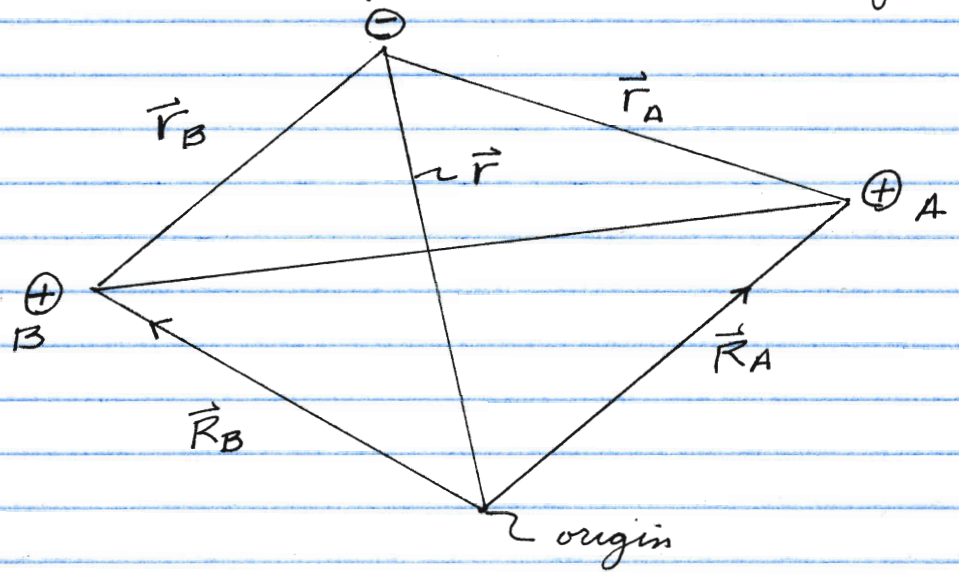
Born Oppenheimer Approximation

Consider the complete Hamiltonian for H_2^+



The separation between A & B is $R = |\vec{R}_A - \vec{R}_B|$

$$\hat{\mathcal{H}}_T = -\frac{1}{2M_P}\nabla_A^2 - \frac{1}{2M_P}\nabla_B^2 - \frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

~~We with~~ The Born Oppenheimer approximation recognizes that the mass of the proton M_P is much larger than the mass of the electron & as a result we may consider the nuclei as stationary & solve for the motion of the electron for a fixed R.

The Born-Oppenheimer Hamiltonian for H_2^+ is

$$\hat{H}_{BO} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

If we solve

$$\hat{H}_{BO}\psi_{BO} = \mathcal{E}_{BO}\psi_{BO}$$

we must first fix R & then solve the equation.

Let $\hat{H}_e = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B}$

Then $\hat{H}_{BO} = \hat{H}_e + \frac{1}{R}$

So

$$\left(\hat{H}_e + \frac{1}{R}\right)\psi_{BO} = \mathcal{E}_{BO}\psi_{BO}$$

$$\hat{H}_e\psi_{BO} = \left(\mathcal{E}_{BO} - 1/R\right)\psi_{BO} = \mathcal{E}_e\psi_{BO}$$

Since

$$r_A = \sqrt{(x-x_A)^2 + (y-y_A)^2 + (z-z_A)^2}$$

$\hat{H}_e$, ψ_{BO} & $\mathcal{E}_{BO}$ all depend on R, so

$$\mathcal{E}_{BO}(R) = \mathcal{E}_e(R) + 1/R$$

We know $\mathcal{E}_e(R)$ at two values of R.

