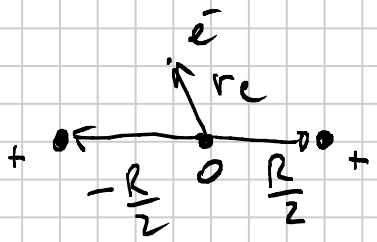
LECTURE # 8

Note Title 9/22/2008

LAST TIME: MOLECULES

BORN - OPPENHEIMER APPROX → $\psi(r_e, R) \simeq \psi_p(R)\,\psi_e^R(r_e)$ (R: PARAMETER)

H_2^+

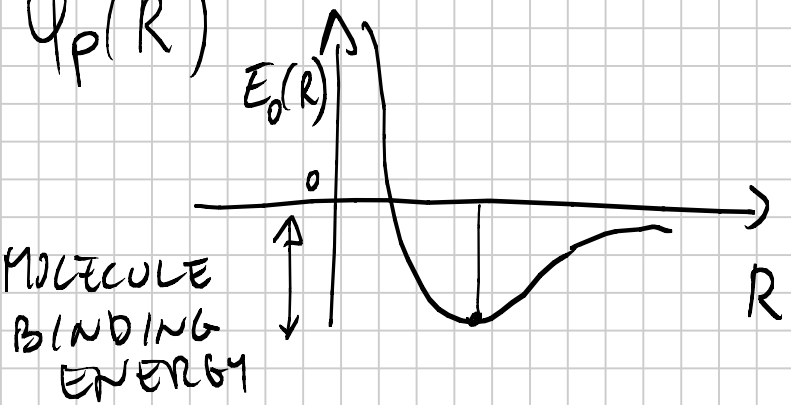


① "CLAMP" PROTONS AT DISTANCE R → $\forall R$, SOLVE SE FOR e^- → $\psi_{e,m}^R$, $E_m(R)$

② Eq. PROTONS:

$$\left(-\frac{\hbar^2 D_R^2}{2\mu_p} + E_m(R)\right)\psi_p(R) = E\,\psi_p(R)$$

HOW DO YOU FIND $E_m(R)$?



$$H = -\frac{\hbar^2}{2m}\nabla_n^2 - \frac{e^2}{\left|\vec{r}+\frac{\vec{R}}{2}\right|} - \frac{e^2}{\left|\vec{r}-\frac{\vec{R}}{2}\right|}$$

$r = r_e$

MOLECULAR ORBITALS AS LINEAR COMBINATION OF ATOMIC ORBITALS

MO - LCAO

$e^{-\alpha r}$

$\psi_{1s}\left(\vec{r}+\frac{\vec{R}}{2}\right) \equiv a(\vec{r})$ = 1S HYDROGEN

$\psi_{1s}\left(\vec{r}-\frac{\vec{R}}{2}\right) \equiv b(\vec{r})$ "

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

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

$$\psi_u(\vec{r}) = N'\left(a(\vec{r}) - b(\vec{r})\right)$$

g = GERADE (EVEN)

SYMMETRIC UNDER INVERSION WITH RESPECT TO THE COM (ORIGIN)

u = UNGERADE (ODD)

GERADE

UNGERADE

$$\psi_g = \frac{1}{\sqrt{1+S}} \cdot \frac{1}{\sqrt{2}} (a+b)$$

$$\psi_u = \frac{1}{\sqrt{1-S}} \frac{1}{\sqrt{2}} (a-b)$$

$$S = \int d\vec{r}\; a^*(\vec{r})\, b(\vec{r}) = \text{OVERLAP OF ATOMIC ORBITALS}$$

