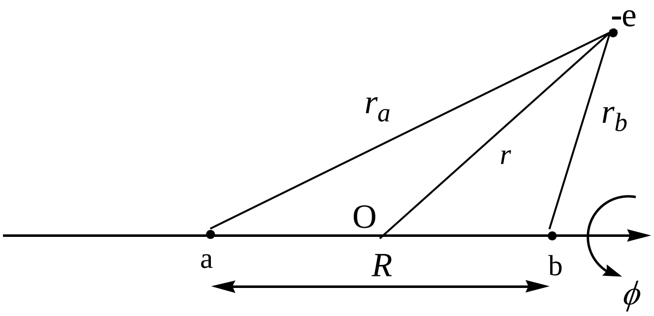
Chapter 7 Electronic Structure of Diatomic Molecules

7.1 The Hydrogen Molecule Ion

1. Accurate solutions



The H_2^+ molecule. The nuclei are at a and b; R is the internuclear distance; r_a and r_b are the distances from the the electron to nuclei a and b.

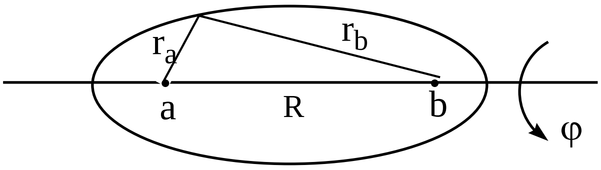
In the BO approximation, the Hamiltonian in atomic units is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

Since the nuclei are fixed, $1/R$ is a constant. The purely electronic Hamiltionian for H_2^+ can be rewritten as

$$\hat{H}_{el} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \tag{7.1}$$

Obviously, the Schroedinger equation is not separable in spherical polar coordinates. In 1927, Burrau showed that the separation of variables is possible using *confocal elliptic coordinates* ξ, η, φ.



The elliptic coordinates with two centers

$$\xi = \frac{r_a + r_b}{R}, \qquad \eta = \frac{r_a - r_b}{R} \qquad (7.2)$$

The ranges of these coordinates are:

$$0 \le \varphi \le 2\pi, \quad 1 \le \xi \le \infty, \quad -1 \le \eta \le 1 \qquad (7.3)$$

We have

$$r_a = \frac{1}{2}R(\xi + \eta), \qquad r_b = \frac{1}{2}R(\xi - \eta) \qquad (7.4)$$

The H_2^+ electronic Hamiltonian (7.1) in the elliptic coordinates has the form

$$\hat{H}_{el} = -\frac{2}{R^2(\xi^2 - \eta^2)}[(\xi^2 - 1)\frac{\partial^2}{\partial \xi^2} + 2\xi\frac{\partial}{\partial \xi} + (1 - \eta^2)\frac{\partial^2}{\partial \eta^2}$$

$$-2\eta\frac{\partial}{\partial \eta} + (\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2})\frac{\partial^2}{\partial \varphi^2}] - \frac{2}{R(\xi + \eta)} - \frac{2}{R(\xi - \eta)} \qquad (7.5)$$

Hence the Schroedinger equation is

$$\hat{H}_{el}\,\Psi(\xi, \eta, \varphi) = E_{el}\Psi(\xi, \eta, \varphi) \qquad (7.6)$$

Let

$$\Psi(\xi, \eta, \varphi) = L(\xi)M(\eta)\Phi(\varphi) \qquad (7.7)$$

Substitution of (7.7) into the Schroedinger equation (7.6) leads to an equation in which the variables are separable.

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) = -m^2\Phi(\varphi) \qquad (7.8)$$

$$(\xi^2 - 1)L'' + 2\xi L' + (A + 2R\xi + \frac{1}{2}E_{el}R^2\xi^2 - \frac{m^2}{\xi^2 - 1})L = 0 \qquad (7.9)$$

$$(1-\eta^2)M''-2\eta M'-(A+\frac{1}{2}E_{el}R^2\eta^2+\frac{m^2}{1-\eta^2})M=0 \qquad (7.10)$$

Solving the equation (7.8), we have

$$\Phi(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi} \qquad (7.11)$$

where m = 0, ±1, ±2, …

or

$$\Phi(\varphi)=\begin{cases}\frac{1}{\sqrt{2\pi}} & when \quad m=0\\ \frac{1}{\sqrt{2\pi}}\cos m\varphi & \\ \frac{1}{\sqrt{2\pi}}\sin m\varphi & \end{cases} \quad when\ m = 1, 2, \ldots \qquad (7.12)$$

The solution for M(η) is an infinite series of associated Legendre functions. L(ξ) also involves an infinite series. The requirement that the wave function be well behaved leads to the conclusion that for a fixed value of R, only certain values of E_{el} are allowed (i.e. discrete); this gives a series of electronic states, corresponding electronic energy

$$E(R)=E_{el}+\frac{1}{R} \qquad (7.13)$$

The electronic energies must be calculated numerically. The series of energy levels are marked by quantum numbers *n*, *l*, and *m*, whose allowed values are

$$\begin{aligned}&n=1,\quad 2,\quad 3,\quad \cdots\\ &l\le n-1\\ &m\le l\end{aligned} \qquad (7.14)$$

l	0, 1, 2, 3, …
	s, p, d, f. …

m	0, 1, 2, 3, …
	σ, π, δ, φ, …

For the ground electronic state, the quantum number m is zero. At $R=\propto$ the H_2^+ ground state is dissociated into a proton and a ground-state hydrogen atom; hence $E_{el}(\propto) = -0.5$ hartree. At R=0, the two protons have come together to form the He^+ ion with ground-state energy of -2 hartrees.