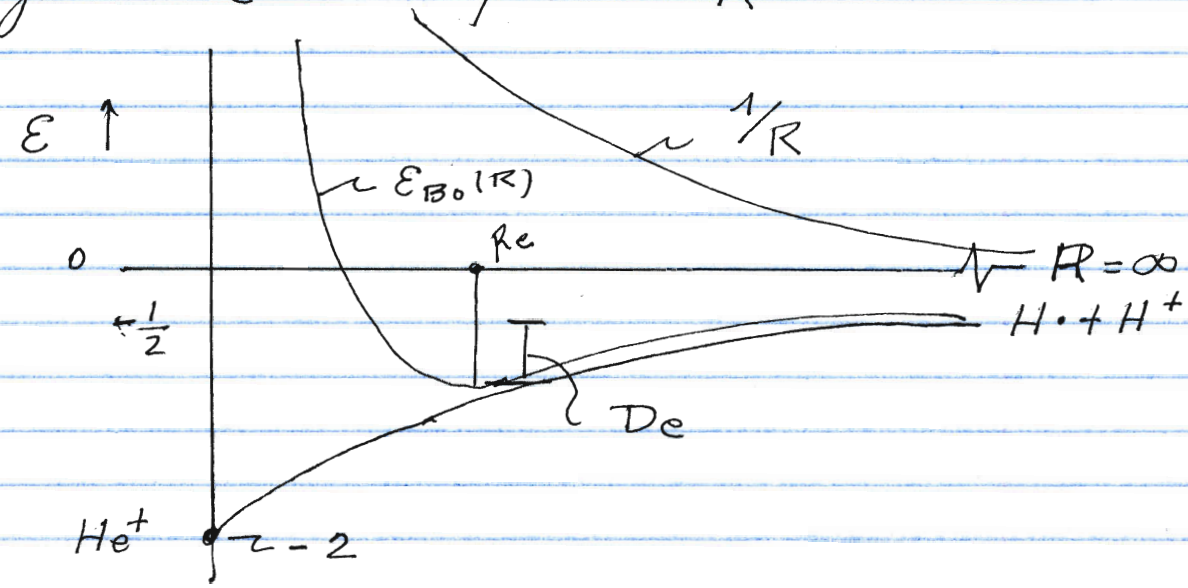
First, when $R = \infty$ $\quad \mathcal{E}_e = -\frac{1}{2}$

because when H_2^+ dissociates it form $H\cdot + H^+$ & the energy of $H\cdot$ is $-\frac{1}{2}$.

Second, when $R = 0$. In this case $r_A = r_B$ & so $\hat{H}_e = -\frac{1}{2}\nabla^2 - \frac{2}{r_A}$ & this is the He^+ Hamiltonian. Consequently $\mathcal{E}_e(0) = -\frac{1}{2}\,4 = -2$

The $R = \infty$ solution is called the separated atom limit while the $R = 0$ is the united atom limit.

The eigenvalue $\mathcal{E}_e(R)$ varies smoothly between these limits. The total $\mathcal{E}_{BO}$ is then the sum of the negative $\mathcal{E}_e$ & the positive $1/R$



Once one has $\mathcal{E}_{BO}(R)$ one forms the Hamiltonian for the nuclear motion

$$\hat{\mathcal{H}}_N = -\frac{1}{2M_P}\nabla_A^2 - \frac{1}{2M_P}\nabla_B^2 + \mathcal{E}_{BO}(R)$$

& Solves

$$\hat{\mathcal{H}}_N \psi(R) = E(R)\psi(R)$$

Once can write $\hat{H}_N$ as $\hat{\mathcal{H}}_{CM} + \hat{\mathcal{H}}_{ROT} + \hat{\mathcal{H}}_{VIB}$

