

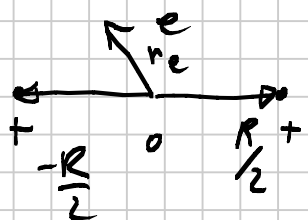
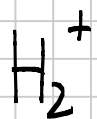
LECTURE # 7

Note Title

9/24/2007

Last time: Molecules

Born-Oppenheimer approx



$$\Psi(r_e, R) \sim \Psi_p(R) \Psi_e^R(r_e)$$

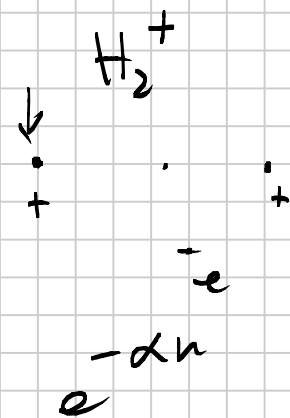
1) "Clamp" protons \rightarrow Solve SE electron $\forall R \rightarrow \Psi_m^{eR} \boxed{E_m(R)}$

2) Eq. for protons

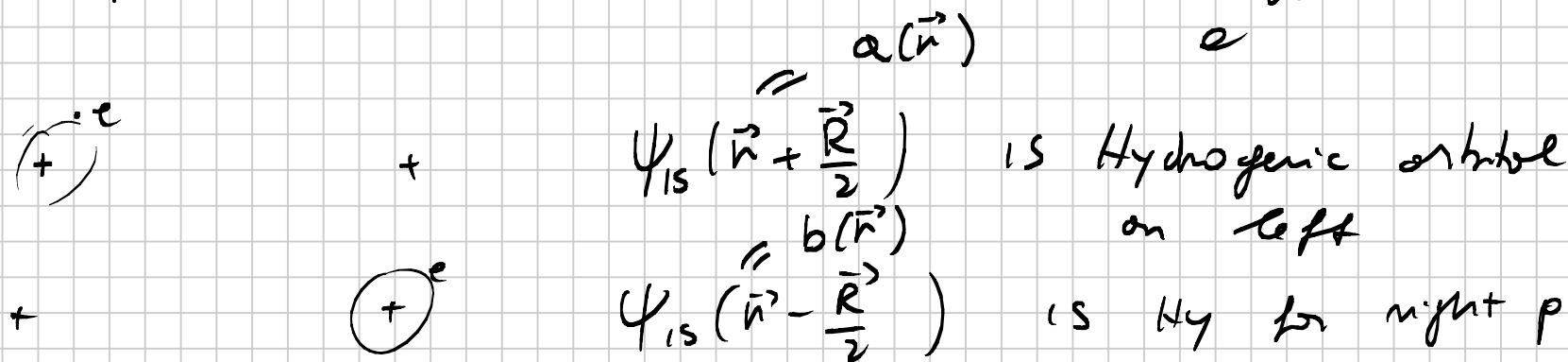
$$\left[-\frac{\hbar^2 \nabla_R^2}{2\mu_p} + E_m(R) \right] \Psi_p(R) = E \Psi_p(R)$$

How do we find $E_m(R)$?

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{|\vec{r}_e + \frac{\vec{R}}{2}|} - \frac{e^2}{|\vec{r}_e - \frac{\vec{R}}{2}|}$$



Find Molecular Orbitals



Molecular Orbitals as Linear Combinations of

Atomic Orbitals MO - LCAO

$$\psi_{MO}(\vec{r}) = c_a a(\vec{r}) + c_b b(\vec{r})$$

Symmetry:
 $|c_a| = |c_b|$

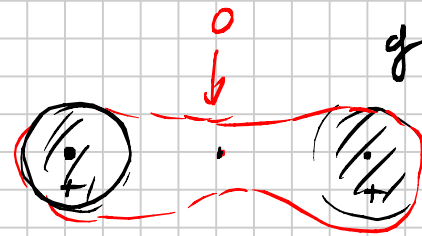
$$\psi_g(\vec{r}) = a(\vec{r}) + b(\vec{r})$$

g \rightarrow GERADE
 Symmetric under inversion with respect to center of molecule

