diagram within the LCAO approximation is given by a correlation diagram (Fig. 6.11), which shows that two 1s atomic orbitals have been combined to give a σ_{g1s} MO with energy lower than the atomic orbitals and a $\sigma*_{u1s}$ MO with higher energy than the atomic orbitals. This diagram 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.
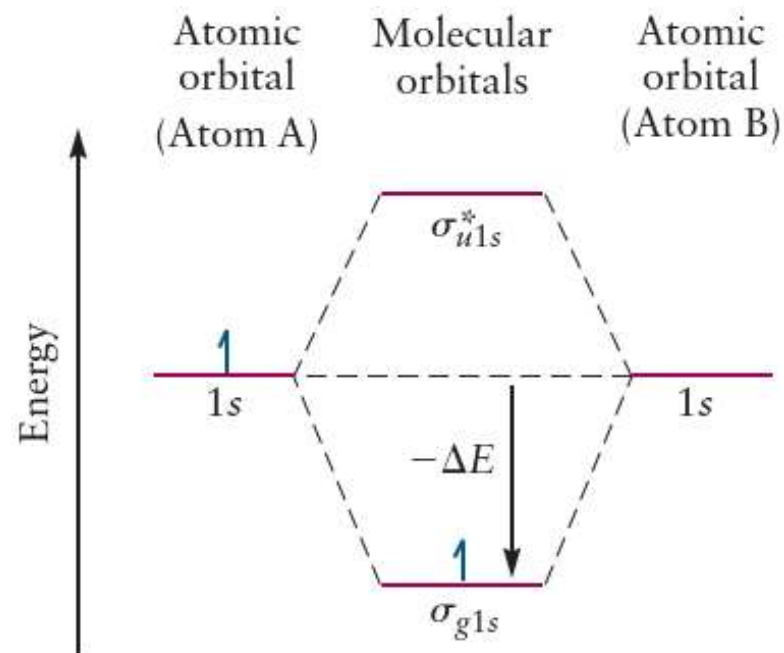

FIGURE 6.11 Correlation diagram for H_2^+ in the linear combination of atomic orbitals (LCAO) approximation. The bonding orbital is stabilized relative to the noninteracting system.
$E_{1s} + (-\Delta E) = E_{\sigma g1s}$ so ΔE is a positive number.

❑ The variation of Eσ* 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.
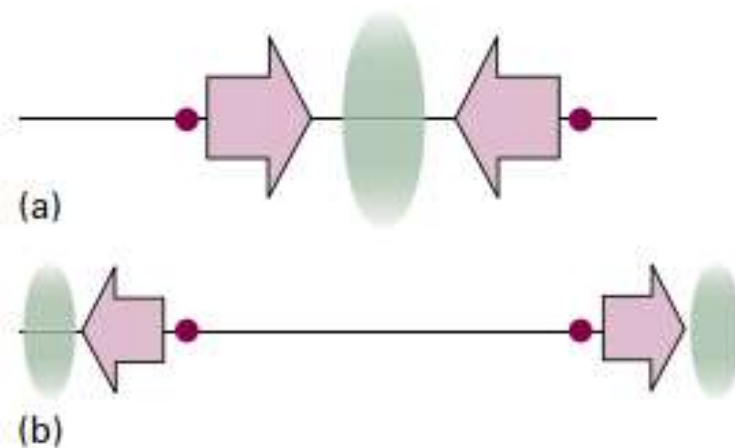
➢ The basic principles dealing with the molecular orbital description of the bonding in diatomic molecules have been presented in the previous section. Atomic orbitals other than ns orbitals can also interact to form molecular orbitals. Because individual p, d, and f orbitals are not spherically symmetrical, 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 σ 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 σ_{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).
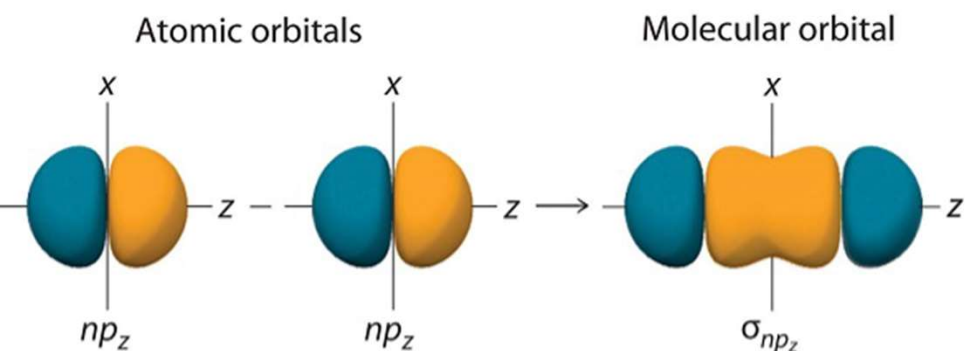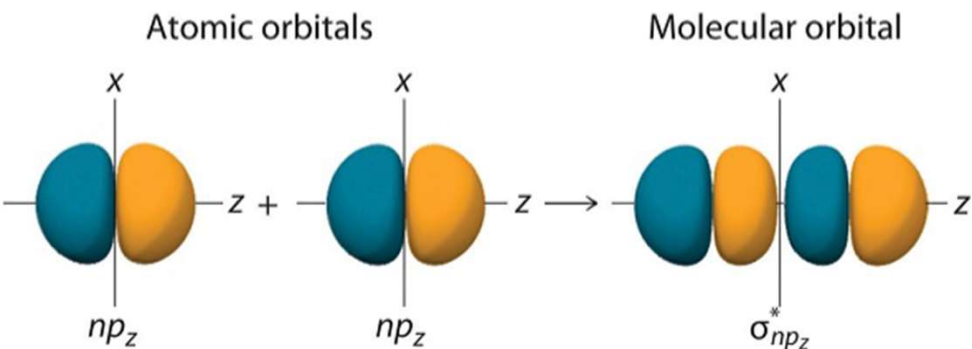
Figure 10.7.5 Formation of Molecular Orbitals from *np* Atomic Orbitals on Adjacent Atoms.

(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 **σ (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 **σ* (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.

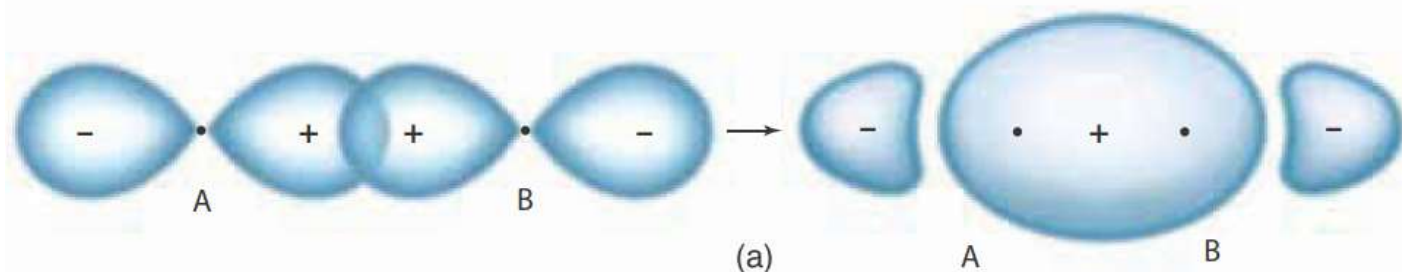➤ $n_{pz}(A) + n_{pz}(B)$
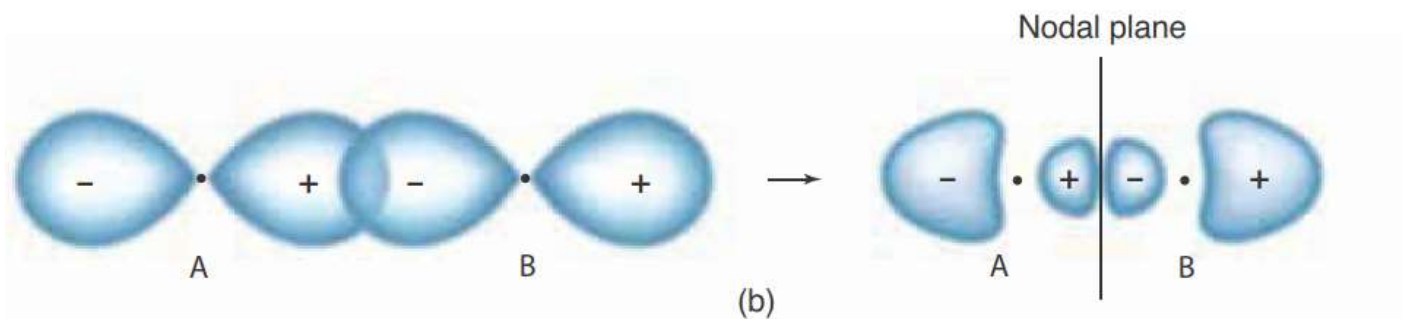
➤ $n_{pz}(A) - n_{pz}(B)$

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 σ_{2pz} orbital. In (b), they are combined such that lobes of different signs overlap, resulting in an antibonding σ^*_{2pz} 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 π orbitals. As before, constructive and destructive interference is possible, giving rise to two molecular orbitals upon interaction, π and π*.

➢ 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 σ 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 (π) 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 (π*) 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.

  ➢ $\pi_{npx} = np_x (A) + np_x (B)$

  ➢ $\pi_{npx}\star = np_x (A) - np_x (B)$

➢ 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 π/π^* orbitals do not possess rotational symmetry, as the sign of those orbitals changes when rotating 180° around the inter-nuclear axis.
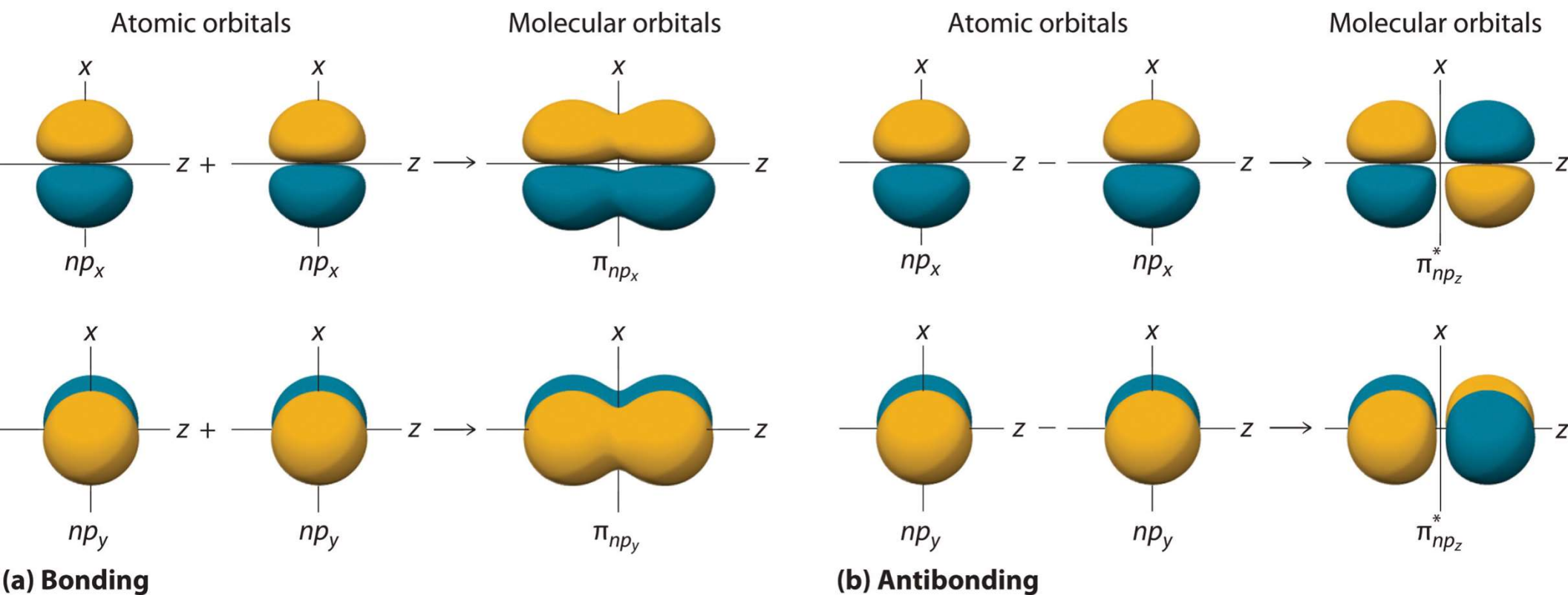
Figure 10.7.6: Formation of π Molecular Orbitals from np and np Atomic Orbitals on Adjacent Atoms. (a) Because the signs of the lobes of both the np and the np atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.
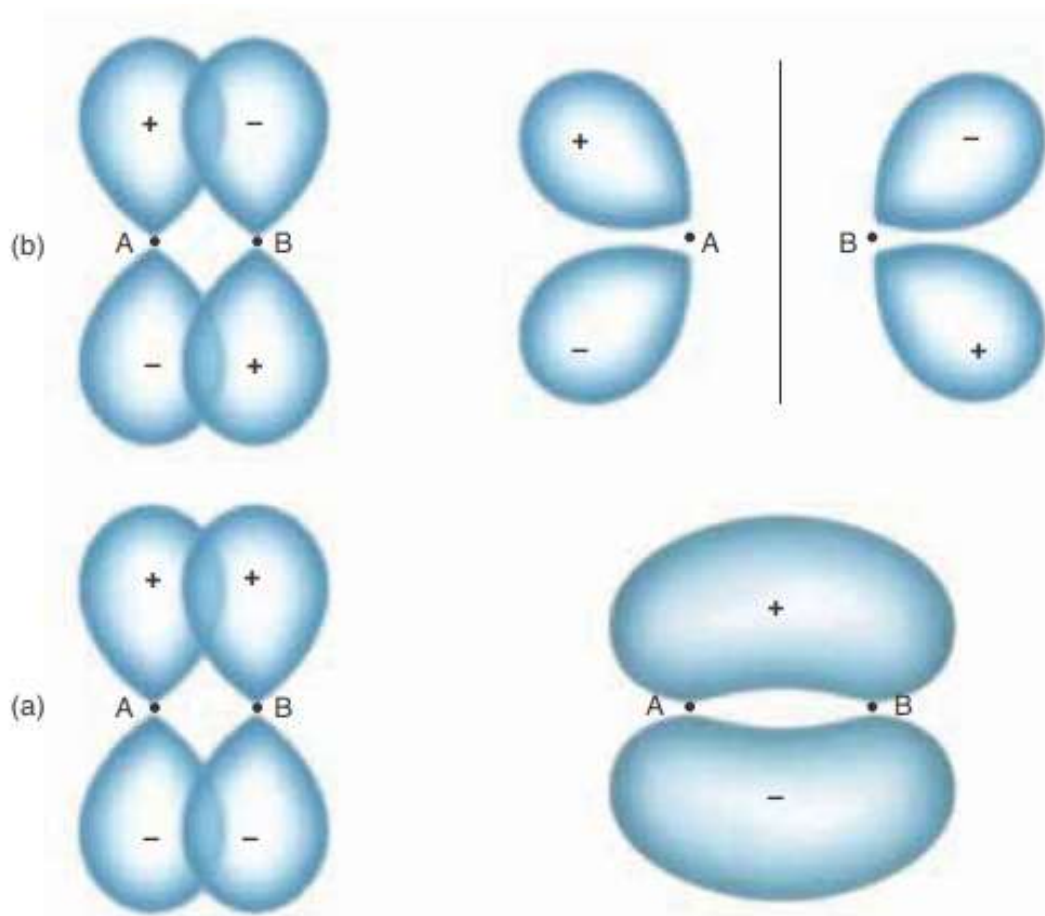
Figure 9.8 The combination of 2p orbitals that lie perpendicular to the internuclear axis. In (a), the p_y orbitals are combined such that lobes of the same sign overlap, resulting in a bonding π_{2py} orbital. In (b), the p_y orbitals are combined such that lobes of opposite sign overlap, resulting in an antibonding π^*_{2py} orbital. There is a similar picture for the px orbitals.
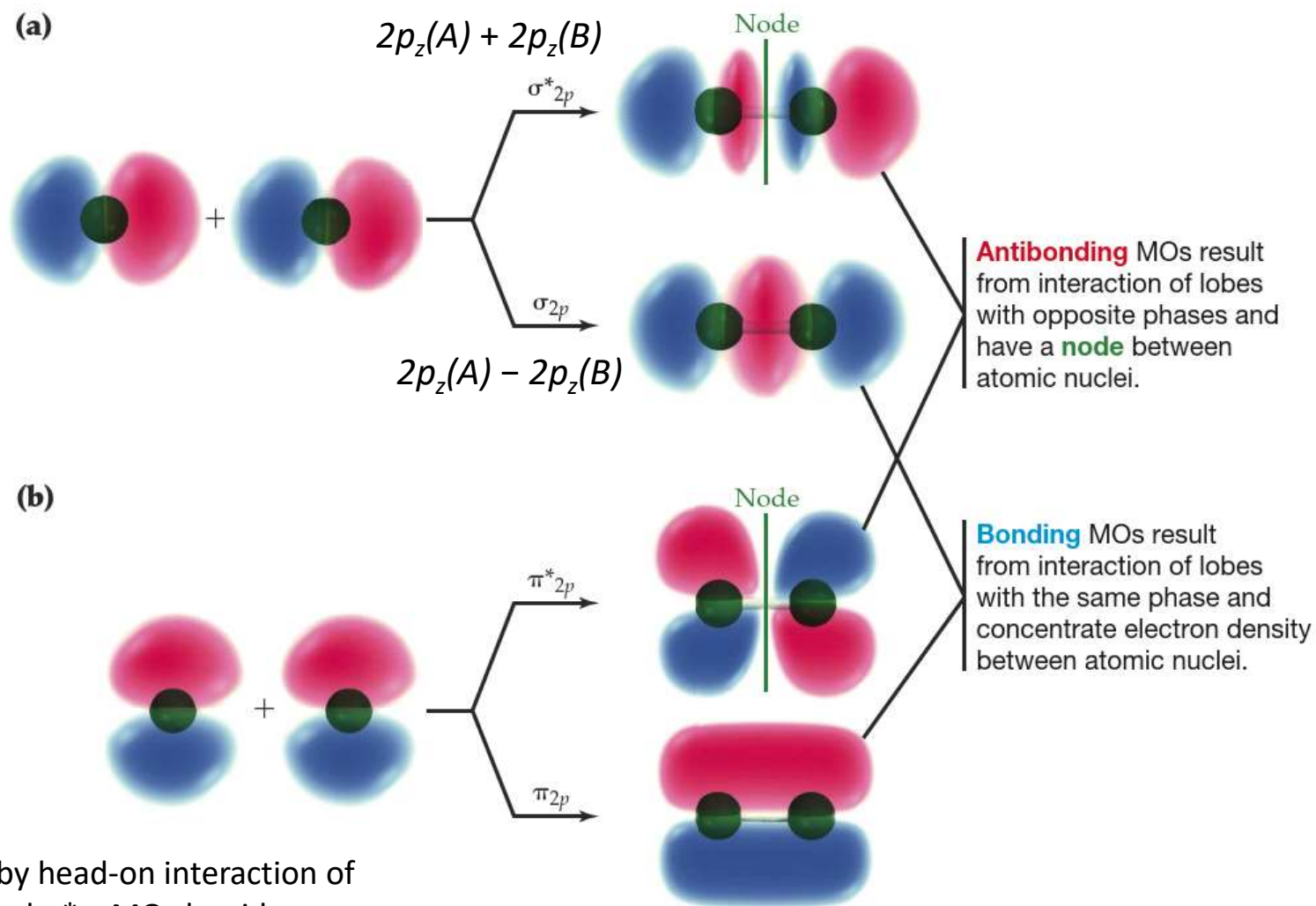
(a)