&

$$\psi(R) = \psi_{CM}\psi_{ROT}\psi_{VIB}$$

& $E(R) = E(R_e) + E_{CM} + E_{ROT} + E_{VIB}$

$E(R_e) = \mathcal{E}_{BO}(R_e)$

E_{CM} = kinetic energy of center of mass

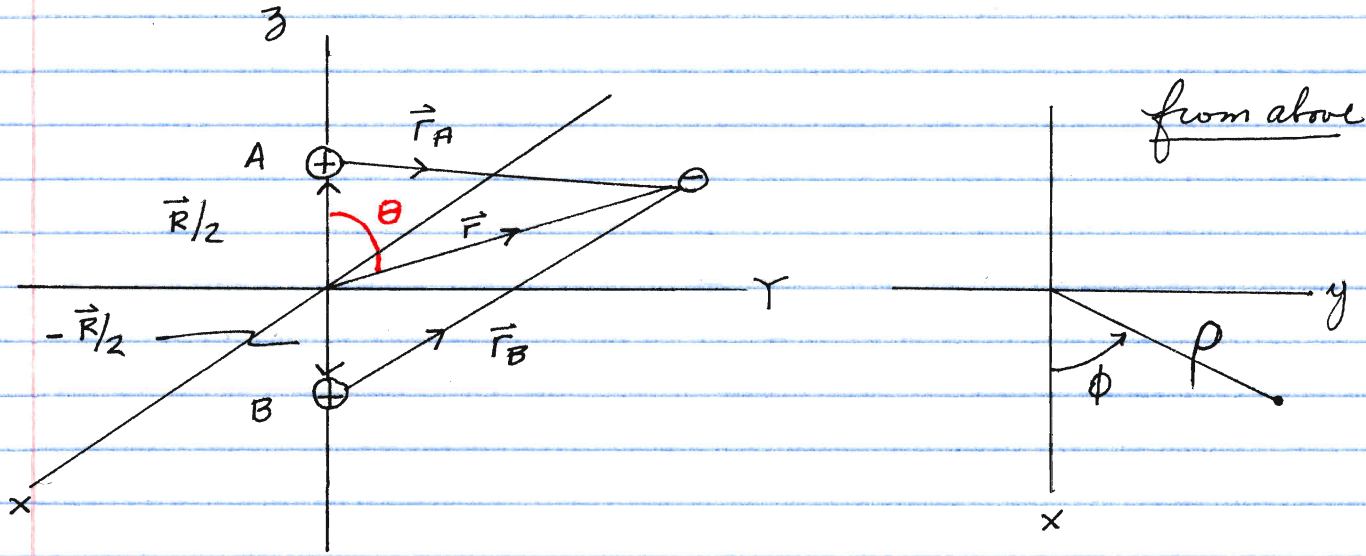
$E_{ROT} = J(J+1)\frac{\hbar^2}{2I}$ as before

$E_{VIB} = h\nu(v+1/2) + \cdots$ as before

We will focus on $\hat{\mathcal{H}}_{BO}$ & simply call it $\hat{\mathcal{H}}$.

Lets see what we can learn about the solutions to $\hat{H}\psi = E\psi$ in the BO approximation

Lets place the protons on the z axis with one at $z = +R/2$ & the other at $z = -R/2$



The x, Y, z coordinates of the electron can be expressed in cylindrical coordinates

$$x = \rho \cos\phi \;,\; Y = \rho \sin\phi \;\&\; z = z$$

& so

$$-\frac{1}{2}\nabla^2 = -\frac{1}{2\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2}$$

recall $\hat{L}_z = -i\frac{\partial}{\partial\phi}$ in atomic units

$$\text{so} \quad \hat{L}_z^2 = -\frac{\partial^2}{\partial \phi^2}$$

& since $-\frac{1}{2}\nabla^2$ contains $\frac{\partial^2}{\partial \phi^2}$ the two operators commute. What about $\frac{1}{r_A}$ & $\frac{1}{r_B}$

$$r_A = \sqrt{x^2 + y^2 + (z - R/2)^2} = \sqrt{\rho^2 + (z - R/2)^2}$$

&

r_A & r_B do not depend on ϕ so

$$[\hat{\mathcal{H}}, \hat{L}_z] = 0$$

This means

$$\psi(\rho, z\, \phi) = \psi(\rho, z)\, e^{im\phi}$$

with $M = 0, \pm 1, \pm 2, \ldots$ & the eigenfunctions must be eigenfunctions of L_z with eigenvals M.

M	0	± 1	± 2	± 3 $\cdots$
letter	σ	π	δ	ϕ $\cdots$
or	Σ	Π	Δ	Φ $\cdots$

Consider the consequence of the two nuclei being identical.

Define an inversion operator $\hat{I}$ which is such that

$$\hat{I} f(\vec{r}) = f(-\vec{r})$$

The eigenvalue problem for $\hat{I}$ is

$$\hat{I} \chi(\vec{r}) = \lambda \chi(\vec{r})$$

but $\hat{I} \chi(\vec{r}) = \chi(-\vec{r})$ by definition. & so

$$\hat{I}^2 \chi(\vec{r}) = \hat{I} \chi(-\vec{r}) = \chi(\vec{r})$$

but $$\hat{I}^2 \chi(\vec{r}) = \hat{I} \lambda \chi(\vec{r}) = \lambda^2 \chi(\vec{r})$$

so $$\lambda^2 = 1 \quad \& \quad \lambda = \pm 1$$

Consider now the commutator of $\hat{I}$ & $\hat{\mathcal{H}}$.

