

Molecular Orbital Theory - Diatomic Molecules

Molecular orbital theory is a conceptual extension of the orbital model, which was successfully applied to atomic structure. As has been playfully remarked, “a molecule is nothing more than an atom with more nuclei”. This may be overly simplistic, but we try to exploit analogies with atomic structure. After introducing the Born-Oppenheimer approximation, we will begin our study of homonuclear diatomic molecules beginning with an exactly solvable prototype – the Hydrogen molecule-ion H_2^+ .

1. The Born-Oppenheimer Approximation

1.1 The Molecular Hamiltonian

Assuming nuclei and electrons are point masses, and ignoring spin-orbit and other relativistic effect, the molecular Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_j \sum_{i > j} \frac{e^2}{r_{ij}} \quad (1)$$

where α and β refer to nuclei and i and j refer to electrons.

The spatial coordinates of nuclei and electrons pose a formidable task for scientists. The Born-Oppenheimer (BO) approximation makes it possible to calculate the total wavefunction in two, less formidable, consecutive steps.

In basic terms, it allows the wavefunction of a molecule to be broken into its electronic and nuclear (vibrational, rotational) components.

$$\Psi_{total} = \psi_{electronic} \times \psi_{nuclear} \quad (2)$$

The key lies in the fact that nuclei are much heavier than electrons. The electrons move much faster than the nuclei and to a good approximation as far as the electrons are concerned, we can regard the nuclei as fixed while the electrons carry out their motion (i.e., the inertia of electrons are negligible compared to the nuclei they are bound to).

In the first step, the motion of nuclei is ignored. The Schrödinger equation for electron motion is

$$(\hat{H}_{el} + V_{NN}) \psi_{el} = U \psi_{el} \quad (3)$$

where the purely electronic Hamiltonian has the form

$$\hat{H}_{el} = \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_j \sum_{i > j} \frac{e^2}{r_{ij}} \quad (4)$$

The electronic Schrödinger equation $\hat{H}_{el} \psi_{el} = E_{el} \psi_{el}$ is the main focus in this class (Note here, $U = V_{NN} + E_{el}$)

In the second step, the Schrödinger equation for nuclear motion is

$$\hat{H}_N \psi_N = E \psi_N \quad (5)$$

$$\hat{H}_N = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 + U(q_{\alpha}) \quad (6)$$

The total energy for an electronic state of a diatomic molecule is the sum of electronic, vibrational, rotational, and translational energies.

1.2 Nuclear Motion in diatomic molecules

The Schrödinger equation for nuclear motion in a diatomic-molecule bound electronic states is

$$\left[-\frac{\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_{\beta}} \nabla_{\beta}^2 + U(R) \right] \psi_N = E \psi_N \quad (7)$$

The two-particle Schrödinger equation can be reduced to two one-particle Schrödinger equations, one for translational energy of the entire molecule, and the one for internal motion of the nuclei relative to each other (see Handout #3, for the example of Hydrogen atom).

The Schrödinger equation for internal motion is

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + U(R) \right] \psi_{N,int} = E_{int} \psi_{N,int} \quad (8)$$

Since the potential energy in equation (8) depends on R only, this is a central-force problem, and it is known that the wavefunction has the form

$$\psi_{N,int} = P(R) Y_J^M(\theta, \phi) \quad (9)$$

The potential energy U(R) can be approximated

$$U(R) = U(R_e) + \frac{1}{2} k_e x^2 \quad (10)$$

After non-trivial mathematical work, we have

$$E_{int} \approx U(R_e) + \left(n + \frac{1}{2}\right) h\nu + \frac{J(J+1)\hbar^2}{2\mu R_e^2} \quad (11)$$

Where $\nu = \sqrt{k_e/\mu}/2\pi$, the harmonic (equilibrium) vibrational frequency.