$2p_z(A) + 2p_z(B)$

σ^*_{2p}

Node

σ_{2p}

$2p_z(A) - 2p_z(B)$

Antibonding MOs result from interaction of lobes with opposite phases and have a **node** between atomic nuclei.

(b)

Node

π^*_{2p}

π_{2p}

Bonding MOs result from interaction of lobes with the same phase and concentrate electron density between atomic nuclei.

FIGURE 5.13
Formation of (a) σ_{2p} and σ^*_{2p} MOs by head-on interaction of two p atomic orbitals, and (b) π_{2p} and π^*_{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 σ and σ* molecular orbitals* is significantly greater** than the difference between the two π and π* sets.

The *reason for this* **is that the atomic orbital overlap and thus the strength of the interaction is greater for a σ bond** than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.
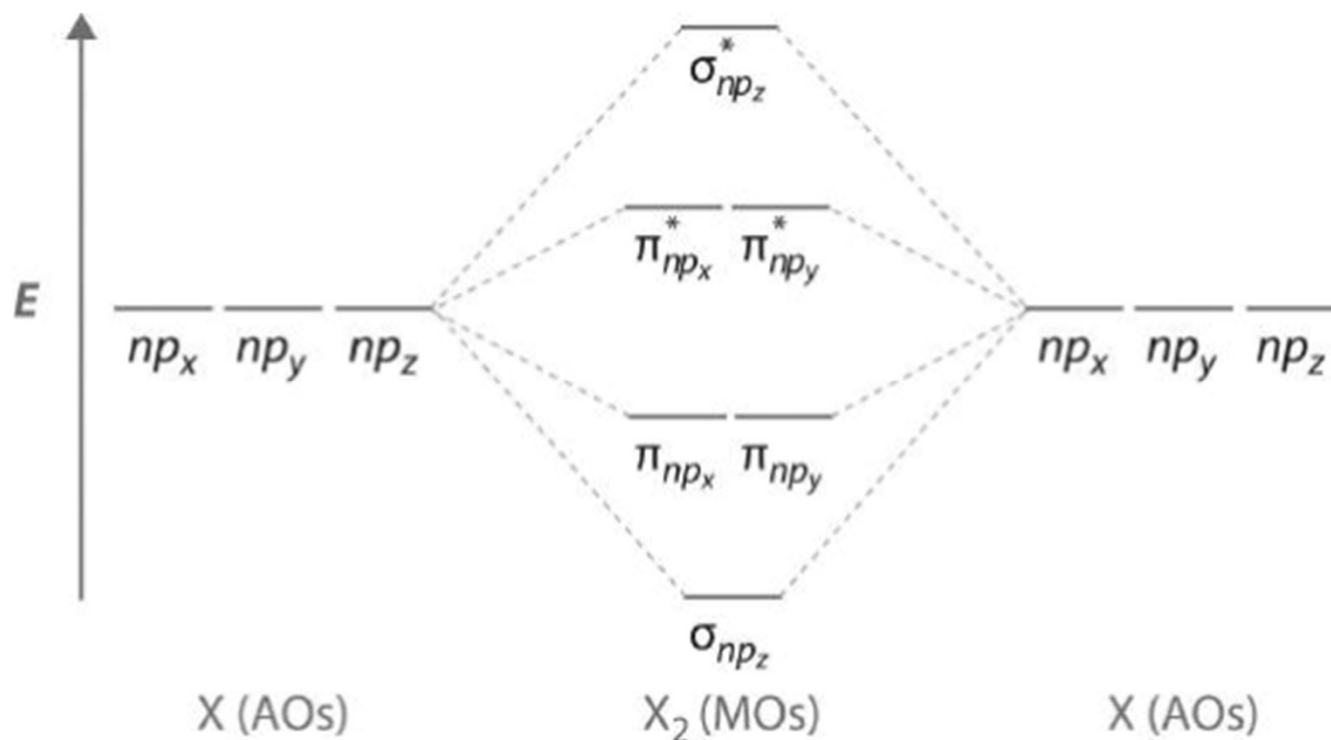
Figure 10.7.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_z, np_x, and np_y Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* 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 σ bonding molecular orbital. Their difference (*ns* – np$_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.
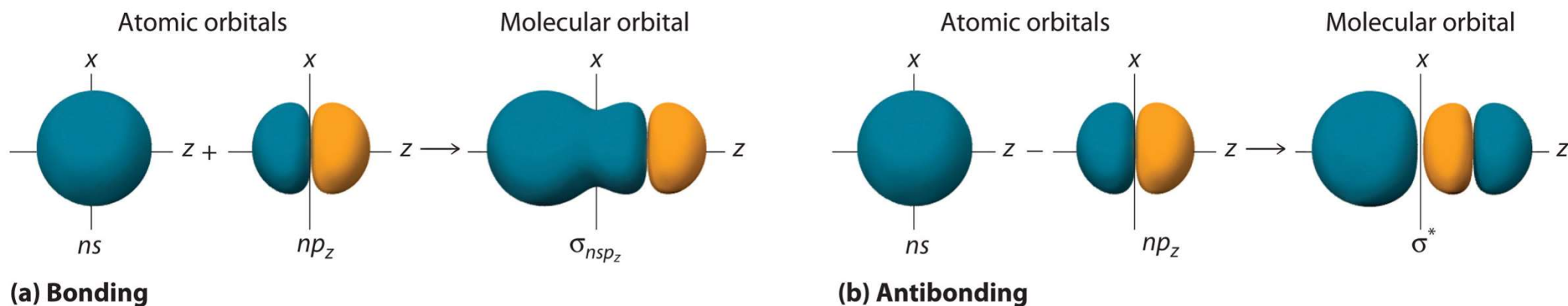
Figure 10.7.8: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np Atomic Orbital on an Adjacent Atom.
(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei.
(b) The mathematical difference results in a σ* (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.
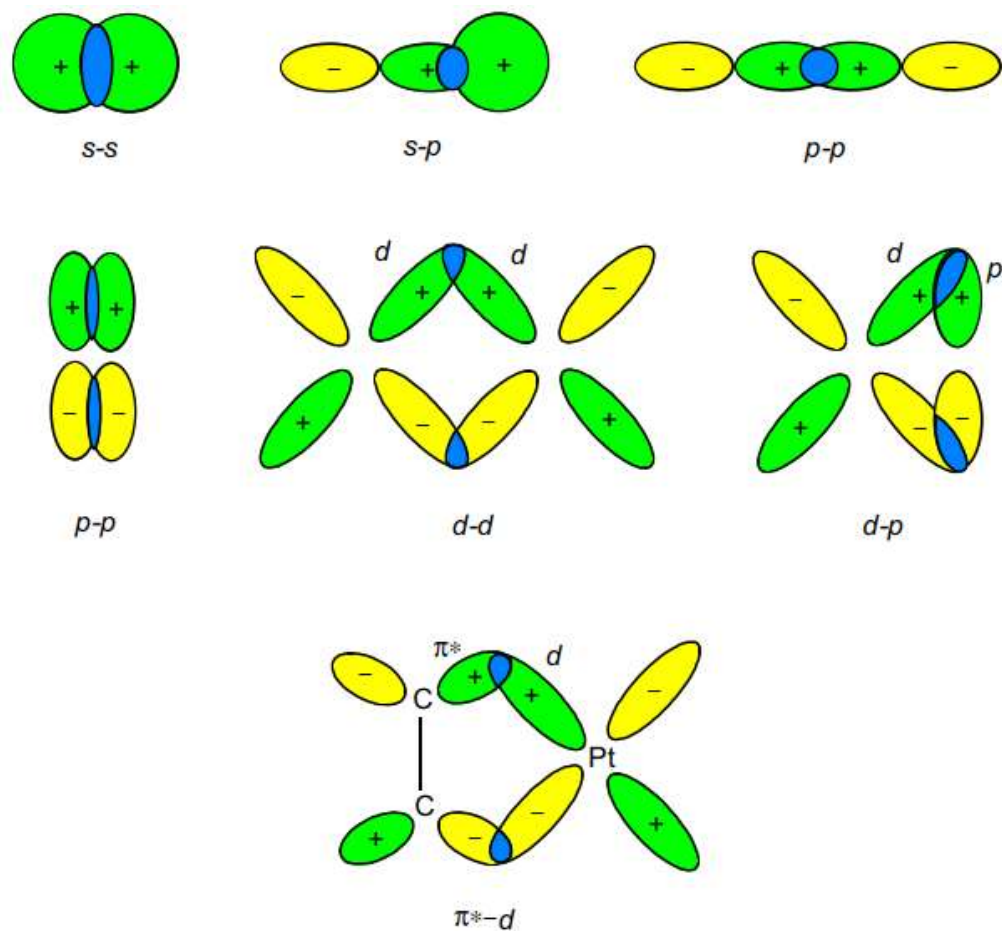
FIGURE 3.6 Some types of orbital overlap that lead to energetically favorable interactions (overlap integral > 0).
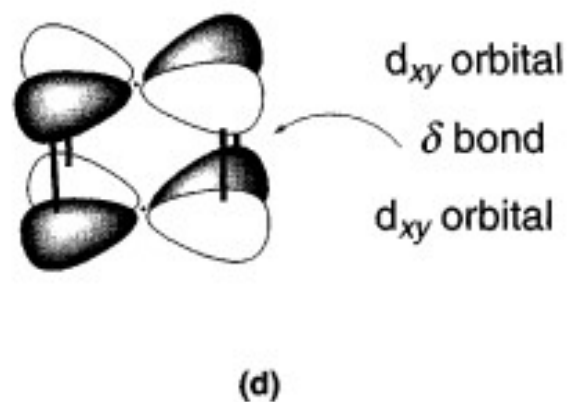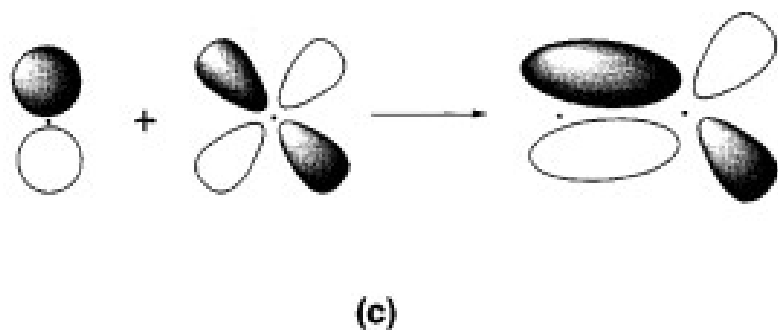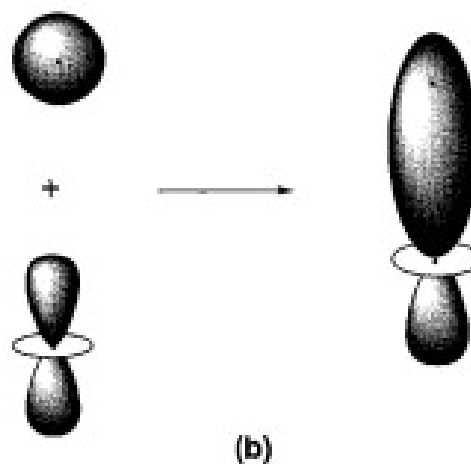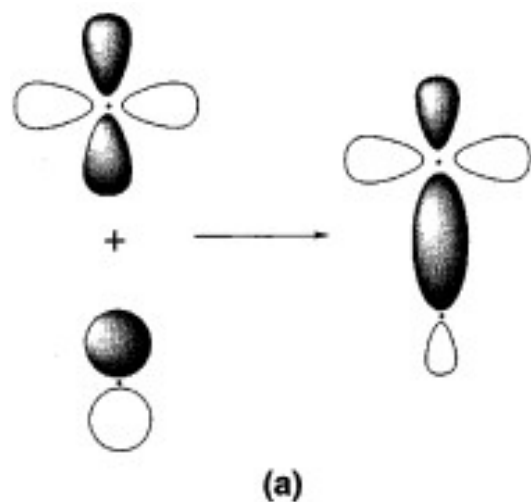
FIG. 3.1 4 Molecular orbitals involving d orbitals. These diagrams indicate the formation of σ, π and δ bonds, involving d orbitals. (a) σ bond between p_y and $d_{x^2-y^2}$, (b) σ bond between s and d_{z^2}, (c) π bond between p_y and d_{xy}, (d) δ bond between two d_{xy} orbitals.
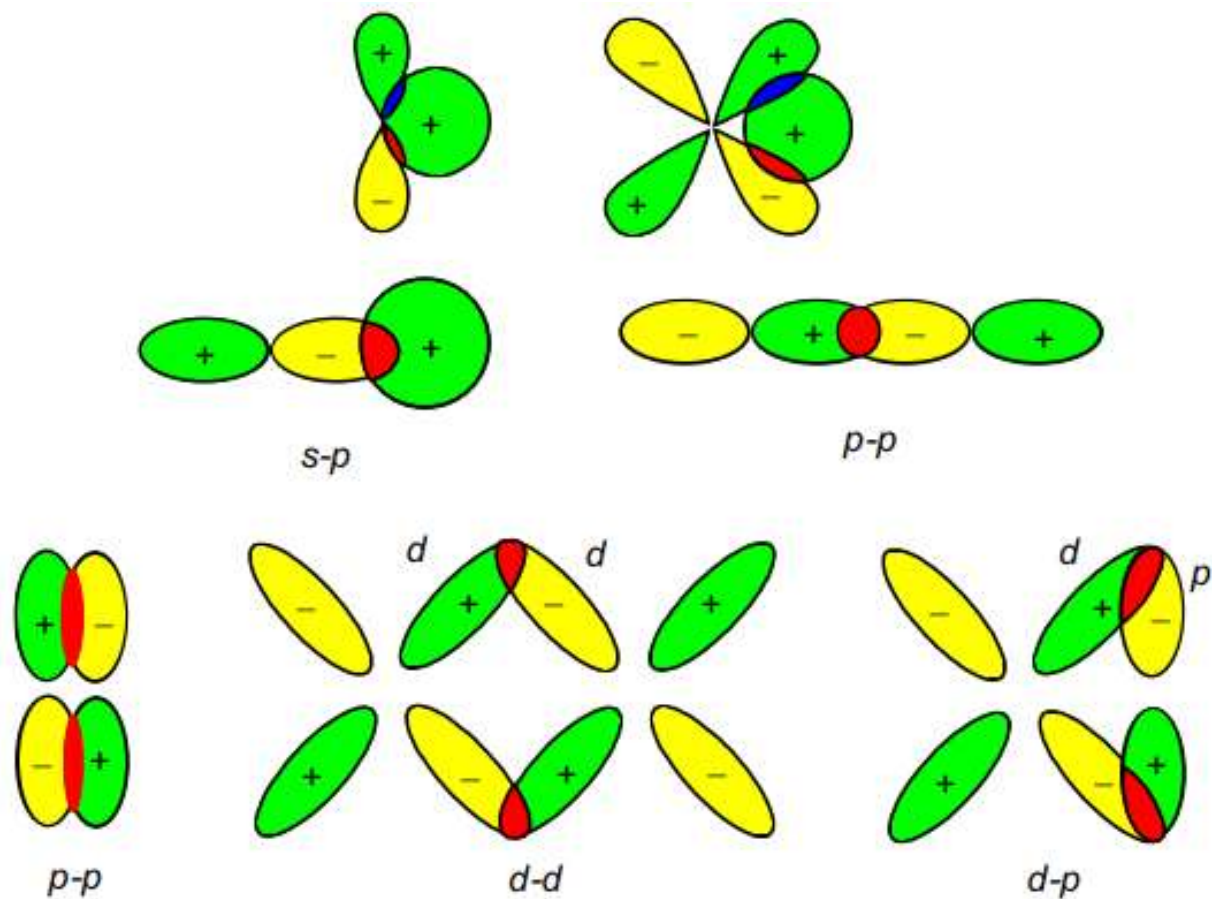
FIGURE 3.7 Patterns of orbital overlap that **do not lead** to bonds.

