18 The Electronic States of Molecules

OBJECTIVES

After studying this chapter, the student should:

1. be familiar with and understand the properties of the electronic states of the hydrogen molecule ion;
2. be able to construct approximate wave functions and electron configurations or homonuclear diatomic molecules;
3. be able to use general properties of molecular orbitals, including criteria for formation of good bonding orbitals, to predict the qualitative properties of electronic states of heteronuclear diatomic molecules;
4. be able to describe qualitatively the bonding in a fairly small polyatomic molecule, including bond angles, bond polarities, and the dipole moment of the molecule, using the criteria for formation of good bonding orbitals;
5. be able to describe qualitatively the bonding in fairly small polyatomic molecule, using the valence bond method;
6. be able to assign molecules to point groups and use some of the elementary applications of group theory to molecular wave functions;
7. be familiar with some of the semi-empirical molecular orbital calculation schemes and be able to use commercially available computer programs to carry out these calculations.

PRINCIPAL FACTS AND IDEAS

1. In the Born–Oppenheimer approximation, the nuclei are assumed to be stationary when the electronic states are studied.
2. The Schrödinger equation for the hydrogen molecule ion, H_2^+, can be solved in the Born–Oppenheimer approximation without further approximations.
3. Molecular orbitals can be represented approximately as linear combinations of atomic orbitals (LCAO-MOs).
4. The electronic states of homonuclear diatomic molecules can be described with a common set of LCAO-MOs.
5. The valence bond method is an alternative to the molecular orbital method.
6. Heteronuclear diatomic molecules are described with molecular orbitals that differ from those of homonuclear diatomic molecules.
7. Qualitative descriptions of the electronic states of molecules can be obtained by using general criteria for forming good bonding LCAO molecular orbitals.
8. The electronic structure of polyatomic molecules can be described with LCAO molecular orbitals.
9. Group theory can be used to obtain useful information about molecular orbitals and wave functions.
10. Various semi-empirical and ab initio techniques exist for carrying out molecular orbital calculations.

18.1 The Born–Oppenheimer Approximation. The Hydrogen Molecule Ion

In a two-particle system such as the hydrogen atom, the Schrödinger equation can be solved in closed form (with solutions that can be represented by formulas). This is done as in Chapter 16 by separating the Schrödinger equation for two particles into one equation for the motion of the center of mass and another for the relative motion. For atoms with more than one electron we had to resort to approximations, including the assumption that in studying the electronic motion in atoms the nucleus was stationary.

Our study of the electronic motion in molecules is based on a similar assumption, the **Born–Oppenheimer approximation,**[1] which is the assumption that the nuclei are stationary when the electronic motion is studied. Fixed bond distances and bond angles are assumed and a Hamiltonian operator is written for electronic motion only. This is a good approximation, since electrons move so rapidly that they adapt to a new electronic wave function as soon as the nuclei move to a new location or conformation.

The energy of the molecule with stationary nuclei is called the Born–Oppenheimer energy. Figure 18.1 shows schematically the ground-state Born–Oppenheimer energy of a diatomic molecule, which depends only on the internuclear distance, R. With polyatomic molecules, the Born–Oppenheimer energy depends on all of the internuclear distances and bond angles. Since the Born–Oppenheimer energy is a function of nuclear positions but not their velocities, it acts as a potential energy for molecular vibrations. Molecular rotations are usually studied with the assumption that the molecule is locked in the conformation of lowest energy (the equilibrium conformation). To a good approximation, the kinetic energy of nuclear motion can be added to the Born–Oppenheimer energy to obtain the total energy of the molecule. We return to study of the nuclear motions in Chapter 19.

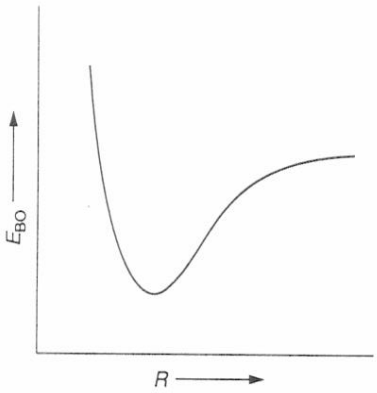

Figure 18.1 Born–Oppenheimer Energy as a Function of Internuclear Distance for a Diatomic Molecule (Schematic). This energy is the total energy of the molecule in the Born–Oppenheimer approximation. It consists of the electronic energy (kinetic plus potential), plus the energy of repulsion of the nuclei for each other.

The Schrödinger Equation for the Hydrogen Molecule Ion

The simplest molecular system is the hydrogen molecule ion, H_2^+, consisting of two nuclei and a single electron, as depicted in Figure 18.2. We apply the Born–Oppenheimer approximation, assuming that the nuclei are stationary with one nucleus at position A on the z axis and the other nucleus at position B on the z axis and with the origin of coordinates midway between the nuclei. The Born–Oppenheimer Hamiltonian operator for the hydrogen molecule ion is