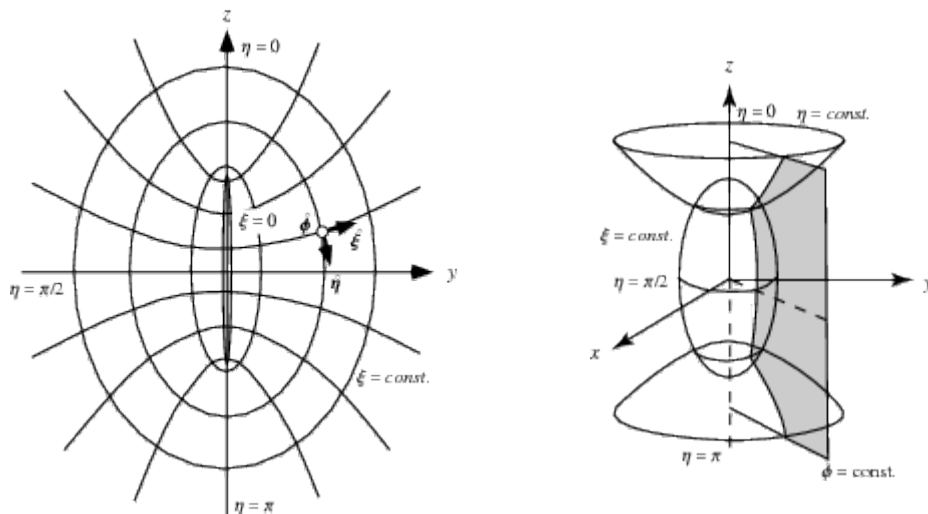
2. The Hydrogen Molecule-Ion

2.1 Analytical solution

The simplest conceivable molecule would be made of two protons and one electron, namely H_2^+ (detected in outer space, or has a transient existence in electrical discharges). The Schrödinger equation for H_2^+ can be solved exactly within the BO approximation. We write (using atomic units)

$$\left[-\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (12)$$

The equation was first solved by Burrau in 1927, after separating the variables in prolate spheroidal coordinates.



The three prolate spheroidal coordinates are designated ζ , η , ϕ . The first two are defined by

$$\zeta = \frac{r_a + r_b}{R} \quad \text{and} \quad \eta = \frac{r_a - r_b}{R} \quad (13)$$

while ϕ is the angle of rotation about the internuclear axis.

The exact Schroedinger equation has the form

$$\Psi_{el} = L(\zeta) M(\eta) (2\pi)^{-1/2} e^{im\phi} \quad (14)$$

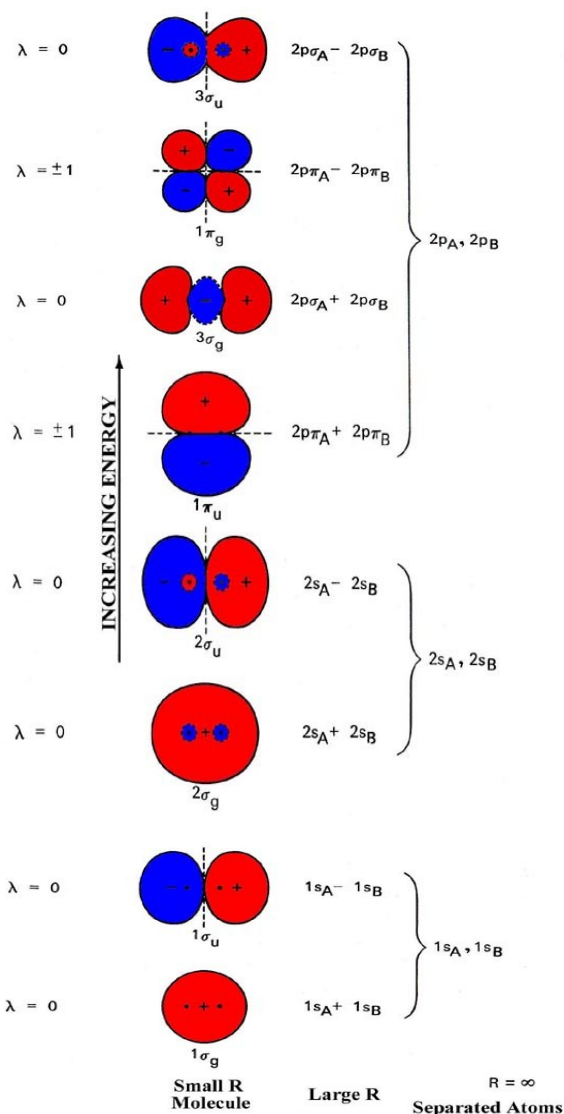
Q: For the *ground state*, how does the electronic energy change with R (e.g. $R=0$, $R=\infty$)?

