

Electronic States of Molecules

8.1 The Born-Oppenheimer approximation

Consider a molecule with M nuclei and N electrons. In Section 6.1.2 we discussed how to write the expression for the total Coulomb potential energy, V . The Hamiltonian for the molecule is (in a.u.)

$$\hat{H} = \hat{T}_n + \hat{T}_e + V \quad \text{Molecular Hamiltonian} \quad \text{eq 8.1}$$

where

$$\hat{T}_n = \sum_a \hat{T}_a \quad \text{with } \hat{T}_a = -\frac{1}{2m_a} \nabla_a^2 \quad \text{eq 8.2}$$

is the contribution to the kinetic energy by the M nuclei, and

$$\hat{T}_e = \sum_{j=1}^N \hat{T}_j \quad \text{with } \hat{T}_j = -\frac{1}{2} \nabla_j^2 \quad \text{eq 8.3}$$

is the kinetic energy operator of the N electrons. The Hamiltonian obtained from the molecular Hamiltonian of eq 8.1 by omitting the nuclear kinetic energy term is called the electronic Hamiltonian:

$$\hat{H}_e = \hat{T}_e + V \quad \text{Electronic Hamiltonian} \quad \text{eq 8.4}$$

The molecular Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad \text{eq 8.5}$$

is universally solved within the Born-Oppenheimer (BO) approximation. One starts by assuming that the total wavefunction Ψ can be written as the product of an electronic and a nuclear wavefunction

$$\Psi(r,R) = \Psi_e(r) \Psi_n(R) \quad \text{eq 8.6}$$

where r and R , collectively, denote the $3N$ variables of the electrons and $3M$ variables for the nuclei, respectively.

8.1.1 The electronic Schrödinger equation

In the recipe for the BO approximation (eq 8.6), the electronic energy E_e (and the associated Ψ_e) must be determined first. They are obtained by solving the “electronic” Schrödinger equation:

$$\hat{H}_e \Psi_e = E_e \Psi_e \quad \text{eq 8.7}$$

The electronic Hamiltonian \hat{H}_e describes the dynamical motion of N electrons in the electrostatic field of M nuclei whose positions are fixed in space. This field depends on the geometric arrangement of the atomic nuclei in 3D space, i.e. the molecular “geometry” (also called, “shape” of the molecule). As a result, solutions of eq 8.7 depend on the particular geometry adopted for the

nuclei in V (and, therefore, in \hat{H}_e). Consequently, the electronic energies and the associated wavefunctions implicitly depend on the shape of the molecule. It is a “parametric” dependence in the sense that we specify a certain geometry R for the molecule, and then solve eq 8.7 for this geometry. We will designate this type of dependence of E_e and Ψ_e on R by the notation $E_e(R)$ and $\Psi_e(r; R)$, respectively.

The geometry of a diatomic molecule, AB, ($M=2$) is determined by just one nuclear variable R ; namely, the distance between the two atoms A and B. In polyatomic molecules where $M \geq 3$, one needs to assign values to $3M-6$ independent (nuclear) variables. For example, in the H_2O molecule, $M=3$ and hence $3M-6=3$. The three variables are usually taken as the two OH bond lengths and the angle between the two bonds.

For a given molecule, the electronic Schrödinger equation must be (numerically) solved for many different geometries of the molecule for the purpose of obtaining $E_e(R)$ as a function of R . Graph of $E_e(R)$ against R is called the electronic “potential energy surface” (PES). Determination of the electronic energy as a function of molecular geometry, i.e. the PES, is needed for the second step in the BO approximation, i.e. for finding the nuclear wavefunctions, $\Psi_n(R)$, of eq 8.6, as will be discussed below. For a diatomic molecule, the PES is a curve. Figure 8.1 shows the typical variation of $E_e(R)$ with the internuclear distance R for the ground electronic state of a diatomic molecule AB.

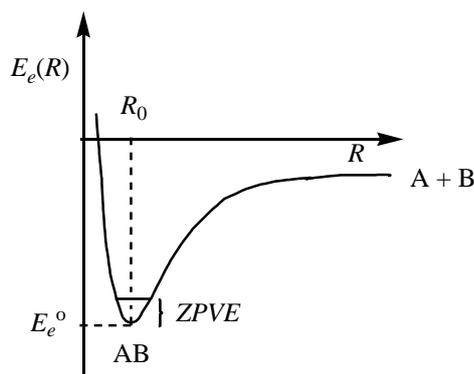


Figure 8.1 Electronic energy as a function of bond length R for a diatomic molecule AB in its ground electronic state.