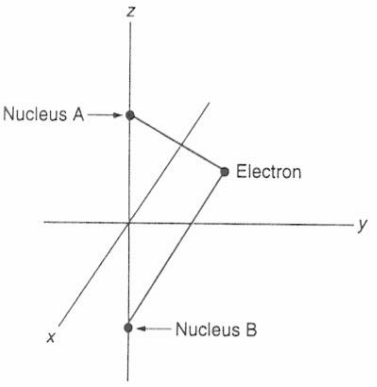

Figure 18.2 The Hydrogen Molecule Ion (H_2^+) System. This system is the simplest molecule, having only one electron. It is the only molecule for which the Schrödinger equation can be solved in the Born–Oppenheimer approximation without any additional appproximations.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B}\right) \qquad (18.1\text{-}1)$$

where ∇^2 is the Laplacian operator for the electron's coordinates, m is the electron mass, R is the internuclear distance, r_A is the distance from the electron to the nucleus at position A, and r_B is the distance from the electron to the nucleus at position B. There are no kinetic energy terms for the nuclei because they are assumed to be fixed. Since

[1] Max Born and J. Robert Oppenheimer, *Ann. Phys.*, **84**, 457 (1927).

the internuclear distance R is constant in the Born–Oppenheimer approximation, the potential energy $\mathscr{V}_{nn}$ of internuclear repulsion is a constant:

$$\frac{e^2}{4\pi\varepsilon_0 R} = \mathscr{V}_{nn} = \text{constant} \tag{18.1-2}$$

We exclude $\mathscr{V}_{nn}$ from the electronic energy and write

$$\hat{H} = \hat{H}_{el} + \mathscr{V}_{nn} \tag{18.1-3}$$

$$\hat{H}_{el} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_A} - \frac{1}{r_B}\right) \tag{18.1-4}$$

The electronic Schrödinger equation is

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el} \tag{18.1-5}$$

where E_{el} is the electronic energy eigenvalue. A constant added to a Hamiltonian operator does not change the energy eigenfunctions and results in adding that constant to the energy eigenvalues. (See Exercise 14.22.) We can write

$$E_{BO} = E_{el} + \mathscr{V}_{nn} \tag{18.1-6}$$

where E_{BO} is the Born–Oppenheimer energy.

The variables can be separated in Eq. (18.1-5) by transforming to a coordinate system that is called confocal polar elliptical coordinates. We will not discuss the solution,[2] but will present some facts about the ground state and first excited state. We call the energies and orbitals of these states the "exact Born–Oppenheimer" energies and orbitals. They contain no approximations other than the Born–Oppenheimer approximation.

Figure 18.3 shows the Born–Oppenheimer energy as a function of R for the two states. The lower curve has a minimum at $R = 1.06 \times 10^{-10}$ m = 106 pm. This value of R is denoted by R_e and is called the **equilibrium internuclear distance**. We consider the molecule to be chemically bonded in the ground state with a bond order of 1/2, since there is one shared electron. For large values of R the energy approaches a constant value. The difference in energy between this constant value and the value of the energy at $R = R_e$ is denoted by D_e and is called the **dissociation energy** of the molecule. For the H_2^+ ion, D_e is equal to 2.8 eV. The first excited state has an energy that decreases monotonically as R increases. If the molecule is in the first excited state it will dissociate, forming a hydrogen atom and an H^+ ion.

Molecular Orbitals

The eigenfunctions of the Hamiltonian of Eq. (18.1-5) are one-electron wave functions that correspond to electronic motion around both nuclei. They are **molecular orbitals**. Figure 18.4 shows qualitatively the orbital regions for the ground state and first excited state. There is some similarity between the ground-state orbital region and that of the $1s$ orbital region for the hydrogen atom and between the orbital region of the first excited state and that of the $2p_z$ orbital of the hydrogen atom. If the mathematical limit is taken as R approaches zero, a hypothetical single atom called the **united atom** is obtained. The united atom for H_2^+ is the He^+ ion with a single electron and $Z = 2$. In this limit

[2] D.R. Bates, K. Ledsham and A. L. Stewart, *Phil. Trans. Roy. Soc.* **A246**, 215 (1963).

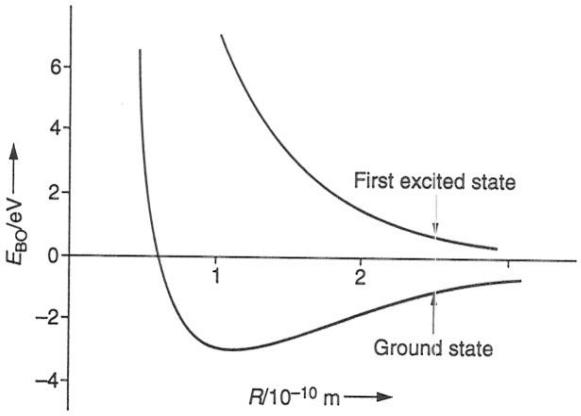

Figure 18.3 The Born–Oppenheimer Energy of the Ground State and First Excited State of the Hydrogen Molecule Ion as a Function of Internuclear Distance. This figure shows the results of solving the Schrödinger equation repeatedly for different internuclear distances in the Born–Oppenheimer approximation and then drawing a smooth curve through the energy eigenvalues as a function of internuclear distance. Both the ground state and the first excited state are shown.

the ground-state molecular orbital turns into the united-atom $1s$ He^+ orbital, and the first excited-state molecular orbital turns into the united-atom $2p_z$ He^+ orbital.

