

# Quantum chemistry 3

Chapter 13-17  
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## CHAPTER 13

Electronic Structure of  
Diatomic Molecules

- There are two principal models of molecular structure: **molecular orbital theory** and **valence bond theory**.
- Even the simplest molecule,  $H_2^+$  consists of three particles, and its Schrodinger equation cannot be solved analytically.
- The Born–Oppenheimer approximation is very reliable for ground electronic states, but it is less reliable for excited states.

## THE BORN-OPPENHEIMER APPROXIMATION

- we assume the nuclei and electrons to be point masses and neglect spin-orbit and other relativistic interactions then the molecular Hamiltonian is

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

The zero level of PE for this eq  $\rightarrow$  all the charges infinitely far from one another

The  $H_2$  molecular Hamiltonian is

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_p} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_p} \nabla_{\beta}^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 \\ & + \frac{e'^2}{r_{\alpha\beta}} - \frac{e'^2}{r_{1\alpha}} - \frac{e'^2}{r_{1\beta}} - \frac{e'^2}{r_{2\alpha}} - \frac{e'^2}{r_{2\beta}} + \frac{e'^2}{r_{12}} \end{aligned}$$

## Born-Oppenheimer approximation

the Schrodinger equation:

$$\hat{H}\psi(q_i, q_\alpha) = E\psi(q_i, q_\alpha)$$

$q_i$  and  $q_\alpha$  symbolize the electronic and nuclear coordinates, respectively.

a highly accurate, simplifying approximation exists.

$$m_\alpha \gg m_e$$

considering the nuclei as fixed, we omit the nuclear kinetic-energy terms

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

## Born-Oppenheimer approximation

**purely electronic Hamiltonian  $\hat{H}_{\text{el}}$**

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

The electronic Hamiltonian including nuclear repulsion is

$$\hat{H}_{\text{el}} + V_{NN}$$

The nuclear- repulsion term  $V_{NN}$  is given by

$$V_{NN} = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta e'^2}{r_{\alpha\beta}}$$

## Born-Oppenheimer approximation

The energy  $U$  is the electronic energy including internuclear repulsion.

The internuclear distances  $r_{\alpha\beta}$  are not variables.

get a set of electronic wave functions and corresponding electronic energies; each member of the set corresponds to a different molecular electronic state. The electronic wave functions and energies thus depend parametrically on the nuclear configuration:

$$\psi_{\text{el}} = \psi_{\text{el},n}(q; q_{\alpha}) \quad \text{and} \quad U = U_n(q_{\alpha})$$

$n$ : electronic quantum numbers

if  $V_{\text{NN}}$  is omitted

$$\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}}$$

purely electronic energy

## Born-Oppenheimer approximation

$$U = E_{\text{el}} + V_{\text{NN}}$$

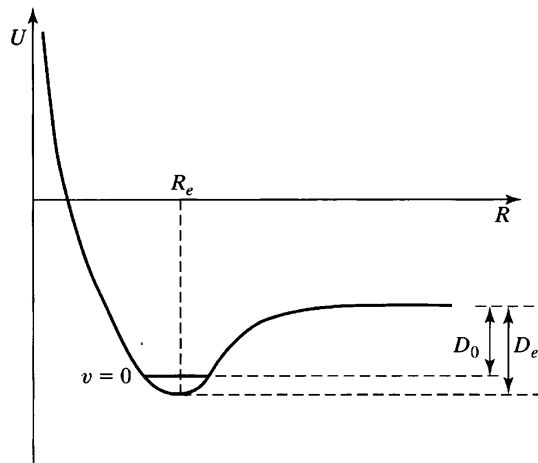
The internuclear separation at the minimum in this curve is called the equilibrium internuclear distance  $R_e$ .

The difference between the limiting value of  $U$  at infinite internuclear separation and its value at  $R_e$  is called the equilibrium dissociation energy  $D_e$ :

$$D_e \equiv U(\infty) - U(R_e)$$

molecular ground-vibrational-state dissociation energy  $D_0$ .

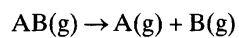
## Born-Oppenheimer approximation



Electronic energy including internuclear repulsion as a function of the internuclear distance  $R$  for a diatomic-molecule bound electronic state.

## Born-Oppenheimer approximation

dissociation of 1 mole of ideal-gas diatomic molecules:



$$N_A D_0 = \Delta U_0^\circ = \Delta H_0^\circ$$

For some diatomic-molecule electronic states, solution of the electronic Schrodinger equation gives a  $U(R)$  curve with no minimum. Such states are not bound and the molecule will dissociate.

## Born-Oppenheimer approximation

$$\hat{H}_N \psi_N = E \psi_N$$

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

The variables in the nuclear Schrodinger equation are the nuclear coordinates, symbolized by  $q_{\alpha}$ .

The energy eigenvalue  $E$  is the total energy of the molecule, since the Hamiltonian includes operators for both nuclear energy and electronic energy.

## Born-Oppenheimer approximation

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

$$E \approx E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{tr}} \quad \text{where } E_{\text{elec}} = U(R_e)$$

The approximation of separating electronic and nuclear motions is called the **Born-Oppenheimer approximation** and is basic to quantum chemistry.

Born and Oppenheimer's mathematical treatment indicated that

$$\psi(q_i, q_{\alpha}) \approx \psi_{\text{el}}(q_i; q_{\alpha}) \psi_N(q_{\alpha}) \quad \text{molecular wave function}$$

if  $(m_e/m_{\alpha})^{1/4} \ll 1$

## Born-Oppenheimer approximation

The Born-Oppenheimer approximation introduces little error for the ground electronic states of diatomic molecules.

