

PART II

Born-Oppenheimer approximation

Electronic, vibrational and rotational spectra

Classification of electronic states

H_2^+ molecule, hybridization and LCAO method

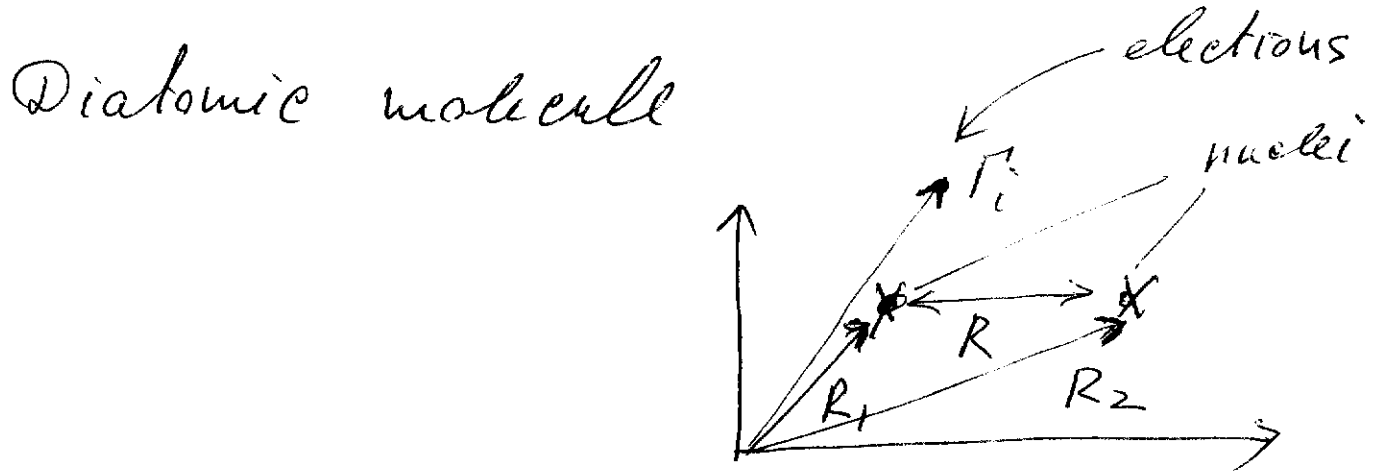
H_2 molecule and Heitler-London method.

Electron correlations, Mott insulator

Exotic atoms and molecules.

(26)

Born-Oppenheimer approximation =
= adiabatic approximation.



Hamiltonian

$$H = \frac{\vec{P}_1^2}{2M_1} + \frac{\vec{P}_2^2}{2M_2} + \sum_i \left[\frac{\vec{P}_i^2}{2m} - \frac{z_1 e^2}{|\vec{R}_1 - \vec{r}_i|} - \frac{z_2 e^2}{|\vec{R}_2 - \vec{r}_i|} \right] +$$

$$+ \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{z_1 z_2 e^2}{|\vec{R}_1 - \vec{R}_2|}$$

$\vec{P}_1 = -i\hbar \frac{\partial}{\partial \vec{R}_1}$ - momentum of the 1st nucleus

$\vec{P}_2 = -i\hbar \frac{\partial}{\partial \vec{R}_2}$ - momentum of the 2nd nucleus

$\vec{P}_i = -i\hbar \frac{\partial}{\partial \vec{r}_i}$ - momentum of the i th electron

$$\left\{ \begin{aligned} \vec{S} &= \frac{M_1 \vec{R}_1 + M_2 \vec{R}_2}{M_1 + M_2} \quad \text{— center of mass of nuclei} \\ \vec{R} &= \vec{R}_1 - \vec{R}_2 \end{aligned} \right.$$

Exclude center of mass motion and get the Hamiltonian for relative motion.

$$H = \frac{\vec{P}^2}{2M} + \sum_i \left[\frac{\vec{p}_i^2}{2m} - \frac{z_i e^2}{|\vec{R}_i - \vec{r}_i|} - \frac{z_2 e^2}{|\vec{R}_2 - \vec{r}_i|} \right] + \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{z_1 z_2 e^2}{R}$$

$$\vec{P} = -i\hbar \frac{\partial}{\partial \vec{R}}$$

Hel. — "electron" Hamiltonian

Schrodinger eq.

$$H \Psi(\vec{R}, \vec{r}_1, \vec{r}_2 \dots) = E \Psi(\vec{R}, \vec{r}_1, \vec{r}_2 \dots)$$

Born-Oppenheimer approximation:

Let us look for solution in the form

$$\Psi = \chi(\vec{R}) \varphi(\vec{R}, \vec{r}_i)$$

where φ satisfies

$$H_{el} \varphi = E_{el} \varphi$$

equation
← here R is just a parameter!

Justification of the approximation. (28)

1) physical: nuclei are very heavy, therefore one can keep their positions fixed when considering electron dynamics.

2) mathematical:

$$\vec{P}_i \psi \sim \frac{\hbar}{a_B} \psi$$

$$\mathcal{P} \psi \sim \frac{\hbar}{a_B} \psi$$

$$\text{Hence terms } \frac{\mathcal{P}^2}{2M} \psi \sim \frac{\hbar^2}{M a_B^2} \psi \sim \frac{m}{M} \left(\frac{\hbar^2}{m a_B^2} \right) \psi$$