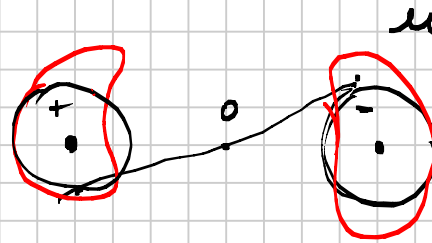
$$\psi_u(\vec{r}) = a(\vec{r}) - b(\vec{r})$$

$n \rightarrow$ UNGERADE

Antisymmetric with respect to center



Molecular O have to be normalized



$$\Psi_g(\vec{r}) = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1+s}} (a+b)$$

$$\Psi_u(\vec{r}) = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1-s}} (a-b)$$

$$S = \int d\vec{r} a^*(r) b(r) =$$

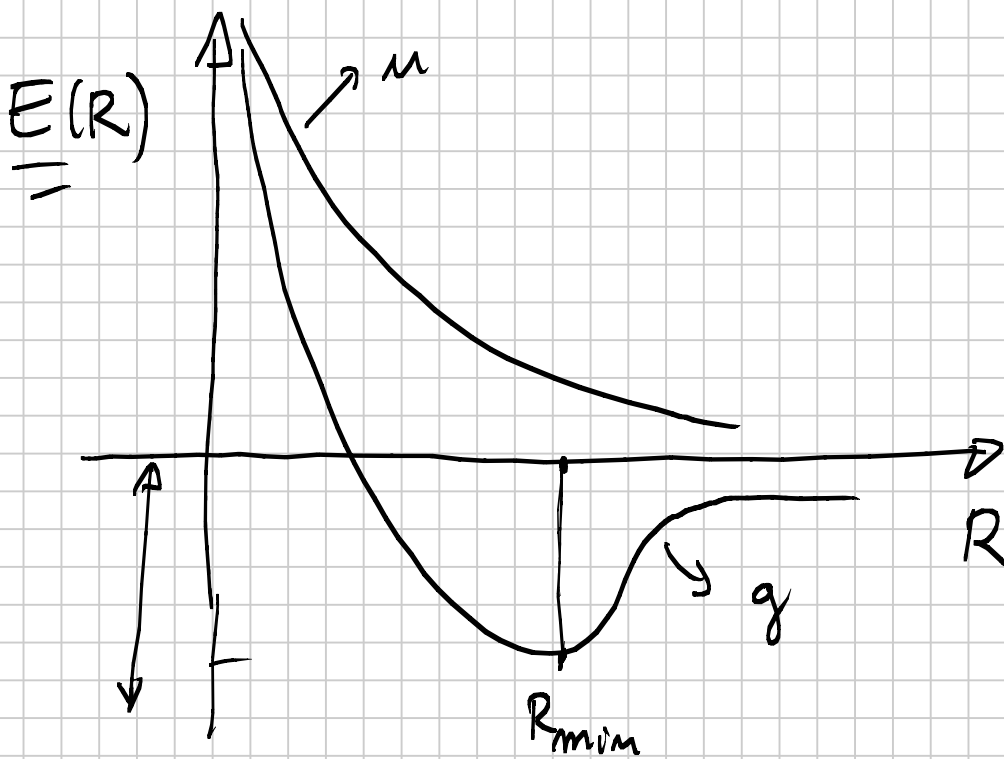
$$\int d\vec{r} \Psi_{1s}(\vec{r} + \frac{\vec{R}}{2}) \Psi_{1s}(\vec{r} - \frac{\vec{R}}{2})$$