1. The one-electron spatial part of a molecular spin-orbital will be called **Molecular Orbitals**.
2. E_{el} Depends on m^2 (quantum number m occurs as m^2 in $L(\zeta)$ and $M(\eta)$)
3. Each electronic level with $m \neq 0$ is doubly degenerate, corresponding to quantum numbers $+|m|$ and $-|m|$. The absolute number m is called $\lambda = |m|$.
4. Name molecular orbitals by $\sigma, \pi, \delta, \phi, \gamma$ corresponding to $\lambda = 0, 1, 2, 3, 4$. (cf. Atomic orbitals: s, p, d, f, g ...)
5. We can also clarify them by their parity, we use subscript g and u to represent symmetric and anti-symmetric wavefunctions. (*gerade*, meaning even; *ungerade*, meaning odd).
6. The molecular orbitals of a given symmetry are numbered in order of increasing energy, for example, $1\sigma_g, 2\sigma_g, 3\sigma_g$

The lowest energy (nodeless) is designated $1\sigma_g$. The next higher orbital have a nodal

plane, and has cylindrical symmetry. $1\sigma_u$. Next come the $2\sigma_g$ and $2\sigma_u$. Two degenerate $1\pi_g$ come next.

Ellipsoidal, and hyperboloidal nodal planes



Alternative notation will be explained later. $\sigma_g 1s$, $\sigma_u 1s$...

2.2 Approximate Treatments For the Ground State

Linear combination of atomic orbitals – MO (LCAO-MO) (variational method)

We take trial function

$$\phi = c_a 1s_a + c_b 1s_b \quad (15)$$

Where the c 's are variational parameters, and

$$1s_a = k^{3/2} \pi^{-1/2} e^{-kr_a}, \quad 1s_b = k^{3/2} \pi^{-1/2} e^{-kr_b} \quad (16)$$

What is the secular equation?

The Hamiltonian for H_2^+ is $\hat{H}_{el} = -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}$ (Using Hartree atomic units).

Coulomb integrals: $H_{aa} = H_{bb}$

Resonance integrals (bond integrals) $H_{ab} = \int 1s_a^* \hat{H} 1s_b d\tau$, $H_{ba} = \int 1s_b^* \hat{H} 1s_a d\tau$ (negative or positive?)

Overlap integrals: $S_{aa} = \int 1s_a^* 1s_a d\tau = 1 = S_{bb}$, $S_{ab} = \int 1s_a^* 1s_b d\tau = S_{ba}$

The secular equation has two roots: $W_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$, and $W_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$

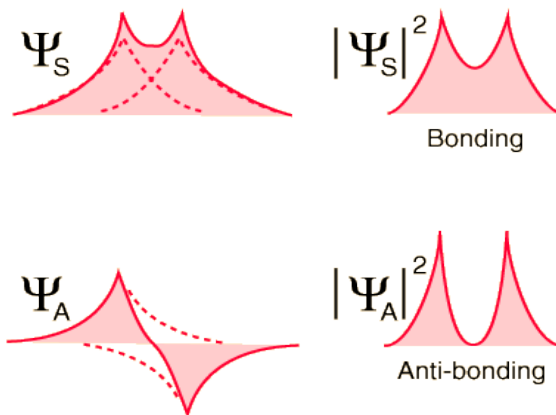
We also find the normalized trial wavefunction becomes

$$\phi_1 = \frac{1s_a + 1s_b}{\sqrt{2(1 + S_{ab})}} \quad (17)$$

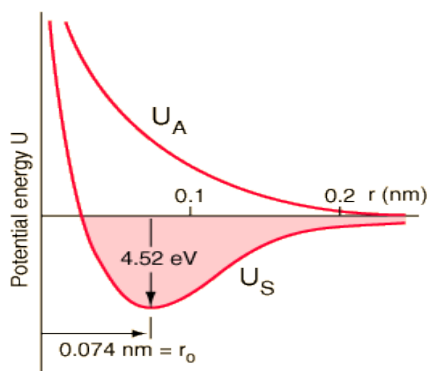
$$\phi_2 = \frac{1s_a - 1s_b}{\sqrt{2(1 - S_{ab})}} \quad (18)$$

Bonding and Anti-bonding

A buildup of charge between nuclei for ϕ_1 ($1s_a + 1s_b$, or $\sigma_g 1s$), there is a minimum in $U(R)$.