Corrections for excited electronic states are larger than for the ground state, but still are usually small as compared with the errors introduced by the approximations used to solve the electronic Schrodinger equation of a many-electron molecule.

## NUCLEAR MOTION IN DIATOMIC MOLECULES

the Schrodinger equation for nuclear motion in a diatomic-molecule bound electronic state

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

$$\Psi_N = \Psi(x_\alpha, y_\alpha, z_\alpha, x_\beta, y_\beta, z_\beta)$$

$$U = U(R) \quad \text{the relative coordinates of the two nuclei}$$



$$\psi_N = \psi_{N,\text{tr}} \psi_{N,\text{int}} \quad \text{and} \quad E = E_{\text{tr}} + E_{\text{int}}$$



Two Schrodinger eq., one for translational motion and one for internal motion

Internal motion

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + U(R) \right] \psi_{N,\text{int}} = E_{\text{int}} \psi_{N,\text{int}}, \quad \mu \equiv m_\alpha m_\beta / (m_\alpha + m_\beta)$$

the potential energy depends on  
R only (a central-force problem)



the spherical coordinates of one  
nucleus relative to the other

$$\psi_{N,\text{int}} = P(R) Y_J^M(\theta_N, \phi_N), \quad J = 0, 1, 2, \dots, \quad M = -J, \dots, J$$

the spherical harmonic functions

$$-\frac{\hbar^2}{2\mu} \left[ P''(R) + \frac{2}{R} P'(R) \right] + \frac{J(J+1)\hbar^2}{2\mu R^2} P(R) + U(R)P(R) = E_{\text{int}} P(R)$$

## NUCLEAR MOTION IN DIATOMIC MOLECULES

is simplified by

$$F(R) \equiv RP(R)$$

$$-\frac{\hbar^2}{2\mu} F''(R) + \left[ U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right] F(R) = E_{\text{int}} F(R)$$

which looks like a one-dimensional Schrodinger equation with  
the effective potential energy.

$$U(R) + J(J+1)\hbar^2/2\mu R^2.$$



1)

- (a) solve the electronic Schrodinger equation at several values of  $R$  to obtain  $E_{el}$  of the particular molecular electronic state one is interested in
- (b) add  $Z_a Z_b e'^2 / R$  to each  $E_{el}$  value to obtain  $U$  at these  $R$  values;
- (c) devise a mathematical function  $U(R)$  whose parameters are adjusted to give a good fit to the calculated  $U$  values;
- (d) insert the function  $U(R)$  found in (c) into the nuclear-motion radial Schrodinger equation and solve by numerical methods.

For a given  $J$ ,  $F(R)$  is characterized by  $v$  (the number of nodes in  $F(R)$ )

$P(R)$  be quadratically integrate depend on  $J$  and  $v \longrightarrow E_{int} = E_{v,J}$ .

$Y_J^M(\theta_N, \phi_N)$   $J$  and  $M$  are rotational quantum numbers.

$v$ , which characterizes  $F(R)$ , is a vibrational quantum number.

## NUCLEAR MOTION IN DIATOMIC MOLECULES

2)

expand  $U(R)$  in a Taylor series about  $R_e$

$$U(R) = U(R_e) + U'(R_e)(R - R_e) + \frac{1}{2}U''(R_e)(R - R_e)^2 + \frac{1}{6}U'''(R_e)(R - R_e)^3 + \dots$$

Defining (equilibrium force constant)  $U'(R_e) = 0$   
 $k_e \equiv U''(R_e)$

harmonic-oscillator  
approximation

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

$$k_e \equiv U''(R_e) \quad \text{and} \quad x \equiv R - R_e$$

$$-\frac{\hbar^2}{2\mu} F''(R) + \left[ U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right] F(R) = E_{\text{int}} F(R)$$

$$x \equiv R - R_e$$



$$-\frac{\hbar^2}{2\mu} S''(x) + \left[ U(R_e) + \frac{1}{2}k_e x^2 + \frac{J(J+1)\hbar^2}{2\mu(x+R_e)^2} \right] S(x) \approx E_{\text{int}} S(x)$$

$$\text{where } S(x) \equiv F(R)$$

rigid-rotor  
approximation

$$\frac{1}{(x+R_e)^2} = \frac{1}{R_e^2(1+x/R_e)^2} = \frac{1}{R_e^2} \left( 1 - 2\frac{x}{R_e} + 3\frac{x^2}{R_e^2} - \dots \right) \approx \frac{1}{R_e^2}$$



$$-\frac{\hbar^2}{2\mu} S''(x) + \frac{1}{2}k_e x^2 S(x) \approx \left[ E_{\text{int}} - U(R_e) - \frac{J(J+1)\hbar^2}{2\mu R_e^2} \right] S(x)$$

## NUCLEAR MOTION IN DIATOMIC MOLECULES

is the same as the Schrodinger equation for a one-dimensional harmonic oscillator

$$E_{\text{int}} - U(R_e) - \frac{J(J+1)\hbar^2}{2\mu R_e^2} \quad \text{Energy eigenvalues}$$

$$E_{\text{int}} - U(R_e) - \frac{J(J+1)\hbar^2}{2\mu R_e^2} \approx (v + \frac{1}{2})h\nu_e$$

$$E_{\text{int}} \approx U(R_e) + (v + \frac{1}{2})h\nu_e + \frac{J(J+1)\hbar^2}{2\mu R_e^2}$$

$$\nu_e = (k_e/\mu)^{1/2}/2\pi, \quad v = 0, 1, 2, \dots$$

harmonic-oscillator and rigid-rotor approximation

$$E \approx E_{\text{tr}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \quad \text{approximately}$$

## NUCLEAR MOTION IN DIATOMIC MOLECULES

the nuclear-motion wave function

$$\psi_N \approx \psi_{N,\text{tr}} S_v(R - R_e) R^{-1} Y_J^M(\theta_N, \phi_N)$$

where  $S_v(R - R_e)$  is a harmonic-oscillator eigenfunction with quantum number  $v$ .

$$E_{\text{int}} \approx U(R_e) + (v + \frac{1}{2})h\nu_e + J(J + 1)\hbar^2/2\mu R_e^2$$

poor agreement with experimentally observed vibration-rotation energy levels of diatomic molecules.