$\hat{I}$ certainly commutes with ∇^2 because of the second derivatives $\frac{\partial^2}{\partial x^2}$ etc. What about r_A & r_B.

$$\hat{I} r_A = \hat{I} \sqrt{x^2 + y^2 + (z - R/2)^2}$$

$$= \sqrt{x^2 + y^2 + (-z - R/2)^2} = r_B$$

& conversely

$$\hat{I} r_B = r_A$$

So the operator $\hat{I}$ commutes with the Hamiltonian for H_2^+. ~~Thus~~ Then if

$$\hat{I}\psi = E\psi$$

we have some ψ which change sign

$$\hat{I}\psi = -\psi$$

& some that don't

$$\hat{I}\psi = +\psi$$

Eigenfunctions that change sign upon inversion are called ungerade (u) functions while those that do not change sign are gerade or g functions.

It is reasonable to assume that the lowest energy state of H_2^+ starts out as the 1s orbital at $R=\infty$ and finishes as the 1s orbital of He^+ at $R=0$. The 1s of He^+ has g symmetry & the 1s of H has $m=0$ & is a σ orbital. The electronic configuration is then $1\sigma_g^1$.

Just as with atoms, diatomic molecules can have term symbols. For H_2^+ we have one electron & so $2S+1 = 2$, a doublet. The ground state term is $^2\Sigma_g^+$ where the + means the wavefunction does not change sign when reflected through any plane containing the two nuclei.

Approximate Wave functions for H_2^+

If we take our variation function as

$$\psi = c_A 1s_A + c_B 1s_B$$

where

$$1s_A = \frac{1}{\sqrt{\pi}} e^{-r_A} \quad \& \quad 1s_B = \frac{1}{\sqrt{\pi}} e^{-r_B}$$

we can determine c_A & c_B in two ways. First, we can insist that ψ be an eigenfunction of $\hat{I}$ & second we can use the variation method.

Eigenfunction of $\hat{I}$

recall

$$\hat{I} r_A = r_B \quad \& \quad \hat{I} r_B = r_A$$

So

$$\hat{I} 1s_A = 1s_B \quad \& \quad \hat{I} 1s_B = 1s_A$$

So

$$\hat{I}\psi = c_A \hat{I} 1s_A + c_B \hat{I} 1s_B = c_A 1s_B + c_B 1s_A$$

If we require ψ to be ψ_g

$$\hat{I}\psi = +\psi$$

&

$$\therefore \quad c_A 1s_B + c_B 1s_A = c_A 1s_A + c_B 1s_B$$

$$(c_A - c_B) 1s_B + (c_B - c_A) 1s_A = 0$$

$$(c_A - c_B)(1s_B - 1s_A) = 0$$

for this to be true for all x, y, z, $c_A = c_B$

So $\psi_g = c_A (1s_A + 1s_B)$

we fix c_A by normalizing ψ_g

$$\langle \psi_g | \psi_g \rangle = c_A^2 \langle 1s_A + 1s_B | 1s_A + 1s_B \rangle = 1$$

So $$c_A = \frac{1}{\sqrt{2+2S}} \quad \text{where } S = \langle 1s_A | 1s_B \rangle$$

S is called the overlap integral & for the orbitals $1s_A$ & $1s_B$ has the form

$$S = e^{-R}\left(1 + R + R^2/3\right)$$

Having ψ_g we can compute the energy as a function of R. The energy is given by

$$E_g = \langle \psi_g | \hat{\mathcal{H}} | \psi_g \rangle = \frac{\langle 1s_A + 1s_B | \hat{\mathcal{H}} | 1s_A + 1s_B \rangle}{2 + 2S}$$

Consider the numerator

$$\langle 1s_A + 1s_B | \hat{\mathcal{H}} | 1s_A + 1s_B \rangle = H_{AA} + H_{BB} + 2H_{AB}$$

Now

$$H_{AA} = \langle 1s_A | -\tfrac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} | 1s_A \rangle$$

$$H_{AA} = -\tfrac{1}{2} - \langle 1s_A | \frac{1}{r_B} | 1s_A \rangle + \frac{1}{R}$$

$-\langle 1s_A | \frac{1}{r_B} | 1s_A \rangle$ = the attraction of the electron on center A (with $\frac{1}{R}$) for nucleus B. Sometimes called (in your text) the Coulomb integral $J = -\langle 1s_A | \frac{1}{r_B} | 1s_A \rangle + 1/R$

$$H_{AA} = -\tfrac{1}{2} + J \quad *$$

Likewise

$$H_{BB} = -\tfrac{1}{2} + J$$

since by symmetry $\langle 1s_B | \frac{1}{r_A} | 1s_B \rangle = \langle 1s_A | \frac{1}{r_B} | 1s_A \rangle$

$$H_{AB} = -\frac{S}{2} - \langle 1s_A | \frac{1}{r_A} | 1s_B \rangle + \frac{S}{R}$$

The quantity $-\langle 1s_A | \frac{1}{r_A} | 1s_B \rangle + S/R = K$

where K is called (in your text) the exchange integral.