$E_n(R)$ →

$$E_g(R) = \langle \psi_g | H | \psi_g \rangle$$

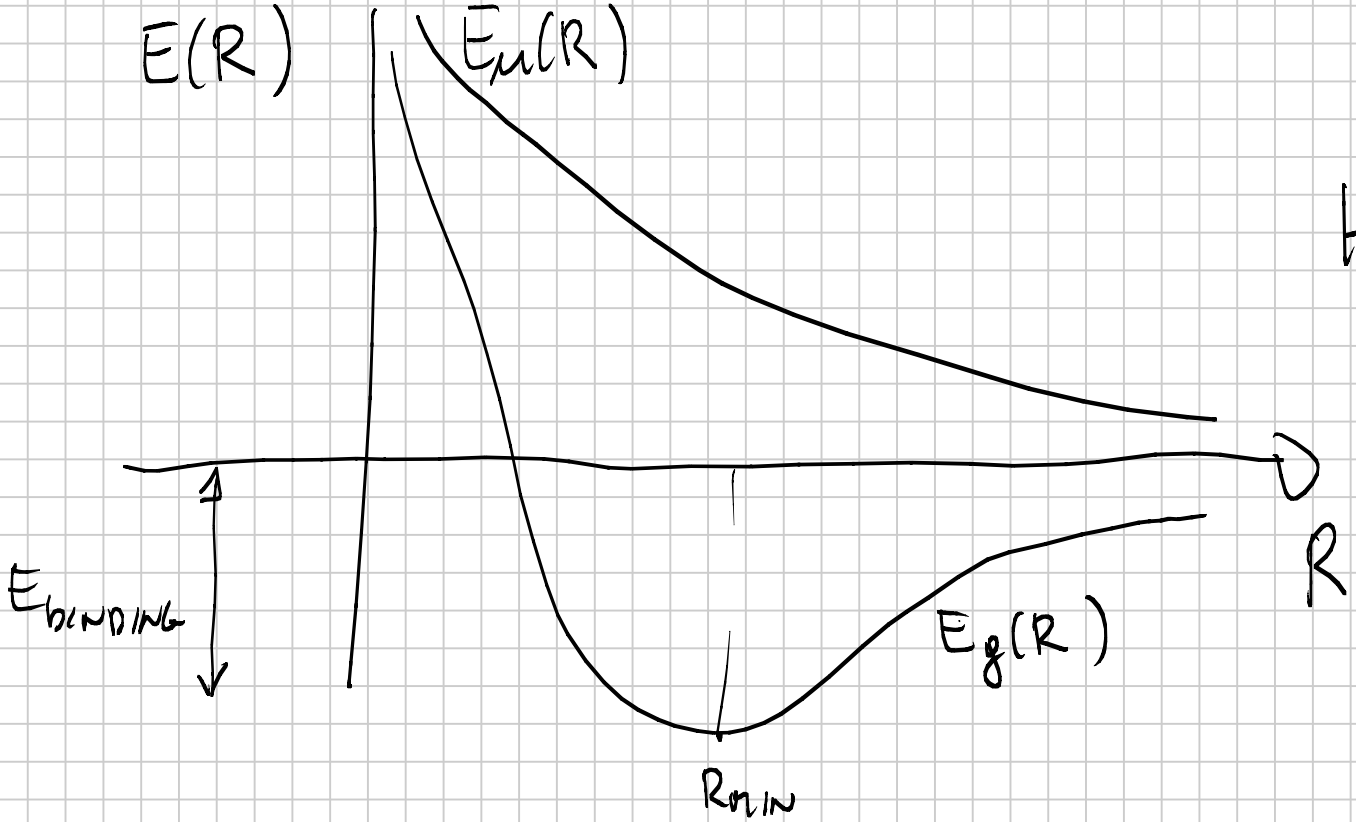
↳

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

$\psi_g(r)$ $(\sigma_g 1s)$ "EQUIVALENT" $\psi_{1s}(r)$ $(1s)$

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

$\psi_u(\vec{r})$ $(\sigma_u 1s)$



H_2^+

MO → $E_b \sim 1.76$ eV

$R_{MIN} \sim 1.32$ Å

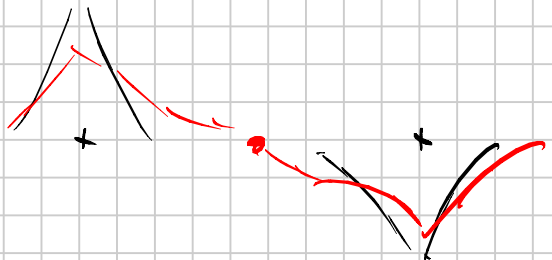
EXPERIMENT

$E_b \sim 2.79$ eV