❑ **The Electronic Structure of Many-Electron 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 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 σ_{2p} and π_{2p} orbitals **interchange** energies so that the energy of the σ_{2p} orbital is less than that of the π_{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 Li_2 through Ne_2 is shown in Figure 9.11.

✓ Observe that the order of the σ_{2p} and π_{2p} orbitals changes in going from N_2 to O_2 molecules.

> The relative order of σ- and π orbitals arising from linear combination of 2p orbitals is shown below.
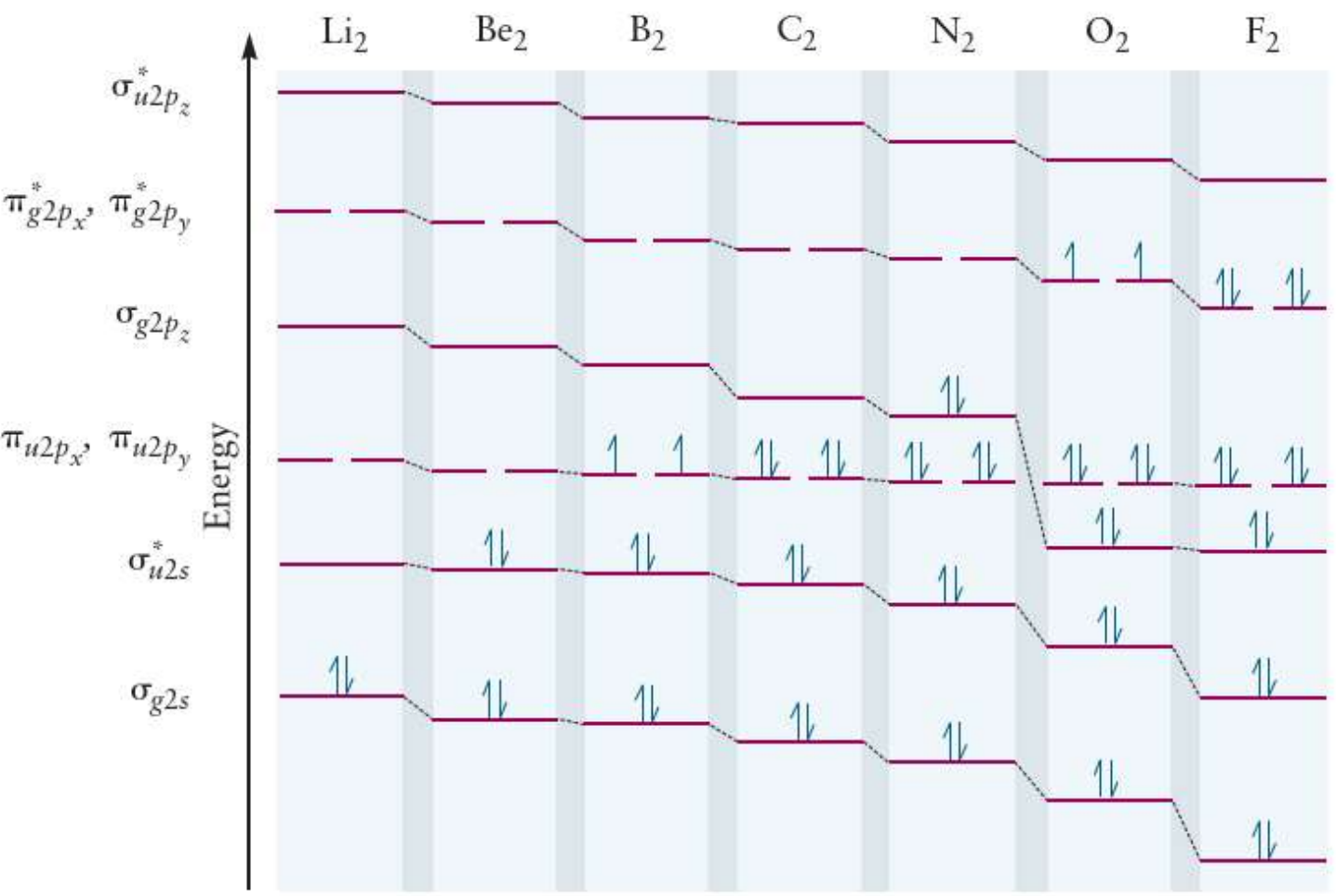
Figure 9.11 The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules Li_2 through F_2. Notice that for O_2 through Ne_2 the energy of the σ_{2pz} orbital is below that of the π_{2p} orbitals.

Spectroscopic evidence shows that in O_2 (and in 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.

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

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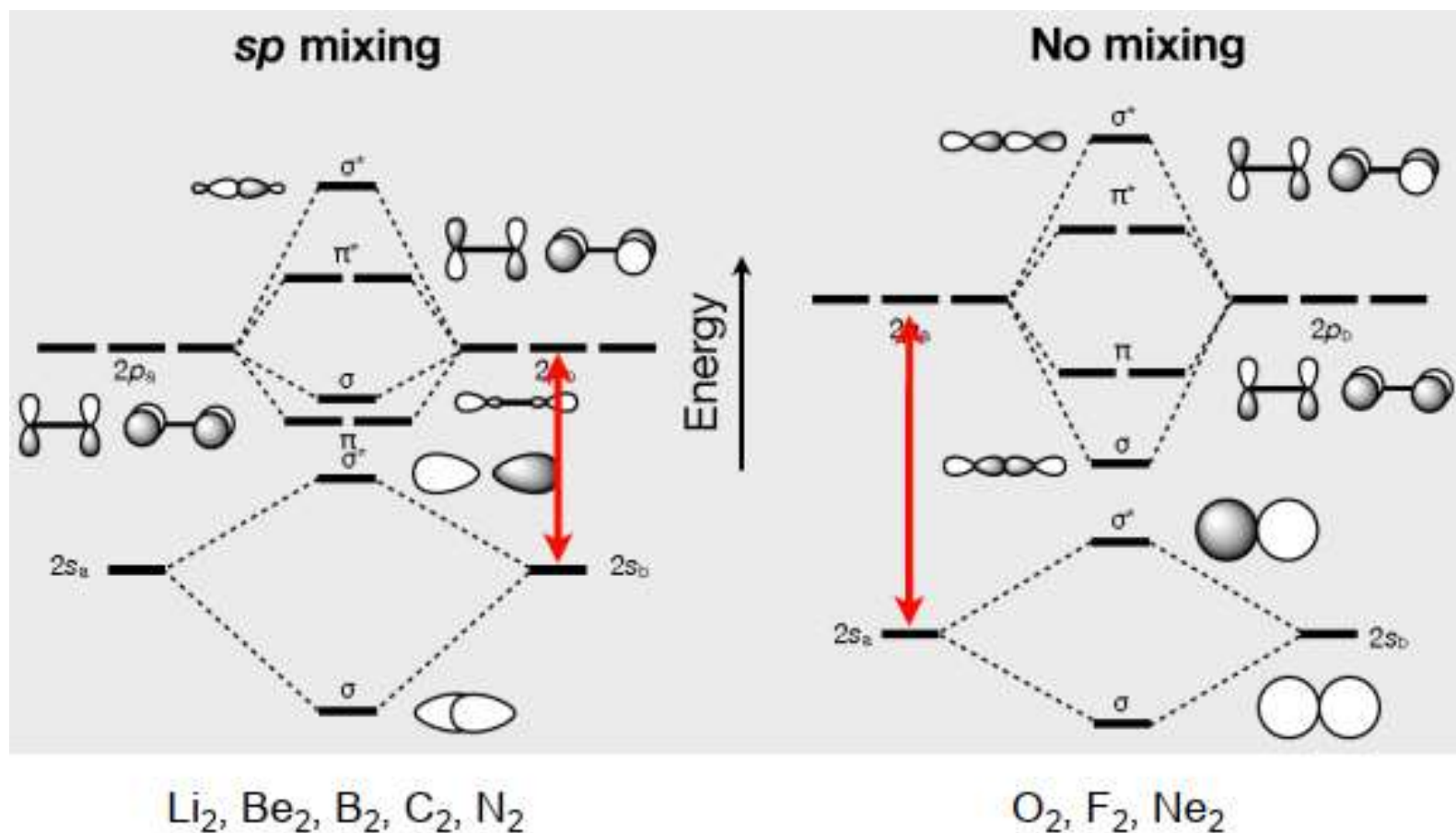
Orbital Mixing