The ground-state orbital has no nodes except at infinite distance from the nuclei, while the first excited-state orbital has a nodal surface between the nuclei. A wave function with more nodes generally corresponds to a higher energy than one with fewer nodes. A molecular orbital without a nodal surface between the nuclei generally corresponds to an electronic energy with a minimum value as a function of R and it is called a **bonding molecular orbital**. An orbital with a nodal surface between the nuclei generally corresponds to an electronic energy that decreases monotonically as R increases and is called an **antibonding molecular orbital**.

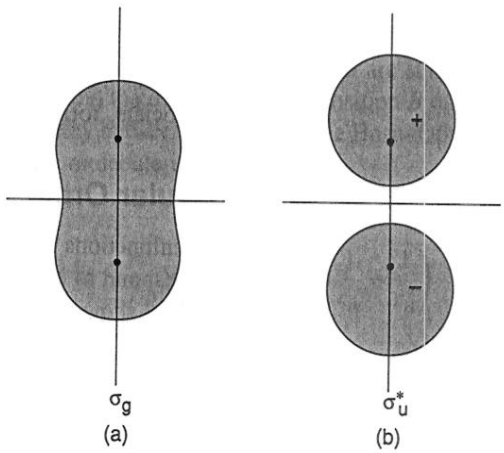

Figure 18.4 The Orbital Regions for the Hydrogen Molecule Ion (Schematic). (a) The ground state. (b) The first excited state. These sketches show the important qualitative properties of these two orbitals. The ground state corresponds to a standing wave with no nodes, and the first excited state corresponds to a standing wave with a nodal plane between the nuclei.

The orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ commute with the electronic Hamiltonian of the hydrogen atom, and energy eigenfunctions could be found that were eigenfunctions of these two operators. The operator $\hat{L}^2$ does not commute with the electronic Hamiltonian of the H_2^+ molecule because all directions are not equivalent due to the two fixed nuclei. However, $\hat{L}_z$ does commute with the electronic Hamiltonian operator if the nuclear axis is chosen as the z axis. The energy eigenfunctions can be eigenfunctions of $\hat{L}_z$, although not necessarily of $\hat{L}^2$. The eigenvalues of $\hat{L}_z$ follow the same pattern as in the atomic case:

$$\hat{L}_z\psi = \hbar m\psi \tag{18.1-7}$$

where the quantum number m equals any integer and where ψ represents an energy eigenfunction. The magnitude of m is not bounded by any quantum number l as for atoms. For molecular orbitals, we define a nonnegative quantum number λ:

$$\lambda = |m| \tag{18.1-8}$$

A nonzero value of λ corresponds to two states because m can be either positive or negative. Each level for $\lambda \neq 0$ has a degeneracy equal to 2 (is "doubly degenerate").

Atomic orbitals corresponding to $l = 0$ were called s orbitals, orbitals with $l = 1$ were called p orbitals, etc. For molecular orbitals we use the following Greek-letter designations:

Value of λ	Symbol
0	σ
1	π
2	δ
3	ϕ
etc.	

Both the ground-state orbital and the first excited-state orbital of the hydrogen molecule ion are σ (sigma) orbitals.

Symmetry Properties of the Molecular Orbitals

There is an important class of operators that can commute with the Born–Oppenheimer electronic Hamiltonian operator for a molecule and can be used to characterize the symmetry properties of molecules and of molecular orbitals. These operators are **symmetry operators**, which move points from one location to another in three-dimensional space. Each symmetry operator is classified and named by the way it moves a point. For each operator, there is a **symmetry element**, which is a point, line, or plane with respect to which the symmetry operation is performed.

The symmetry operators that commute with the Born–Oppenheimer Hamiltonian of a given molecule are said to belong to the molecule. The electronic energy eigenfunctions of the molecule can also be eigenfunctions of these operators. For diatomic molecules, we consider several symmetry operators. The **inversion operator**, $\hat{i}$, is defined to move a point on a line through the origin of coordinates to a location that is at the same distance from the origin as the original location. If the cartesian coordinates of the original location are (x, y, z), the inversion operator moves the point to $(-x, -y, -z)$. For a general operation, we denote the final coordinates by (x', y', z'), so that for the

inversion operator $x' = -x$, $y' = -y$, and $z' = -z$. We denote the operation by the equation

$$\hat{i}(x, y, z) = (x', y', z') = (-x, -y, -z) \tag{18.1-9}$$

The symmetry element for the inversion operator is the origin. Since there is only one origin, there is only one inversion operator. **Point symmetry operators** are symmetry operators that leave a point at its original location if that location is at the origin. The inversion operator is an example of a point symmetry operator. The symmetry elements of point symmetry operators always include the origin.

A **reflection operator** is defined to move a point along a line perpendicular to a specified plane to a location on the other side of the plane at the same distance from the plane as the original location. It is said to "reflect" the point through the plane, which is the symmetry element. The reflection operator $\hat{\sigma}_h$ reflects through a horizontal plane:

$$\hat{\sigma}_h(x, y, z) = (x', y', z') = (x, y, -z) \tag{18.1-10}$$

There is only one horizontal plane through the origin, so there is only one $\hat{\sigma}_h$ operator among the point symmetry operators. A symmetry operator that reflects through a vertical plane is denoted by $\hat{\sigma}_v$. Since there are infinitely many vertical planes containing the origin, there are infinitely many $\hat{\sigma}_v$ operators among the point symmetry operators. It is convenient to attach subscripts or other labels to distinguish them from each other.