$R_{MIN} \sim 1.06$ Å

UNGERADE NOT STABLE

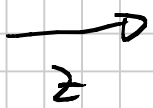
GERADE



H_2

$\psi_e^R(r_1, r_2)$

$(\sigma_g 1s)^2$



($\vec{L}_{TOT}$ NOT A GOOD QUANTUM #)

L_z (TOTAL) IS A GOOD QUANTUM # $L_z = \sum_i l_{z_i}$

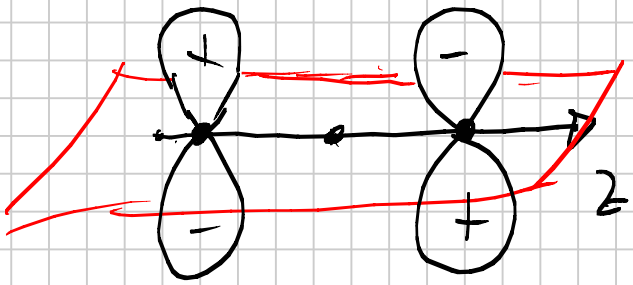
S_z

4

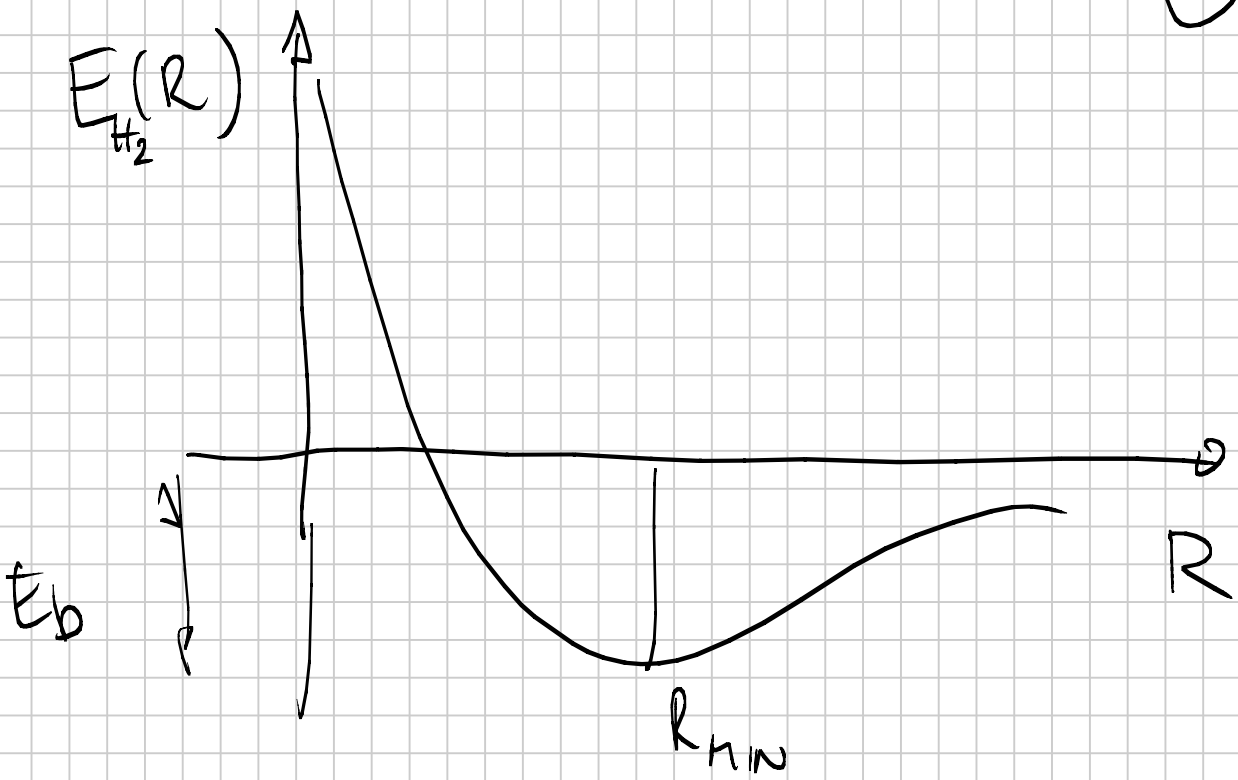
ATOMS	s	p	d	f	...	L_{TOT} CONSERVED FOR ATOMS
	S	P	D	F	..	
MOLECULES (AXIAL SYMMETRY)	σ	π	δ	φ		L_z CONSERVED
	Σ	Π	Δ	Φ		