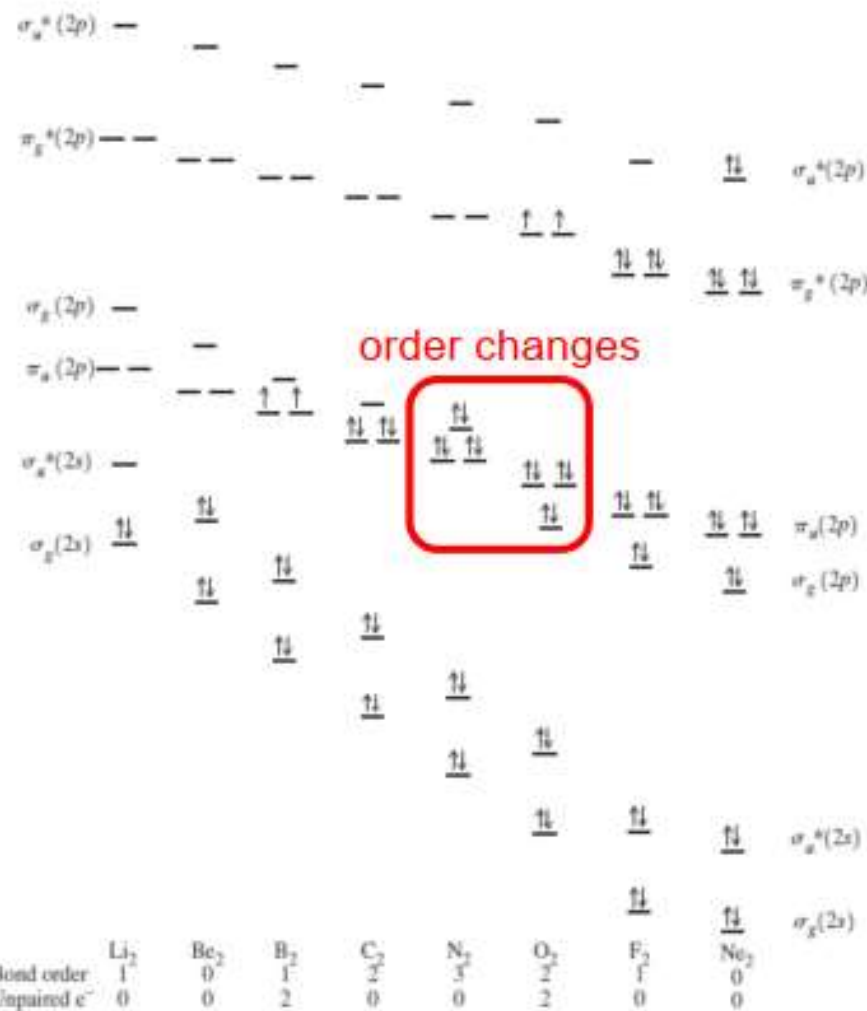**The size of the effect depends on the 2s-2p energy difference.**

$\sigma_u^*(2p)$

$\pi_g^*(2p)$

$\sigma_u^*(2p)$

$\pi_g^*(2p)$

$\sigma_g(2p)$

$\pi_u(2p)$

order changes

$\sigma_u^*(2s)$

$\pi_u(2p)$

$\sigma_g(2s)$

$\sigma_g(2p)$

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

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

$\sigma_u^*(2s)$

$\sigma_g(2s)$

	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	0	1	2	3	2	1	0
Unpaired e⁻	0	0	2	0	0	2	0	0

➢ 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.

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

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

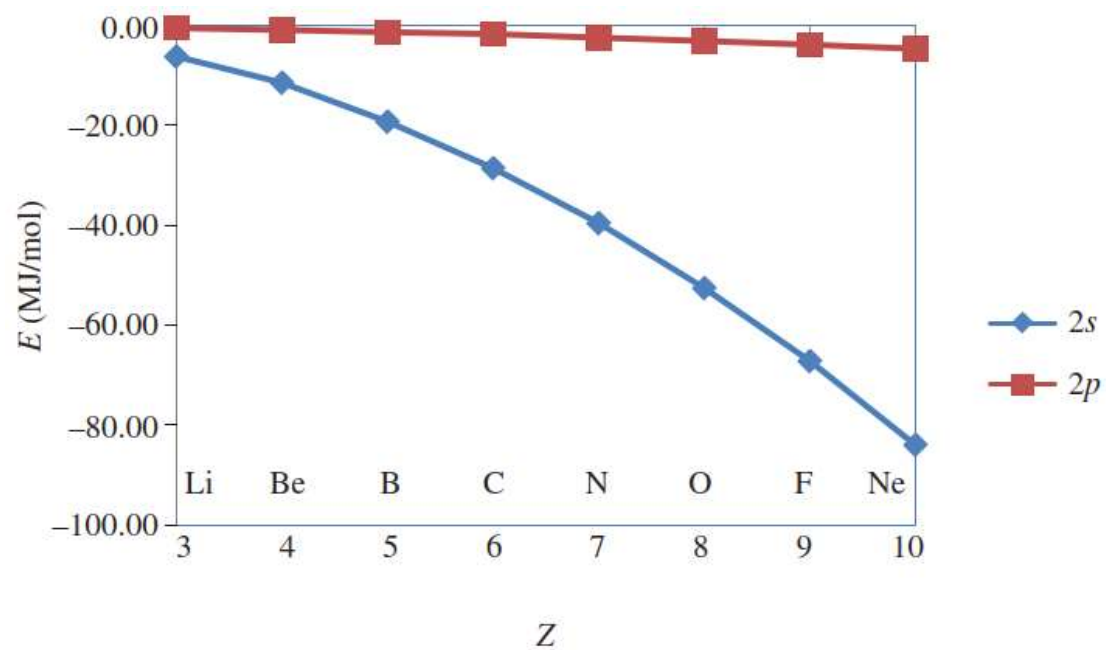| Element	Li	Be	B	C	N	O	F
$-E(2s)$, eV	5.39	9.32	12.9	16.6	20.3	28.5	37.8
$-E(2p)$, eV	3.54	6.59	8.3	11.3	14.5	13.6	17.4
$[E(2p) - E(2s)]$, eV	1.85	2.73	4.6	5.3	5.8	14.9	20.4

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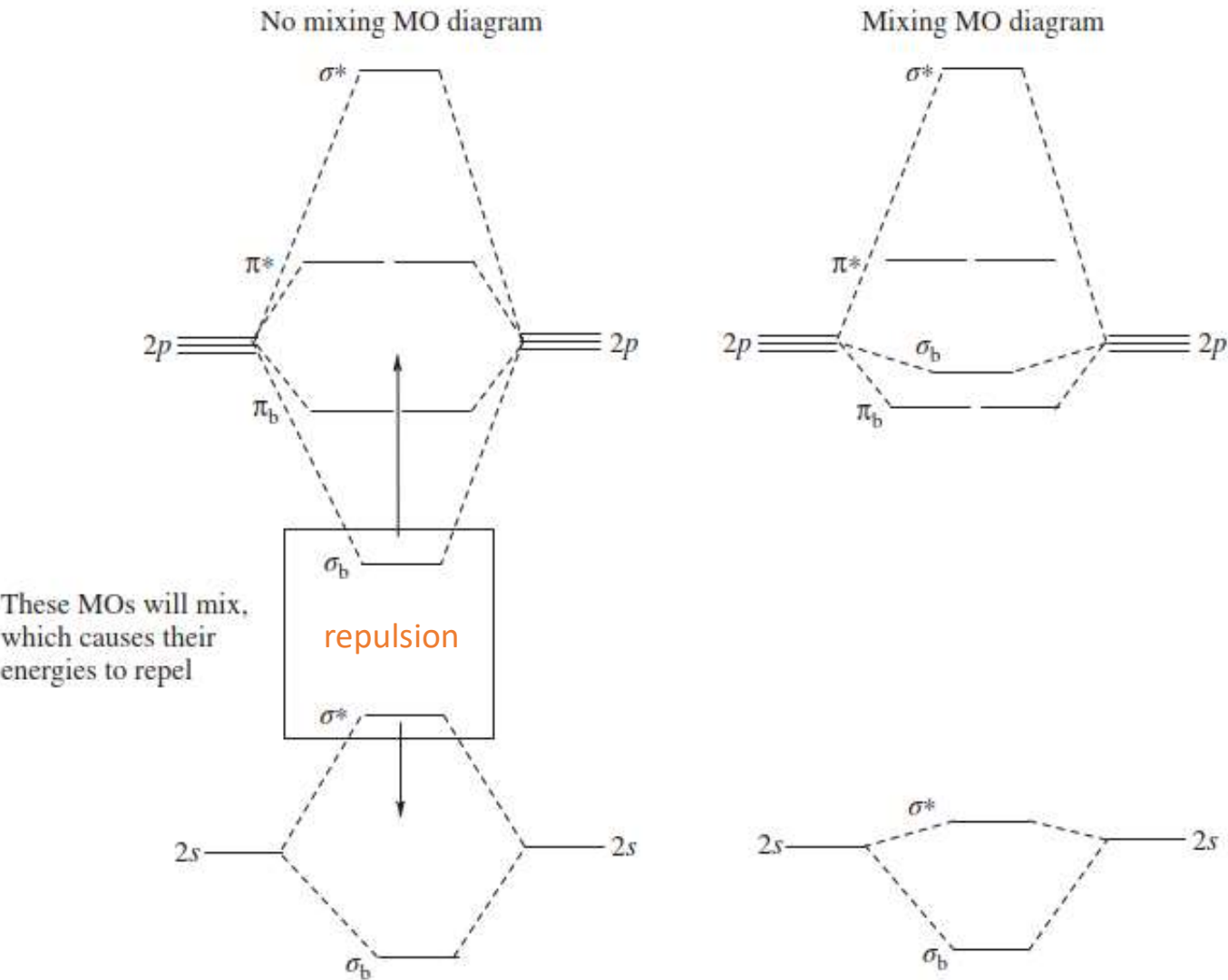Relative energies of the valence MOs for the Period 2 homonuclear diatomics.

➢ 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 Li_2, Be_2, B_2, C_2, and N_2 but not in O_2 and F_2, as shown in Figure 10.27.

➢ Further *evidence that mixing occurs in N_2*, which lies close to the mixing/nonmixing border, is supported by the PES spectrum of N_2, which shows that the four π^b electrons are ionized at slightly higher energies than the two σ^b ($2p_z$) 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 σ_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 σ_b MO.*

➢ Likewise, for the highest energy σ^* MO, the coefficients for the $2p_z$ wavefunctions will be much greater than those for the 2s wavefunctions.

➢ However, for the σ^* and σ_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