*Exercise 18.1

Find the coordinates of the points resulting from the operations:

a. $\hat{i}(1, 2, 3)$

b. $\hat{\sigma}_h(4, -2, -2)$

c. $\hat{\sigma}_{vyz}(7, -6, 3)$ where $\hat{\sigma}_{vyz}$ is the reflection operator that reflects through the yz plane.

Rotation operators cause a point to move as it would if it were part of a rigid body rotating about a specified axis, which is the symmetry element. The point moves around a circle that is centered on the axis of rotation and perpendicular to it. By convention, all rotations are counterclockwise when viewed from the end of the rotation axis that is designated as the positive end. There are infinitely many lines that pass through the origin, and for each rotation axis there can be rotations by infinitely many different angles. We consider only rotation operators that produce a full rotation (360°) when applied an integral number of times. A rotation operator that produces one full rotation when applied n times is denoted by $\hat{C}_n$. It is convenient to add subscripts to denote the axis. For example, the $\hat{C}_{4z}$ operator rotates by 90° about the z axis, and its effect on a point at (x, y, z) is

$$\hat{C}_{4z}(x, y, z) = (x', y', z') = (-y, x, z) \tag{18.1-11}$$

Figure 18.5 shows the effect of the operators $\hat{i}$, $\hat{\sigma}_h$, and $\hat{C}_{4z}$ on a point in the first octant.

*Exercise 18.2

Find the following locations:

a. $\hat{C}_{2x}(1, 2, 3)$ (the axis of rotation is the x axis).

b. $\hat{C}_{3y}(1, 1, 1)$ (the axis of rotation is the y axis).

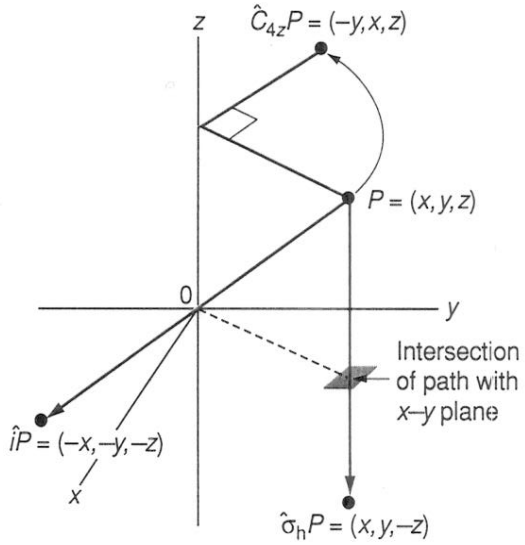

Figure 18.5 The Effect of the Symmetry Operators $\hat{i}$, $\hat{\sigma}_h$, and $\hat{C}_{4z}$. These mathematical operators move a point in three-dimensional space in ways defined in the text.

In addition to the above operators there is the **identity operator**, which does nothing. It is denoted by $\hat{E}$. The letter E is used because it is the first letter of the German word "Einheit," meaning "unity."

$$\hat{E}(x, y, z) = (x, y, z) \tag{18.1-12}$$

The Operation of Symmetry Operators on Functions

Ordinary mathematical operators operate on functions, not on isolated points. We define a mode of operation so that symmetry operators also operate on functions. Let $f(x, y, z)$ be some function of the coordinates x, y, and z, and let $\hat{O}$ be some symmetry operator that carries a point at (x, y, z) to a location (x', y', z'):

$$\hat{O}(x, y, z) = (x', y', z') \tag{18.1-13}$$

When the operator $\hat{O}$ operates on the function f it produces a new function g, defined to be the function that has the same value at the location (x', y', z') that the function f has at the location (x, y, z). If

$$\hat{O}f(x, y, z) = g(x, y, z) \tag{18.1-14}$$

then

$$g(x', y', z') = f(x, y, z) \tag{18.1-15}$$

A function can be an eigenfunction of a symmetry operator. The only eigenvalues that occur are $+1$ and -1.

EXAMPLE 18.1

Show that the hydrogenlike $1s$ orbital is an eigenfunction of the inversion operator $\hat{i}$. Find the eigenvalue.

Solution

$$\psi_{1s} = \sqrt{\frac{1}{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

where Z is the number of protons in the nucleus, a is the Bohr radius, and r is the distance from the nucleus:

$$r = (x^2 + y^2 + z^2)^{1/2}$$

When x is replaced by $-x$, y is replaced by $-y$, and z is replaced by $-z$, the value of r is unchanged so that

$$\hat{i}\psi_{1s} = \psi_{1s}$$

The ψ_{1s} function is an eigenfunction of the inversion operator with eigenvalue 1.

Exercise 18.3

***a.** Determine the spherical polar coordinates of $\hat{i}P$ and $\hat{\sigma}_h P$ if P represents a point whose location is (r, θ, ϕ).

b. Show that the ψ_{2p_z} hydrogenlike orbital is an eigenfunction of the $\hat{\sigma}_h$ operator with eigenvalue -1.