The first- and second-order perturbation-theory energy corrections additional terms corresponding to vibrational anharmonicity, vibration-rotation interaction, and rotational centrifugal distortion of the molecule.

## NUCLEAR MOTION IN DIATOMIC MOLECULES

**EXAMPLE** An approximate representation of the potential-energy function of a diatomic molecule is the Morse function

$$U(R) = U(R_e) + D_e[1 - e^{-a(R - R_e)}]^2$$

Use of  $U''(R_e) = k_e$  [Eq. (4.61)] and (13.27) gives  $a = (k_e/2D_e)^{1/2} = 2\pi\nu_e(\mu/2D_e)^{1/2}$  (Problem 4.29; the Morse functions in Problem 4.29 and in this example differ because of different choices for the zero of energy). Use the Morse function and the Numerov method (Section 4.4) to: (a) find the lowest six vibrational energy levels of the  $^1\text{H}_2$  molecule in its ground electronic state, which has  $D_e/hc = 38297 \text{ cm}^{-1}$ ,  $\nu_e/c = 4403.2 \text{ cm}^{-1}$ , and  $R_e = 0.741 \text{ \AA}$ , where  $h$  and  $c$  are Planck's constant and the speed of light; (b) find  $\langle R \rangle$  for each of these vibrational states.

## Atomic units

- The system of atomic units that is based on Gaussian units:
- Mass:  $m_e \rightarrow g$
- Charge:  $e' \rightarrow \text{statcoulomb}$
- angular momentum:  $\hbar \rightarrow g \text{ cm}^2/s$

to change a formula from cgs Gaussian units to atomic units, we simply set these quantities equal to 1.

Hydrogen-atom Hamiltonian is  $-1/2\nabla^2 - 1/r$

Ground-state energy of the hydrogen atom:  $-1/2(e'^2/a_0)$

$a_0 = \hbar^2/m_e e'^2$ :  $a_0$  in atomic units is 1

the ground-state energy of H atom:  $-1/2$

Atomic unit of energy,  $e'^2/a_0$

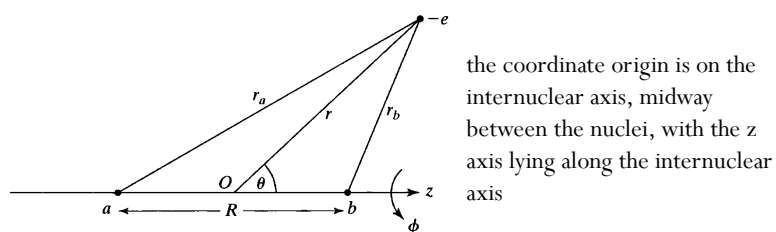
1 Hartree =  $E_0 = e'^2/a_0 = e'^2/4\pi a_0 \epsilon_0$

1 bohr =  $a_0 = \hbar^2/m_e e'^2 = 0.529177 \text{ \AA}$

## The hydrogen molecule ion

We now begin the study of the electronic energies of molecules.  
We shall use the Born- Oppenheimer approximation,  
We shall usually be considering an isolated molecule, ignoring intermolecular

We start with diatomic molecules, the simplest of which is  $H_2^+$



The electronic Schrodinger equation for  $H_2^+$  is separable, and we can get exact solutions for the eigenfunctions and eigenvalues.

Since the nuclei are fixed, we have a one-particle problem whose purely electronic Hamiltonian is

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e'^2}{r_a} - \frac{e'^2}{r_b}$$

The first term is the electronic kinetic-energy operator; the second and third terms are the attractions between the electron and the nuclei.

In atomic units

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

The  $H_2^+$  electronic Schrodinger equation is not separable in spherical coordinates. However, separation of variables is possible using confocal elliptic coordinates  $\xi$ ,  $\eta$  and  $\phi$ . The coordinate  $\phi$  is the angle of rotation of the electron about the internuclear ( $z$ ) axis,

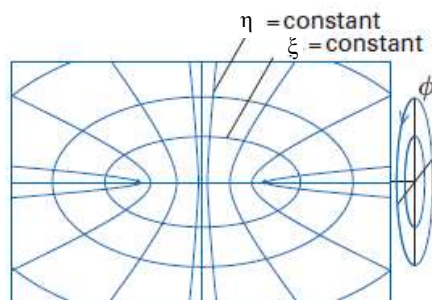
$$\xi \equiv \frac{r_a + r_b}{R}, \quad \eta \equiv \frac{r_a - r_b}{R}$$

The ranges of these coordinates

$$0 \leq \phi \leq 2\pi, \quad 1 \leq \xi \leq \infty, \quad -1 \leq \eta \leq 1$$

We have

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



The elliptical coordinates  $\xi$ ,  $\eta$ , and  $\phi$  used for the separation of variables in the exact treatment (within the Born–Oppenheimer approximation) of the hydrogen molecule–ion.

**Exercise:**

Express the Laplacian in confocal elliptic coordinates.

For the hydrogen atom, with spherical symmetry, the electronic angular-momentum operators  $\hat{L}^2$  and  $\hat{L}_z$  both commute with  $\hat{H}$ . The  $H_2^+$  ion does not have spherical symmetry, and one finds that  $[\hat{L}^2, \hat{H}_{\text{el}}] \neq 0$  for  $H_2^+$ .

