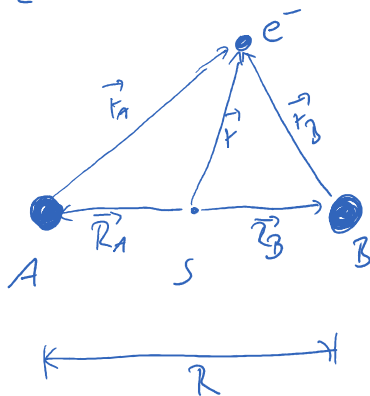


H_2^+ molecular ion



SE:

$$\left[-\frac{\hbar^2}{2M} (\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R} \right) \right] \psi = E \psi$$

$\uparrow$
 square of gradient
 along $\vec{r}_A, \vec{r}_B$

Coul. Interaction

neglected $\hbar \nabla^2$

→ "fixed" nuclei

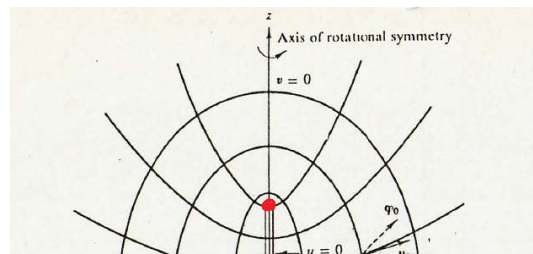
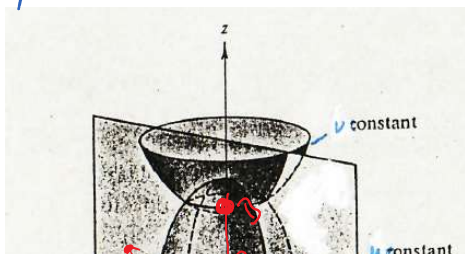
This can be solved analytically in elliptic coordinates

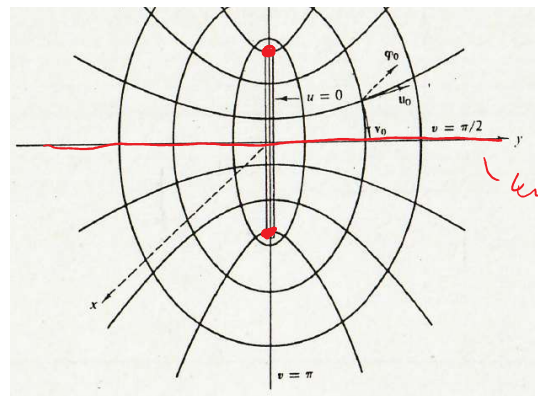
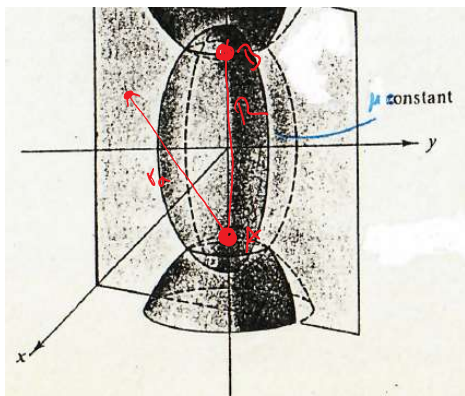
$$\mu = \frac{r_A + r_B}{2}$$

$$\nu = \frac{r_A - r_B}{2}$$

$$\tan \varphi = \frac{y}{x}$$

⇒ Separation $\psi(\vec{r}_A, \vec{r}_B, R) = M(\mu) \cdot N(\nu) \cdot \Phi(\varphi)$
 elliptic coordinates





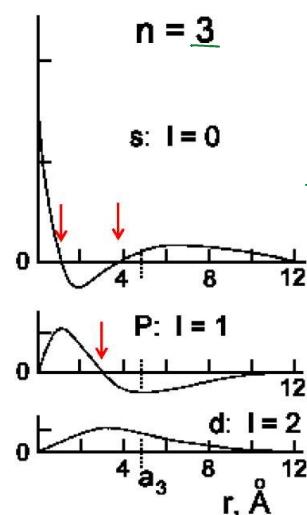
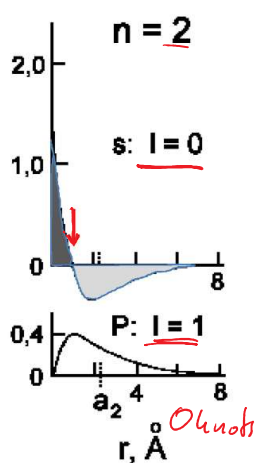
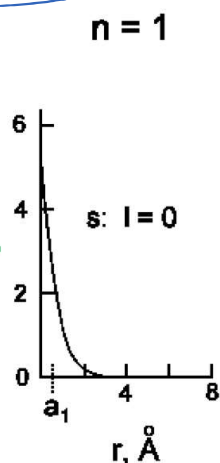
$u = \text{const} \hat{=} \text{ellipses}$
 $v = \text{const} \hat{=} \text{hyperbolas}$
 protons in the foci of ell./hyp.