The E(R) curve is found to have a minimum at

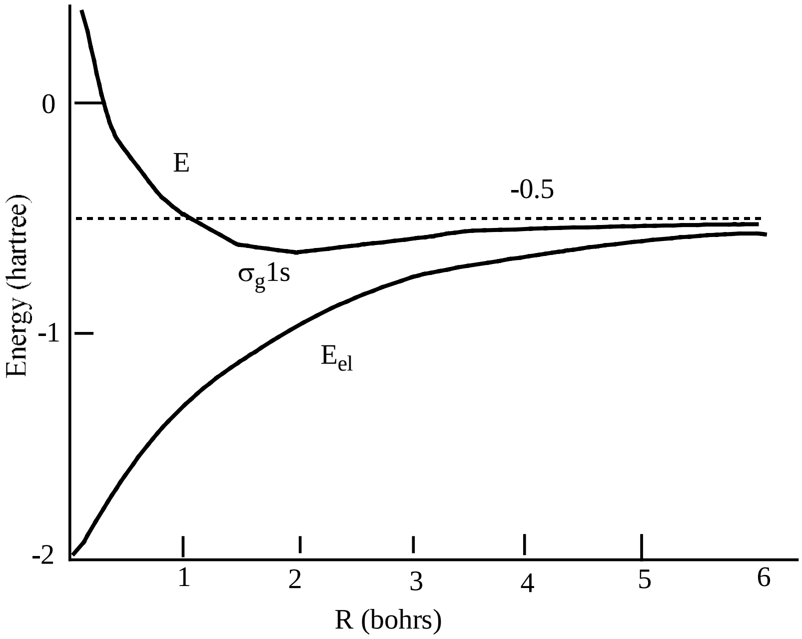
$R_e = 1.9972$ bohrs ≈ 2.0 bohrs = 1.06 Å.

$E_{el} = -1.1033$ hartree, $E(R) = -0.6026$ hartree

The ground-state binding energy is

$$D_e = 0.1026 \text{ hartree} = 2.79 \text{ eV} = 64.4 \text{ kcal/mol} \qquad (7.15)$$

Experiment: $R_e = 1.06$ Å, $D_e = 2.791$ eV.



Electronic energy with (E) and without nuclear repulsion for the H_2^+ ground state

Similarly, we have the first other electronic states, such as $\sigma_u{}^*1s$, $\sigma_g 2s$, $\sigma_u{}^*2s$, $\sigma_g 2p$, $\pi_u 2p$, …

2. Approximate Treatment of the H_2^+

Trial function:

Consider a limiting behavior of the H_2^+ ground-state electronic wave function as R approaches $\propto$.

$$\varphi = c_a 1s_a + c_b 1s_b \qquad (7.16)$$

$$1s_a = \frac{1}{\sqrt{\pi}} e^{-r_a}, \quad 1s_b = \frac{1}{\sqrt{\pi}} e^{-r_b}$$

When R goes zero, we get the He^+ ion, which has the ground-state wave function (Z=2)

$$\sqrt{\frac{2^3}{\pi}} e^{-2r} \qquad (7.17)$$

Note that at the R = 0 the trial function (7.16) goes to

$$(c_1 + c_2)\sqrt{\frac{1}{\pi}} e^{-r} .$$

Comparing with (7.17), we see that (7.16) has the wrong limiting behavior at R = 0. We can fix things by multiplying r_a and r_b in the exponentials by a variational parameter k = k(R). For correct limiting behavior at zero and infinite internuclear distance, we have

K(0) = 2, k($\propto$) =1

We thus take as the trial function

$$\varphi = c_a \phi_{1sa} + c_b \phi_{1sb} \qquad (7.18)$$

where

$$\phi_{1sa} = \sqrt{\frac{k^3}{\pi}} e^{-kr_a}, \quad \phi_{1sb} = \sqrt{\frac{k^3}{\pi}} e^{-kr_b} \qquad (7.19)$$

The molecular orbital (MO) (7.18) is a linear combination of atomic orbitals, an LCAO-MO. (Exponential parameter—effective nuclear charge)

For the trial function (7.18), the secular equation is

$$\begin{vmatrix} H_{aa} - WS_{aa} & H_{ab} - WS_{ab} \\ H_{ba} - WS_{ba} & H_{bb} - WS_{bb} \end{vmatrix} = 0 \qquad (7.20)$$

The integrals H_{aa} and H_{bb} are

$$H_{aa} = \int \phi_{1sa}^{*} \hat{H} \phi_{1sa} d\nu, \quad H_{bb} = \int \phi_{1sb}^{*} \hat{H} \phi_{1sb} d\nu \qquad (7.21)$$

These two integrals are called *Coulomb integrals*. Since the H_2^+ is a homonuclear diatomic system, $H_{aa} = H_{bb}$. We have

$$H_{ab} = \int \phi_{1sa}^{*} \hat{H} \phi_{1sb} d\nu, \quad H_{ba} = \int \phi_{1sb}^{*} \hat{H} \phi_{1sa} d\nu \qquad (7.22)$$