However,  $H_2$  does have axial symmetry, and one can show that  $\hat{L}_z$  commutes with  $\hat{H}_{\text{el}}$  of  $H_2^+$ . Therefore the electronic wave functions can be chosen to be eigenfunctions of  $\hat{L}_z$ .

$$\text{constant} \cdot (2\pi)^{-1/2} e^{im\phi}, \quad \text{where } m = 0, \pm 1, \pm 2, \pm 3, \dots$$

$$L_z = m\hbar \text{ (or } m \text{ in atomic units).}$$

$L$  is not a constant for  $H_2^+$ .

The "constant" is a constant only as far as  $\partial/\partial\phi$  is concerned,

$$\psi_{\text{el}} = L(\xi)M(\eta)(2\pi)^{-1/2}e^{im\phi}$$

Substitution into

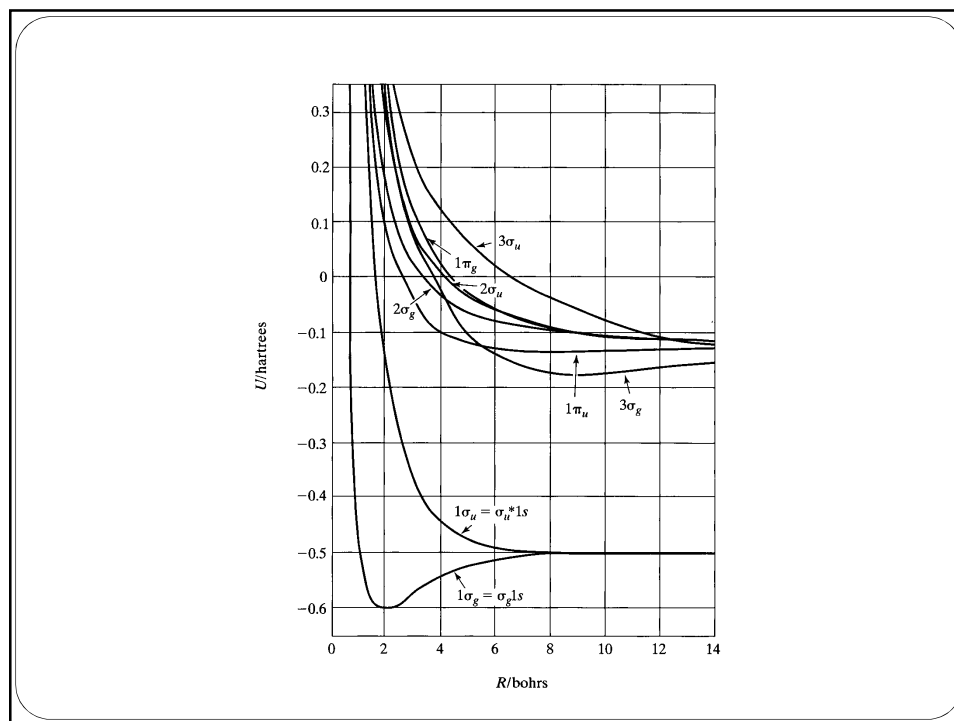
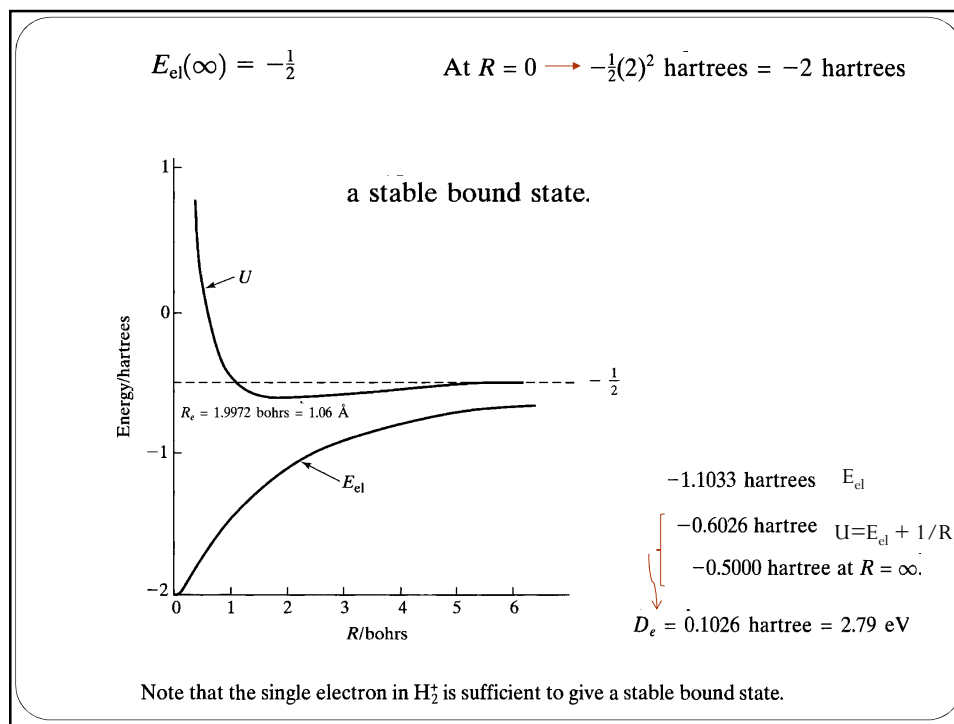
$$\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}}$$

the variables are separable; one gets two ordinary differential equations, one for  $L(\xi)$  and one for  $M(\eta)$ .

the condition that  $\psi_{\text{el}}$  be well-behaved requires that, for each fixed value of  $R$ , only certain values of  $E_{\text{el}}$  are allowed;