No mixing MO diagram

Mixing MO diagram

These MOs will mix, which causes their energies to repel

repulsion

Orbitals of similar but unequal energies can interact if they have the same symmetry. The 2s and $2p_z$ orbitals form MOs with the same sigma symmetry (σ_g and σ_u). *s-p* mixing causes the σ_g and σ_u MOs to be pushed apart in energy:
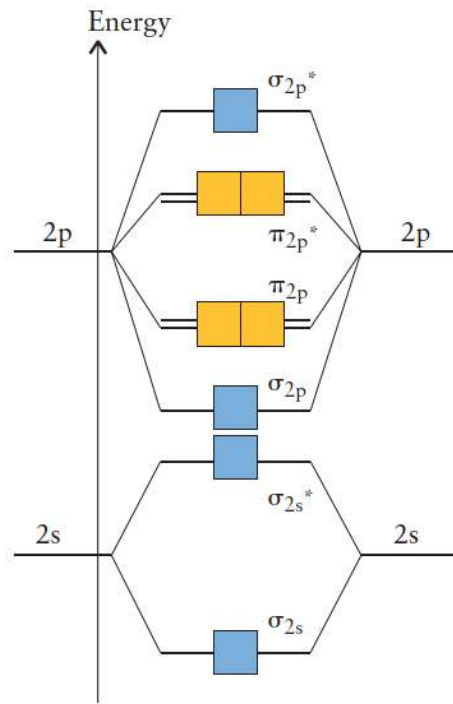
FIGURE 10.26
Whenever two MOs have the same symmetry and similar energies, they will mix with each other; in extreme cases, this can lead to the MO diagram shown at right.
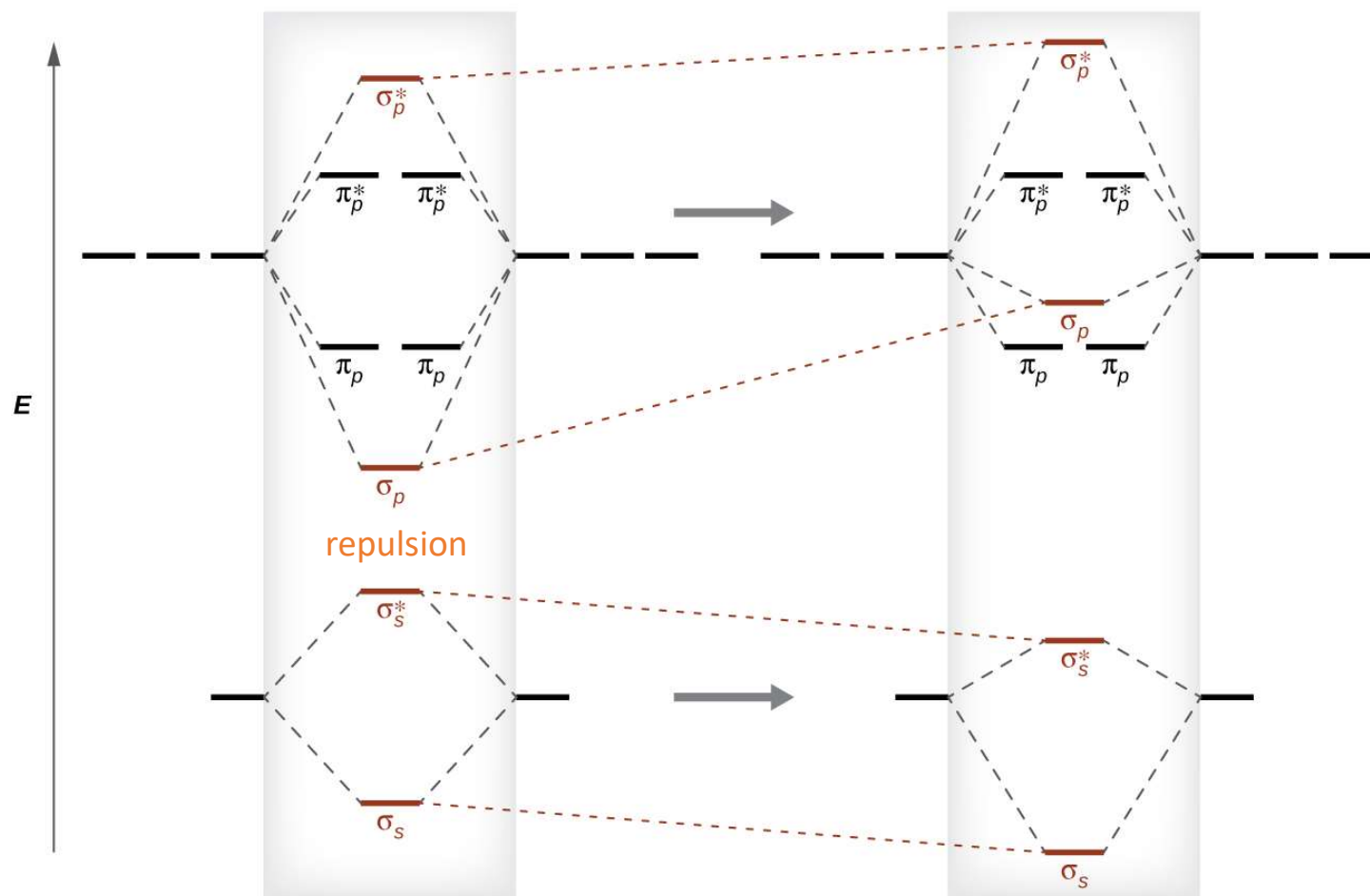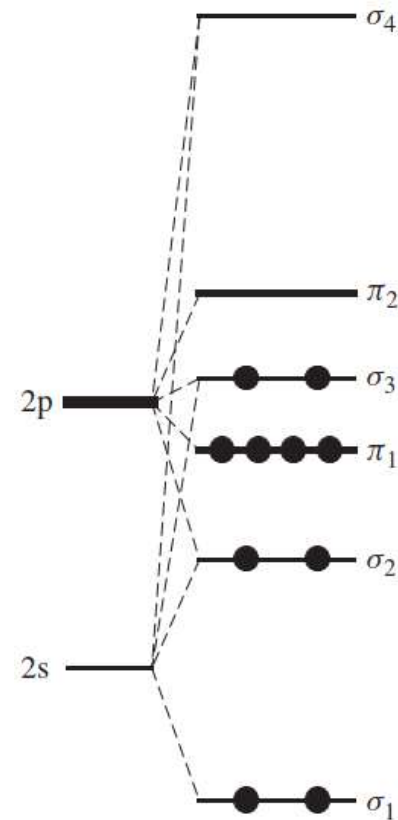
❑ Molecular Orbital theory Predicts the Electron Configurations of Diatomic Molecules
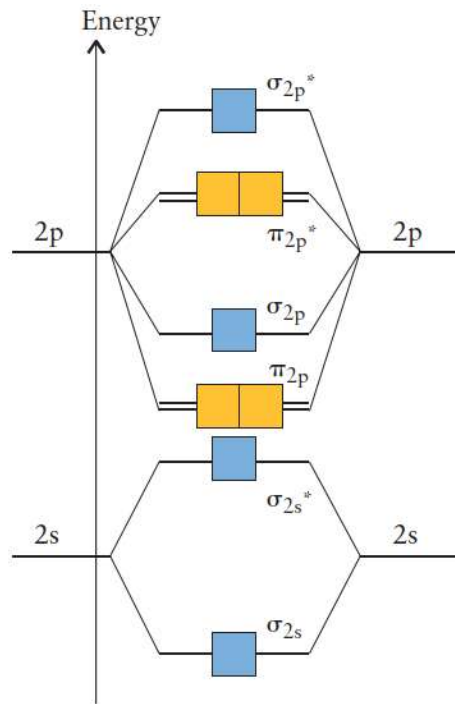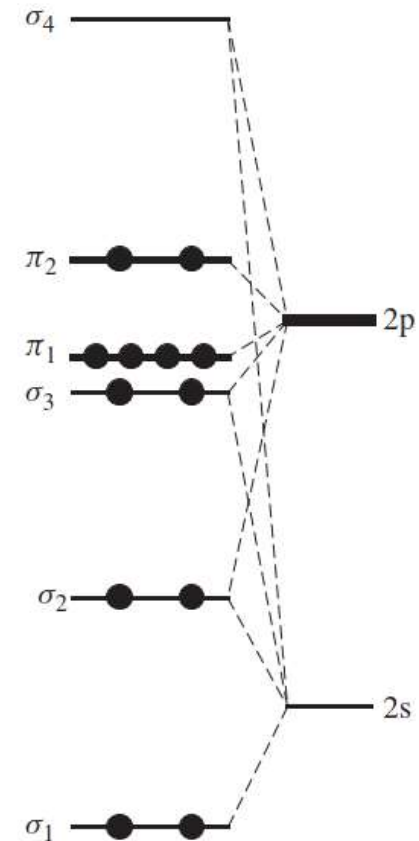

Molecules Li$_2$ through N$_2$

Molecules O$_2$ & F$_2$

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

(a) Lithium to nitrogen

(b) Oxygen and fluorine

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

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

❖ A bond order of ½ 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, H_2^+, H_2, He_2^+, and He_2.

TABLE 9.1 Molecular properties of H_2^+, H_2, He_2^+, and He_2

Species	Number of electrons	Ground state configuration	Bond order	Bond length/pm	Bond energy/aJ
H_2^+	1	$(\sigma_{1s})^1$	½	106	0.423
H_2	2	$(\sigma_{1s})^2$	1	74	0.724
He_2^+	3	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	½	108	0.400
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 N_2 is bonding, and in going from the ground state of N_2 to that of N_2^+ the dissociation energy decreases (and the bond length increases).

✓ In contrast, the highest filled MO of O_2 is antibonding, and in going from O_2 to 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 $O_2(g)$ is related to its electron structure.

➢ The **Lewis formula** of an O_2 molecule does not account for the paramagnetism of $O_2(g)$. According to the octet rule, we should write the Lewis formula of an O_2 molecule as $\ddot{\text{O}}=\ddot{\text{O}}$, 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_2 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^*_{2p} orbitals. As in the atomic case, we apply Hund's rule.

➢ Because the two π^*_{2p} orbitals have the same energy (degenerate), we place one electron in each π^*_{2p} orbital such that the two electrons have unpaired spins, as shown in Figure 9.11.

➢ The ground state electron configuration of an O_2 molecule is:

$$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2px})^1(\pi^*_{2py})^1.$$
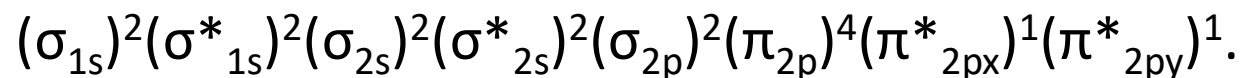
➢ According to Hund's rule, each π^*_{2p} orbital is occupied by one electron and the spins are unpaired, we get *a **triplet** term*. By Hund's rule this is the ground term.

➢ Therefore, ***an oxygen molecule has a net electron spin and so acts like a tiny magnet***. Thus, $O_2(g)$ is attracted into a region between the poles of a magnet.

➢ This explanation of the paramagnetism of O_2 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_2 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*.
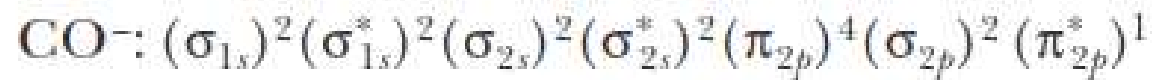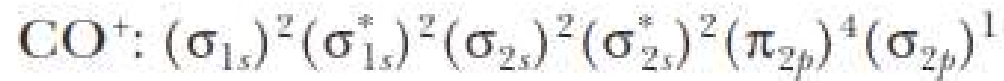
➢ Note, the bond order for the O_2 molecule is $(8 - 4)/2 = 2$, and we say that a bond order of **2 is equivalent to a double bond**.

➢ 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 π*** (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 π^* 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 kJ.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^-, 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:

CO^+: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$

CO: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$

CO^-: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^1$

with bond orders of 2½, 3, and 2½, respectively. Thus, we predict that a CO molecule has the shortest bond, which is correct.

| Homonuclear | $1\sigma_g$ | $1\sigma_u^*$ | $2\sigma_g$ | $2\sigma_u^*$ | $1\pi_u$ | $3\sigma_g$ | $1\pi_g^*$ | $3\sigma_u^*$ | .... |
| Heteronuclear | 1σ | 2σ | 3σ | 4σ | 1π | 5σ | 2π | 6σ | .... |

❑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**, χ (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.

$$\Psi_a = c_A' \phi_A + c_B' \phi_B$$

Fig. 1 A schematic representation of the relative contribu-
tions 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.

Energy →

Less electronegative atom

ϕ_A

ϕ_B
More electronegative atom

$$\Psi_b = c_A \phi_A + c_B \phi_B$$
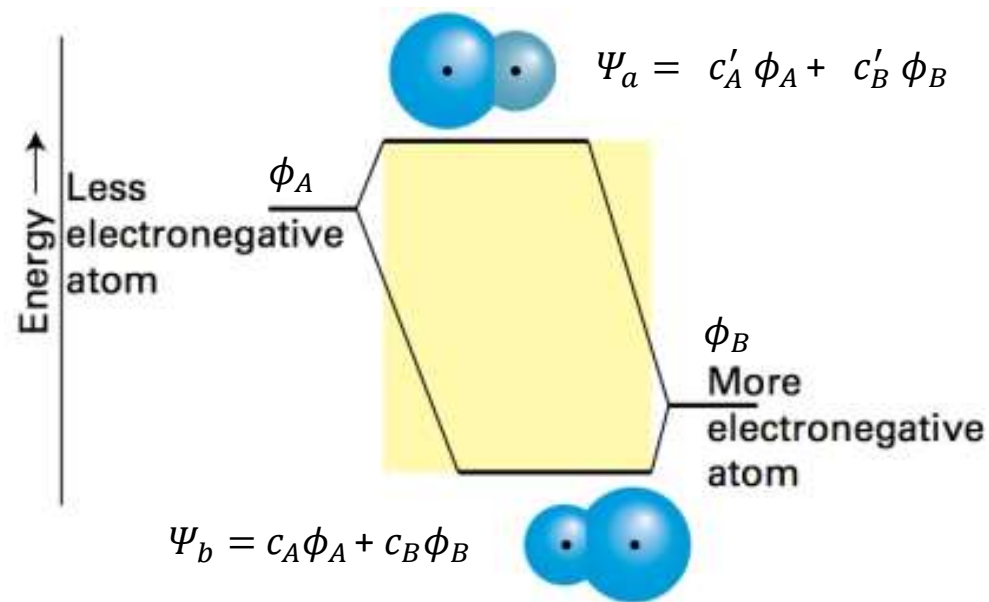
➢ A molecular orbital energy-level diagram is *always skewed toward the more electronegative* atom.

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*.

A (AOs)
Less electronegative

B (AOs)
More electronegative
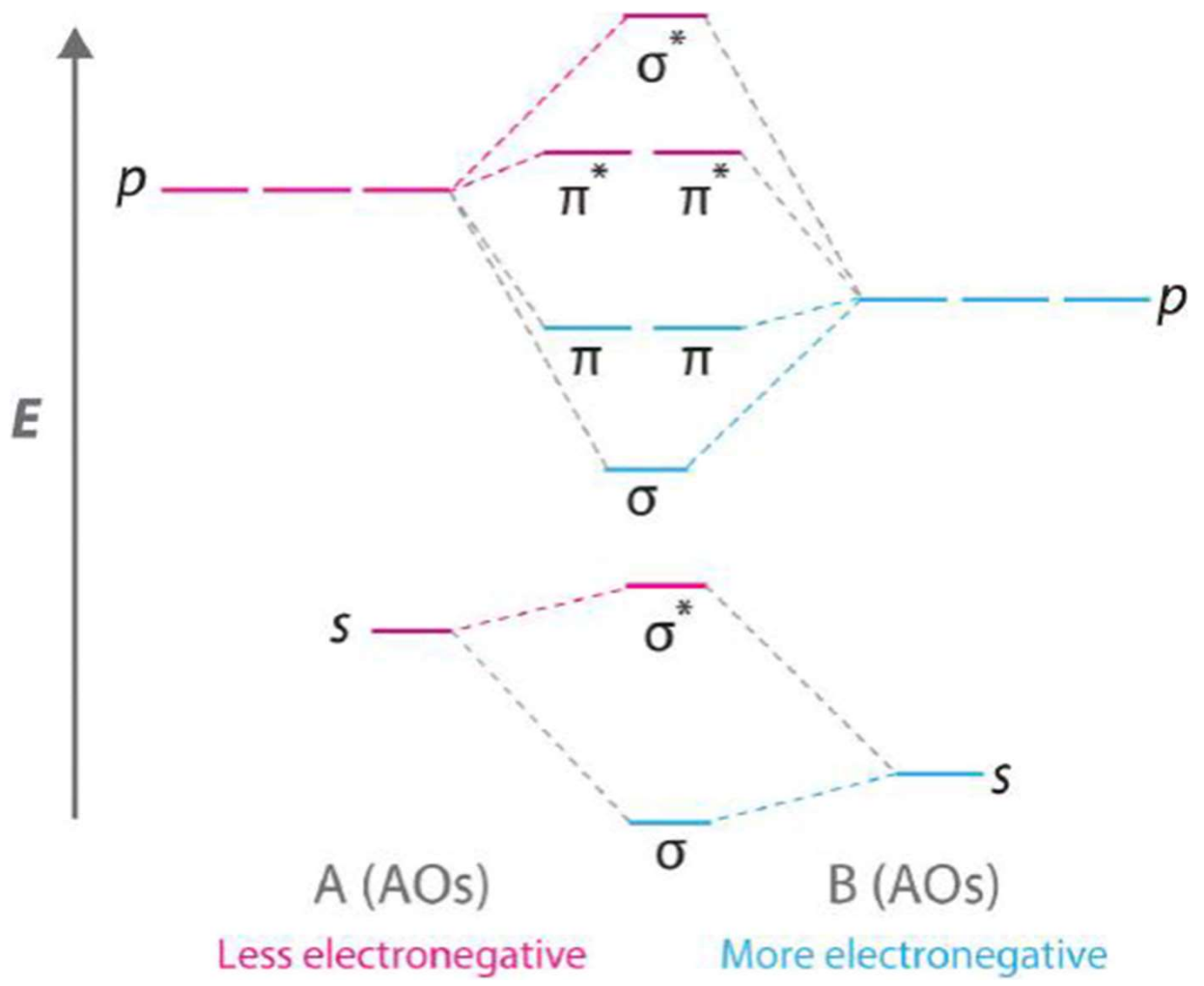
MO Description of A-B Covalent, Polar-Covalent, and Ionic Bonds