can be neglected

compared to

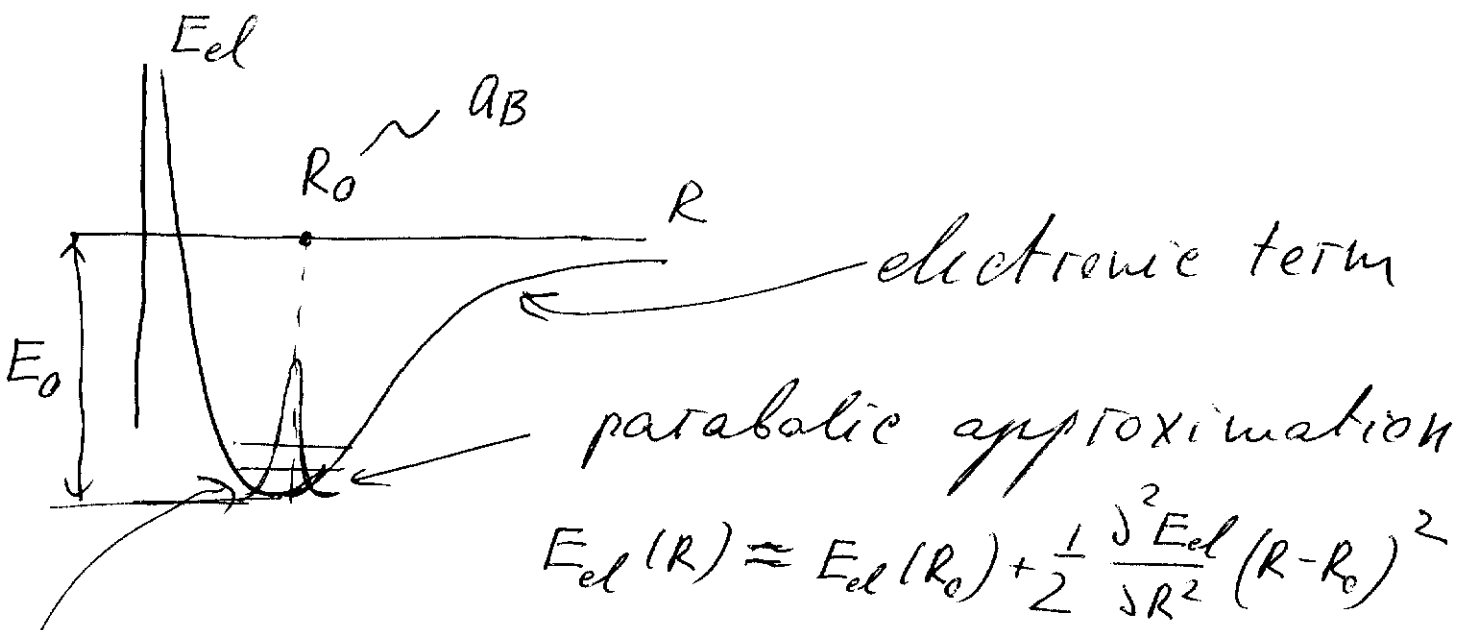
$$\frac{P^2}{2m} \psi \sim \frac{\hbar^2}{m a_B^2} \psi$$

↑
typical
atomic
energy

$$E_{el} = E_{el}(R)$$

this is the effective potential for nuclear motion

$$\left[\frac{P^2}{2M} + E_{el}(R) \right] \chi(R) = E \chi(R)$$



Harmonic oscillator

$$M\omega^2 = \frac{\partial^2 E_{el}}{\partial R^2} \sim \frac{1}{a_B^2} \left(\frac{me^4}{\hbar^2} \right) \sim R_y = \frac{me^4}{2\hbar^2}$$

typical atomic energy

$$\Rightarrow \hbar\omega \sim \sqrt{\frac{\hbar^2}{M a_B^2} R_y} \sim \sqrt{\frac{m}{M}} R_y \ll R_y$$

$$\frac{m}{M} < 2000$$

↑ typical vibrational energy

$$\frac{P^2}{2M} \sim \hbar\omega \Rightarrow$$

$$P \sim \left(\frac{M}{m} \right)^{1/4} \frac{\hbar}{a_B} \leftarrow \text{typical momentum of the nucleus.}$$

$$\chi(\vec{R}) = \chi_0(R) Y_{LM}(\vec{R})$$

$$M = L_z$$

$$\frac{\mathcal{P}^2}{2M} \rightarrow \frac{\mathcal{P}_R^2}{2M} + \frac{\hbar^2 L(L+1)}{2MR^2}$$

↑
radial
part

↑
centrifugal
part.

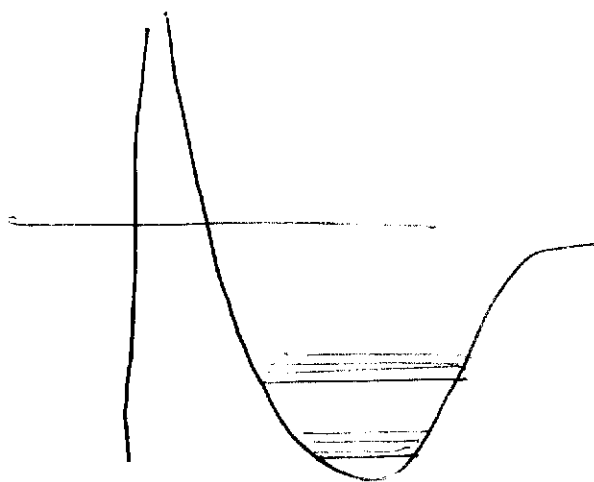
So spectrum of excitations built on a given electronic term is

$$E(n, L) = E_0 + \hbar\omega\left(n + \frac{1}{2}\right) + \frac{\hbar^2 L(L+1)}{2I}$$

$$I = MR_0^2$$

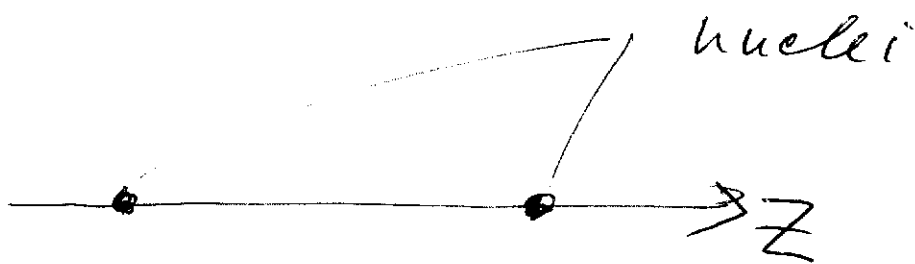
$$\frac{\hbar\omega}{E_0} \sim \sqrt{\frac{m'}{M}}$$

$$\frac{\hbar^2/I}{\hbar\omega} \sim \sqrt{\frac{m}{M}}$$



Usually there are several electronic terms that have different, E_0 , ω , and I

Classification of electronic states



$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots \quad \text{— total electron angular momentum}$$