Since $\hat{H}$ is Hermitian and the functions in these integrals are real, we conclude that $H_{ab} = H_{ba}$. The integral H_{ab} is called a resonance (or bond) integral. Since ϕ_{1sa} and ϕ_{1sb} are normalized and real. We have

$$\begin{aligned} S_{aa} &= <\phi_{1sa} \mid \phi_{1sa}> = \int \phi_{1sa}^{*} \phi_{1sa} dv = 1 = S_{bb} \\ S_{ab} &= \int \phi_{1sa}^{*} \phi_{1sb} dv = S_{ba} \end{aligned} \qquad (7.23)$$

The secular equation (7.20) becomes

$$\begin{vmatrix} H_{aa} - W & H_{ab} - WS_{ab} \\ H_{ab} - WS_{ab} & H_{aa} - W \end{vmatrix} = 0 \qquad (7.24)$$

$$H_{aa} - W = \pm(H_{ab} - S_{ab}W) \qquad (7.25)$$

$$W_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}, \quad W_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \qquad (7.26)$$

These two roots are upper bounds for the energies of the ground and the first excited electronic states of H_2^+.

We now find the coefficients in (7.18) for each of the roots of the secular equation. From the linear homogeneous equations in Chapter 5, we have

$$(H_{aa} - W)c_a + (H_{ab} - S_{ab})c_b = 0 \qquad (7.27)$$

Substituting in W_1 from (7.26), we get

$$\frac{c_a}{c_b} = 1 \qquad (7.28)$$

$$\varphi_1 = c_a(\phi_{1sa} + \phi_{1sb}) \qquad (7.29)$$

We fix c_a by normalization:

$$< \varphi_1 | \varphi_1 > = | c_a |^2 \int (\phi_{1sa}^2 + \phi_{1sb}^2 + 2 \cdot \phi_{1sa}\phi_{1sb})dv = 1$$

$$| c_a | = \frac{1}{\sqrt{2 + 2S_{ab}}} \qquad (7.30)$$

The normalized trial function corresponding to the energy W_1 is thus:

$$\varphi_1 = \frac{1}{\sqrt{2 + 2S_{ab}}}(\phi_{1sa} + \phi_{1sb}) \qquad (7.31)$$

For the root W_2, we find $c_b = -c_a$ and

$$\varphi_2 = \frac{1}{\sqrt{2 - 2S_{ab}}}(\phi_{1sa} - \phi_{1sb}) \qquad (7.32)$$

Let us evaluate H_{aa}, H_{ab}, and S_{ab}.

Overlap integral S_{ab}

$$S_{ab} = e^{-kR}[1 + kR + \frac{1}{3}k^2R^2] \qquad (7.34)$$

Coulomb integral H_{aa}

$$H_{aa} = \frac{1}{2}k^2 - k - \frac{1}{R} + e^{-2kR}(k + \frac{1}{R}) \qquad (7.35)$$

Resonance integral H_{ab}

$$H_{ab} = -\frac{1}{2}k^2 S_{ab} + k(k-2)(1+kR)e^{-kR} \qquad (7.36)$$

The final task is to vary the parameter k, setting

$$\frac{\partial W_1}{\partial k} = 0, \qquad \frac{\partial W_2}{\partial k} = 0$$

The results are that for the $\varphi_1 (1s_a + 1s_b)$ function (7.31), the parameter k increases monotonically from 1 to 2 as R decreases from $\propto$ to 0; for the $\varphi_2 (1s_a - 1s_b)$ function (7.32), k decreases monotonically from 1.0 to 0.4 as R decreases from $\propto$ to 0. Since k is positive and never greater than 2, and since the overlap integral S_{ab} is positive, we see from (7.36) that the resonance integral H_{ab} is always negative.

The ground state σ_g 1s :

$$W_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}, \qquad \varphi_1 = \frac{1}{\sqrt{2 + 2S_{ab}}}(\phi_{1sa} + \phi_{1sb})$$

$k(R_e) = 1.24$

R_e = 2.02 bohrs, Binding energy: **2.35 eV**. (Expt. **2.00 bohrs, 2.79 eV**).

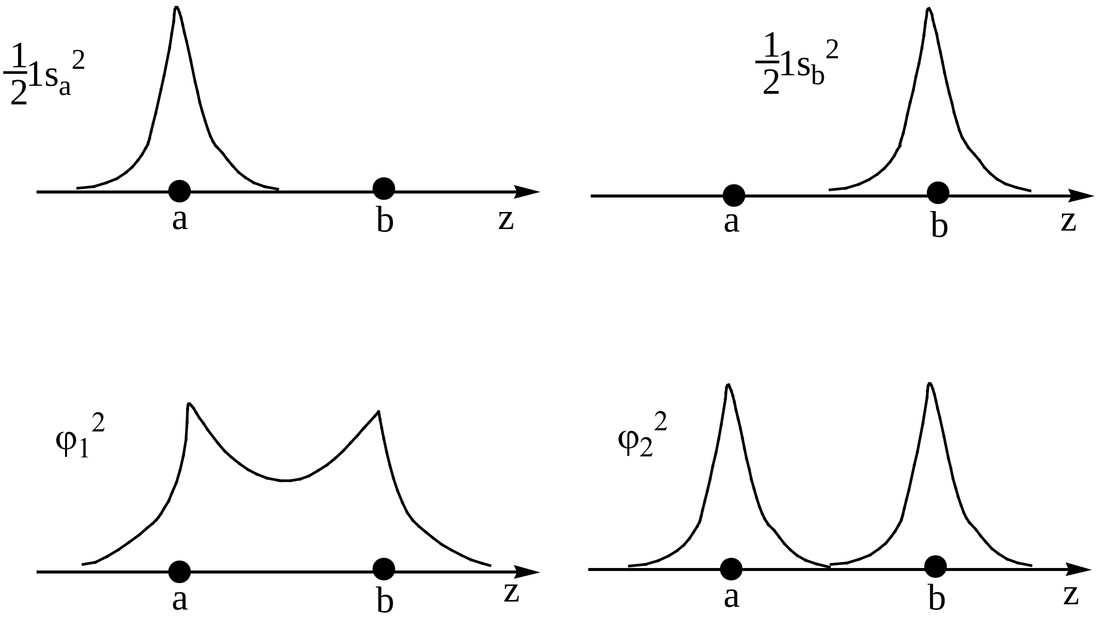
If we **omit varying k**, but simply set it equal to 1, we get