No buildup of charge between nuclei for ϕ_2 ($1s_a - 1s_b$, $\sigma_u^* 1s$), and the $U(R)$ curve has no minimum.



Two different notations: **Separated-atom description vs United-atom Description**

Hybridization: the mixing of two or more atomic orbitals on the same atom is called hybridization.

2.3 Molecular Orbitals For H_2^+ Excited States

We still use LCAO-MOs to approximate higher H_2^+ molecular orbitals. For the six lowest σ states, we use a linear combination of the three hydrogenic atomic orbitals ($m=0$) on each atom:

$$\phi = c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a + c_4 2s_b + c_5 2s_b + c_6 (2p_0)_b \quad (19)$$

This can be transformed to

$$\phi = [c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a] \pm [c_4 2s_b + c_5 2s_b + c_6 (2p_0)_b] \quad (20)$$

where the upper sign goes with the even states.

To obtain the six molecular orbitals, one has to solve the secular equations for the coefficients. Here, using a first order approximation, we obtain the following six MOs ($m=0$):

$$\begin{aligned} \sigma_g 1s: & 1s_a + 1s_b \\ \sigma_u^* 1s: & 1s_a - 1s_b \\ \sigma_g 2s: & 2s_a + 2s_b \\ \sigma_u^* 2s: & 2s_a - 2s_b \\ \sigma_g 2p: & (2p_0)_a + (2p_0)_b \\ \sigma_u^* 2p: & (2p_0)_a - (2p_0)_b \end{aligned}$$

For the other two $2p$ orbitals, we either use either the complex functions ($2p_{+1}$ and $2p_{-1}$) or the real functions $2p_x$ and $2p_y$ (note $2p_{+1} \sim r e^{-r/2} \sin \theta e^{i\phi}$). Now we have

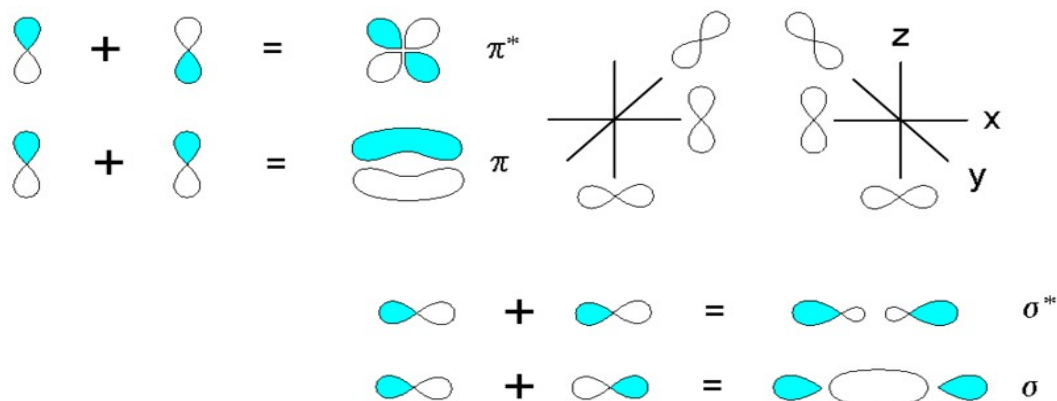
$$\pi_u 2p_{+1}: (2p_{+1})_a + (2p_{+1})_b$$

$$\pi_u 2p_{-1}: (2p_{-1})_a + (2p_{-1})_b$$

$$\pi_g^* 2p_{+1}: (2p_{+1})_a - (2p_{+1})_b$$

$$\pi_g^* 2p_{-1}: (2p_{-1})_a - (2p_{-1})_b$$

We can also form molecular orbitals by taking LCAO of $2p_x$ and $2p_y$.