$\Lambda = L_z$ is conserved

notation: $\Lambda = 0, 1, 2, \dots$

$\Sigma, \Pi, \Delta, \dots$

for single electron $\lambda = l_z$

$\lambda = 0, 1, 2, \dots$

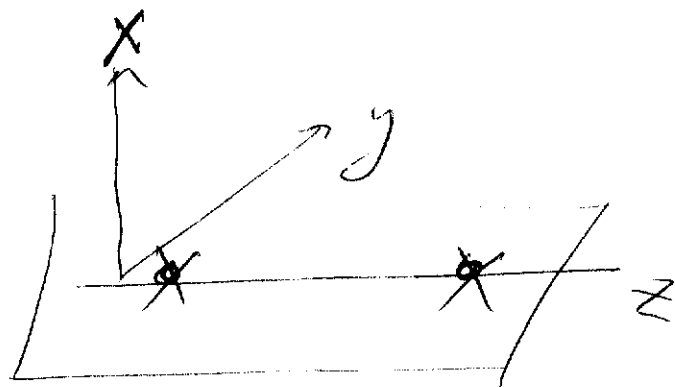
$\sigma, \pi, \delta, \dots$

This is similar to notations in atomic spectroscopy:

single electron: s, p, d, f, \dots

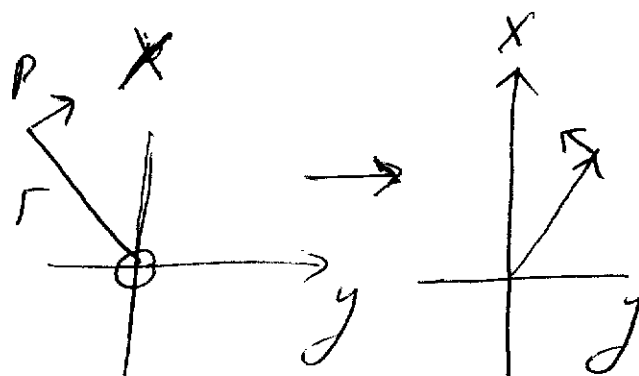
total L : S, P, D, F, \dots

Symmetry operation: reflection in the xz -plane



$$xz, y \rightarrow xz, -y$$

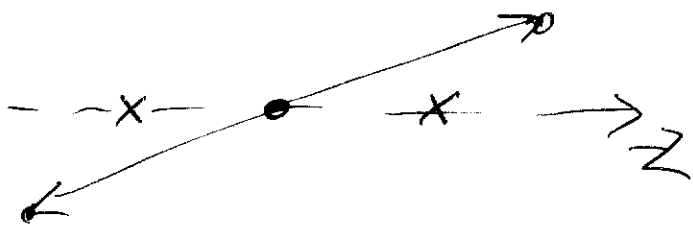
$$\Lambda \rightarrow -\Lambda$$



Hence all states with $\Lambda \neq 0$ are double degenerate.

Under this operation a Σ -state can stay the same or change sign. They are called Σ^+ and Σ^- respectively.

If the molecule consists of two identical atoms then there is an additional symmetry operation: reflection with respect to the middle of the distance between nuclei



under this operation Λ is unchanged since $\Lambda \sim x p_y - y p_x$ while the operation is $z \rightarrow -z, p_z \rightarrow -p_z$

The states that do not change sign under the operation are called g-states, the states that change sign are called u-states.

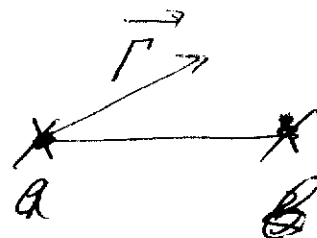
For example Σ_g and Σ_u
 Π_g and Π_u

The simplest molecule, H_2^+

(34)

Hamiltonian (electronic)

$$\hat{H}_{el} = \frac{p^2}{2m} - \frac{e^2}{|\vec{r} - \vec{R}_a|} - \frac{e^2}{|\vec{r} - \vec{R}_b|} + \frac{e^2}{R}$$



In atomic units, $E \rightarrow \frac{E}{(me^4/\hbar^2)}$, $r \rightarrow r/a_B$


$$\boxed{H_{el} = -\frac{1}{2}\Delta - \frac{1}{|\vec{r} - \vec{R}_a|} - \frac{1}{|\vec{r} - \vec{R}_b|} + \frac{1}{R}}$$

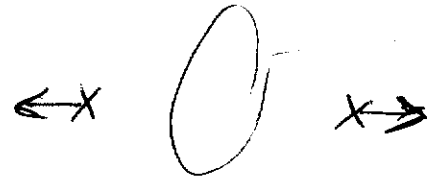
The LCAO method (Linear Combination of Atomic Orbitals)

$$|1\sigma_g\rangle = C_+ (\psi_a + \psi_b) \leftarrow \text{bonding orbital}$$

$$|1\sigma_u\rangle = C_- (\psi_a - \psi_b) \leftarrow \text{antibonding orbital}$$

$$\Psi_a = \frac{1}{\sqrt{\pi}} e^{-|\vec{r}-\vec{R}_a|}, \quad \Psi_b = \frac{1}{\sqrt{\pi}} e^{-|\vec{r}-\vec{R}_b|}$$

bonding:  enhanced charge density due to constructive interference

antibonding:  depleted charge density due to destructive interference.