The geometry R_0 at the minimum of the PES is called the “equilibrium geometry” of the molecule. For a diatomic molecule, R_0 is simply the equilibrium bond length. The electronic energy of the molecule at its equilibrium geometry is

$$E_e^0 = E_e(R_0) \quad \text{The electronic energy} \quad \text{eq 8.8}$$

As with any Schrödinger equation, eq 8.7 has infinitely many solutions. Thus there are many excited PESs besides the ground electronic PES. The ground PES of a stable molecule always has at least one minimum. Excited electronic states may or may not have a minimum in their PESs.

8.1.2 The Schrödinger equation for the nuclei

In the second step of the BO procedure, the function $\Psi_n(R)$ of eq 8.6 is determined by solving the following Schrödinger equation for the motion of the nuclei

$$[\hat{T}_n + E_e(R)]\Psi_n(R) = E\Psi_n(R) \quad \text{eq 8.9}$$

where the electronic PES, determined as described above, plays the role of the potential energy function. Note that E is the total energy of the molecule. Defining the vibrational potential energy function,

$$U(R) = E_e(R) - E_e^o \quad \text{eq 8.10}$$

eq 8.9 may be rewritten in the form

$$[\hat{T}_n + U(R)]\Psi_n(R) = E_n\Psi_n(R) \quad \text{eq 8.11}$$

where $E_n = E - E_e^o$ is the energy associated with the motion of the nuclei alone. The kinetic energy term \hat{T}_n is a function of $3M$ independent variables whereas the vibrational potential $U(R)$ depends only on $3M-6$ ($3M-5$ for linear molecules) variables. It can be shown that by an appropriate choice of the $3M$ independent variables, Ψ_n of eq 8.11 is (approximately) factorized: $\Psi_n = \psi_t\psi_r\psi_v$, where the three factors are the translational, rotational, and vibrational wavefunctions, respectively.

Substitution of this product function into eq 8.11 gives a Schrödinger equation for ψ_t and associated translational energy E_t , another equation for ψ_r and the rotational energy E_r , and finally a third equation for ψ_v and the vibrational energy E_v . The total energy of the nuclear motion is

$$E_n = E_t + E_r + E_v \quad \text{eq 8.12}$$

Combining these with the contribution from the electronic motion, the final result of the Born-Oppenheimer approximation for the solution of the molecular Schrödinger equation (eq 8.5) is

$$\Psi(r, R) = \psi_t\psi_r\psi_v\Psi_e^o \quad \text{where} \quad \Psi_e^o = \Psi_e(r; R_0) \quad \text{eq 8.13}$$

$$E = E_t + E_r + E_v + E_e^o \quad \text{BO approximation} \quad \text{eq 8.14}$$

The Born-Oppenheimer approximation is basic to all quantum chemical calculations. It allows the extremely complicated 3D motions of electrons and nuclei in a molecule to be analyzed in terms of independent contributions from the translational, rotational, vibrational, and electronic motions.

The translational motion of the molecule is that of a free particle with mass, $m=m_{molecule}$ moving in a 3D macroscopic box (e.g. a test tube); its variables are the three center of mass coordinates of the nuclei in the molecule. Particle-in-a-box problem was discussed in Lecture Notes 3. Since box size is large, the allowed translational energies of the molecule are continuous, ranging from 0 to ∞ . In most applications, the translational energy is not involved, and it may be omitted from the total energy.

The allowed rotational and vibrational energies of a diatomic molecule were discussed in Lecture Notes 4 and 5. Description of rigid rotation in 3D of a linear molecule about the *c.m.* involves two independent angle variables, θ and ϕ . For a nonlinear molecule, one more angle variable, usually

denoted by χ , is required. The remaining independent variables, $3M-6$ for nonlinear molecules and $3M-5$ for linear ones, describe the vibrational motion of the molecule. It can be shown that in the harmonic approximation for $U(R)$, a nonlinear molecule has $3M-6$ vibrational frequencies whereas for a linear molecule this number is $3M-5$.¹ The zero-point vibrational energy (ZPVE) of a molecule is its lowest vibrational energy level (Figure 8.1), and is given by

$$ZPVE = \frac{h}{2} \sum_j \nu_j \quad \text{eq 8.15}$$

where the sum is over the $3M-6$ or $3M-5$ vibrational frequencies, depending on whether the molecule is nonlinear or linear, respectively. The lowest possible value for the total energy of the molecule follows from eq 8.14 as

$$E_{ground} = E_e^0 + ZPVE \quad \text{eq 8.16}$$

In the remainder of this course, we will discuss methods for solving the electronic Schrödinger equation (eq 8.7) for a given geometry of the molecule.

Exercise 8.1 Find the number of vibrational frequencies in the following molecules: i) Benzene, ii) Ammonia, iii) Acetylene.

Exercise 8.2 The vibrational frequencies of the water molecule are (in cm^{-1}): 3657, 1595, and 3756. Calculate ZPVE in kJ/mol. *Ans.* 53.9 kJ/mol.