3. MO Configurations of (Homonuclear) Diatomic Molecules

For Many-electron homonuclear diatomic molecules, if we ignore the inter-electronic repulsions, the wavefunction is a Slater-determinant of H_2^+ like one-electron orbitals. Treatments that go beyond this will be discussed in a later section.

The sizes and energies of the MOs vary with varying internuclear distance for each molecule. Despite numerous crossings, the following is the order in which the MOs will fill as we go across the periodic table:

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p_{+1} = \pi_u 2p_{-1} < \sigma_g 2p < \pi_g^* 2p_{+1} = \pi_g^* 2p_{-1} < \sigma_u^* 2p \quad (21)$$

3.1 Molecular Orbital Diagram:

A molecular orbital diagram is a qualitative descriptive tool explaining chemical bonding in molecules in terms of molecular orbital theory in general and the LCAO method in particular. This tool is very well suited for simple diatomic molecules such as dihydrogen, dioxygen and carbon monoxide.

It explains why some molecules exist and not others, how strong bonds are, and what electronic transitions take place.

Constructing an MO diagram by filling the molecular orbitals with electrons:

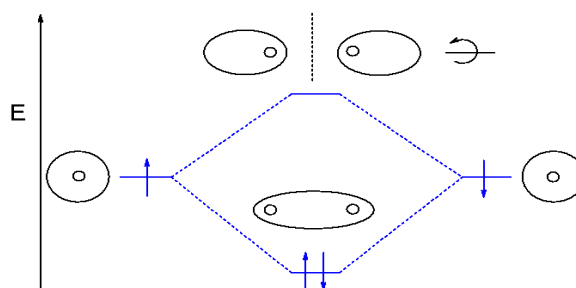
The Aufbau principle; The Pauli exclusion principle; Hund's rule.

HOMO: Highest Occupied Molecular Orbitals

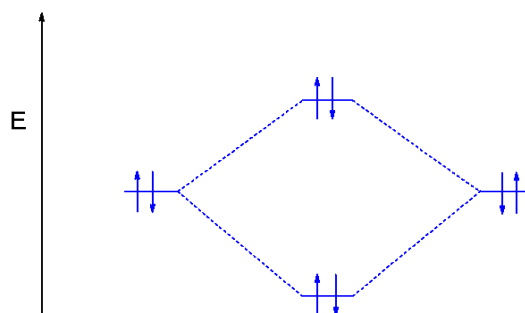
LUMO: Lowest Unoccupied Molecular Orbitals

$$\text{Bond order} = \frac{\text{number of electrons in bonding MOs} - \text{number of electrons in anti-bonding MOs}}{2}$$

Bond order must be larger than 0.

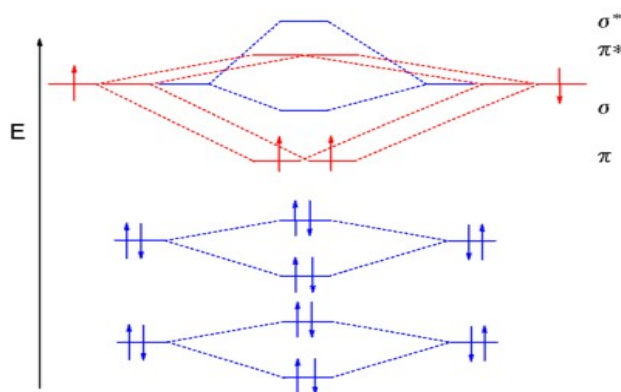


Dihelium MO diagram



Bond order of He₂ = 0. Bond order of He₂⁺ = 1/2.

Diboron MO Diagram:



3.2 Electronic Terms of Diatomic Molecules

We define a molecular electronic configuration by giving the number of electrons in each shell, for example: $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^3$

The component of electronic orbital angular momentum along the molecular axis has the possible values $M_L \hbar$, where $M_L = 0, \pm 1, \pm 2, \dots$. To calculate M_L , we simply add algebraically m_l 's of the individual electrons, and

$$\Lambda = |M_L| \quad (22)$$

Λ	0	1	2	3	4
letter	Σ	Π	Δ	Φ	Γ

The individual electron spins add vectorially to give a total electronic spin S . The quantity $2S+1$ is called the **spin multiplicity**.