Normalization:

$$1 = |C_{\pm}|^2 \langle \Psi_a \pm \Psi_b | \Psi_a \pm \Psi_b \rangle = |C_{\pm}|^2 (1 \pm \langle \Psi_a | \Psi_b \rangle)$$

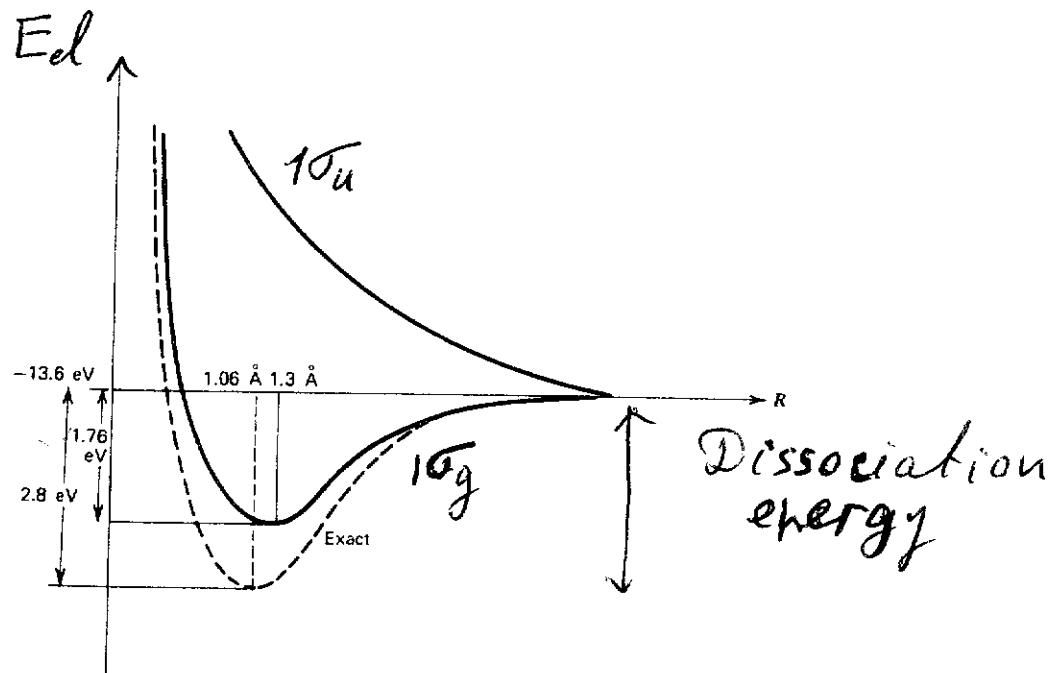
$$\langle \Psi_a | \Psi_b \rangle = \frac{1}{\pi} \int d^3r e^{-r} e^{-|\vec{r}-R|} = (1+R+\frac{1}{3}R^2)e^{-R}$$

$$\Rightarrow |C_{\pm}|^2 = \frac{1}{2(1 \pm \langle \Psi_a | \Psi_b \rangle)}$$

$$\langle H_{el} \rangle = |C_{\pm}|^2 \langle \Psi_a \pm \Psi_b | H_{el} | \Psi_a \pm \Psi_b \rangle =$$

$$= \frac{1}{[1 \pm \langle \psi_a | \psi_b \rangle]} \left\{ \langle \psi_a | U_{\text{el}} | \psi_a \rangle \pm \langle \psi_a | U_{\text{el}} | \psi_b \rangle \right\}$$

$$\left\{ \begin{aligned} \langle \psi_a | U_{\text{el}} | \psi_a \rangle &= -\frac{1}{2} - \frac{1}{R} (1+R) e^{-2R} \\ \langle \psi_a | U_{\text{el}} | \psi_b \rangle &= \left(-\frac{1}{2} + \frac{1}{R}\right) \langle \psi_a | \psi_b \rangle - (1+R) e^{-R} \end{aligned} \right.$$



Results of LCAO calculation
for H_2^+ (solid lines)

Variational LCAO method

still

$$\bar{\Psi}_{\pm} = C(\Psi_a \pm \Psi_b)$$

However instead of

$$\Psi_a = \frac{1}{\sqrt{\pi}} e^{-|\vec{r} - \vec{R}_a|}, \quad \Psi_b = \frac{1}{\sqrt{\pi}} e^{-|\vec{r} - \vec{R}_b|}$$

We take

$$\Psi_a = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha|\vec{r} - \vec{R}_a|}, \quad \Psi_b = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha|\vec{r} - \vec{R}_b|}$$