There is no algebraic formula for  $E_{\text{el}}$ ;

the quantum numbers are  $m$ ,  $n_\xi$  and  $n_\eta$  (give the number of nodes in the  $L(\xi)$  and  $M(\eta)$  factors)





$\phi$  occurs in  $\hat{H}_{el}$  of  $H_2^+$  only as  $\partial^2/\partial\phi^2$ .  $\longrightarrow$   $E_{el}$  depends on  $m^2$ ,

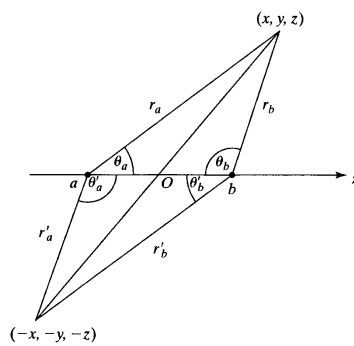
level with  $m \neq 0$  is doubly degenerate

$$\lambda \equiv |m|$$

$\lambda$	0	1	2	3	4
letter	$\sigma$	$\pi$	$\delta$	$\phi$	$\gamma$

Thus the lowest  $H_2^+$  electronic state is a  $\sigma$  state.

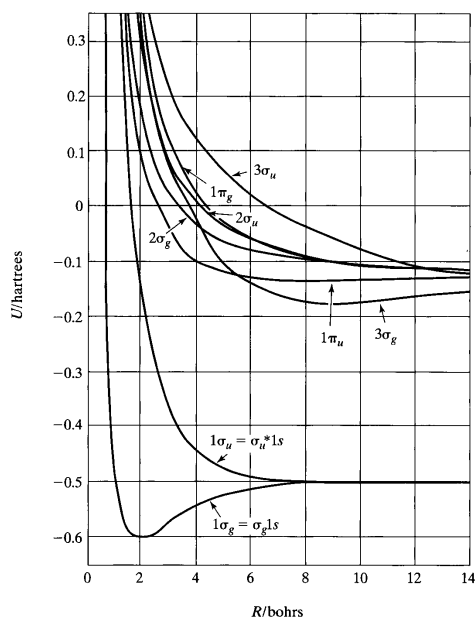
Besides classifying the states of  $H_2^+$  according to  $\lambda$ , we can also classify them according to their parity



The effect of inversion of the electron's coordinates in  $H_2^+$ .

We have  $r'_a = r_b$ ,  $r'_b = r_a$ , and  $\phi' = \phi + \pi$ .

This leaves the potential-energy part of the electronic Hamiltonian unchanged. The kinetic-energy operator is invariant under inversion. Hence the **parity operator commutes with the Hamiltonian**, and the  $H_2^+$  electronic wave functions can be classified as either **even or odd**. For even electronic wave functions, we use the subscript **g** (from the German word gerade, meaning even); for odd wave functions, we use **u** (from ungerade).



alternative notation  $\sigma_g 1s$  indicates that this level dissociates to a  $1s$  hydrogen atom.

- ✓ Also, we must take spin into account (multiply spatial  $H_2^+$  electronic wave functions by  $\alpha$  or  $\beta$ )
- ✓  $\alpha$ : the component of electron spin along the internuclear axis is  $+1/2$
- ✓  $\beta$ : the component of electron spin along the internuclear axis is  $-1/2$
- ✓ Inclusion of spin doubles the degeneracy of all levels.

## APPROXIMATE TREATMENTS OF THE $H_2^+$ GROUND ELECTRONIC STATE

### For a many-electron atom:

By the self-consistent-field (SCF) method

an approximate  
wave function

~

a Slater determinant of (one-electron) **spin-orbitals**

↑ spatial part  
an atomic orbital (AO)

each AO

≡

a spherical harmonic × a radial factor

As an initial approximation

hydrogenlike radial functions with effective nuclear charges

### For many-electron molecules

We use many of the ideas of the SCF treatment of atoms.

an approximate molecular  
electronic wave function

~

a Slater determinant of (one-  
electron) **spin-orbitals**

↑  
spatial part

will be called a molecular orbital (MO)

Each MO can hold no more than two electrons (the Pauli principle)

### What kind of functions do we use for the MOs?

the analytic form of each MO is found by an SCF calculation

simple approximations for the MOs

the **angular part** of  
each diatomic MO

≡

$$(2\pi)^{-1/2} e^{im\phi}$$

as in  $H_2^+$ .

the  **$\xi$  and  $\eta$  factors** in  
the  $H_2^+$  wave functions  
are complicated  
functions not readily  
usable in MO  
calculations.



**simpler functions** that will  
provide reasonably accurate  
approximations to the  $H_2^+$  wave  
functions and that can be used to  
construct molecular orbitals for  
many-electron diatomic molecules.

The variation method approach,

writing down some function containing several parameters

minimize the variational integral

an approximation to the ground-state wave function  
and an upper bound to the ground- state energy

By use of the factor  $e^{im\phi}$  in the trial function, we can get an upper bound to the energy of the lowest  $H_2^+$  level for any given value of  $m$

linear variation  
functions



approximations for  
excited states

The  $H_2^+$  ground state has  $m = 0$ , and the wave function depends only on  $\xi$  and  $\eta$ .

We could try any well-behaved function of these coordinates as a trial variation function.

for large values of the internuclear separation  $R$

When the electron is near nucleus a:  $\pi^{-1/2}e^{-r_a}$

When the electron is near nucleus b:  $\pi^{-1/2}e^{-r_b}$

we try as a variation function

$$c_1 \pi^{-1/2} e^{-r_a} + c_2 \pi^{-1/2} e^{-r_b}$$

variational parameters.