The equilibrium nuclear conformations of many molecules are symmetrical. Our first use of symmetry operators is to apply them to the nuclei of a molecule in their equilibrium conformation. Our second use is to apply them to the electrons of the molecule or to an orbital function, leaving the nuclei fixed in their equilibrium positions. If a symmetry operator moves every nucleus to a location previously occupied by a nucleus of the same kind (same isotope of the same element) it belongs to the molecule. A symmetry operator that belongs to the molecule will not change the value of the potential energy when it is applied to the electrons with the nuclei fixed. It will bring every electron to a point in which it either is at the same distance from each nucleus as it was in its original position or is at the same distance from a different nucleus of the same kind. The operation of the inversion operator on the electron of an H_2^+ molecule ion is illustrated in Figure 18.6. This motion brings the electron to the same distance from nucleus A as it originally was from nucleus B and vice versa, and thus does not change the potential energy. Any symmetry operator that belongs to a molecule will not change the potential energy when it is applied to its electrons and will commute with the Born–Oppenheimer electronic Hamiltonian operator of that molecule.

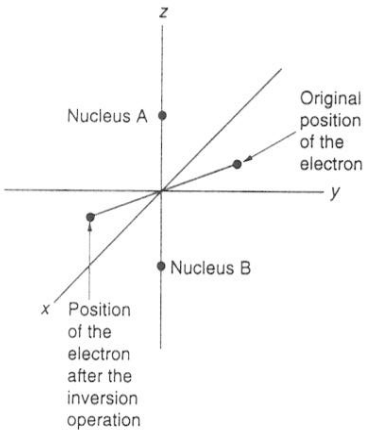

Figure 18.6 The Effect of the Symmetry Operator $\hat{i}$ on the electron of the H_2^+ Ion. This symmetry operator moves the electron so that its distance from nucleus B is the same as its original distance from nucleus A.

Exercise 18.4

Show that the symmetry operators $\hat{i}$, $\hat{\sigma}_h$, $\hat{C}_{nz}$, and $\hat{C}_{2a}$ belong to the H_2^+ molecule, where n is any positive integer and where a stands for any axis in the x–y plane. Show also that if these operators are applied to the electron position with fixed nuclei, the potential energy is unchanged.

A symmetry operator can operate on electronic wave functions as defined in Eq. (18.1-15), and electronic wave functions can be eigenfunctions of symmetry operators that commute with the electronic Hamiltonian operator. The ground-state electronic orbital of H_2^+ is an eigenfunction of each of the symmetry operators in Exercise 18.4, and each eigenvalue is equal to $+1$. The orbital of the first excited state is also an

eigenfunction of these operators, but the eigenvalues of $\hat{i}$, $\hat{\sigma}_h$, and $\hat{C}_{2a}$ are equal to -1. An eigenfunction having an eigenvalue of $\hat{i}$ equal to $+1$ is denoted by a subscript g (from the German *gerade*, meaning "even") and an eigenvalue of $\hat{i}$ equal to -1 is denoted by a subscript u (from the German *ungerade*, meaning "odd"). An eigenvalue of $\hat{\sigma}_h$ equal to -1 is denoted by an asterisk (*). Orbitals with asterisks are antibonding since they have a nodal plane through the origin perpendicular to the bond axis. No superscript or subscript is used to denote an eigenvalue of $\hat{\sigma}_h$ equal to $+1$, corresponding to a bonding orbital. The sigma orbitals are generally numbered from the lowest to the highest orbital energy, so the ground-state orbital of the hydrogen molecule ion is denoted by $\psi_{1\sigma_g}$ and the first excited state is denoted by $\psi_{2\sigma_u^*}$.

18.2 LCAO-MOs—Molecular Orbitals That Are Linear Combinations of Atomic Orbitals

The exact Born–Oppenheimer solutions to the Schrödinger equation for the hydrogen molecule ion are expressed in an unfamiliar coordinate system, and we did not explicitly display them. It will be convenient to have some easily expressed approximate molecular orbitals. We define **molecular orbitals that are linear combinations of atomic orbitals**, abbreviated LCAO-MO. If $f_1, f_2, f_3, \ldots$ are a set of functions, then g is called a **linear combination** of these functions if it equals a sum of these functions times constant coefficients:

$$g = c_1 f_1 + c_2 f_2 + c_3 f_3 + \cdots \tag{18.2-1}$$

We say that the function g is **expanded** in terms of the set of **basis functions** $f_1, f_2, \ldots$. The coefficients $c_1, c_2, \ldots$ are called **expansion coefficients**. If the linear combination can be an exact representation of an arbitrary function obeying the same boundary conditions as the basis set, the basis set is said to be a **complete set**. In Chapter 15 we introduced the assumption that the set of all eigenfunctions of a hermitian operator is a complete set for expansion of any function obeying the same boundary conditions as the eigenfunctions. We will not attempt to use a complete set of functions for our LCAO-MOs, but will begin with a basis set consisting of two atomic orbitals centered on two different nuclei.

LCAO-MOs for the First Two States of the H_2^+ Molecule Ion

We seek LCAO-MO representations for the $\psi_{1\sigma_g}$ and $\psi_{2\sigma_u^*}$ molecular orbitals. Let r_A be the distance from nucleus A to the electron, and let r_B be the distance from nucleus B to the electron. We take two hydrogenlike orbitals as our first basis set: one with r_A as its independent variable and one with r_B as its independent variable. We use the abbreviations:

$$\psi_{1sA} = \psi_{1s}(r_A) \tag{18.2-2a}$$

$$\psi_{1sB} = \psi_{1s}(r_B) \tag{18.2-2b}$$

The orbital ψ_{1sA} has its orbital region centered at location A and the orbital ψ_{1sB} has its orbital region centered at location B. We now form molecular orbitals that are linear combinations of the basis functions:

$$\psi_{MO} = c_A\psi_{1sA} + c_B\psi_{1sB} \tag{18.2-3}$$

The number of possible independent linear combinations is always equal to the number of independent basis functions. We have two basis functions so it is possible to make two independent linear combinations. We seek two molecular orbitals that are approximations to the ground state orbital and the first excited state orbital of the H_2^+ ion.