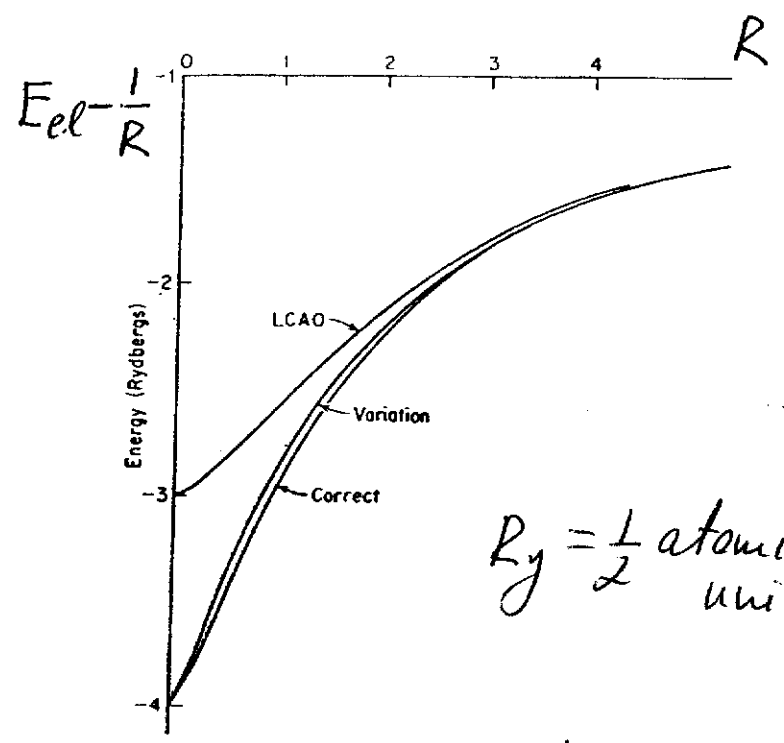
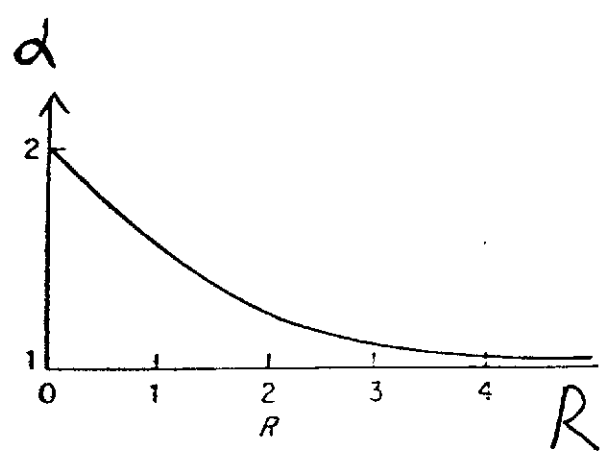
where α is a variational parameter that depends on R and at any given R the α has to be found by minimizing the energy.

Asymptotic values of α are obvious.

$\left\{ \begin{array}{l} R \rightarrow \infty : \text{hydrogen atom} \\ \text{hence } \alpha(R \rightarrow \infty) = 1 \end{array} \right.$

$\begin{array}{c} x \\ \uparrow \\ \text{proton} \end{array}$

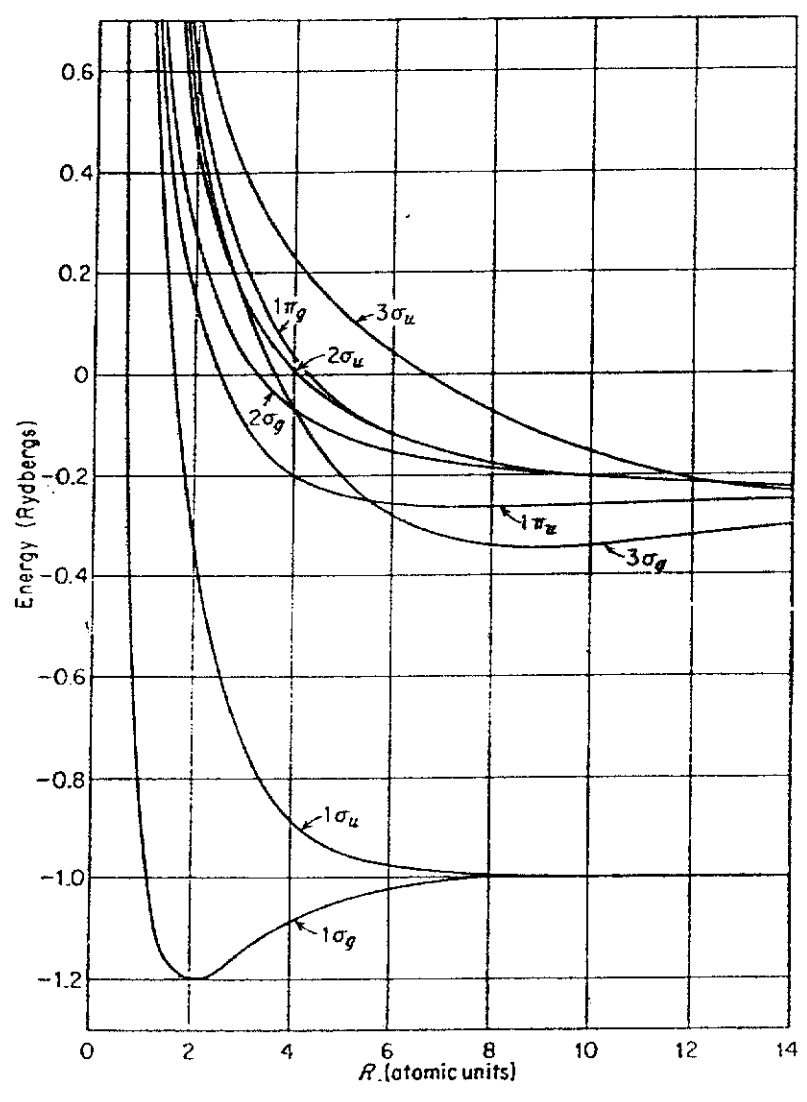
$\left\{ \begin{array}{l} R = 0 : \text{hydrogen-like He ion} \\ \text{hence } \alpha(R = 0) = 2 \end{array} \right.$



$R_y = \frac{1}{2}$ atomic unit.