R_e = 2.50 bohrs, Binding energy: **1.76 eV**.

The excited state σ_u 1s :

$$W_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}, \qquad \varphi_2 = \frac{1}{\sqrt{2 - 2S_{ab}}}(\phi_{1sa} - \phi_{1sb})$$

The appearance of the trial functions for σ_g 1s and σ_u 1s

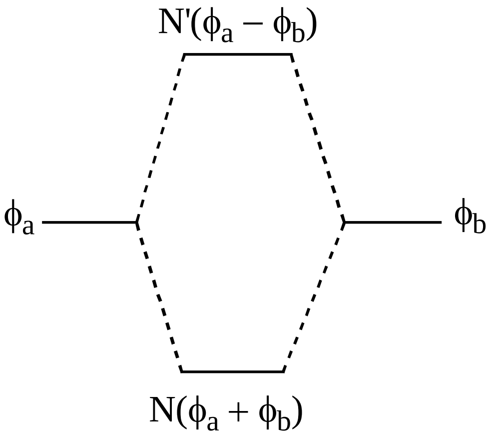


Charge probability density

In summary, we have formed the two H_2^+ molecular orbitals (MO), one bonding and one antibonding, from the atomic orbitals $1s_a$ and $1s_b$. The MO energy are given by (7.26) as

$$W_{1,2} = H_{aa} \pm \frac{H_{ab} - H_{aa} S_{ab}}{1 \pm S_{ab}} \qquad (7.37)$$

A schematic representation of MO formation from AO's



Trial function from hybridized AO's (Dickinson in 1933)

$$\varphi = [1s_a + c(2p_0)_a] + [1s_b + c(2p_0)_b] \qquad (7.38)$$

where c is variational parameter, and where

$$\phi_{1sa} = \sqrt{\frac{k^3}{\pi}} e^{-kr_a}, \quad (2p_0)_a = (2p_z)_a = \frac{\xi^{5/2}}{4(2\pi)^{1/2}} e^{-\xi r_a/2} r_a \cos\theta_a$$

Final results:

K = 1.246, ξ =2.965, c = 0.138

R_e = 2.01 bohrs, Binding energy: 2.73 eV.

3. Molecular Orbitals for H_2^+ Excited States

Method of the linear variation function

LCAO-MO's

$$\varphi = c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a + c_4 1s_b + c_5 2s_b + c_6 (2p_0)_b$$

The symmetry of the homonuclear diatomic molecule makes the coefficients of the atom b orbitals equal to ±1 times the corresponding atom a orbital coefficients:

$$\varphi = [c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a] \pm [c_1 1s_b + c_2 2s_b + c_3 (2p_0)_b] \quad (7.39)$$

where the upper sign goes with the even (g) states (i.e. +: g; -: u).

Relative magnitudes of the coefficients in (7.39)

For the electronic states that dissociate into a 1s hydrogen atom: Large c_1, Small c_2 and c_3. As a first approximation, we set c_2 and c_3 equal to zero, taking

$$\varphi = c_1(1s_a \pm 1s_b) \tag{7.40}$$

as an approximation for the wave functions of these two states (σ_g 1s, σ_u* 1s). The same argument for the two states that dissociate to 2s hydrogen atom gives as approximate wave functions for them:

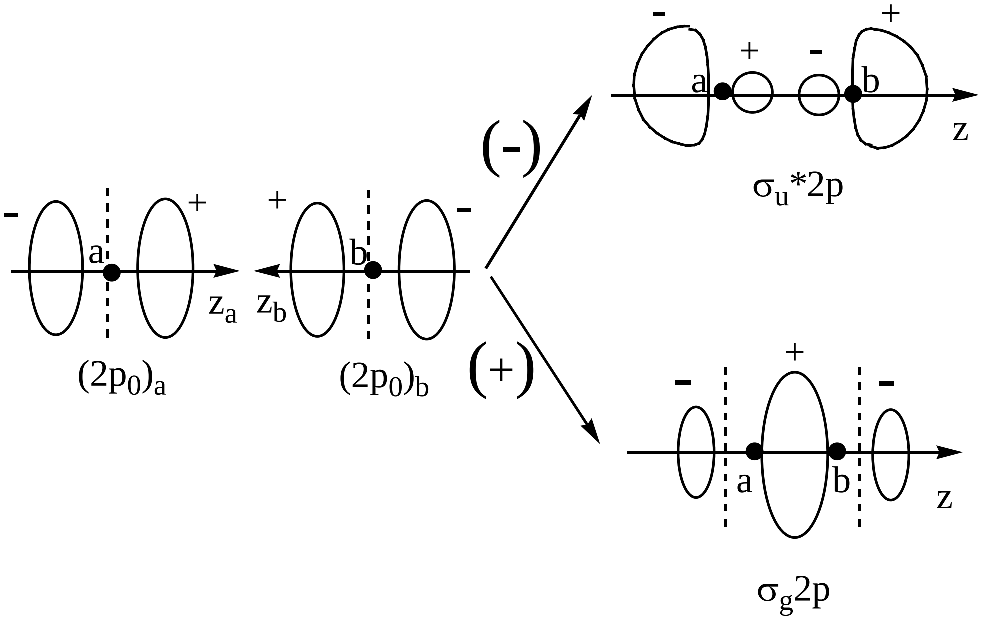
$$\varphi = c_2(2s_a \pm 2s_b) \tag{7.41}$$