There are at least two ways to find the appropriate values of c_A and c_B for the ground state. One procedure is to regard ψ_{MO} as a variational trial function and to minimize the variational energy as a function of c_A and c_B. We do not present this calculation, but the result is that the variational energy is minimized when $c_A = c_B$. An approximation to the first excited state is obtained when the energy has its maximum value, and this corresponds to $c = -c_B$.[3] Another procedure is to choose values of c_A and c_B so that the approximate orbital is an eigenfunction of the same symmetry operators as the exact orbitals. The ground-state exact Born–Oppenheimer orbital is an eigenfunction of the inversion operator with eigenvalue $+1$. In order to obtain an LCAO-MO with this eigenvalue, we choose

$$c_A = c_B \tag{18.2-4}$$

Since the origin is midway between the two nuclei, inversion from any point leads to a point that is the same distance from nucleus B that the original point was from nucleus A and vice versa. If $c_A = c_B$ each term in the linear combination becomes equal to the original value of the other term, so that the molecular orbital is an eigenfunction of the inversion operator with eigenvalue 1 if $c_A = c_B$.

In order to obtain a molecular orbital with the same symmetry properties as the exact Born–Oppenheimer orbital of the first excited state, we must choose

$$c_A = -c_B \tag{18.2-5}$$

The symmetry properties are sufficiently fundamental that choosing the molecular orbitals to be their eigenfunctions leads to the same LCAO-MOs as the variation procedure. These LCAO-MOs are eigenfunctions of the other symmetry operators that belong to the H_2^+ molecule.

Exercise 18.5

a. Argue that $c_A = c_B$ leads to an eigenvalue of $+1$ for the $\hat{\sigma}_h$ operator and for the $\hat{C}_{2a}$ operator, where $\hat{C}_{2a}$ is a rotation operator whose symmetry element lies somewhere in the x–y plane.

b. Argue that $c_A = -c_B$ leads to an eigenvalue of -1 for the $\hat{\sigma}_h$ operator and for the $\hat{C}_{2a}$ operator.

We introduce the symbols for our two LCAO-MOs:

$$\psi_{\sigma_g 1s} = C_g[\psi_{1sA} + \psi_{1sB}] \tag{18.2-6}$$

$$\psi_{\sigma_u^* 1s} = C_u[\psi_{1sA} - \psi_{1sB}] \tag{18.2-7}$$

[3] J. C. Davis, Jr., *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, p. 404.

where the $1s$ subscripts indicate the atomic orbitals from which the LCAO-MOs were constructed. The value of the constants C_g and C_u can be chosen to normalize the molecular orbitals.

Figure 18.7 schematically shows the orbital regions for the $\sigma_g 1s$ *LCAO – MO* and the $\sigma_u^* 1s$ LCAO-MO, as well as the orbital regions for the $1s$ atomic orbitals. The intersection of the two atomic orbital regions is called the **overlap region**. This is the only region where both atomic orbitals differ significantly from zero. For the $\sigma_g 1s$ orbital the two atomic orbitals combine with the same sign in the overlap region, producing an orbital region characteristic of a bonding orbital with no nodal surfaces. For the $\sigma_u^* 1s$ orbital the atomic orbitals combine with opposite signs in the overlap region, canceling to produce a nodal surface between the nuclei, characteristic of an antibonding orbital. This addition and cancellation are similar to constructive and destructive interference of waves, but should not be interpreted as actual interference.

Figure 18.8 shows the electronic energy for each of these LCAO molecular orbitals along with the exact Born–Oppenheimer energies. The value of D_e for the $\sigma_g 1s$ orbital is equal to 1.76 eV, with a value of R_e equal to 1.32×10^{-10} m. As we expect from the variational theorem, the approximate energies lie above the exact energies for all values of R. The energies can be improved by "scaling" the atomic orbitals: that is, by replacing the atomic number Z in the orbital exponent by a variable parameter.

LCAO-MOs can be constructed that are linear combinations of more than two atomic orbitals. For example, for the ground state of the hydrogen molecule ion, we could write

$$\begin{aligned}\psi_{MO} = {} & c_{1sA}\psi_{1sA} + c_{1sB}\psi_{1sB} + c_{2sA}\psi_{2sA} \\ & + c_{2sB}\psi_{2sB} + c_{2p_zA}\psi_{2p_zA} + c_{2p_zB}\psi_{2p_zB}\end{aligned} \tag{18.2-8}$$

When the variational energy is minimized with respect to the c coefficients, a better (lower) value is obtained than with the $\sigma_g 1s$ orbital. However, we will use linear combinations of only two atomic orbitals as much as possible, since we will content ourselves with qualitative description rather than quantitative calculation. The $2p_x$ and $2p_y$ atomic orbitals are not included in Eq. (18.2-8) because they have different