8.2 Electronic states of the hydrogen molecule

The H_2 molecule is the simplest (neutral) molecule. It has $N=2$ electrons. Figure 8.2 shows the interparticle distances involved. The electronic Hamiltonian (in a.u.), describing the motion of two electrons in the field of two protons separated by a distance R , is

$$\hat{H}_e = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} + \frac{1}{R} \quad \text{eq 8.17}$$

¹ It is possible in some molecules that several vibrational frequencies have the same numerical value. Such frequencies are said to be “degenerate”.

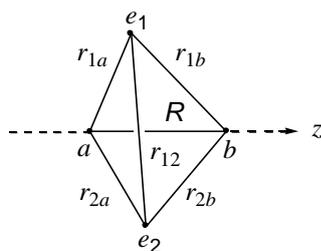


Figure 8.2 Interparticle distances in the H₂ molecule for a given bond length R . The two protons a and b are fixed in space; only the electrons are moving.

Solutions of the electronic Schrödinger equation (eq 8.7) with this hamiltonian have the following properties.

- i) As in the He atom, the total spin quantum number S has only two allowed values: 0 and 1. Thus the multiplicities of the electronic states of H₂ are either singlet or triplet. Energies of singlet and triplet states are different.
- ii) The \hat{L}^2 operator does not commute with the Hamiltonian of eq 8.17; and as a consequence, the angular momentum quantum number L is not useful in molecules. On the other hand, it can be shown that the component of the angular momentum vector along the molecular axis (see Figure 8.2), \hat{L}_z , commutes with the electronic Hamiltonian of a linear molecule. This means that the electronic wavefunctions of a linear molecule may be chosen to be eigenfunctions of \hat{L}_z with eigenvalues $M=0, \pm 1, \pm 2, \dots$. The corresponding energies depend only on the absolute value of M so that all states with $M \neq 0$ are doubly degenerate.² The absolute value of M is denoted by $\Lambda \equiv |M|$, and a capital letter code is assigned to it (Table 8.1).

Table 8.1 Symbols for many-electron states in linear molecules.

Λ	0	1	2	3	4
Letter	Σ	Π	Δ	Φ	Γ

Electronic states of linear molecules are designated by “molecular term symbols”: $^{2S+1}\Lambda$. For example, the electronic states of H₂ have the term symbols $^1\Sigma, ^1\Pi, \dots$ for singlet states, and $^3\Sigma, ^3\Pi, \dots$ for triplets.

- iii) The electronic wavefunctions of a molecule must obey the Pauli principle; i.e. they must be antisymmetric in the exchange of two electrons.

² This is a spatial degeneracy. If $S \neq 0$, there will also be spin degeneracy.

8.2.1 The orbital approximation in molecules: Molecular Orbitals

Since $N=2$ in the H_2 molecule, the wavefunction is factorized as in the He atom:

$$\Psi(1,2) = \Psi_{space}(1,2) \Psi_{spin}(1,2) \quad \text{eq 8.18}$$

The two-electron spin functions here are the same as in Table 7.5 for He. For singlet states, the two-electron spin function is antisymmetric in spin exchange and must be combined with a symmetric spatial function in eq 8.18. On the other hand, in triplet states $\Psi_{space}(1,2)$ must be antisymmetric in electron exchange because the spin functions are symmetric. We need to devise approximate expressions for Ψ_{space} with these and other properties summarized above.

The V_{nn} term, $1/R$, in eq 8.17 is a constant since R has a predefined value in the Born-Oppenheimer procedure. Its contribution to the electronic energy may be included afterwards. The troublesome term in eq 8.17 is the electronic interaction term, $1/r_{12}$, as in the He atom. Dropping these two terms from eq 8.17, one obtains the “molecular core” Hamiltonian of H_2 :

$$\hat{H}_{core} = \hat{h}(1) + \hat{h}(2) \quad \text{eq 8.19}$$

where the molecular one-electron Hamiltonian \hat{h} is

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \quad \text{eq 8.20}$$

Here, r_a and r_b may be either (r_{1a}, r_{1b}) or (r_{2a}, r_{2b}) in Figure 8.2 since the two electrons are indistinguishable. The solutions, ψ , of the Schrödinger equation with \hat{h} as the hamiltonian are called the molecular orbitals (MO) of H_2 in the “core hamiltonian” approximation. They are classified according to the eigenvalues $m=0, \pm 1, \pm 2, \dots$ of the one-electron \hat{l}_z operator. The MOs of a linear molecule are labeled by lowercase letters depending on $\lambda \equiv |m|$, similar to that in Table 8.1 for the many-electron case where capital letters are employed.

Table 8.2 Symbols for MO types in a linear molecule.