The perturbation theory approach

the unperturbed system

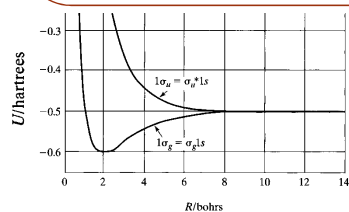
$H_2^+$  molecule with  $R = \infty$

$$\pi^{-1/2} e^{-r_a}$$

$$\pi^{-1/2} e^{-r_b}$$

In each case:  $E^{(0)} = -1/2$  hartree

a doubly degenerate unperturbed energy level



Bringing the nuclei in from infinity gives rise to a perturbation that splits the doubly degenerate unperturbed level into two levels.

The correct zeroth-order wave functions for the perturbed levels

$$c_1 \pi^{-1/2} e^{-r_a} + c_2 \pi^{-1/2} e^{-r_b}$$

A linear combination



led to a secular equation

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W \end{vmatrix} = 0$$

$$W = E^{(0)} + E^{(1)}$$

improve the trial function

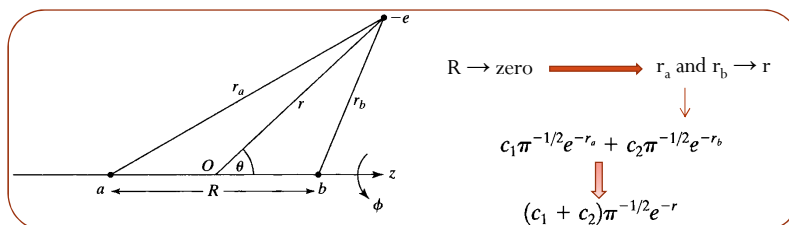
$$R \rightarrow 0 \quad \longrightarrow \quad H_2^+ \rightarrow \text{He}^+ \quad (Z = 2)$$

the ground-state wave function of  $H_2^+$



the ground-state wave function of  $\text{He}^+$

$$2^{3/2} \pi^{-1/2} e^{-2r}$$



Thus, trial function has the wrong limiting behavior at  $R = 0$

it should go to  $e^{-2r}$ , not  $e^{-r}$

$k(0) = 2$  and  $k(\infty) = 1$  for the  $H_2^+$  ground electronic state

Physically,  $k$  is some sort of effective nuclear charge.

$k^{3/2}$  normalizes  $1s_a$  and  $1s_b$

$$c_1 \pi^{-1/2} e^{-r_a} + c_2 \pi^{-1/2} e^{-r_b}$$

Multiplying  $r_a$  and  $r_b$  in the exponentials by a variational parameter  $k$ , which  $k = k(R)$

variational parameters

$$\phi = c_a 1s_a + c_b 1s_b$$

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

$$\phi = c_a 1s_a + c_b 1s_b$$

linear combination of atomic orbitals,  
an LCAO-MO.

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

$$H_{aa} = \int 1s_a^* \hat{H} 1s_a dv, \quad H_{bb} = \int 1s_b^* \hat{H} 1s_b dv \quad \text{Coulomb integrals}$$

$$\hat{H}_{\text{el}} = -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \quad H_{aa} = H_{bb}$$

$$H_{ab} = \int 1s_a^* \hat{H} 1s_b dv, \quad H_{ba} = \int 1s_b^* \hat{H} 1s_a dv \quad \text{resonance (or bond) integral.}$$

$\hat{H}$  is Hermitian and the functions are real  $\rightarrow H_{ab} = H_{ba}$

$$S_{aa} = \int 1s_a^* 1s_a dv = 1 = S_{bb} \quad S_{ab} = \int 1s_a^* 1s_b dv = S_{ba} \quad \text{overlap integral}$$



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



$$\begin{vmatrix} H_{aa} - W & H_{ab} - S_{ab}W \\ H_{ab} - S_{ab}W & H_{aa} - W \end{vmatrix} = 0$$

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

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

$H_{ab}$  is negative, so  $W_1$  is the lower-energy root.

For the root  $W_1$ ,  $(H_{aa} - W)c_a + (H_{ab} - S_{ab}W)c_b = 0$

$$\downarrow \quad W_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$c_a/c_b = 1$$

$$\phi_1 = c_a(1s_a + 1s_b)$$



$$|c_a|^2 \int (1s_a^2 + 1s_b^2 + 2 \cdot 1s_a 1s_b) dv = 1$$

$$|c_a| = \frac{1}{(2 + 2S_{ab})^{1/2}}$$

$$\boxed{\phi_1 = \frac{1s_a + 1s_b}{\sqrt{2}(1 + S_{ab})^{1/2}}}$$

For the root  $W_2$ ,  $(H_{aa} - W)c_a + (H_{ab} - S_{ab}W)c_b = 0$



$$W_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

$$c_b = -c_a$$



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

Evaluation of the integrals  $H_{aa}$ ,  $H_{ab}$ , and  $S_{ab}$

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

$$\xi \equiv \frac{r_a + r_b}{R}, \quad \eta \equiv \frac{r_a - r_b}{R}$$

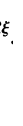


$$1s_a 1s_b = k^3\pi^{-1}e^{-k(r_a+r_b)} = k^3\pi^{-1}e^{-kR\xi}$$

$$S_{ab} = \int 1s_a^* 1s_b dv = S_{ba}$$

$$1s_a 1s_b = k^3\pi^{-1}e^{-k(r_a+r_b)} = k^3\pi^{-1}e^{-kR\xi}$$

$$dv = \frac{1}{8}R^3(\xi^2 - \eta^2) d\xi d\eta d\phi$$



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

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

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

Problem 13.18

$$W_{1,2} = -\frac{1}{2}k^2 + \frac{k^2 - k - R^{-1} + R^{-1}(1 + kR)e^{-2kR} \pm k(k - 2)(1 + kR)e^{-kR}}{1 \pm e^{-kR}(1 + kR + k^2 R^2/3)}$$

approximations to the  
purely electronic energy  $E_{\text{el}}$

+ : for  $W_1$ - : for  $W_2$ 

$$U_{1,2}(R) = W_{1,2} + 1/R$$

At many fixed  $R$  : vary  $k$  to minimize first  $U_1(R)$  and then  $U_2(R)$

Solve problems 13.19 (analytically) and 13.20 (numerically).