since c_1 and c_3 will be small for these states.

Next, we have the combinations

$$(2p_0)_a \pm (2p_0)_b = (2p_z)_a \pm (2p_z)_b \tag{7.42}$$

giving the σ_g 2p and σ_u* 2p molecular orbitals.



Similarly, for the other two 2p atomic orbitals, they can be formed the 4 MO's:

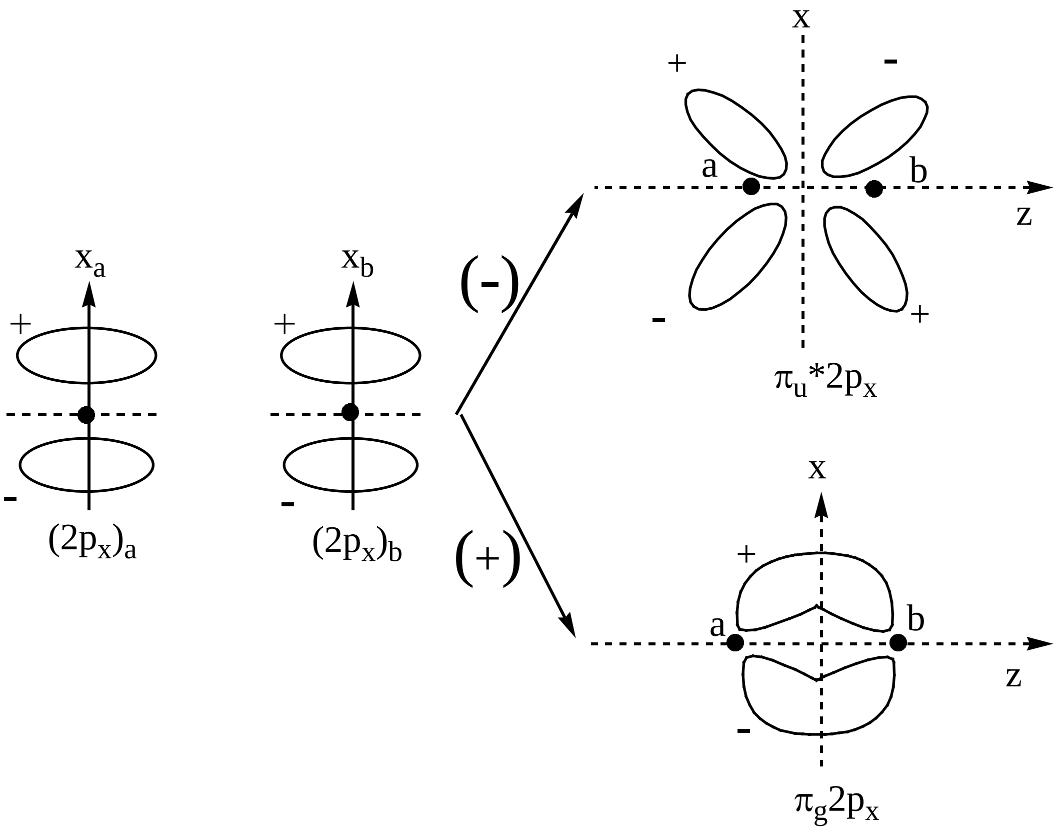
$$(2p_{+1})_a + (2p_{+1})_b \qquad (7.43)$$

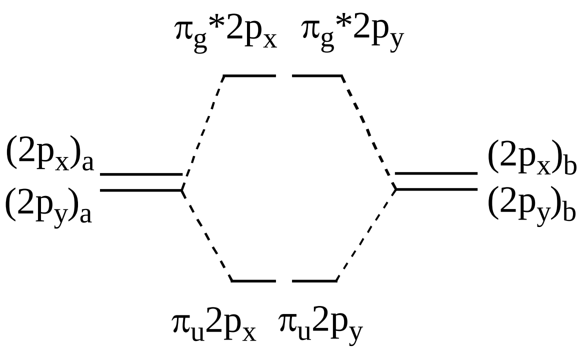
$$(2p_{+1})_a - (2p_{+1})_b \qquad (7.44)$$

$$(2p_{-1})_a + (2p_{-1})_b \qquad (7.45)$$

$$(2p_{-1})_a - (2p_{-1})_b \qquad (7.46)$$

Obviously, the MO (7.43) and MO (7.45) have the same energy, i.e. they are doubly degenerate. The functions (7.44) and (7.46) give the π_g*$2p_{+1}$ and π_g*$2p_{-1}$ MO’s. Both have the same shapes and the same energy.