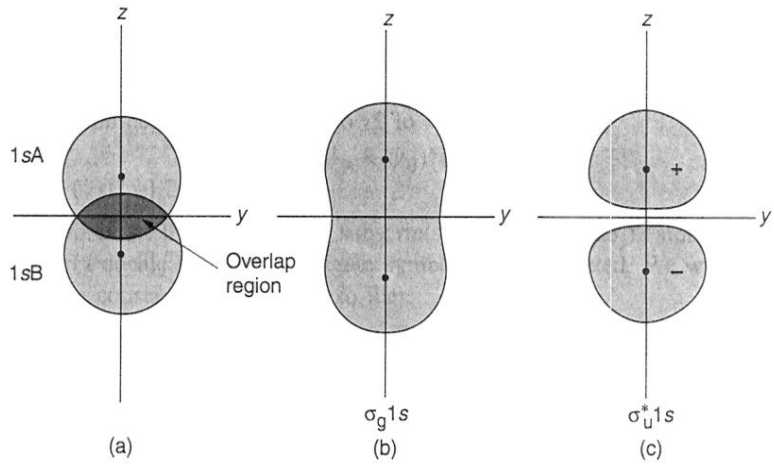

Figure 18.7 The Orbital Region for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. (a) The overlapping orbital regions of the $1s$A and $1s$B atomic orbitals. (b) The orbital region of the $\sigma_g 1s$ LCAO-MO. (c) The orbital Region of the $\sigma_u^* 1s$ LCAO-MO. The orbital regions of the LCAO molecular orbitals have the same general features as the "exact" Born Oppenheimer orbitals whose orbital regions were depicted in Figure 18.4.

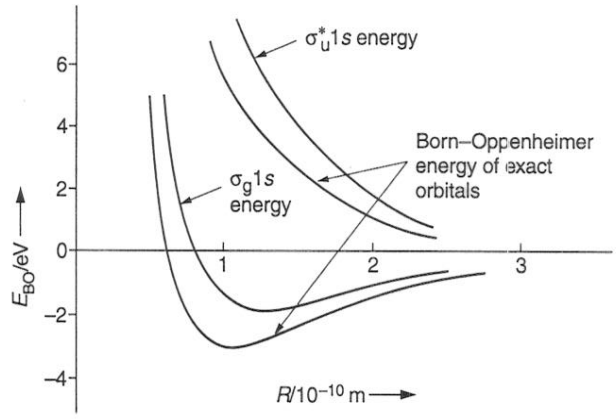

Figure 18.8 The Orbital Energies for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. This diagram shows qualitatively how the Born–Oppenheimer energies of the LCAO molecular orbitals compare with the Born Oppenheimer energies of the "exact" orbitals. The approximate orbital energies must lie above the corresponding exact energies for all internuclear distances.

symmetry about the bond axis than does the exact ground-state orbital. If they were included with nonzero coefficients, the LCAO-MO would not be an eigenfunction of the same symmetry operators as the exact orbitals.

Exercise 18.6

Argue that the $2p_x$ and $2p_y$ atomic orbitals are eigenfunctions of the $\hat{C}_{2z}$ operator with eigenvalue -1, while the $2p_z$ orbital is an eigenfunction with eigenvalue $+1$. Argue that a linear combination of all three of these orbitals is not an eigenfunction of the $\hat{C}_{2z}$ operator.

LCAO-MOs for Additional Excited States of H_2^+

The wave functions for additional excited states of H_2^+ are approximated by LCAO-MOs using higher-energy hydrogenlike orbitals. For example, two linear combinations of $2s$ orbitals that are eigenfunctions of the appropriate symmetry operators are

$$\psi_{\sigma_g 2s} = C_g[\psi_{2s}(r_A) + \psi_{2s}(r_B)] = C_g[\psi_{2sA} + \psi_{2sB}] \tag{18.2-9}$$

$$\psi_{\sigma_u^* 2s} = C_u[\psi_{2s}(r_A) - \psi_{2s}(r_B)] = C_u[\psi_{2sA} - \psi_{2sB}] \tag{18.2-10}$$

The $\sigma_g 2s$ orbital is a bonding orbital, and the $\sigma_u^* 2s$ orbital is an antibonding orbital. The $\sigma_g 2s$ orbital energy is higher than that of the $\sigma_u^* 1s$ antibonding orbital since the molecule dissociates from the $\sigma_g 2s$ state to a hydrogen nucleus and a hydrogen atom in the $2s$ state, as shown schematically in Figure 18.9.

Exercise 18.7

Draw sketches of the orbital regions for the functions in Eq. (18.2-9) and (18.2-10). Argue that the designations σ_g and σ_u^* are correct.