| covalent	polar- covalent	ionic
$\chi(B) = \chi(A)$	$\chi(B) > \chi(A)$	$\chi(B) \gg \chi(A)$
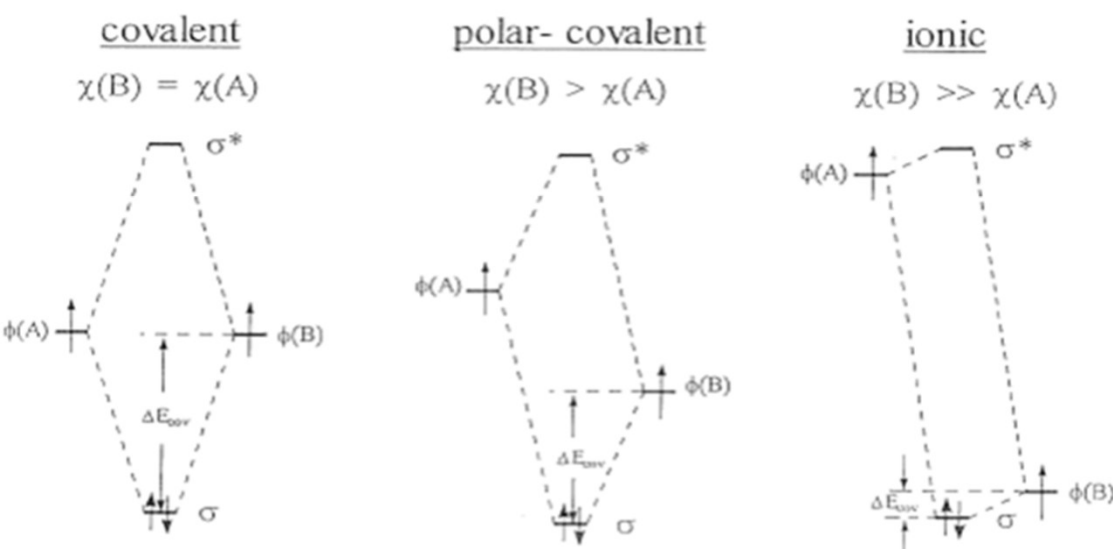
Key Features:

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:
   $$\psi_b(\sigma) \sim \phi(B), \quad \psi_a(\sigma^*) \sim \phi(A)$$

➢ 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.
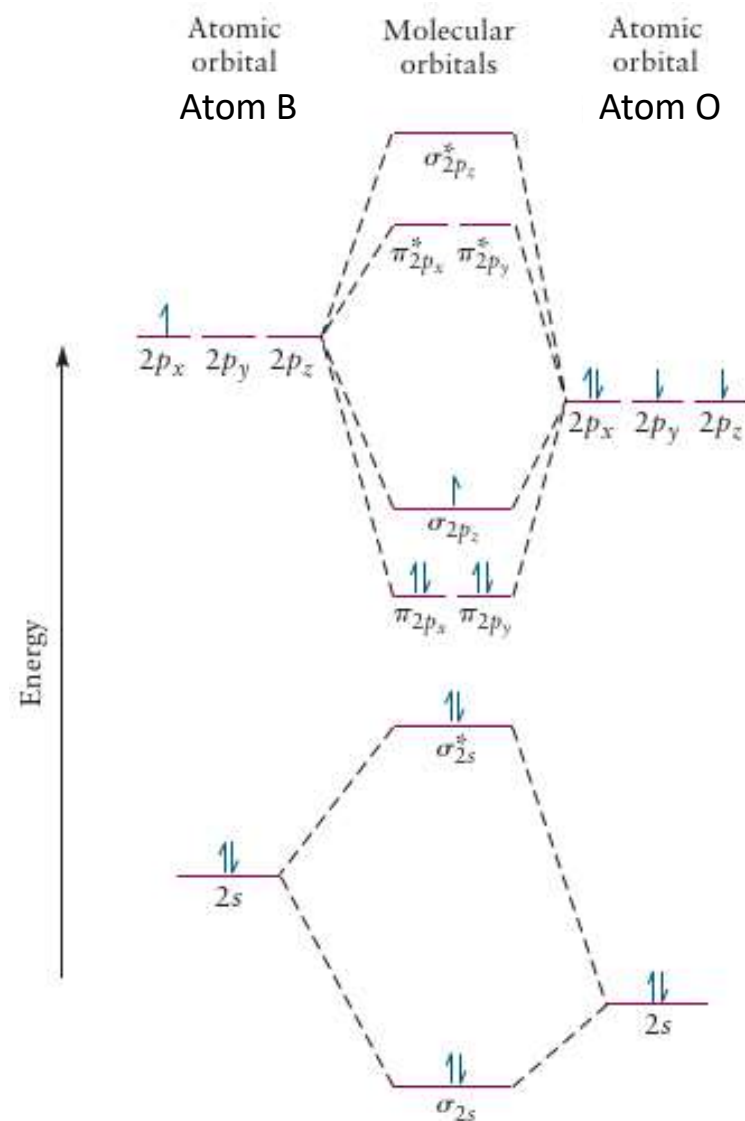
❑ Next, **we consider HF molecule** to illustrate the differences between homonuclear and heteronuclear diatomic molecules.

  ❑ **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 $2p_z$ and $2p_x$ orbitals with the hydrogen 1s orbital.
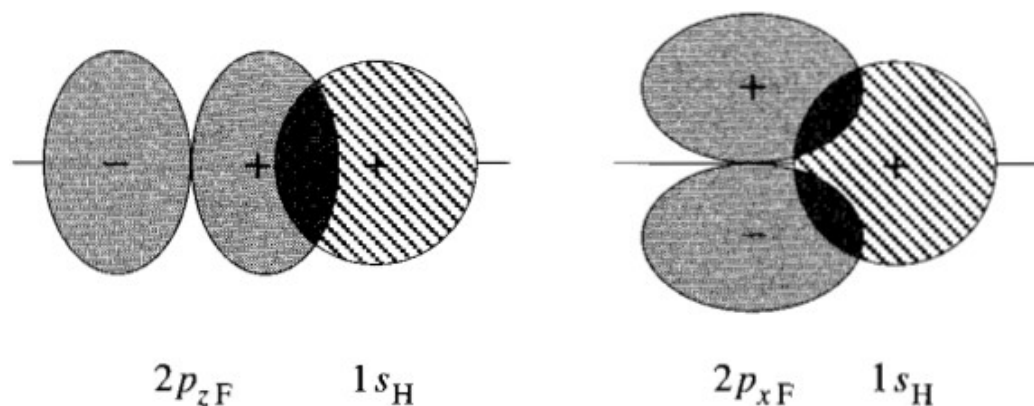

FIGURE 9.18
The overlap of the fluorine $2p_z$ and $2p_x$ atomic orbitals with the hydrogen 1s atomic orbital. Because of the change in sign of the $2p_x$ wave function, the net overlap between the $2p_x$ and hydrogen 1s is zero for all internuclear distance. A set of two a molecular orbitals result from the overlap of the fluorine $2p_z$ atomic orbital and the hydrogen 1s atomic orbital. The bonding σ orbital, σ_b, is the one shown.
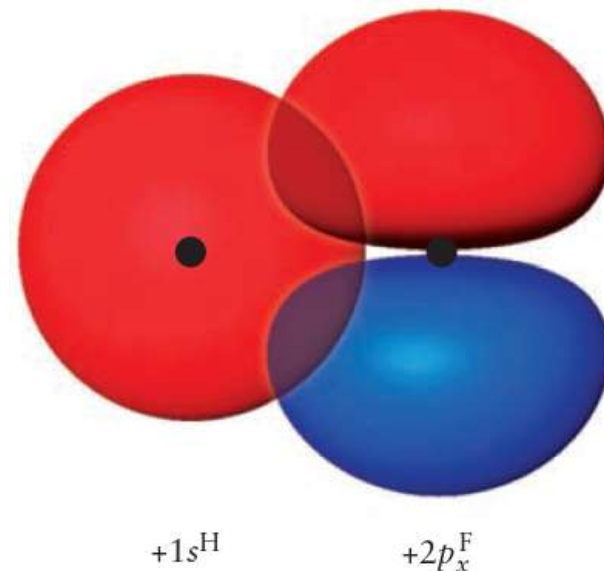

FIGURE 6.22 The H 1s and F $2p_x$ (or $2p_y$) orbitals have no net overlap in HF.

➤ 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 σ molecular orbitals (one bonding, σ_b, and one antibonding, σ_a).

➤ Figure 3.4.8.2 shows the molecular-orbital energy-level diagram for HF. (The $1s_F$ orbital is not shown.)
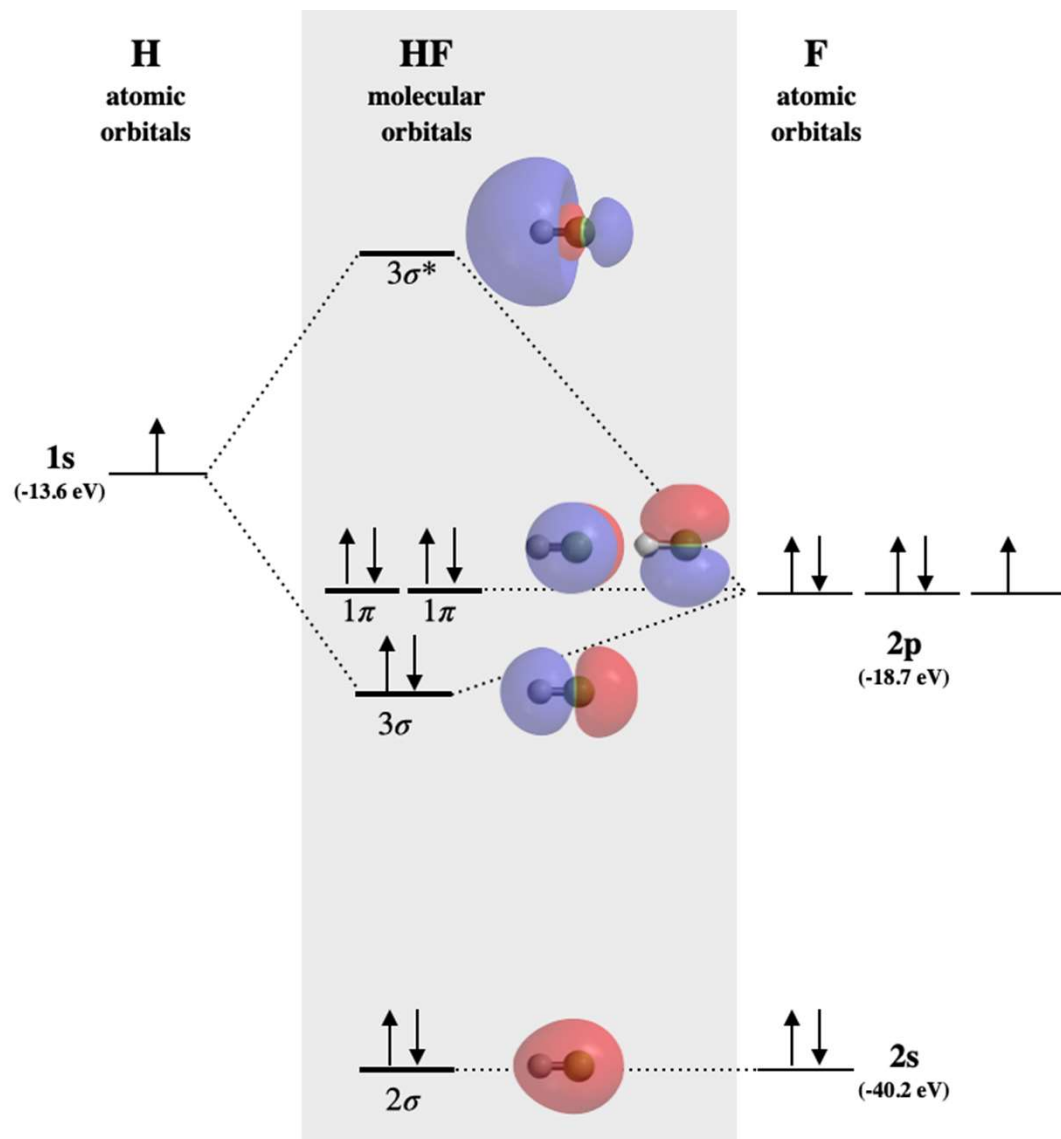
Figure 3.4.8.2: Molecular Orbital diagram of **hydrogen fluoride** (**HF**). Molecular orbitals calculated using Spartan software.

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 **1σ 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 **2σ orbital is more bonding than the 1σ orbital** *and has both H1s and F2p character.*

➢ The *3σ* 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 2σ orbital, forming a bond between the two atoms. **Six more enter the 1σ and 1π 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 $2\sigma^2 3\sigma^2 1\pi^4$.

➢ The $2s_F(2\sigma)$, $2p_{xF}$ and $2p_{yF}$ (1π) 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 1π 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 3σ and $4\sigma^*$ MOs changes the electron distribution in the HF molecule somewhat when compared with a homonuclear diatomic molecule. *The 3σ 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 2σ MO is largely localized on the F atom, the 3σ MO is not totally bonding, and the 1π MOs are completely localized on the F atom. The MO energy diagram depicts the MOs in terms of their constituent AOs.
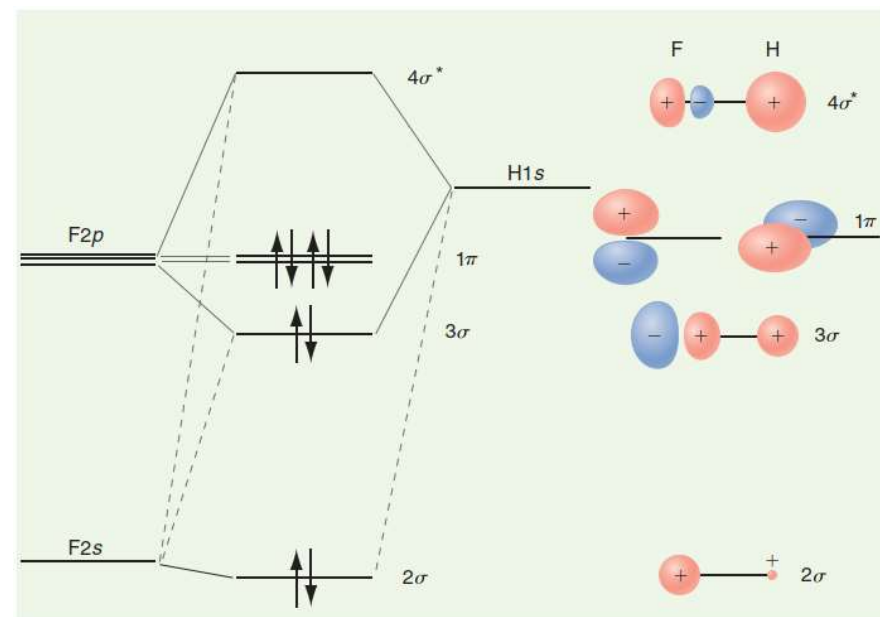

FIGURE 12.22 Schematic energy diagram (Correlation diagram) showing the relationship between the atomic and molecular orbital energy levels for the valence electrons in HF. The degenerate p and π orbitals are shown slightly offset in energy. The dominant atomic orbital contributions to the MOs are shown 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 1σ MO, which is localized on the F atom.