4. Molecular-Orbital Configurations of Homonuclear Diatomic Molecules

Approximate MO order

The sizes and energies of the MO's vary with varying internuclear distance for each molecule, and vary as we go from one molecule to another. Hence we cannot give a definitive order. However, the following is the order in which the MO's fill as we go across the periodic table:

$$\sigma_g 1s < \sigma_u{*}1s < \sigma_g 2s < \sigma_u{*}2s < \pi_u 2p_{+1} = \pi_u 2p_{-1} < \sigma_g 2p < \pi_g{*}2p_{+1}$$

$$= \pi_u{*}2p_{-1} < \sigma_u{*}2p$$

Each bonding orbital fills before the corresponding antibonding orbital. The $\pi_u 2p$ orbitals are close in energy to the $\sigma_g 2p$ orbital, and it formerly believed that the $\sigma_g 2p$ MO filled first.

MO Nomenclature for Homonuclear Diatomic Molecules

$\sigma_g 1s$	$\sigma_u{*}1s$	$\sigma_g 2s$	$\sigma_u{*}2s$	$\pi_u 2p$	$\sigma_g 2p$	$\pi_g{*}2p$	$\sigma_u{*}2p$
$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$1\sigma_g$	$1\pi_g$	$2\sigma_u$

MO configuration

H_2: $(\sigma_g 1s)^2$. The two bonding electrons give a single bond H-H. D_e = 4.75 eV < 2 D_e $(H_2^+) \approx$ 5.6 eV. (H_2^+: De =2.79 eV)

He_2: $(\sigma_g 1s)^2$ $(\sigma_u{*}1s)^2$. No net bonding electrons, in agreement with the well-known fact that the ground electronic state of He_2 is unstable, showing no minimum in the potential-energy curve.

He_2^+: $(\sigma_g 1s)^2 (\sigma_u{*}1s)^1$. One net bonding electron.

Li_2: $(\sigma_g 1s)^2 (\sigma_u{*}1s)^2 (\sigma_g 2s)^2$. Two net bonding electrons.

Be_2: KK $(\sigma_g 2s)^2 (\sigma_u{*}2s)^2$. No net bonding electrons.

B_2: KK $(\sigma_g 2s)^2 (\sigma_u{*}2s)^2 (\pi_u 2p)^2$. By Hund's rule, the ground state of B_2 will have 2S+1=3. Experimentally, the ground state of B_2 is observed to be a triplet (Actually, the ground state is uncertain.)

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Properties of Homonuclear Diatomic Molecules in their Ground Electronic States

Molecule	Ground Term	Bond Order	De (eV)	Re (Å)
H_2^+	$^2\Sigma_g^+$	1/2	2.8	1.06
H_2	$^1\Sigma_g^+$	1	4.75	0.742
He_2^+	$^2\Sigma_u^+$	1/2	3	1.08
He_2	$^1\Sigma_g^+$	0	—	—
Li_2	$^1\Sigma_g^+$	1	1.1	2.67
Be_2	$^1\Sigma_g^+$	0	—	—
B_2	$^3\Sigma_g^-$ (?)	1	2.9	1.59
N_2^+	$^2\Sigma_g^+$	2.5	8.9	1.12
N_2	$^1\Sigma_g^+$	3	9.9	1.10
O_2^+	$^2\Pi_g$	2.5	6.8	1.12
O_2	$^3\Sigma_g^-$	2	5.2	1.21
F_2	$^1\Sigma_g^+$	1	1.6	1.42
Ne_2	$^1\Sigma_g^+$	0	—	—

5. Molecular Electronic Terms

For a many-electron diatomic molecule, the component of electronic orbital angular momentum along the molecular axis has the possible values $M_L(h/2\pi)$ where $M_L = 0, \pm1, \pm2, \pm3, \ldots$. We define Λ as

$$\Lambda \equiv |M_L|$$

The following code is used to indicate the value of Λ.

Λ	0	1	2	3	4
letter	Σ	Π	Δ	Φ	Γ

For $\Lambda\neq0$, there are two possible value of M_L: $+\Lambda$ and $-\Lambda$; so that there is a double degeneracy associated with the two values of M_L.

Just as in atoms, the individual electronic spin add vectorially to give a total electronic spin **S**, whose magnitude has the possible values $\sqrt{S(S+1)}\hbar$, with S =0, 1/2, 1, 3/2, …. The component of S along an axis has the possible values $M_s\hbar$, where M_s = S, S-1, …, -S. The quantity (2S+1) is called the *multiplicity*.

Now consider the molecular electronic terms. A closed-subshell molecular configuration has both S and Λ equal to aero and gives rise to a single $^1\Sigma$ term. For example, H_2: $(\sigma_g 1s)^2$, S = 1/2 + (–1/2) =0, $M_L = 0 + 0 = 0$, $^1\Sigma_g^+$. Thus, in deriving molecular terms, we need only consider electrons outside filled subshells.

H_2^+: (σ_g 1s), $^2\Sigma_g^+$

πδ: π: m =±1, δ: m = ±2; M_L = +3, -3, +1, and –1. Λ = 3 or 1.

Possible terms: $^1\Pi$, $^3\Pi$, $^1\Phi$, $^3\Phi$.

ππ: π: m =±1, π: m =±1; M_L = +2, -2, 0, 0. Λ = 2, 0, and 0.

Possible terms: $^1\Delta$, $^3\Delta$, $^1\Sigma$, $^3\Sigma$, $^1\Sigma$, and $^3\Sigma$.