A single σ electron gives a $^2\Sigma$ term; a single π electron gives a $^2\Pi$ term.

4. The Hydrogen Molecule

4.1 The MO approach

The ground state electronic configuration of H_2 is $(\sigma_g 1s)^2$, term symbol?, we can write an approximate wavefunction as the Slater determinant

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g 1s(1)\alpha(1) & \sigma_g 1s(2)\alpha(2) \\ \sigma_g 1s(1)\beta(1) & \sigma_g 1s(2)\beta(2) \end{vmatrix} = \sigma_g 1s(1)\sigma_g 1s(2) 2^{-1/2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (23)$$

Our task becomes to choose a proper function for $f = \sigma_g 1s$, so as to minimize

$$\frac{\int \int f^*(1) f^*(2) \hat{H} f(1) f(2) d\tau_1 d\tau_2}{\int \int |f(1)|^2 |f(2)|^2 d\tau_1 d\tau_2}$$

trial function 1: $\frac{k^{3/2}}{(2^{\pi})^{1/2} (1+S_{ab})^{1/2}} (e^{-kr_a} + e^{-kr_b})$

trial function 2: $e^{-\alpha\zeta} \sum_{p,q} a_{p,q} \zeta^p \eta^q$

More will be discussed later.

4.2 The valence-bond treatment

The first quantum mechanical treatment of the hydrogen molecules was by Heitler and London in 1927. This idea has been extended to give a general theory of chemical bonding called “valence bond” theory. It treats atoms as composed of atomic cores and bonding valence shells. For H_2 , the two electrons are all valence electrons.

The wavefunction for two non-interaction electrons is

$$f(1) = 1s_a(1)1s_b(2) \quad \text{Or} \quad f(2) = 1s_a(2)1s_b(1) \quad (24)$$

This suggests a variational wavefunction of

$$c_1 f_1 + c_2 f_2 = c_1 1s_a(1)1s_b(2) + c_2 1s_a(2)1s_b(1) \quad (25)$$

This linear variation function leads to the determinantal secular wavefunction $\det(H_{ij} - S_{ij}W) = 0$.

The Heitler-London wavefunction for the ground state is found to be

$$\frac{1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)}{\sqrt{2}(1 + S_{ab}^2)^{1/2}} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (26)$$

We can also find the wavefunctions for the next excited states.

To calculate the energies of the states, two integrals will be evaluated:

$$\text{Coulomb integral} \quad \int \int 1s_a^*(1)1s_b(2) \hat{H} ' 1s_a(1)1s_b(2) d\tau_1 d\tau_2$$

Exchange integral $\int \int 1s_a^*(2)1s_b(1) \hat{H} ' 1s_a(1)1s_b(2) d\tau_1 d\tau_2$. (This is the most difficult part, it is called *two-center, two-electron* integration).

4.3 Comparison of the VB and MO method

The unnormalized LCAO-MO wavefunction for the H_2 ground state is

$$[\phi_a(1) + \phi_b(1)][\phi_a(2) + \phi_b(2)] \quad (27)$$

This function equals:

$$\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2) + \phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1) \quad (28)$$

The first two terms are called ionic terms (corresponding to the chemical structures H^+H^- and H^-H^+). The last two terms are covalent terms.

According to this MO description, there is a 50-50 chance as to whether the H_2 deassociates into two neutral H atoms or to a proton and a hydride ion. (This does not agree with the real scenario).

The simple MO functions give the wrong limiting value as the energy as R goes to infinity.

A remedy is to omit the two ionic terms. Equation 28 now is equivalent to the VB function.

An improvement on VB functions is to include *ionic-covalent resonance*

$$\phi_{VB,imp} \phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1) + \delta[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)] \quad (29)$$

This actually corresponds to LCAO-MO CI trial function. (why?)

4.4 MO and VB wavefunctions for Homonuclear Diatomic Molecules

We compared the two methods for H_2 . Now let's consider other diatomic molecules.

For the ground state of He_2 , the separated helium atoms each have the ground-state configuration of $1s^2$.

- closed subshell
- no unpaired electrons to form valence bond.