$$E_m(R) \rightarrow E_g(R) = \langle \Psi_g | H | \Psi_g \rangle$$

$$E_u(R) = \langle \Psi_u | H | \Psi_u \rangle$$

$$\Psi_g(r) \sim (\sigma_g | s)$$

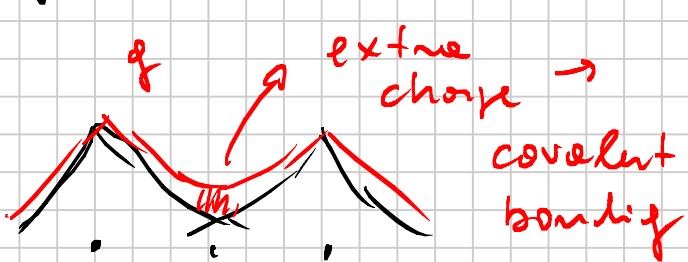
$$\Psi_u(r) \sim (\sigma_u | s)$$



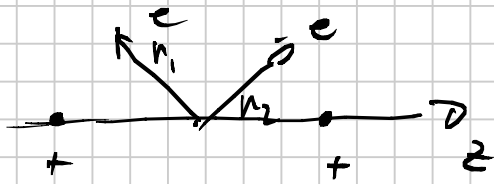
gerade \rightarrow Bound Molecule Stable system

		Experiment
Binding energy	$E_b = 1.76 \text{ eV}$	$E_b \sim 2.79 \text{ eV}$
	$R_{\min} = 1.32 \text{ \AA}$	$R_{\min} \sim 1.06 \text{ \AA}$

ungerade \rightarrow not stable



H₂ 2 electrons $\psi_e(r_1, r_2)$



$$(\sigma_g 1s)^2$$

L_z is a good quantum number $L_z = \sum_i l_{i,z}$

S_z $S_z = \sum_i s_{i,z}$

Atoms	s	p	d	f ...	} L_{TOT} conserved
	S	P	D	F ...	

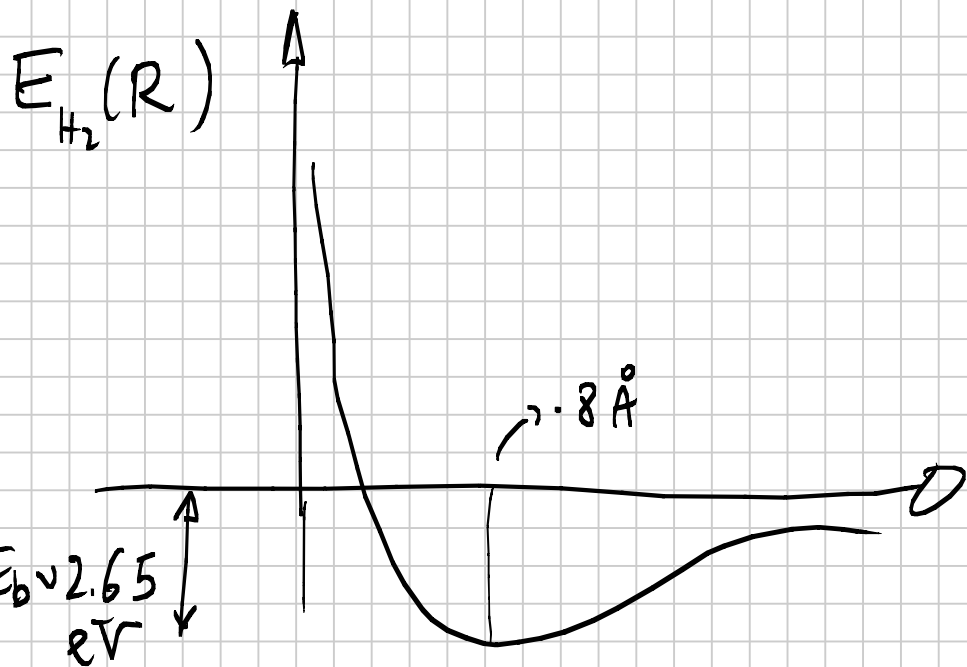
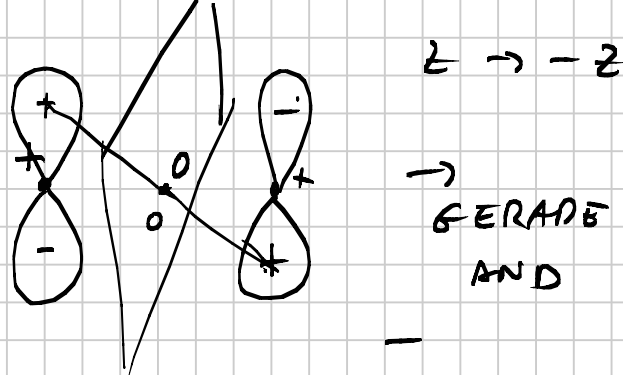
Molecules (axial symmetry)	σ	π	δ	ϕ ...	} L_z conserved
	Σ	Π	Δ	Φ	