Results for $E_{el} - \frac{1}{R}$

- 1) LCAO
- 2) Variational LCAO
- 3) Exact

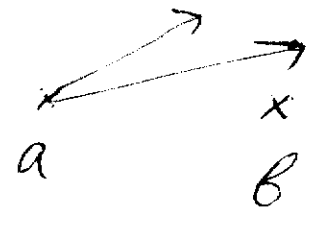


Lowest energy levels of H_2^+ as function of internuclear distance, .

H₂ molecule

Heitler-London (Valence-bond) method.

two electrons



$$H_{el} = \frac{p_1^2}{2} + \frac{p_2^2}{2} - \frac{1}{|\vec{r}_1 - \vec{R}_a|} - \frac{1}{|\vec{r}_1 - \vec{R}_b|} - \frac{1}{|\vec{r}_2 - \vec{R}_a|} - \frac{1}{|\vec{r}_2 - \vec{R}_b|} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{R}$$

Heitler-London wave function

$$\Psi(\vec{r}_1, \vec{r}_2, \zeta_1, \zeta_2) \propto [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)] \chi(\zeta_1, \zeta_2)$$

$$\psi_a(\vec{r}_1) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha|\vec{r}_1 - \vec{R}_a|}$$

, α is variational parameter.

total spin; $S=0 \Rightarrow \chi(\zeta_1, \zeta_2) = \frac{1}{\sqrt{2}} [\uparrow\downarrow_1 \downarrow\downarrow_2 - \downarrow\downarrow_1 \uparrow\downarrow_2]$

$$S=1 \Rightarrow \chi(\zeta_1, \zeta_2) = \begin{cases} \uparrow\uparrow_1 \uparrow\uparrow_2 \\ \frac{1}{\sqrt{2}} [\uparrow\uparrow_1 \downarrow\downarrow_2 + \downarrow\downarrow_1 \uparrow\uparrow_2] \\ \downarrow\downarrow_1 \downarrow\downarrow_2 \end{cases}$$

So if $S=0$ one must take the sign $(+)$ in the coordinate wave function (Fermi statistics) and this is the

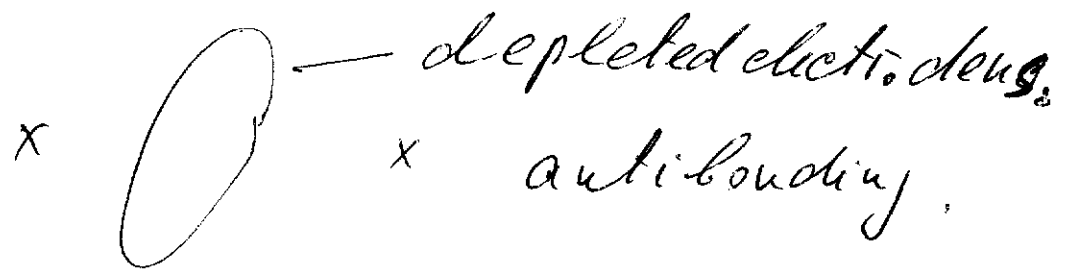
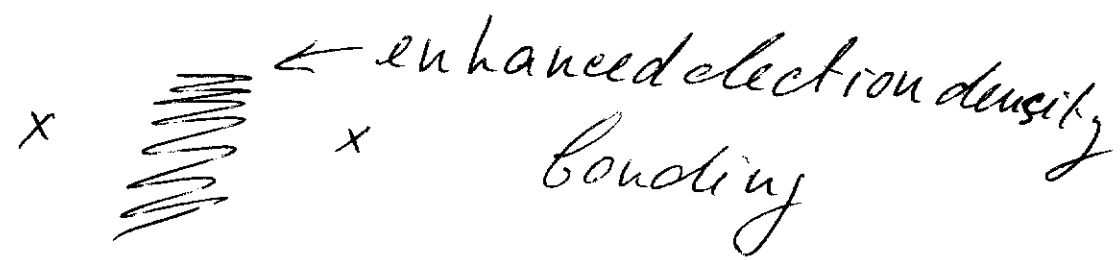
$$1 \sum_{g}^{2S+1} \text{state (bonding)}$$

If $S=1$ one must take $(-)$ in the coordinate wave function and

$$\text{this is } 3 \sum_{u}^{+} \text{state (antibonding)}$$

Short notation: instead of $\psi_a(1) \rightarrow a(1)$

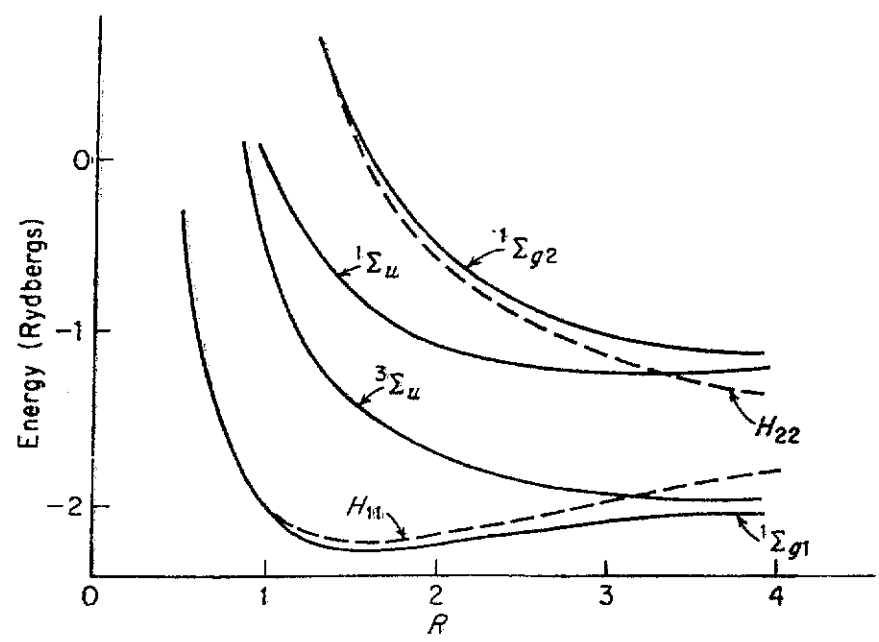
$$\psi(r_1, r_2) = C_{\pm} [a(1)b(2) \pm a(2)b(1)]$$



Because of this bonding mechanism spin of the ground state is typically zero.