λ	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

Energies of MOs depend on $|m|$, i.e. λ . MOs of σ type are nondegenerate, and they are real functions. All other types π , δ , etc. are doubly degenerate, i.e. there are two MOs with same energy. The two degenerate MOs are designated by attaching $\pm m$ as a subscript to the λ symbol. For example, π_1 and π_{-1} for π type MOs; δ_2 and δ_{-2} for δ type MOs, and so on. Degenerate MOs shown by this notation are complex functions. As in the atomic orbitals, in place of a pair of degenerate complex MOs we are allowed to use a pair of real MOs. As an example, instead of the degenerate pair π_1 and π_{-1} we may use the two real MOs denoted by π_x and π_y .

Nodal planes. If an MO has zero value at all points in a plane, the plane is called a nodal plane of this MO. The nodal planes of main interest in linear molecules are those that contain all points of the molecular axis, i.e. the entire z-axis in Figure 8.2. The importance of such nodal planes arises from the following simple rule: When real MOs are employed, the number of nodal planes for a given type

of MO is equal to λ . Thus, σ MOs have no nodal planes, π MOs have 1, δ MOs have 2 nodal planes, etc.

8.2.2 Molecular Orbitals as Linear Combination of Atomic Orbitals (LCAO)

The one-electron Hamiltonian in eq 8.20 describes the motion of the electron in an H_2^+ molecule ion (Figure 8.3).

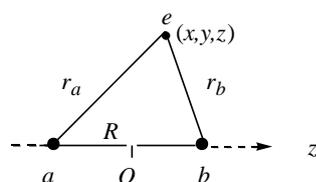


Figure 8.3 Interparticle distances in H_2^+ . The point O is the midpoint between the two nuclei.

Due to the presence of two nuclear force centers, there is no simple analytical solution of the Schrödinger equation for the molecular orbitals.

$$\hat{h}\psi = \epsilon\psi \quad \text{MO equation} \quad \text{eq 8.21}$$

We must resort to approximation methods even though this is a one-electron problem. The standard procedure is to express the MOs in terms of AOs centered on each nucleus in the molecule.

As an example of this procedure, let us consider the problem of finding the MO that has the lowest energy. In the simplest approximation, this MO is expressed as

$$\psi = c_1 1s_a + c_2 1s_b \quad \text{eq 8.22}$$

where c_1 and c_2 are constants to be determined, and the subscripts a and b indicate the nucleus on which a $1s$ AO is centered (Figure 8.4). Such an expression for an MO in terms of AOs centered on various nuclei is called "linear combination of atomic orbitals" (LCAO).

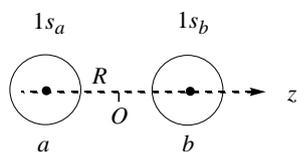


Figure 8.4 Two identical $1s$ AOs, one centered on nucleus a and the other on nucleus b .

The coefficients in LCAO expressions for MOs are found by the variation method (eq 7.3a). The calculations can be simplified by noting "symmetry properties" of the potential energy function, V . In a homonuclear diatomic molecule $Z_a = Z_b$, and this fact leads to an important symmetry property. Consider a Cartesian coordinate system with origin at point O in Figure 8.3. Now compare the value of $V = -1/r_a - 1/r_b$ when the electron is at a point $P(x, y, z)$ with that at the "inverted" point $P'(-x, -y, -z)$

(Figure 8.5). You see that V has the same value at the two points. We say that V is invariant under the inversion operation. The kinetic energy term in the Hamiltonian is always invariant under such geometric transformations. Thus when V is invariant under a symmetry operation, the Hamiltonian is also invariant. The point O through which the inversion operation is carried out is called the “inversion center” or “center of symmetry”. It is at the geometrical center of the two nuclei in a homonuclear diatomic molecule.

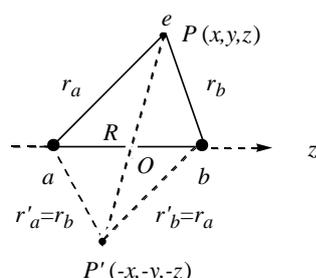


Figure 8.5 Inversion of coordinates of the electron through the inversion center O .

For the purpose of analyzing the consequences of inversion symmetry, we introduce the inversion operator \hat{i} . Its action on an arbitrary function $f(x, y, z)$ is defined as, $\hat{i}f(x, y, z) = f(-x, -y, -z)$. One has $\hat{i}^2 = 1$, the identity operator, and therefore \hat{i} has only two eigenvalues: +1 and -1. Since \hat{i} commutes with the electronic Hamiltonian of any homonuclear diatomic molecule, solutions ψ of the associated Schrödinger equation must be eigenfunctions of the inversion operator. Wavefunctions with eigenvalue +1 are said to have “gerade” symmetry, and labeled by subscript “g”. Similarly, the functions with eigenvalue -1 are labeled by subscript “u” (meaning “ungerade”).³