π^2: π: m =±1, π: m =±1; M_L = +2, -2, 0, 0. Λ = 2, 0, and 0. $^1\Delta$, $^1\Sigma^+$, $^3\Sigma^-$.

…

Molecular Electronic Terms

Configuration	Terms
σσ	$^1\Sigma^+$, $^3\Sigma^+$
σπ	$^1\Pi$, $^3\Pi$
ππ	$^1\Sigma^+$, $^3\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^-$, $^1\Delta$, $^3\Delta$
πδ	$^1\Pi$, $^3\Pi$, $^1\Phi$, $^3\Phi$
σ	$^2\Sigma^+$
σ^2; π^4; δ^4	$^1\Sigma^+$
π; π^3	$^2\Pi$
δ; δ^3	$^2\Delta$
δ^2	$^1\Sigma^+$, $^3\Sigma^-$, $^1\Gamma$

For homonuclear diatomic molecules, a g or u right subscript is added to the term symbol to show the parity of the electronic states belonging to the term.

7.2 SCF Wave Functions for Diatomic Molecules

1. Hartree-Fock equation

A very important developmemt in quantum chemistry has been the computation of accurate self-consistent-field wave functions for many diatomic and polyatomic molecules.

The molecular wave function—Slater determinant

$$\Psi(x_1, x_2, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \quad (7.47)$$

where the molecular orbital (spin-orbital) is a product of a spatial orbital and a spin function (either α or β), i.e.

$$\chi_i = \begin{cases} \varphi_i \alpha \\ \varphi_i \beta \end{cases} \quad (7.48)$$

The spatial orbitals are found by solving the Hartree-Fock differential equations, which are

$$H^{eff}(1)\varphi_i(1) = \varepsilon_i \varphi_i(1) \quad (7.49)$$

where ε_i is the orbital energy and where the effective Hartree-Fock Hamiltonian operator is (in atomic units)

$$H^{eff}(1) = -\frac{1}{2}\nabla_1^2 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}} + \sum_j [2\hat{J}_j(1) - \hat{K}_j(1)] \quad (7.50)$$

where the Coulomb operator and the exchange operator are defined by

$$\hat{J}_j(1)\varphi_i(1) = \varphi_i(1)\int |\varphi_j(2)|^2 \frac{1}{r_{12}} dv_2 \quad (7.51)$$

$$\hat{K}_j(1)\varphi_i(1) = \varphi_j(1)\int \frac{\varphi_j*(2)\varphi_i(2)}{r_{12}}dv_2 \qquad (7.52)$$

The Coulomb integral

$$<\varphi_i(1)\,|\,\hat{J}_j(1)\,|\,\varphi_i(1)> = \int |\varphi_j(2)|^2 \frac{1}{r_{12}} |\varphi_i(1)|^2\, dv_2 dv_1$$

The exchange integral

$$<\varphi_i(1)\,|\,\hat{K}_j(1)\,|\,\varphi_i(1)> = \int \varphi_j*(2)\varphi_i(2)\frac{1}{r_{12}}\varphi_i(1)*\varphi_j(1)dv_1 dv_2$$

All the molecular orbitals φ_i are eigenfunctions of the same Hartree-Fock Hamiltonian operator H^{eff}; moreover, this operator is Hermitian. Hence themolecular orbitals φ_i are (or can be chosen to be) orthogonal.

The expression for the Hartree-Fock molecular energy E_{HF} involves Coulomb and exchange integrals in addition to the orbital energies (closed-shell systems):

$$E_{HF} = 2\sum_i \varepsilon_i - \sum_i \sum_j (2J_{ij} - K_{ij}) + V_{NN} \qquad (7.53)$$

where the sums are over the n/2 occupied spatial orbitals.

2. MO-LCAO

In 1951 Roothaan proposed expanding the spatial orbitals as linear combinations of a complete set of basis functions f_k:

$$\varphi_i = \sum_k c_{ik} f_k \qquad (7.54)$$

Substitution of this expression into the HF equation (7.49) gives

$$\sum_k c_{ik} H^{eff} f_k = \varepsilon_i \sum_k c_{ik} f_k$$

Multiplication by f_j* and integration gives

$$\sum_k c_{ik}(H_{jk}^{eff} - \varepsilon_i S_{jk}) = 0, \quad j = 1,2,3,... \qquad (7.55)$$

where

$$H_{jk}^{eff} = < f_j \mid H^{eff} \mid f_k >, \quad S_{jk} = < f_j \mid f_k >$$

For a nontrivial solution, we must have

$$\mathbf{det} \mid H_{jk}^{eff} - \varepsilon_i S_{jk} \mid = 0 \qquad (7.56)$$

This is a secular equation whose roots give the orbital energies. The Roothaan equations (7.55) must be solved by an iterative process, since the H_{jk}^{eff} integrals depend on the orbitals φ_i, which in turn depend on the unknown coefficients c_{ik}. —SCF method.

As an example, the SCF MO's (using a minimal basis set) for the ground state of Li_2 [MO configuration $(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$] at $R = R_e$ are:

$$\begin{aligned} 1\sigma_g &= 0.706(1s_a + 1s_b) + 0.009(2s_a + 2s_b) + 0.0003(2p_{za} + 2p_{zb}) \\ 1\sigma_u &= 0.709(1s_a - 1s_b) + 0.009(2s_a - 2s_b) + 0.0003(2p_{za} - 2p_{zb}) \qquad (7.57) \\ 2\sigma_g &= -0.059(1s_a + 1s_b) + 0.523(2s_a + 2s_b) + 0.114(2p_{za} + 2p_{zb}) \end{aligned}$$

— **Ransil**, B.J. *Rev. Mod. Phys.*, 1960, 32, 245.