The numerator is then

$$-1 + 2J - S + 2K = -(1+S) + 2(J+K)$$

Dividing by $2+2S$

$$E_g = \underbrace{-\frac{1}{2}}_{\text{energy of } H_2^+ \text{ at } R=\infty} + \underbrace{\frac{J+K}{1+S}}_{\text{energy change upon molecule formation}}$$

Define $\Delta E_+ = E_g + 1/2 = \frac{J+K}{1+S} = \Delta E_+(R)$

One can evaluate $J = e^{-2R}(1 + 1/R)$

$$K = \frac{S}{R} - e^{-R}(1+R)$$

The minimum occurs at $\frac{\partial \Delta E_+}{\partial R} = 0$

we find $R_{min} = R_e = 2.50\, a_0$ & $\Delta E_+(R_e) = -1.76$ eV

H_2^+ is bound in this approximation but since the experimental $R_e = 2.00\, a_0$ & experimental $\Delta E_+ = -2.79$ eV we are not close.

We can improve these results by generalizing the trial function & introducing a variational parameter

Let $1s_A = \sqrt{\frac{\alpha^3}{\pi}}\, e^{-\alpha r_A}$ & $1s_B = \sqrt{\frac{\alpha^3}{\pi}}\, e^{-\alpha r_B}$

We find $\Delta E_+(R, \alpha)$

So forming $\frac{\partial \Delta E_+}{\partial R} = 0$ & $\frac{\partial \Delta E_+}{\partial \alpha} = 0$

we find $\alpha_{opt} = 1.24$ & $R_e = 2.02\, a_0$ & then

$\Delta E_+(R_e, \alpha_{opt}) = -2.35\ eV$, a significant improvement.

We could also use the Linear Variation Method to determine C_A & C_B.

taking $\psi = C_A 1s_A + C_B 1s_B$

& forming $E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = E(C_A, C_B)$

we determine $\frac{\partial E}{\partial C_A} = \frac{\partial E}{\partial C_B} = 0$

which results in the simultaneous equations

$$C_A(H_{AA}-E) + C_B(H_{AB}-ES) = 0$$

$$C_A(H_{AB}-ES) + C_B(H_{BB}-E) = 0$$

The solution requires the secular equation

$$\begin{vmatrix} H_{AA}-E & H_{AB}-ES \\ H_{AB}-ES & H_{BB}-E \end{vmatrix} = 0$$

We have seen $H_{AA} = H_{BB}$, So

$$(H_{AA}-E)^2 = (H_{AB}-ES)^2$$

& $\therefore \pm(H_{AA}-E) = (H_{AB}-ES)$

~~pro~~ substituting into the simultaneous equation

$$C_A(H_{AA}-E) + C_B(\pm)(H_{AA}-E) = 0$$

requires $C_A = \pm C_B$

& $\therefore \quad \psi_g = C_A(1s_A + 1s_B)$

$$\psi_u = C_A(1s_A - 1s_B)$$

We can then compute the energy as before or solve for E in

$$H_{AA}-E = \pm(H_{AB}-ES)$$

Taking the negative sign

$$E_g = \frac{H_{AA} + H_{AB}}{1+S}$$

we have seen $H_{AA} = -\frac{1}{2} + J$ & $H_{AB} = -\frac{S}{2} + K$

So

$$E_g = \frac{-\frac{1}{2} + J. -\frac{S}{2} + K}{1+S} = -\frac{1}{2} + \frac{J+K}{1+S}$$ as found earlier.