The VB wavefunction is simply

$$\frac{1}{\sqrt{24}} \begin{vmatrix} 1s_a(1) & \bar{1}s_a(1) & 1s_b(1) & \bar{1}s_b(1) \\ 1s_a(2) & \bar{1}s_a(2) & 1s_b(2) & \bar{1}s_b(2) \\ 1s_a(3) & \bar{1}s_a(3) & 1s_b(3) & \bar{1}s_b(3) \\ 1s_a(4) & \bar{1}s_a(4) & 1s_b(4) & \bar{1}s_b(4) \end{vmatrix} \quad (30)$$

In the shorthand notation, this is

$$|1s_a \bar{1}s_a 1s_b \bar{1}s_b| \quad (31)$$

The MO approximation to the wavefunction is

$$|\sigma_g 1s \bar{\sigma}_g \bar{1}s \sigma_u^* 1s \bar{\sigma}_u^* 2s| \quad (32)$$

Taken MOs as LCAO: $\sigma_g 1s = 1s_a + 1s_b$, $\sigma_u^* = 1s_a - 1s_b$, equation 32 becomes

$$|(1s_a + 1s_b)(\bar{1}s_a + \bar{1}s_b)(1s_a - 1s_b)(\bar{1}s_a - \bar{1}s_b)| \quad (33)$$

This is equivalent to the VB wavefunction shown in equation 31. (Why?)

Heitler-London's VB wavefunction (ground state) can be written as

$$\frac{1}{2} (1 + S_{ab}^2)^{-1/2} \{ |1s_a \bar{1}s_b| - |\bar{1}s_a 1s_b| \} \quad (34)$$

Singlet: $|1s_a \bar{1}s_b| - |\bar{1}s_a 1s_b|$

Triplet: $\begin{vmatrix} |1s_a 1s_b| \\ |1s_a \bar{1}s_b| + |\bar{1}s_a 1s_b| \\ |\bar{1}s_a \bar{1}s_b| \end{vmatrix}$

Li_2 : ground state configuration is $1s^2 2s$

The Lewis structure is $\text{Li}-\text{Li}$

The ground state VB function uses 6×6 Slater Determinant

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} 2s_a \overline{2s_b}| - |1s_a \overline{1s_a} 1s_b \overline{1s_b} 2s_a \overline{2s_b}| \quad (35)$$

The MO wavefunction is

$$|\sigma_g 1s \overline{\sigma_g} 1s \sigma_u^* 1s \overline{\sigma_u^*} 1s \sigma_g 2s \overline{\sigma_g} 2s| \quad (36)$$

This can be simplified as

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} \sigma_g 2s \overline{\sigma_g} 2s| \quad (37)$$

VB treatment for the ground state of N_2 : electronic configuration $1s^2 2s^2 2p^3$

What is the ground state term symbol according to Hund's rule?

The Lewis structure is $\text{N} \equiv \text{N}$:

There are 8 possible Slater determinant that we can write.

$$D_1 = |1s_a \overline{1s_a} 2s_a \overline{2s_a} 1s_b \overline{1s_b} 2s_b \overline{2s_b} 2p_{xa} \overline{2p_{xb}} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}|$$

$$D_2 = |1s_a \overline{1s_a} 2s_a \overline{2s_a} 1s_b \overline{1s_b} 2s_b \overline{2s_b} 2p_{xa} \overline{2p_{xb}} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}|$$

...

$$D_8 = |1s_a \overline{1s_a} 2s_a \overline{2s_a} 1s_b \overline{1s_b} 2s_b \overline{2s_b} 2p_{xa} \overline{2p_{xb}} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}|$$

The VB function is a linear combination of eight Slater determinants, and the coefficient of each determinant is either 1 or -1.

The single determinant MO wavefunction is much easier (why?)

Computational Homework (Due April 8, 2008):

(1) Propose a simple computational problem and solve it using Gaussian03. Report the results.

(2) Perform HF/STO-3G calculations on Oxygen diatomic molecules. (a) Estimate the equilibrium internuclear distance of O_2 . (b) Present visualization results of O_2 molecular orbitals (see, e.g. <http://educ.gaussian.com/visual/index.html> for a visualization tutorial).