Returning to eq 8.22, let us note that $\hat{i}(1s_a) = 1s_b$ and $\hat{i}(1s_b) = 1s_a$ (see Figure 8.4). It follows that $c_2 = c_1$ for gerade symmetry, and $c_2 = -c_1$ for ungerade symmetry. Further, it is seen from Figure 8.4 that the 1s AOs have no nodal plane containing the molecular axis. Thus both ψ are of σ type (i.e. $\lambda = 0$). Renaming the MOs of eq 8.22 as 1σ , we have

$$1\sigma_g = c_1(1s_a + 1s_b) \quad \text{eq 8.23}$$

$$1\sigma_u^* = c_1(1s_a - 1s_b) \quad \text{eq 8.24}$$

where c_1 is a normalization constant. The two MOs are real functions. The relative energies of these MOs must be found by evaluating the variational integral, $\epsilon(R) = \int \psi \hat{h} \psi d\tau_{electron}$, with each one of the functions above. Value of this integral depends on the internuclear separation. At very large values of R , ϵ is the same for both functions, equal to the 1s AO energy. For R near the equilibrium bond length it is found that ϵ for the $1\sigma_g$ MO is lower than the 1s AO energy, and ϵ for $1\sigma_u^*$ is higher than that of 1s. Figure 8.6 depicts a qualitative energy level diagram summarizing these computational results.

³ In discussions of electronic states in atoms, the inversion operator here is called the “parity” operator. The eigenvalues +1 and -1 are then referred to as the “even parity” and “odd parity”, respectively.

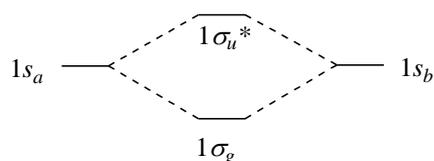


Figure 8.6 Relative energies of diatomic MOs formed from the 1s AOs.

The lower energy $1\sigma_g$ is a bonding MO whereas the $1\sigma_u^*$ is antibonding since the energy of the latter increases as R approaches the equilibrium bond length, while that of the former decreases. It is conventional to mark antibonding MOs by a star. Figure 8.7 shows simplified graphs of these MOs. We have multiplied the 1s AOs in Figure 8.4 by relative values of their coefficients (i.e. $c_2/c_1 = \pm 1$), and redrawn them in Figure 8.7. We next “visualize” the results of arithmetical addition or subtraction in eqs 8.22-23 by looking at Figure 8.7. It is seen that the xy -plane passing through the middle of the molecule is a nodal plane⁴ for the antibonding $1\sigma_u^*$ MO while the bonding $1\sigma_g$ is nonzero at all points between the nuclei. The electron charge density at a point in 3D space is proportional to ψ^2 . At points between the two nuclear centers, the charge density of $1\sigma_g$ is clearly larger than that of $1\sigma_u^*$ since the latter becomes very small near the midpoint. This observation is consistent with the lower energy of $1\sigma_g$ because we expect that there should be a buildup of electronic charge density between the nuclei in order to keep them together, i.e. for a chemical bond to form.

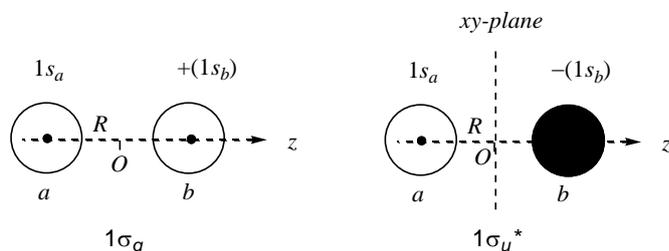


Figure 8.7 Simplified representation of the bonding and antibonding MOs formed from the 1s AOs. Relative signs of the AOs in the two MOs are indicated by shading.

Exercise 8.3 Is there a center of symmetry in: i) LiH, ii) O_2^+ molecules?

8.2.3 Low-lying electronic states of H_2

An approximate function for eq 8.18, expected to give the lowest electronic energy in H_2 , is $\Psi_{space}(1,2) = 1\sigma_g(1) 1\sigma_g(2)$, denoted by the MO electron configuration $(1\sigma_g)^2$. Being symmetric in electron exchange, this spatial function can only be combined with a singlet spin function ($S=0$). Thus

⁴ Note that such a nodal plane that passes through the molecular axis at only one point should not be counted in the exploration of the σ , π , etc. types of the MOs.

the ground electronic state of H_2 should be a singlet; its term symbol is $^1\Sigma_g$, where the subscript g is added to indicate that it does not change sign under (simultaneous) inversion of coordinates of the two electrons.