This is opposite to Hund's rule for atoms!!!

Two exclusions: NO: ${}^2\Pi$ ground state
 O_2 ${}^3\Sigma_g^-$ ground state



Energy of hydrogen molecule as function of internuclear distance. Full curves, energies as derived from secular equation. Dashed curves, diagonal energies of ${}^1\Sigma_g$ states constructed from molecular-orbital wave functions, without configuration interaction.

A problem with molecular orbital method, correlations, metal - Mott insulator transition

Molecular orbital method: independent motion of electrons.

1) single electron orbitals

$$\psi_g(r) = C_+ [a(r) + b(r)] \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha|\vec{r}-\vec{R}_B|}$$

$$\psi_u(r) = C_- [a(r) - b(r)]$$

hybridization

2) Two electron states

$$\left\{ \begin{aligned} {}^1\Sigma_g^+ &= \psi_g(1) \psi_g(2) \chi_{S=0} \\ {}^3\Sigma_u^+ &= \frac{1}{\sqrt{2}} [\psi_g(1) \psi_u(2) - \psi_g(2) \psi_u(1)] \chi_{S=1} \end{aligned} \right.$$

One can evaluate the electron energy (like we did it before)

$$E_{el} = \langle {}^1\Sigma_g | H_{el} | {}^1\Sigma_g \rangle$$

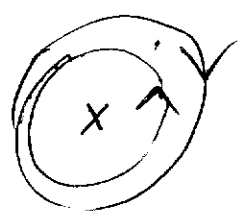
and find that the energy is wrong and especially wrong is the dissociation energy.

Why??

$$| {}^1\Sigma_g \rangle \approx [a(1) + b(1)][a(2) + b(2)] =$$

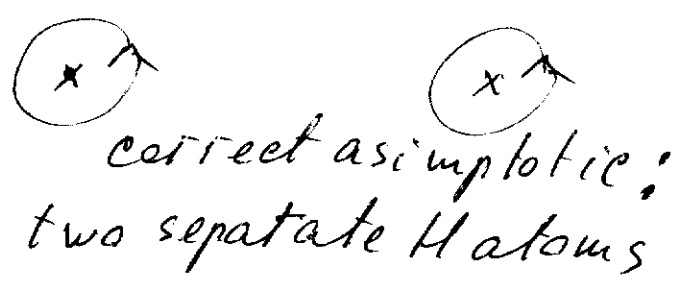
$$= \underbrace{a(1)a(2) + b(1)b(2)}_{\text{Heitler-London part.}} + \underbrace{a(1)b(2) + a(2)b(1)}_{\text{at } R \rightarrow \infty}$$

$\sqrt{R \rightarrow \infty}$



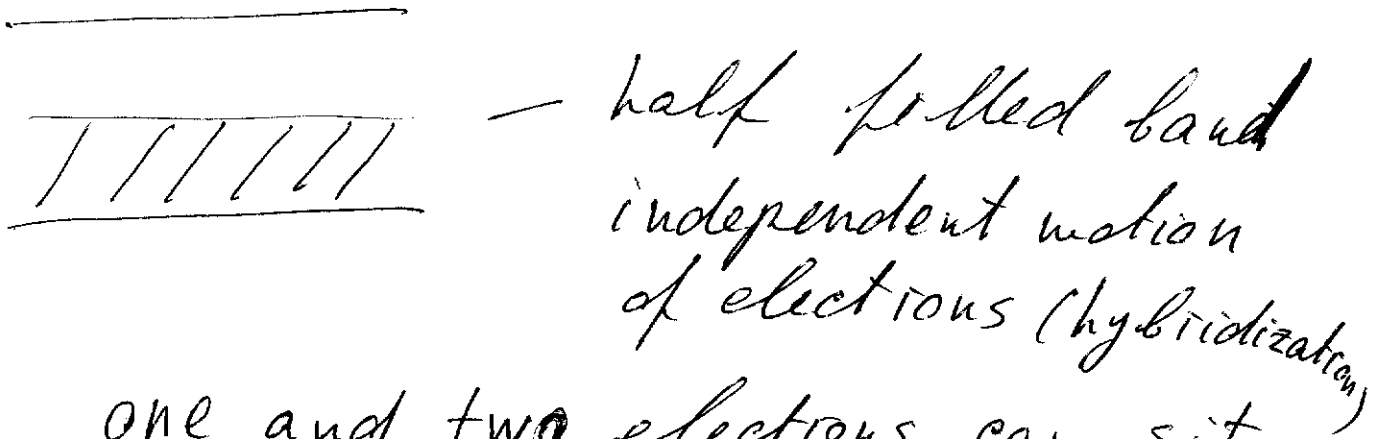
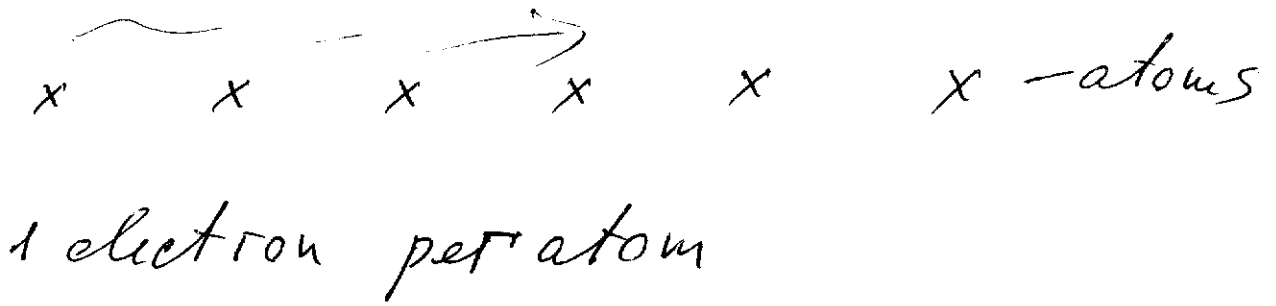
wrong asymptotic behaviour.