For H₂⁺ $(\sigma_g 1s)^2 \sum_g^+$ \rightarrow ^(2s+1) symmetric with respect to a plane passing by center

Fon

H₂

$$(\sigma_g 1s)^2 \quad \uparrow \quad \downarrow$$



Experiment gives

$$E_0 \sim \underline{\underline{4.72 \text{ eV}}}$$

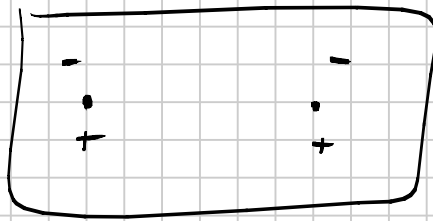
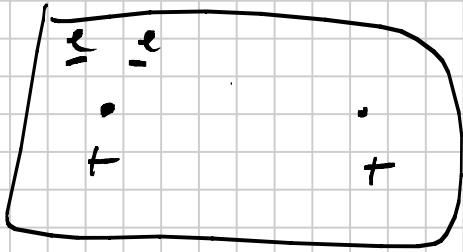
$$R_{\text{min}} \sim 0.7 \text{ \AA} \text{ or}$$

Molecular orbitals (Hund-Mulliken method)

$$(\sigma_g 1s)^2 \rightarrow \psi_g(r_1) \psi_g(r_2)$$

$$\left(a(\vec{r}_1) + b(\vec{r}_1) \right) \left(a(\vec{r}_2) + b(\vec{r}_2) \right)$$

$$\psi_{MO} \sim \underbrace{a(r_1)a(r_2)}_{\text{I}} + \underbrace{a(r_1)b(r_2) + b(r_1)a(r_2)}_{\text{II}} + b(r_1)b(r_2)$$



$\psi_{MO} \rightarrow$ Type I and Type II have the same probability \rightarrow NOT GOOD

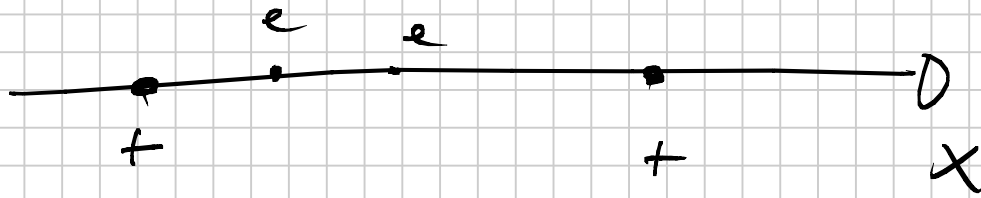
Heitler-London approximation

Keep only terms of type II

$$\psi_{HL} \sim N [a(r_1)b(r_2) + a(r_2)b(r_1)]$$

$$E_{\text{binding}} \sim 3.14 \text{ eV}$$

$$R_{\text{min}} \sim 8 \text{ \AA}$$



H_2 1D
m

$$V(x) = -e^2 \delta(x)$$