For the lowest excited states, the natural choice of MOs is $1\sigma_g 1\sigma_u^*$. This configuration can yield both a singlet and a triplet wavefunction since the two MOs are different. The parity of Ψ_{space} is $g\chi u = u$ for both spin states. The triplet wavefunction $^3\Sigma_u$ is expected to have a lower energy than the singlet, $^1\Sigma_u$, assuming Hund's rule is applicable to the molecules.

These theoretical predictions about the first three electronic states of H_2 are confirmed by experimental observations. The ground state is $^1\Sigma_g$, followed by $^3\Sigma_u$ and then $^1\Sigma_u$ (in increasing order of energy).

8.3 Homonuclear diatomic molecules of Period 2 atoms

In studying the electronic states of any molecule, we always start with the ground state first, and then consider a few excited states. Due to Pauli principle, even for the ground electronic state we need at least $N/2$ MOs where N is the total number of electrons in the molecule. For the neutral diatomic molecules Li_2, Be_2, \dots, F_2 , composed of atoms in second period, N ranges from 6 to 18 so that for the F_2 molecule, at least 9 MOs are required for just the ground electronic state, and more are needed for excited states. We will now give a qualitative discussion of the LCAO MOs that can be constructed from the 2s and 2p atomic orbitals centered on each nucleus.

We need a systematic nomenclature for the MOs. We know that the exact MOs are classified according to their λ values as σ, π , etc., and also by "g" and "u" subscripts depending on their parities. We will use the following symbols in numbering the MOs by an integer n in increasing order of their energies:

$$n\lambda_p \quad \text{where } n=1, 2, \dots \quad \lambda = \sigma, \pi, \dots \quad \text{and } p=g \text{ or } u \quad \text{eq 8.25}$$

Note that MOs of each symmetry type (i.e. a given λ and p) are numbered separately. E.g. MOs of σ_g type are numbered as $1\sigma_g, 2\sigma_g, \dots$; those of σ_u type as $1\sigma_u, 2\sigma_u, \dots$; and similarly for the π_g and π_u type MOs. We have already used this notation for the first two MOs in the H_2 molecule (eqs 8.23-24).

The approximate forms of the $2\sigma_g$ and $2\sigma_u^*$ MOs are similar to those in eqs 8.23-24 except that the 1s AOs are replaced by the 2s AOs:

$$2\sigma_g = c_1(2s_a + 2s_b) \quad \text{eq 8.26}$$

$$2\sigma_u^* = c_1(2s_a - 2s_b) \quad \text{eq 8.27}$$

Simplified graphs of these MOs are similar to those in Figure 8.7, and their energies are near the 2s AO energy, just like the energies of the $1\sigma_g$ and $1\sigma_u^*$ MOs are nearby the 1s AO energy (Figure 8.6).

We next consider MOs containing 2p AOs. There are three 2p AOs for each atom in the molecule, the total number on both centers being six. Hence we must construct six MOs. Since AOs other than the s

type have directional properties, they must be appropriately defined before they are used. We will employ the definitions shown in Figure 8.8. It should be noted from the figure that the two $2p_z$ AOs lying along the molecular axis have no nodal plane containing the (entire) z -axis. Thus they can contribute to only σ type MOs in LCAO expressions, just like the $1s$ and $2s$ AOs above. On the other hand, the $2p_x$ and $2p_y$ AOs have one nodal plane (the yz - and xz -planes, respectively). Hence, they will form π type MOs.

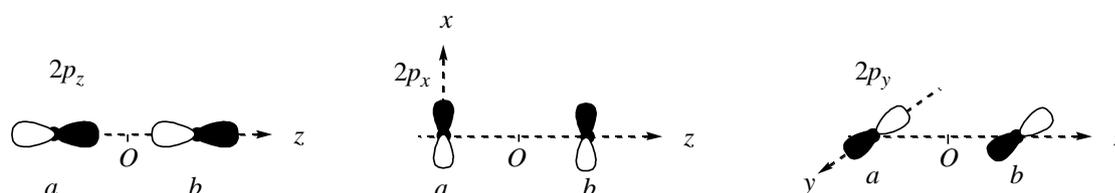


Figure 8.8 Definitions of $2p_z$, $2p_x$, and $2p_y$ AOs centered on nuclei a and b . The two centers are separated by a distance R .

Let us note that all three $2p$ AOs centered on either nucleus have the same property under inversion through the center of symmetry O .

$$i(2p_q)_a = -(2p_q)_b, \quad q = x, y, z \quad \text{eq 8.28}$$

Using this property, you should convince yourself that σ type MOs formed from the two $2p_z$ AOs have the expressions:

$$3\sigma_g = c_1[(2p_z)_a - (2p_z)_b] \quad \text{eq 8.29}$$

$$3\sigma_u^* = c_1[(2p_z)_a + (2p_z)_b] \quad \text{eq 8.30}$$

Simplified graphs of these MOs are depicted in Figure 8.9.