Heitler-London part. at $R \rightarrow \infty$



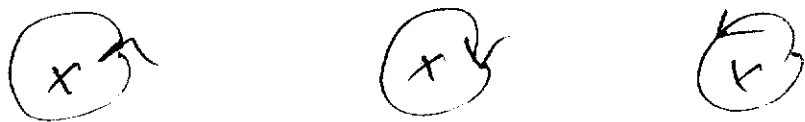
correct asymptotic: two separate H atoms

A similar effect in condensed matter physics; metal \rightarrow Mott insulator transition



one and two electrons can sit at the same atom.

If electron-electron repulsion is sufficiently strong then the state with localized electrons has lower energy (Mott insulator)

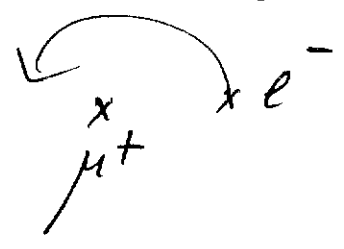


Exotic atoms and molecules

1) positronium $\begin{matrix} \circ e^+ \\ \circ e^- \end{matrix}$ $\mu = \frac{m}{2} \rightarrow$

$\rightarrow E_0 = \frac{E_H}{2} = -\frac{13.6}{2} eV$ $\tau \sim 10^{-7} \text{ sec}, 10^{-10}$
annihilation

2) muonium

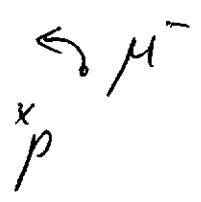


like hydrogen

$m_\mu = 207 m_e$

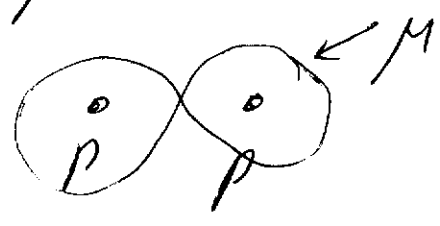
$\tau_\mu = 2.2 \cdot 10^{-6} \text{ sec}$

3) μ -hydrogen



$\Gamma \sim \frac{a_B}{207}$, $E \sim 207 \cdot 13.6 eV$

4) μ -molecule and μ -catalysis of fusion



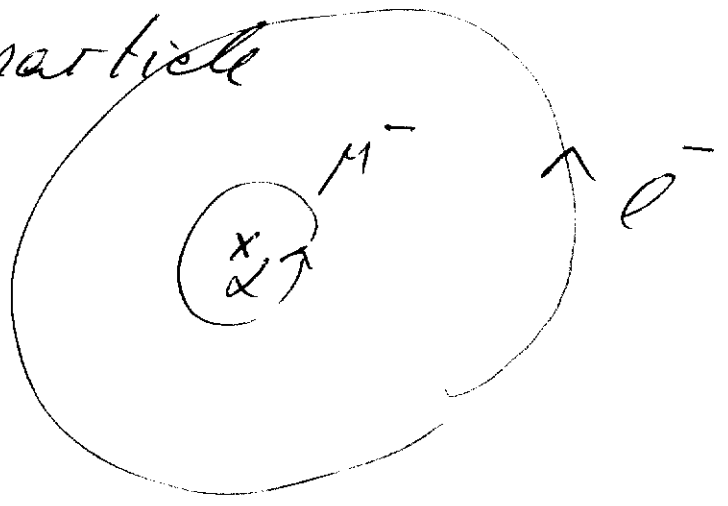
$\Gamma \sim \frac{1}{207} \Gamma_{H_2}$

take $d(pn)$ and $t(pnn)$ instead of protons

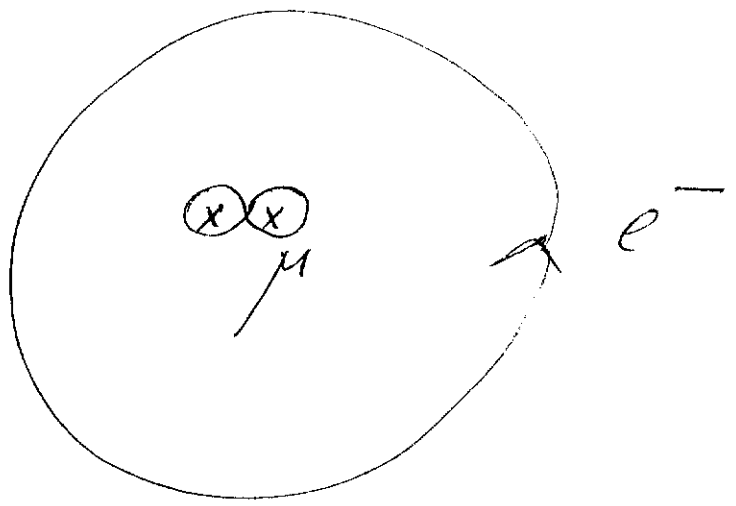
Probability of fusion $P_\mu = (207)^3 P_{H_2}$

5) $\alpha \mu^- e^-$

$\alpha = p p n n$, α -particle



6) $p p \mu^- e^-$



μ -molecule as nucleus of H-atom.