The 2s, 2px, and 2py 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.)
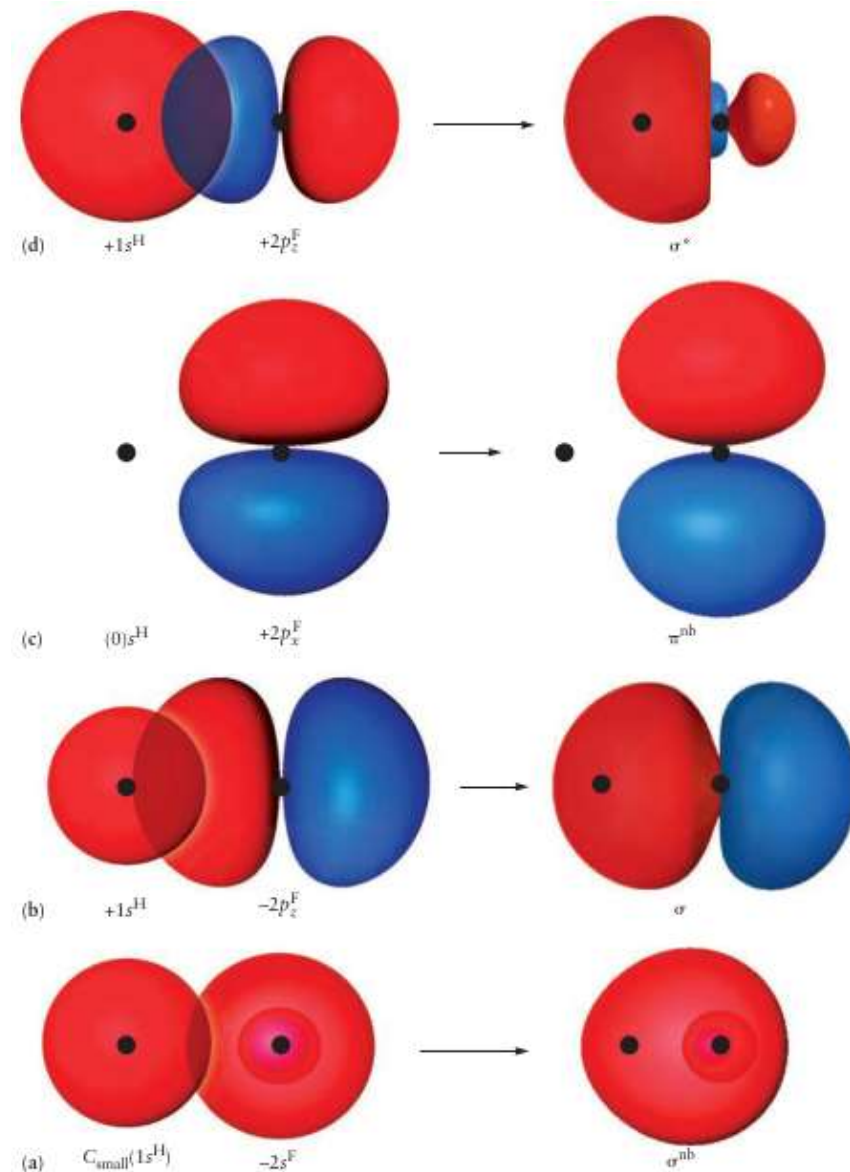
✓ As expected, in the σ bonding orbital the electron density is much greater on the more electronegative fluorine than on the hydrogen.

✓ However, in the σ*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 3*s*, $3p_x$, 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) ÷ 2 = 1.

➤ Because *the σ bonding molecular orbital is closer in energy to the Cl 3p* than to the H 1s atomic orbital, *the electrons in the σ 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 $H^{\delta+}$–$Cl^{\delta-}$.

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 σ orbital is occupied by electrons, giving a bond order of 1.
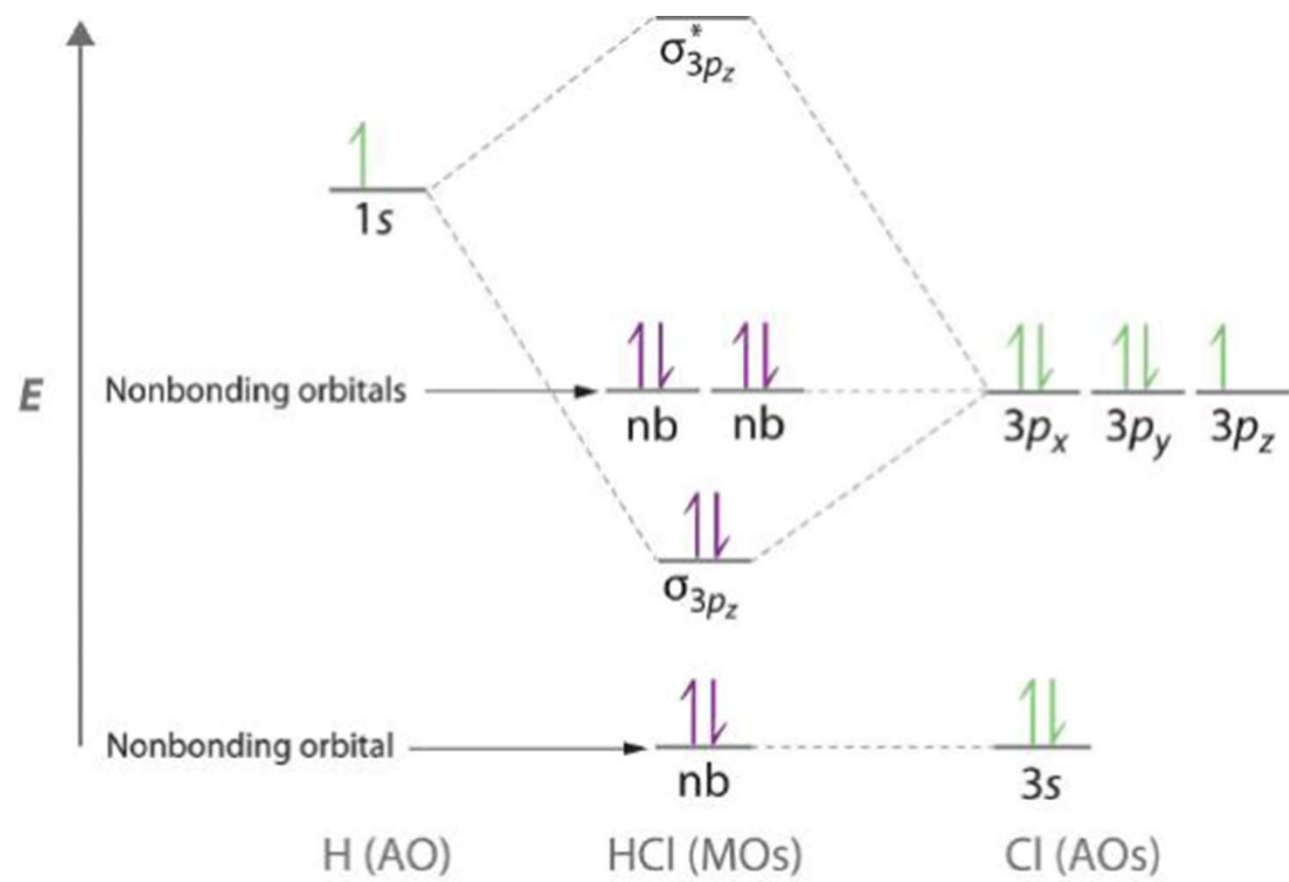
➢ An **energy-level diagram for O–H** radical calculated for the experimentally observed O–H bond length of 97.0 pm is shown in Figure 6.10.

➢ On the far right of the figure, *the coefficients of the AOs, i.e., C_1, C_2 and C_3, for each σ 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.
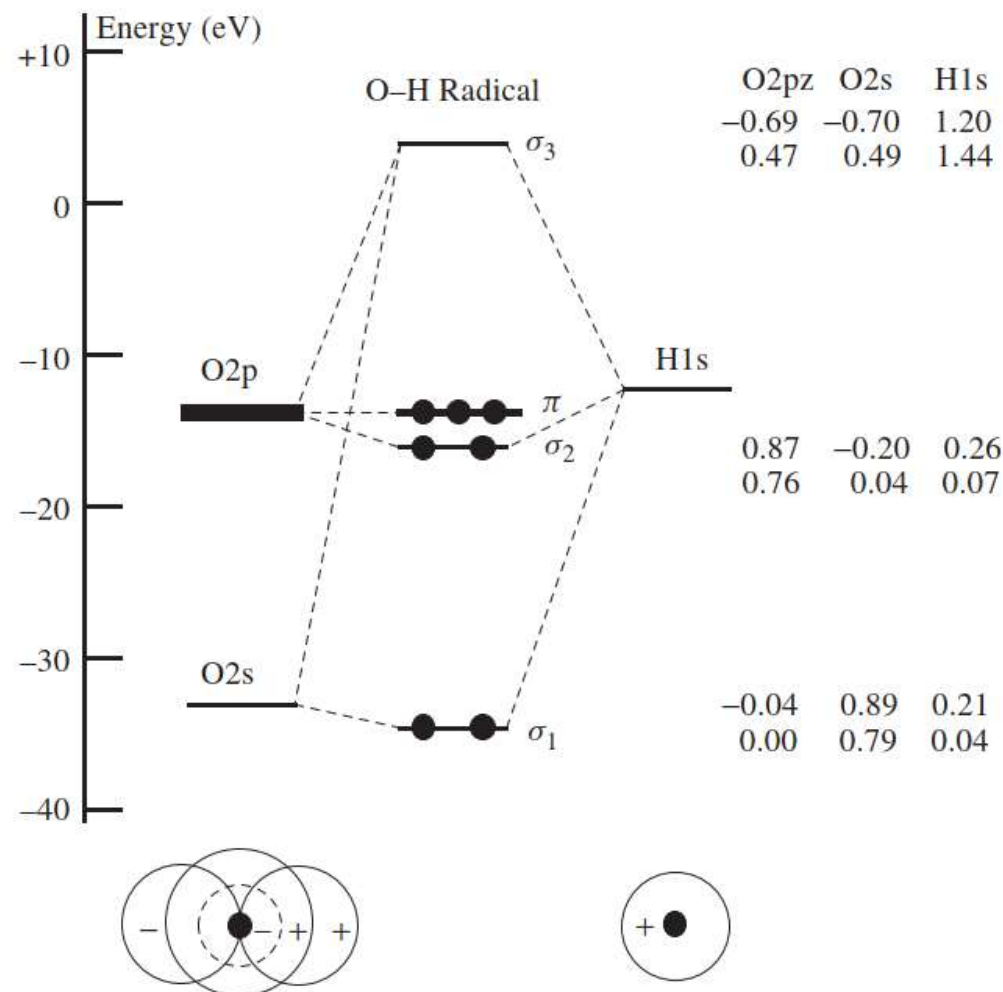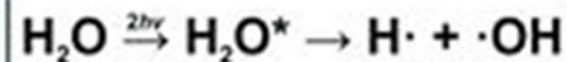

Figure 6.10 A molecular orbital energy-level scheme for the OH radical.

❖ **Energy-level diagram for O–H Radical** $H_2O \xrightarrow{2h\nu} H_2O^* \rightarrow H\cdot + \cdot OH$

➢ 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 σ 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; σ_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 $2p_z$ is too small to concern us. Note that **the orbital is bonding, because the two AO contributors overlap in phase, and of σ type**.

✓ *We place **two of our seven electrons** in this MO.*

➢ The MO next in energy (σ_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 π symmetry at E = −14.80 eV, are ***non-bonding MOs***.

✓ The π-type oxygen $2p_x$ and oxygen $2p_y$ AOs have zero overlap with the σ-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 (σ_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_2*, 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⁻, 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 σ orbital largely localized on C; the LUMO is an antibonding π 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 σ and π 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 σ orbital largely localized on C; the LUMO is an antibonding π orbital.

predominantly C2pz in character, largely nonbonding

bonding

bonding

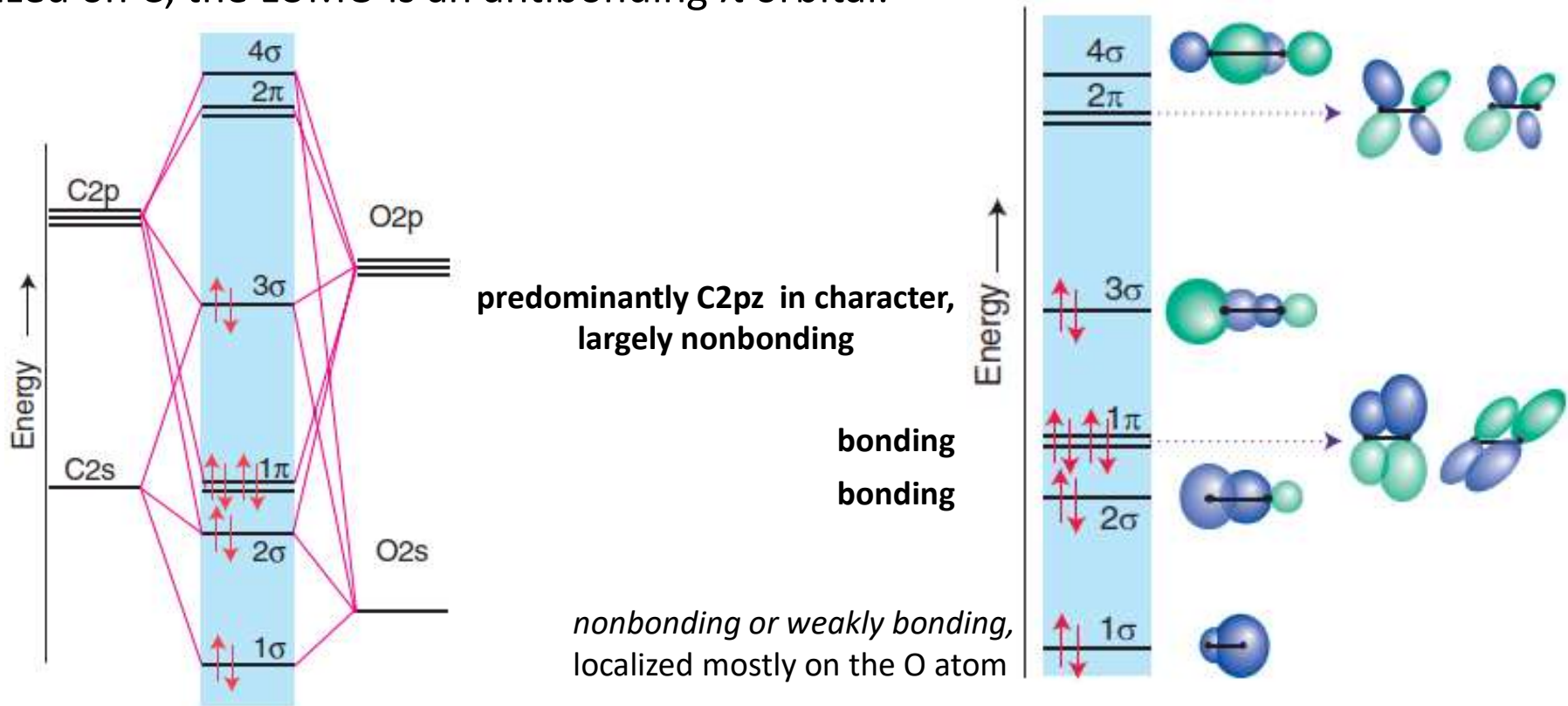*nonbonding or weakly bonding,* localized mostly on the O atom

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: $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$

➤ The 1σ orbital is localized mostly on the O atom and therefore essentially *nonbonding or weakly bonding*. The **2σ orbital is bonding**. The 1π orbitals constitute the doubly degenerate pair of **bonding π orbitals**, with *mainly C2p orbital character*.