$$\text{For } (1s_a + 1s_b) : R (\infty \rightarrow 0) \rightarrow k (1 \rightarrow 2)$$

$$\text{For } (1s_a - 1s_b) : R (\infty \rightarrow 0) \rightarrow k (1 \rightarrow 0.4)$$

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

$$0 < k \leq 2 \text{ and } S_{ab} > 0$$

$H_{ab}$  is negative

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

$W_1$  corresponds to the ground electronic state ( $\sigma_g 1s$ ) of  $H_2^+$

For the ground state:  $k(R_e) = 1.24$

For  $(1s_a - 1s_b) : R (\infty \rightarrow 0) \rightarrow k (1 \rightarrow 0.4)$  **why?**

$\sigma_u^* 1s$

~~$k (1 \rightarrow 2.0)$~~

$\sigma_u^* 1s$  (odd parity)

zero electronic orbital  
angular momentum along  
the internuclear (z) axis



$2p$

The lowest odd  
states of  $\text{He}^+$

$2p_0$

for  $m = 0$

$$W_{1,2} = -\frac{1}{2}k^2 + \frac{k^2 - k - R^{-1} + R^{-1}(1 + kR)e^{-2kR} \pm k(k - 2)(1 + kR)e^{-kR}}{1 \pm e^{-kR}(1 + kR + k^2R^2/3)}$$

$+ 1/R$

1)  $k(R)$  for  $W_1$   
2)  $k(R)$  for  $W_2$

$U(R)$  curves

The calculated ground-state :

calculated:

$R_e = 2.0$  bohrs

(true  $R_e = 2.0$  bohrs)

$U(R_e) = -15.96$  eV  $\rightarrow D_e = 2.36$  eV

(true  $D_e = 2.79$  eV)

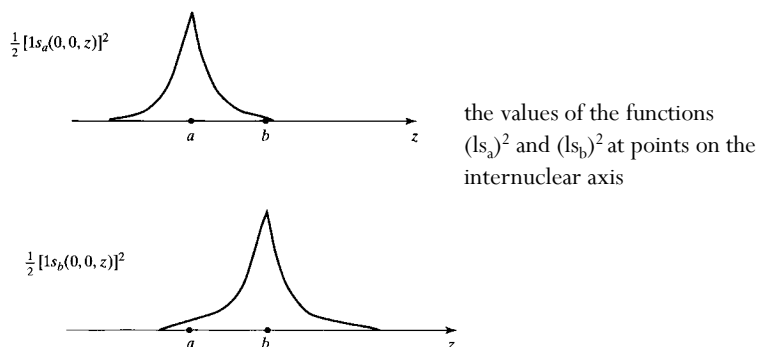
calculated  $R_e = 2.49$  and  $D_e = 1.76$  if  $k = 1$

The appearance of the trial functions for the  $\sigma_g 1s$  and  $\sigma_u^* 1s$  states at intermediate values of  $R$

$$\frac{1}{2}(1s_a^2 + 1s_b^2)$$

The probability density for an electron in a  $1s_a$  atomic orbital

The probability density for half an electron in a  $1s_a$  AO and half an electron in a  $1s_b$  AO

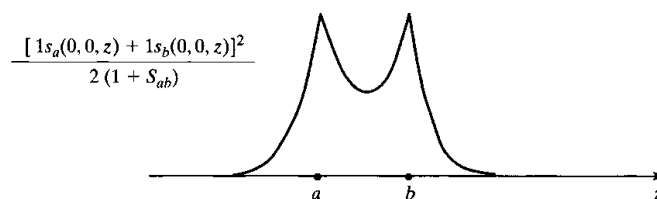


### The $H_2^+$ ground-state probability density

For the  $\sigma_g 1s$  function  $(1s_a + 1s_b)$  : a buildup of electronic probability density between the nuclei

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

$$\phi_1^2 = \frac{1}{2(1 + S_{ab})} [1s_a^2 + 1s_b^2 + 2(1s_a 1s_b)]$$



It is especially significant that the buildup of charge between the nuclei is greater than that obtained by simply taking the sum of the separate atomic charge densities.

$$\phi_1^2 - \frac{1}{2}(1s_a^2 + 1s_b^2) = \frac{1}{2(1 + S_{ab})} [2(1s_a 1s_b) - S_{ab}(1s_a^2 + 1s_b^2)] \equiv \mathbf{D}$$

$$S_{ab} = e^{-kR}(1 + kR + \frac{1}{3}k^2R^2) \xrightarrow{R=2.0 \quad k=1.24} S_{ab} = 0.46 \text{ at } R_e$$

?