H_2^+ $(\sigma_g 1s)\ ^2\Sigma_g^+$ ⟶ SYMMETRIC WITH RESPECT TO A PLANE PASSING BY AXIS

H_2 $(\sigma_g 1s)^2\ {}^1\Sigma_g^+$



GERADE AND — WITH RESPECT TO PLANE



MOLECULAR ORBITAL

$E_D \sim 2.65$ eV

$R_{MIN} \sim .8$ Å

EXPERIMENT

$E_D \sim 4.72$ eV

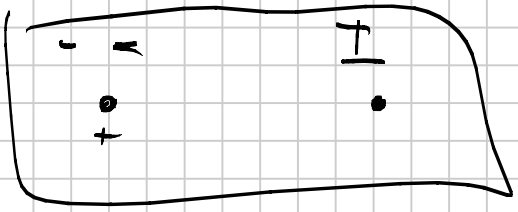
$R_{MIN} \sim .7$ Å

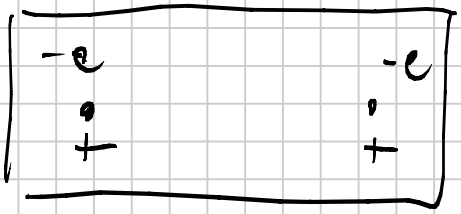
MOLECULAR ORBITAL FOR H_2 (A.K.A. HUND-MULLIKEN) CAN BE IMPROVED USING

HEITLER–LONDON APPROXIMATION

MO $\quad (\sigma_g 1s)^2 = \psi_g(r_1)\,\psi_g(r_2) = \big(a(r_1)+b(r_1)\big)\big(a(r_2)+b(r_2)\big)$

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



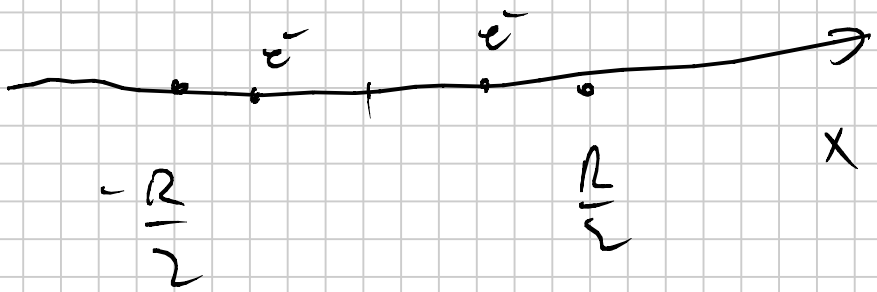


HEITLER–LONDON
KEEP ONLY TERMS OF TYPE II

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

$E_b \sim 3.14$ eV $\qquad R_{MIN} \sim .8$ Å

1D IMMAGINE H_2



$$\frac{e^2}{r} \rightarrow e^2 \delta(x)$$

$$\psi_{1S}(x) = e^{-|x|}$$