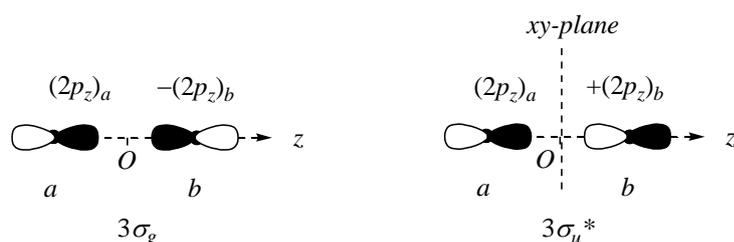


Figure 8.9 MOs formed from the $2p_z$ AOs centered on the two nuclei. The MO on the right has a nodal plane passing through O .

The relative energies of these MOs can be guessed by comparing the relative charge densities of the two MOs in the region between the nuclei. For the same reasons as in the case of the $1\sigma_g$ and $1\sigma_u^*$ MOs (Figure 8.7), we expect the MO energy of $3\sigma_g$ to be lower than that of $3\sigma_u^*$. This anticipation is verified by actual calculations.

The π type MOs from the $2p$ AOs are shown in Figure 8.10. In contrast to σ type MOs that concentrate the charge density at points near the molecular axis between the two nuclei, charge densities of π orbitals are concentrated above and below the nodal plane (yz -plane for $1\pi(x)$ and xz -plane for $1\pi(y)$ in Figure 8.10). We know from general principles discussed above that π type MOs are doubly degenerate. Thus the x and y components of $1\pi_u$ MOs have the same energy; same is true for $1\pi_g^*$. Relative energy of $1\pi_u$ is lower than that of $1\pi_g^*$ because the former MO places higher electron density between the two nuclei than the latter.

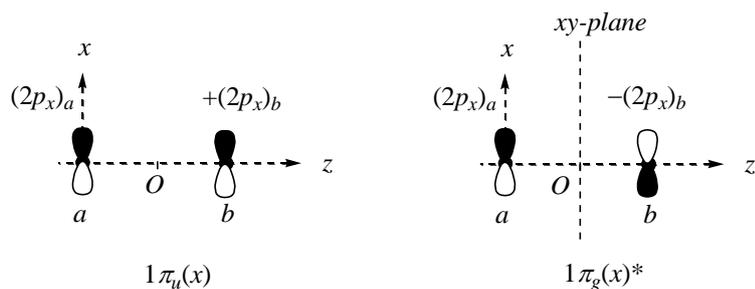


Figure 8.10 MOs formed from $2p_x$ AOs centered on the two nuclei. MOs from $2p_y$ AOs are obtained by rotating these MOs around the z -axis by 90° .

The 6 MOs formed from $2p$ AOs have 4 different energies. These MO energies are all nearby the atomic $2p$ energy, and above the $2s$ energy. The charge density argument works in deciding which MO of a related pair such as $1\pi_u$ and $1\pi_g^*$ has a lower energy, but it does not help us in finding the relative energies of e.g. $3\sigma_g$ and $1\pi_u$. Calculations must be done to determine the correct order. Results are graphically shown in Figure 8.11.

Exercise 8.4 Classify the five real d type AOs centered on the two nuclei according to diatomic molecular symmetry types σ , π , etc.

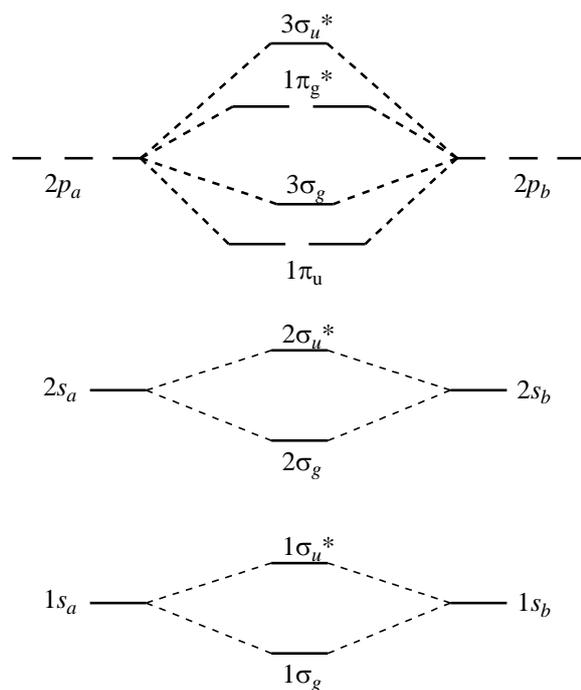


Figure 8.11 Order of MO energies in homonuclear diatomic molecules.