Our previous simple expressions for these MO's were

$$\begin{aligned} 1\sigma_g &= \sigma_g 1s = 2^{-1/2}(1s_a + 1s_b) \\ 1\sigma_u &= \sigma_u * 1s = 2^{-1/2}(1s_a - 1s_b) \qquad (7.58) \\ 2\sigma_g &= \sigma_g 2s = 2^{-1/2}(2s_a + 2s_b) \end{aligned}$$

Comparison of (7.58) with (7.57) shows the simple LCAO functions to be reasonable first approximations to the minimal-basis-set SCF MO's.

Hartree-Fock wave functions are only approximations to the true wave functions. It is possible to prove that a Hartree-Fock wave function gives a very good approximation to the electron probability density. The prime example is the molecular dipole moment.

LiH: Theor. 6.00D, Expt. 5.83 D.

NaCI: Theor. 9.18D, Expt. 9.02D.

CO: Theor. HF: 0.27D (C^+O^-), post-HF: 0.12D(C^-O^+); Expt. 0.27D(C^-O^+).

3. Main defects of Hartree-Fock wavefunctions

HF calculations do not give good values for dissociation energies.

The HF energy approaches the wrong limit for large values of R.

N_2: An extended-basis-set calculation gives De = 5.3 eV.

Expt. De = 9.9 eV

F_2: HF calculations: De = -1.4 eV

Expt. De = 1.65 eV

H_2: HF calculation predicts a wrong dissociation limit: $H^+ + H^-$.

To overcome such defects of Hartree-Fock formalism, post-HF methodologies, such as CI, CASSCF, MRCI, MP2, CCSD,…, have been developed.

7.3 MO Treatment of Heteronuclear Diatomic Molecules

Suppose the two atoms have atomic numbers that differ only slightly; an example is CO.

MO description

N_2	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$3\sigma_u$
CO	1σ	2σ	3σ	4σ	1π	5σ	2π	6σ

MO's of the same symmetry are numbered in order of increasing energy.

The ground-state configuration

CO: $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2$ or $KK\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2$

N_2: $(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2$

or $KK(2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2$

As in homonuclear diatomic molecules, the heteronuclear diatomic MO's are approximated as linear combinations of atomic orbitals.

For qualitative discussion it is useful to have simple approximations for heteronuclear diatomic MO's.

In general, from two AO's φ_a and φ_b, we can form two MO's

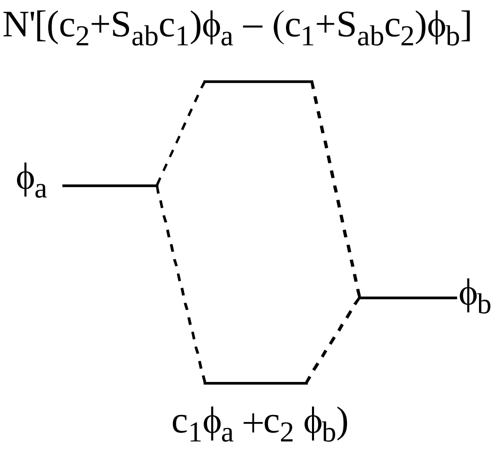
$$c_1\varphi_a + c_2\varphi_b \quad and \quad c_1'\varphi_a + c_2'\varphi_b \tag{7.59}$$

The coefficients are determined by solving the secular equation:

$$\begin{vmatrix} H_{aa} - W & H_{ab} - WS_{ab} \\ H_{ab} - WS_{ab} & H_{bb} - E \end{vmatrix} = 0 \tag{7.60}$$

$$(H_{aa} - W)(H_{bb} - W) - (H_{ab} - WS_{ab})^2 = 0 \tag{7.61}$$

Suppose that $H_{aa} > H_{bb}$, and let *f(W)* be defined as the left side of (7.61). The overlap S_{ab} is less than 1. The coefficient of W^2 in *f(W)* is $(1-S_{ab}^2)>0$; hence we have $f(\propto) = f(-\propto)=+\propto >0$. Because of $f(H_{aa})< 0$ and $f(H_{bb})< 0$, the roots of (7.61) occur where *f*(W) equals 0; one root must be between $+\propto$ and H_{aa} and the other between the H_{bb} and $-\propto$. Therefore the orbital energy of on MO is less than both H_{aa} and H_{bb}, while the energy of the other MO is greater than both H_{aa} and H_{bb}.



A minimal-basis-set SCF calculation using Slater orbitals with optimized exponents gives for the HF MO’s:

$$\begin{aligned}
1\sigma &= \mathbf{1.000}(1s_F)+0.012(2s_F)+0.002(2p_z)-0.003(1s_H)\\
2\sigma &= -0.018(1s_F)+\mathbf{0.914}(2s_F)+0.090(2p_z)+0.154(1s_H)\\
3\sigma &= -0.023(1s_F)-\mathbf{0.411}(2s_F)+\mathbf{0.711}(2p_z)+\mathbf{0.516}(1s_H) \qquad (7.62)\\
1\pi_{+1} &= (2p_{+1})_F\\
1\pi_{-1} &= (2p_{-1})_F
\end{aligned}$$

The ground-state MO configuration of HF is $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi^4$.