➤ The **HOMO in CO is 3σ, which is predominantly C2pz in character, largely nonbonding**, and *located on the C atom*.

➤ The **LUMO** *is the doubly degenerate* **pair of antibonding π orbitals**, with mainly C2p orbital character (Fig. 2.23).

➤ This combination of frontier orbitals—*a full σ orbital largely localized on C* and a *pair of empty π 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 σ bond and the LUMO antibonding π orbital participates in the formation of π bonds to the metal atom.

- The HOMO lone pair orbital (**σ orbital largely localized on C)** of CO participates in the formation of a σ bond.
- The LUMO antibonding π orbital participates in the formation of π 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.
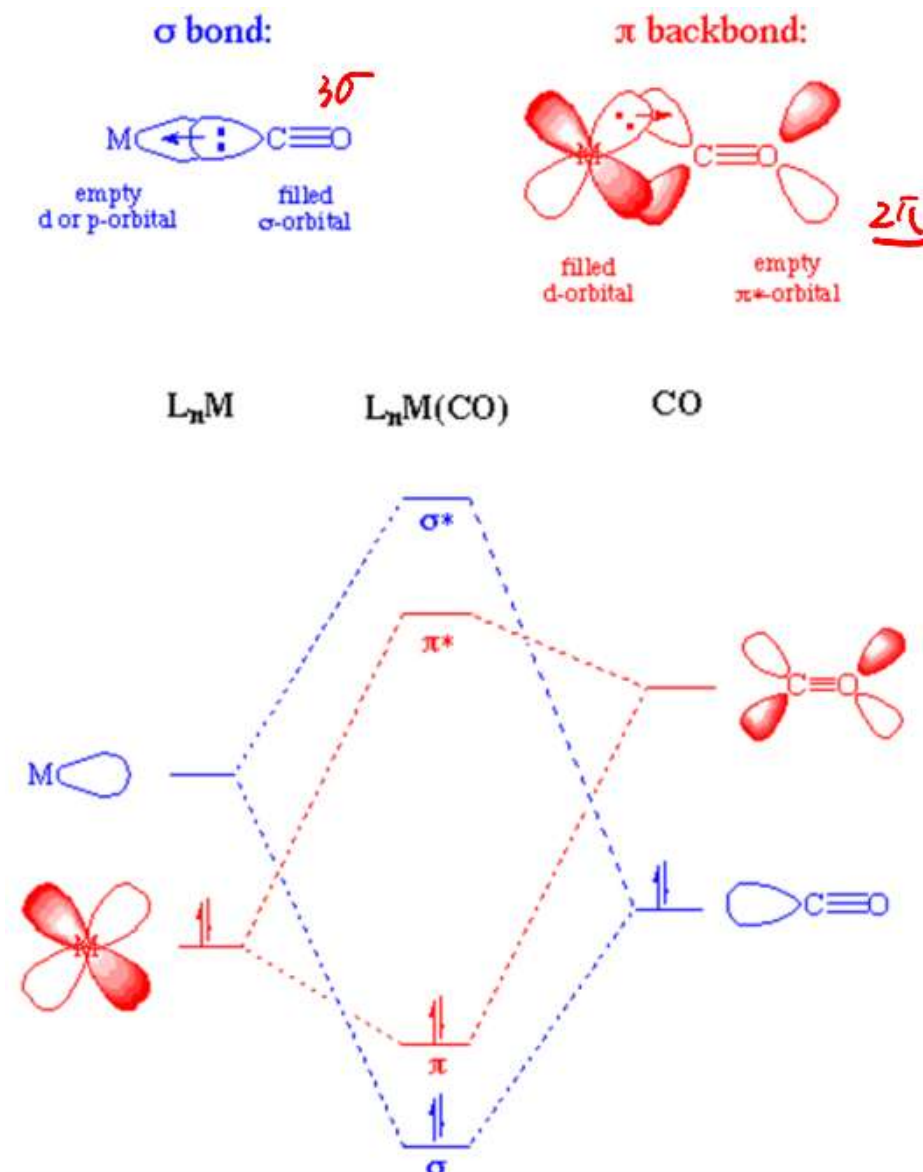
- ➤ ***Nonbonding MOs are not counted*** in the determination of the ***bond order***. Thus, ***the overall bond order for CO is 3***, *consistent with its Lewis structure.*

- ➤ 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 Na^+F^-.

Note that if we were to **excite an electron** from ψ_1 MO to ψ_2 MO using light, the resulting electronic configuration would be ($\psi^1\psi^1$) and we would be Na^0F^0. **This is called a charge transfer transition.**

Figure 2.2.8 : Molecular orbital energy diagram illustrating ionic bonding in the NaF molecule
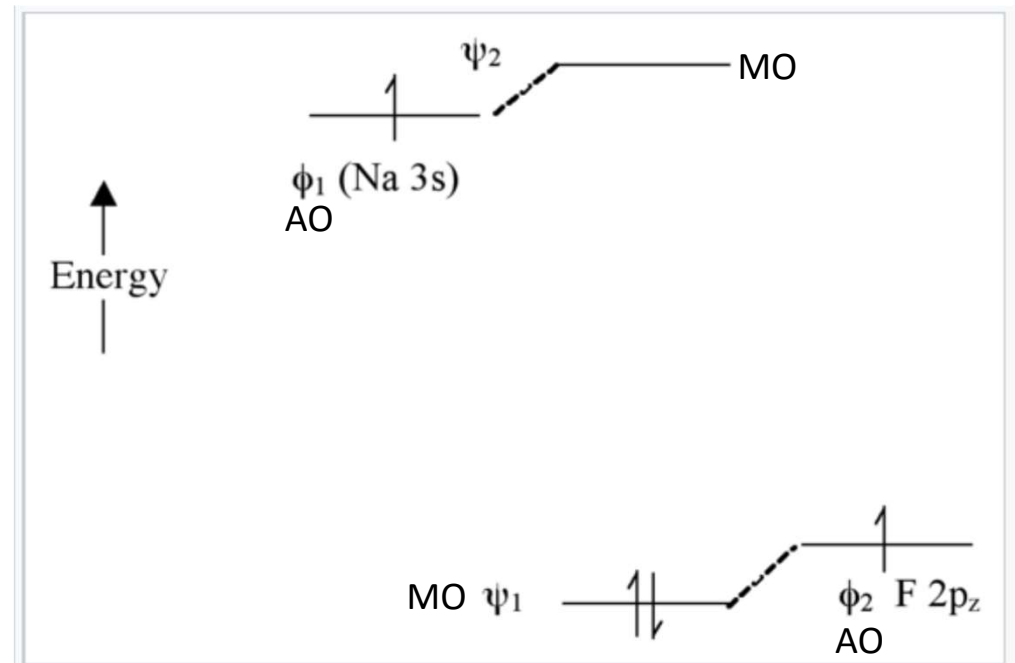
- In NaCl, the **sodium 3s orbital** (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals.
- The chlorine 3s and $3p_z$ orbitals *have compatible symmetry*, yet only the **$3p_z$ orbital** (-13.8 eV) is **close enough** in energy to interact with the Na 3s; still, the *energy difference is large enough to make bonding weak*.
- The Na 3s orbital combines with Cl $3p_z$ 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 $3p_z$ 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.
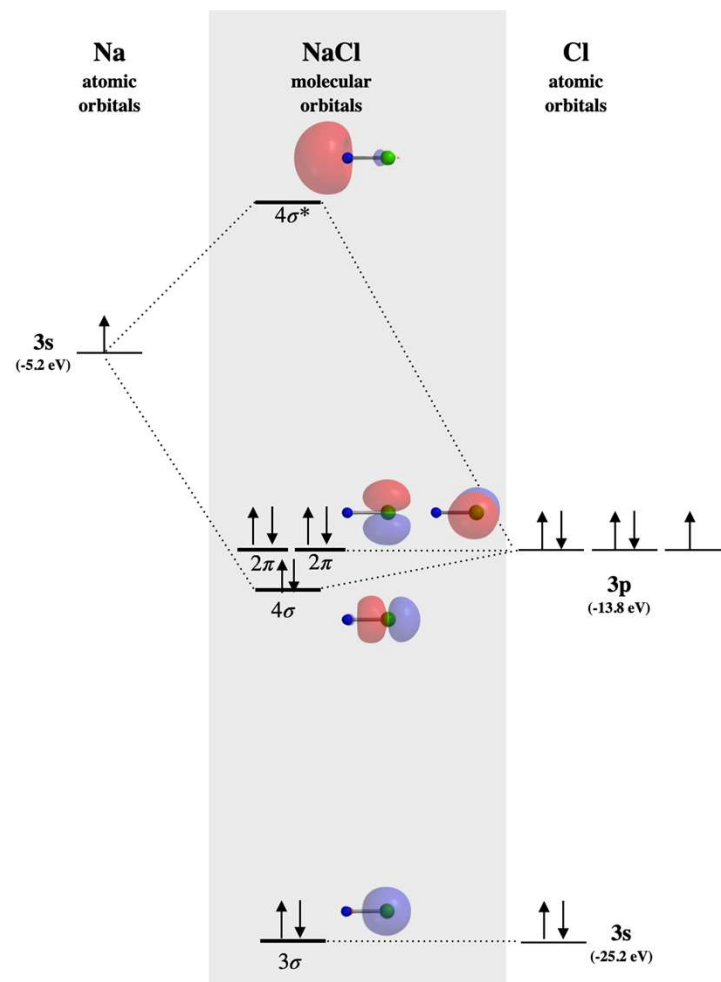

Figure 5.3.2.1: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding.

❑ 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 **λ 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 λ 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 μ arises from a charge separation in space, and is thus defined as

$$\mu = Q \cdot r, \tag{11.15}$$

➤ where Q is the separated charge (e.g., 1 e = 1.602 x 10⁻¹⁹ 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 x 10⁻³⁰ 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 Å = 0.1 nm = 10⁻¹⁰ 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 = (μ(observed) / μ(theoretical)) *100

➢ where, **μ = Dipole moment in Debye.**

❖ **Calculate the percentage ionic and covalent character in HF molecules having bond distance = 0.92Å and dipole moment=1.78D?**

Ans: Given, μ(observed) = 1.78D= $1.78*10^{-18}$ esu.cm   ($1D = 10^{-18}\ esu.cm$)

r = 0.92Å = $0.92*10^{-8}$ cm

We know,   % ionic character = (μ(observed)/μ(theoretical))*100

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

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

Ionic character = 40.3%

Hence, Covalent character = 100 – 40.3 = 59.7%.

Electronegativity Difference

| Nonpolar Covalent Bond | 0.4 | Polar Covalent Bond | 1.8 | Ionic Bond |

Examples:

C-H   C-O   NaCl

2.5-2.1 = 0.4   3.5 − 2.5 = 1.0   3.0 − 0.9 = 2.1
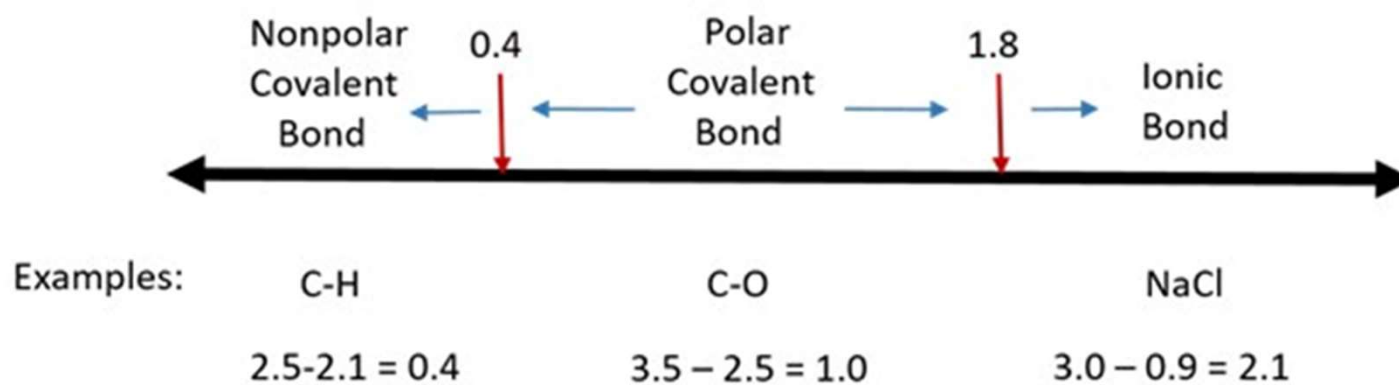
Dipole Moment of Ionic Compounds

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 $+1 \cdot e$, and the charge on the chlorine $-1 \cdot e$. With an inter-nuclear distance of 2.36 Å, this results in a dipole moment of $\mu = 11.34$ D. The experimental value of the dipole moment can be obtained by microwave spectroscopy and yields $\mu = 9.001$ D. The ratio of the experimental and theoretical dipole moments

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

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