8.3.1 Term symbols of homonuclear diatomic molecules

Having determined the energetic ordering of low lying MOs, finding the term symbols of a given diatomic molecule proceeds very similarly to finding atomic term symbols. The main difference is in the notation of the orbitals. Similar to the concept of “subshells” in atoms, we define a “molecular shell” as the group of MOs with a given n and a given λ and a given parity (g or u). A σ shell has only one MO, and its maximum occupation number is 2. Shells with $\lambda > 0$ have two degenerate MOs, and their maximum occupation numbers are 4. Electronic configurations are written by assigning electrons to a selected set of shells, within the stated restrictions. Closed shells do not contribute to either the total spin quantum number S or to Λ of the molecular term. Thus electronic configurations in which all shells are closed give only a singlet term symbol: $^1\Sigma_g$. Higher spin multiplicities and “ungerade” symmetry is possible only if there are open shells. We now consider several examples.

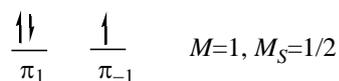
Li₂: The molecule has $N=6$ electrons. The ground electronic configuration is $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2$. The net number of bonding electrons is 2; i.e. there is a single bond of σ type in the Li₂ molecule. Since all shells are closed, the term symbol for the ground state of Li₂ molecule is $^1\Sigma_g$. The first few excited electronic states of this molecule arise from the configuration $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)(2\sigma_u^*)$, obtained by transferring one of the electrons in the highest energy $2\sigma_g$ shell in the ground configuration to the lowest unoccupied $2\sigma_u^*$ shell. This electronic configuration has two different open shells with one electron in each. Thus, both $S=0$ and 1 are possible. The M quantum number is zero since both electrons in the open shells have $m=0$. Thus $\Lambda=0$, the overall parity of the states is “ u ”, and the allowed term symbols are $^1\Sigma_u$ and $^3\Sigma_u$. From Hund’s rule, $^3\Sigma_u$ should be the first excited state.

B₂: The molecule has $N=10$ electrons. The ground electronic configuration is $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^2$. The net number of bonding electrons is 2. Hence there is a single bond, but it is interesting that the bonding electrons are π electrons in this molecule. There is one open shell, $1\pi_u$, with two electrons. The situation here is similar to the np^2 subshell configuration in atoms. However, it is simpler here since the $1\pi_u$ shell has only two MOs whereas the p subshell has 3 AOs. The overall parity of the electronic states is $uxu=g$. The total spin $S=0$ or 1. We need to determine the allowed values of M . We prefer to use complex MOs for this purpose because then M can be found simply by adding m values of the two electrons in orbital products. We designate the two complex MOs of the $1\pi_u$ shell by π_1 and π_{-1} . There are 4 different orbital products from which one antisymmetric and three symmetric space functions of two electrons can be constructed as shown in Table 8.3 (*cf.* Table 7.6). Thus this configuration gives rise to three molecular terms with distinct energies: a triply degenerate $^3\Sigma_g$ term, a doubly degenerate $^1\Delta_g$, and a nondegenerate $^1\Sigma_g$. The term symbol for the ground state of B₂ molecule is $^3\Sigma_g$, by Hund's rule.

Table 8.3 Two-electron spatial functions for a π^2 shell configuration.

S	Two-electron space functions	M	Term Symbol
1	$\pi_1\pi_{-1} - \pi_{-1}\pi_1$	0	$^3\Sigma_g$
0	$\pi_1\pi_1$	2	$^1\Delta_g$
	$\pi_{-1}\pi_{-1}$	-2	
0	$\pi_1\pi_{-1} + \pi_{-1}\pi_1$	0	$^1\Sigma_g$

B₂⁻ negative ion: There are $N=11$ electrons in this anion. The ground electronic configuration is $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^3$ with three net bonding electrons. Since the number of bonds (or the "bond order") is 1.5, the equilibrium bond length in the anion is expected to be shorter than that in the neutral molecule. The open $1\pi_u$ shell has 3 electrons, one less than the maximum of 4. Parity of the state(s) is $uxuxu=u$. The diagram below shows that there is only one possibility for $|M_S|$, namely 1/2, and also $|M|=1$. Therefore, $S=1/2$ and $\Lambda=1$. The ground state of the anion is a doublet: $^2\Pi_u$.



The same term symbol would be obtained if the $1\pi_u$ shell had only one electron (i.e. $4-3=1$). This is generally true in other open molecular shell types, also (*cf.* Section 7.6).

Exercise 8.5 Find the molecular term symbols for the electronic configuration: (closed shells)($1\pi_u$)($1\pi_g^*$).

Exercise 8.6 i) The experimental bond lengths of N_2^+ and N_2 are 112 and 110 pm, respectively. Find all term symbols of each species arising from their ground electronic configurations. Interpret the difference in the bond lengths of these two species. ii) Same question as above for O_2^+ and O_2 where the bond lengths are 112 and 121 pm, respectively.