Also E_u = (~~positive~~ sign) $= \frac{H_{AA} - H_{AB}}{1-S}$

$$E_u = \frac{-\frac{1}{2} + J + \frac{S}{2} - K}{1-S} = -\frac{1}{2} + \frac{J-K}{1-S}$$

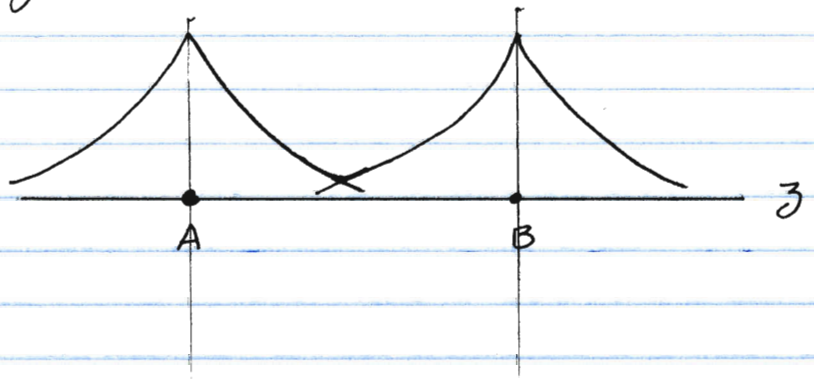
The Ψ_u state does not result in a stable molecule.

Bonding & Anti bonding Orbitals

If one plots the square of Ψ_g function

$$\Psi_g^2 = \left(\frac{1s_A + 1s_B}{\sqrt{2+2S}}\right)^2$$

along the internuclear line (z) -

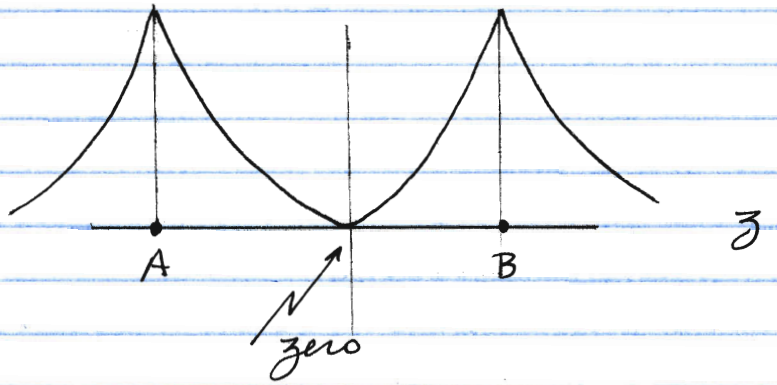


One finds that there is more electron density in the region between the two nuclei than if one simply plotted the sum of the non interacting atomic densities. The ψ_g is a bonding orbital.

On the other hand, the ψ_u function

$$\psi_u = \frac{1s_A - 1s_B}{\sqrt{\quad}}$$

has a node exactly half way between the two nuclei & when squared the node remains, so ψ_u^2 looks like



& there is a decrease in the electron density relative to the ~~two~~ non interacting atoms. The ψ_u is an antibonding orbital.

Improvements

We took the variation function (for the g state) as

$$1s_A + 1s_B$$

but there is no reason to stop with the 1s orbitals. We could, for example write:

$$\psi_g = C_{1s}(1s_A + 1s_B) + C_{2s}(2s_A + 2s_B) + C_{2p}(2p_{zA} - 2p_{zB})$$
$$+ C_{3s}(3s_A + 3s_B) + C_{3p}(3p_{zA} - 3p_{zB})$$
$$+ C_{3d}(3d_{z^2A} + 3d_{z^2B}) + \cdots .$$

& determine the coefficients using the linear variation method. When we do this we are using the SCF-LCAO-MO method. The basis functions

$$1s_A + 1s_B$$

$$2s_A + 2s_B$$

$$2p_{zA} - 2p_{zB}$$

are called symmetry orbitals and one can write them down immediately. The weight (the C's) with which

the symmetry orbitals enter the molecular orbital is determined by the secular equations. The symmetry orbitals can be labelled as

$\sigma_g 1s = (1s_A + 1s_B) N$ ← normalization

$\sigma_g 2s = (2s_A + 2s_B) N'$

$\sigma_g 2p_z = (2p_{zA} - 2p_{zB}) N''$

$\sigma_u 1s = (1s_A - 1s_B) N$

$\sigma_u 2s = (2s_A - 2s_B) N$

$\sigma_u 2p_z = (2p_{zA} - 2p_{zB}) N$