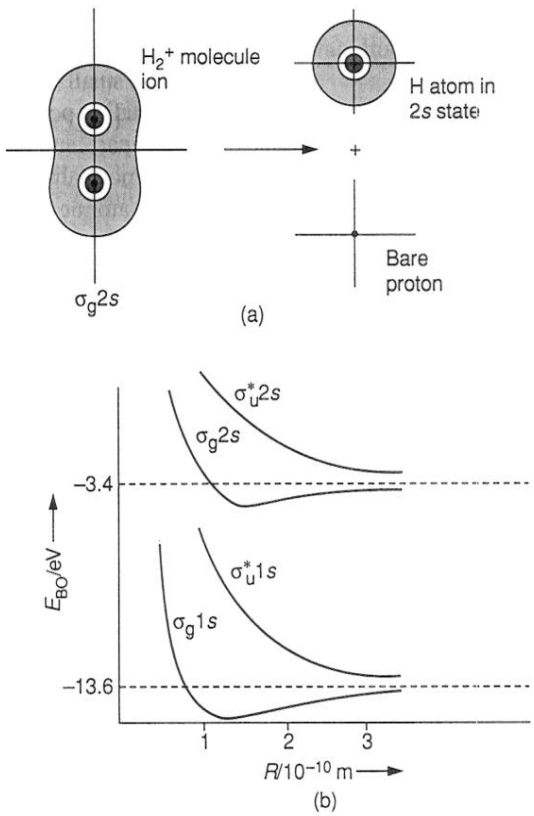

Figure 18.9 Dissociation of a Hydrogen Molecule Ion in the $\sigma_g 1s$ and $\sigma_g 2s$ States. (a) The orbital regions before and after dissociation. (b) The energy levels of the LCAO molecular orbitals as a function of internuclear distance. If a molecule in the $\sigma_g 2s$ state dissociates, an atom in a $2s$ state and a bare nucleus result. A molecule in the $\sigma_g 1s$ state dissociates to form an atom in the $1s$ state and a bare nucleus.

Normalization of the LCAO-MOs

To normalize the $\sigma_g 1s$ orbital we write

$$1 = |C_g|^2 \int (\psi_A + \psi_B)^* (\psi_A + \psi_B)\, d^3\mathbf{r} \tag{18.2-11}$$

where we abbreviate the $1s$A and $1s$B subscripts by A and B. The $1s$ atomic orbitals are real functions, so the complex conjugate symbol can be omitted. We will choose the normalization constant C_g to be real so that

$$1 = C_g^2 \int (\psi_A^2 + 2\psi_A\psi_B + \psi_B^2)\, d^3\mathbf{r} \tag{18.2-12}$$

The atomic orbitals ψ_A and ψ_B are normalized, so that the first term and the last term in the integral will each yield unity when the integration is done. The second term gives an integral that is denoted by S:

$$\int \psi_A \psi_B\, d^3\mathbf{r} = S \tag{18.2-13}$$

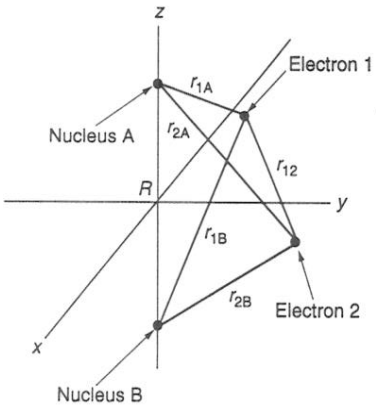

Figure 18.10 The Hydrogen Molecule System. This system is analogous to the helium in having two electrons. Our treatment of it is similar to the treatment of the helium atom, except for using molecular orbitals instead of atomic orbitals.

The integral S is called the **overlap integral** because the major contribution to its integrand comes from the overlap region. In other regions at least one of the factors in the integrand is small. Since the $1s$ orbitals are positive everywhere the overlap integral for two $1s$ orbitals is positive. Its value depends on R, approaching zero if the two nuclei are very far apart and approaching unity when R approaches zero since it then approaches a normalization integral. Similar overlap integrals can be defined for other pairs of atomic orbitals, and it is convenient to attach two subscripts to the symbol S to indicate which two orbitals are involved. The overlap integral in Eq. (18.2-13) would be denoted as $S_{1s,1s}$. For any normalized atomic orbitals, the values of overlap integrals must lie between -1 and $+1$, and approach zero as R is made large. If we had an overlap integral between a $1s$ and a $2p_z$ orbital on different nuclei, it would approach zero as the nuclei approach each other, because it would approach an othogonality integral instead of a normalization integral.

We now have

$$1 = C_g^2(1 + 2S + 1) \tag{18.2-14}$$

so that the normalized LCAO-MO is

$$\psi_{\sigma_g 1s} = \frac{1}{\sqrt{2 + 2S}}(\psi_A + \psi_B) \tag{18.2-15}$$

Exercise 18.8

Show that the normalization constant for the $\sigma_u^* 1s$ LCAO-MO is

$$C_u = \frac{1}{\sqrt{2 - 2S}} \tag{18.2-16}$$

18.3 Homonuclear Diatomic Molecules

Homonuclear diatomic molecules have two nuclei of the same kind. We discuss the homonuclear diatomic molecules of the first and second rows of the periodic table, and will base our discussion on the H_2^+ molecular orbitals in much the same way as we based our discussion of multielectron atoms on the hydrogen atom atomic orbitals in Chapters 16 and 17.

The Hydrogen Molecule

Figure 18.10 shows the hydrogen molecule, consisting of two nuclei at locations A and B and two electrons at locations 1 and 2. With its two electrons the hydrogen molecule bears the same relationship to the hydrogen molecule ion that the helium atom does to the hydrogen atom, and our treatment of it resembles that of the helium atom. We apply the Born–Oppenheimer approximation, assuming the nuclei to be fixed on the z axis