Outside ab region:  $1s_a$  or  $1s_b$  is very small

↓  
 $D < 0$

At the midpoint of the internuclear axis

↓  
 $1s_a = 1s_b$

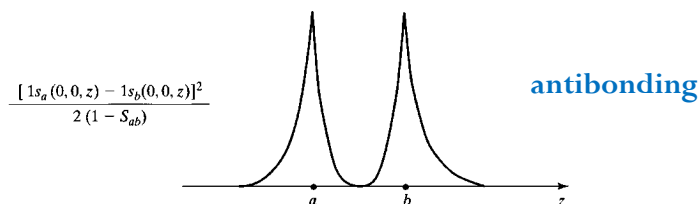
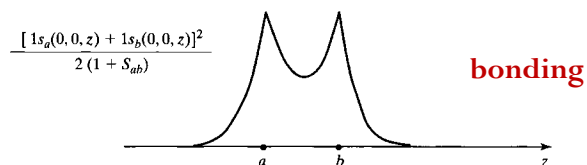
the bracketed terms  $= 2(1s_a)^2 - 0.92(1s_a)^2 \approx 1s_a^2 > 0$

buildup of charge probability density between the nuclei in the molecule

$$\sigma_u^* 1s \equiv (1s_a - 1s_b) \propto (e^{-ra} - e^{-rb}) \quad = \mathbf{0 \text{ at } r_a = r_b}$$

a nodal plane

$\sigma_g 1s$  orbital is bonding and the  $\sigma_u^* 1s$  orbital is antibonding



to the lowering in the average electronic potential energy

the decrease in electronic potential energy due to the sharing is of the same order of magnitude as the nuclear repulsion energy  $1/R$  and hence is insufficient by itself

Two other effects also contribute to the bonding:

The increase in atomic orbital exponent

( $k = 1.24$  at  $R_e$  versus  $1.0$  at  $\infty$ )

Moreover, the buildup of charge in the internuclear region makes  $d\psi/dz$  zero at the midpoint of the molecular axis and small in the region close to this point, thus

$$\frac{1}{2} \int |\partial\psi/\partial z|^2 d\tau < \langle T_z \rangle$$

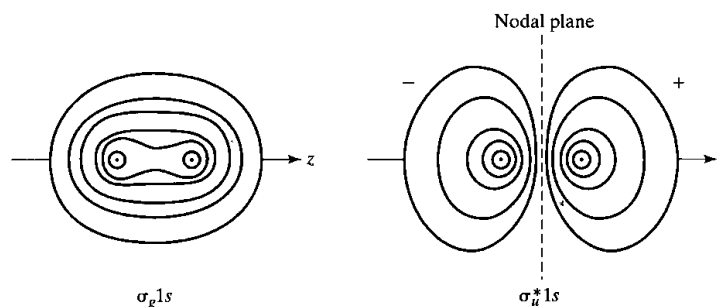
z component of the average                      the atomic value  
electronic kinetic energy

Reflection of the electron's coordinates in the  $\sigma_h$  symmetry plane perpendicular to the molecular axis and midway between the nuclei .

The operator  $\hat{O}\sigma_h$  commutes with the electronic Hamiltonian and with the parity (inversion) operator (eigenvalues must be  $+1$  and  $-1$  )

star

**starred orbitals are antibonding.**



Contour (of constant  $|\psi|$ ) diagrams of the orbitals

**comparison**

helium

 $1s(1)2s(2)$  $1s(2)2s(1)$ 

degenerate functions

 $[1s(1)2s(2) \pm 1s(2)2s(1)]/\sqrt{2}$  the correct zeroth-order functions $H_2^+$  $1s_a$  and  $1s_b$ 

degenerate functions

 $(1s_a \pm 1s_b)/\sqrt{2(1 \pm S_{ab})^{1/2}}$  the correct zeroth-order functionsbinding in  $H_2^+$ resonance integral  $H_{ab}$ 

arises out of the nature of the LCAO approximation

the AOs  $1s_a$  and  $1s_b$ 

LCAO

the two  $H_2^+$  MOs

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

$$H_{aa} = \langle 1s_a | \hat{H} | 1s_a \rangle$$

purely electronic Hamiltonian



### H<sub>aa</sub>

- ✓ the molecule's purely electronic energy if the electron's wave function in the molecule were 1s<sub>a</sub>.
- ✓ is the energy of the 1s<sub>a</sub> orbital in the molecule (in the limit R = ∞, becomes the 1s AO energy in the H atom)

In the molecule, H<sub>aa</sub> is substantially lower than the electronic energy of an H atom because the electron is attracted to both nuclei.

**separated-atoms description**

$\sigma_g 1s$

$\sigma_u^* 1s$

**united-atom description**

$1s\sigma_g$

$2p\sigma_u^*$

$2p_0\sigma_u^*$

not necessary

the fact that it is a  $\sigma$  state tells us that it correlates with the united-atom 2p<sub>0</sub> state

For the united-atom description, the subscripts g and u are not needed, since molecular states correlating with s, d, g,... atomic states must be g, while states correlating with p, f, h,... atomic states must be u.

how the trial function can be improved?

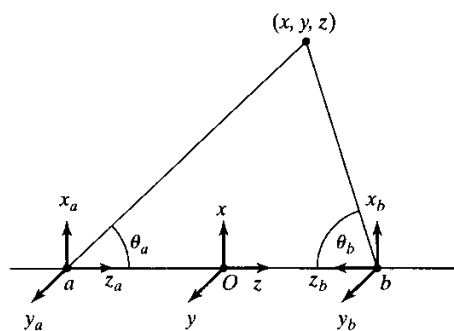
the perturbation of molecule formation will mix in other hydrogen-atom states besides 1s.

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

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

c, k, and  $\beta$  are variational parameters

$\theta_a$  and  $\theta_b$  refer to two sets of spherical coordinates,



using a right-handed coordinate system on atom a and a left-handed system on atom b.

hybridization

$1s + c2p_0$  is a hybridized atomic orbital

$R_e = 2.01$  bohrs.

$k = 1.246$ ,  $\beta = 2.965$ , and  $c = 0.138$

$D_e = 2.73$  eV (true value = 2.79 eV)

in atomic units

$$1s_a = k^{3/2} \pi^{-1/2} e^{-kr_a}$$

in ordinary units

$$1s_a = (k/a_0)^{3/2} \pi^{-1/2} e^{-kr_a/a_0}$$