quantum numbers

$n_u = \text{number of knots in the wf. } M(u)$
 (elliptical part)

$n_v = \dots$
 (hyperbolic part) $N(u)$

c.f. H atom



knots = $n - l - 1$

2

1

0

LCAO in H_2^+

Lm. Combination of Atomic Orbitals

H_2^+ molecular ion $\hat{=} 1$ H atom in ground state

+ 1 proton

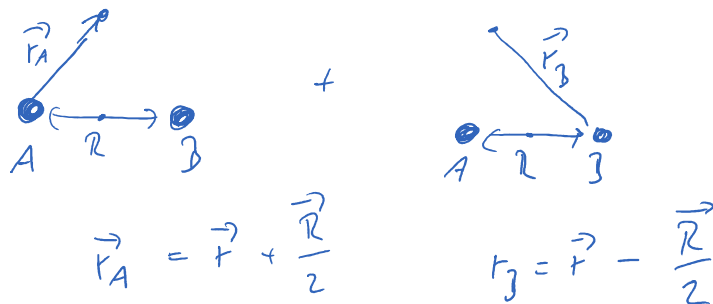
e^- can be either at proton A or B

$$\psi(\vec{r}, \vec{R}) = c_1 \phi_A(\vec{r}_A) + c_2 \phi_B(\vec{r}_B)$$

$$\text{with } \phi_A(\vec{r}_A) = \phi_A(r_A) = \frac{1}{\sqrt{\pi} a_0^3} e^{-\frac{r_A}{a_0}}$$

ground state H wavefunction

same for $\phi_B(\vec{r}_B)$



Normalization of $\psi \Rightarrow$

$$c_1^2 + c_2^2 + 2c_1c_2 S_{AB} = 1$$

$$S_{AB} = \int \phi_A(\vec{r}_A) \phi_B(\vec{r}_B) d^3r$$

overlap integral

Integration over all electron coordinates

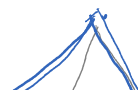
$$\text{symmetry} \Rightarrow |c_1|^2 = |c_2|^2$$

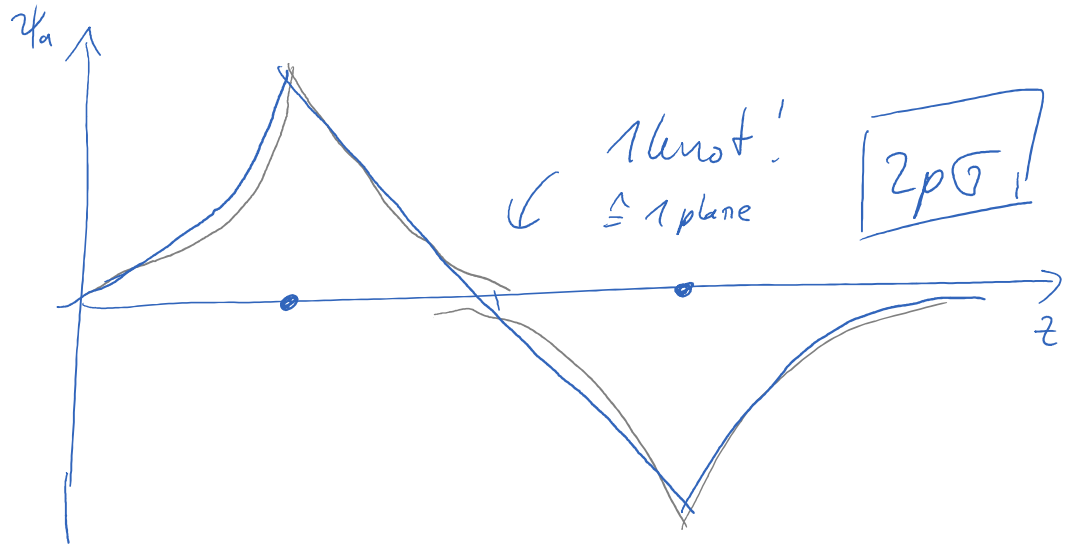
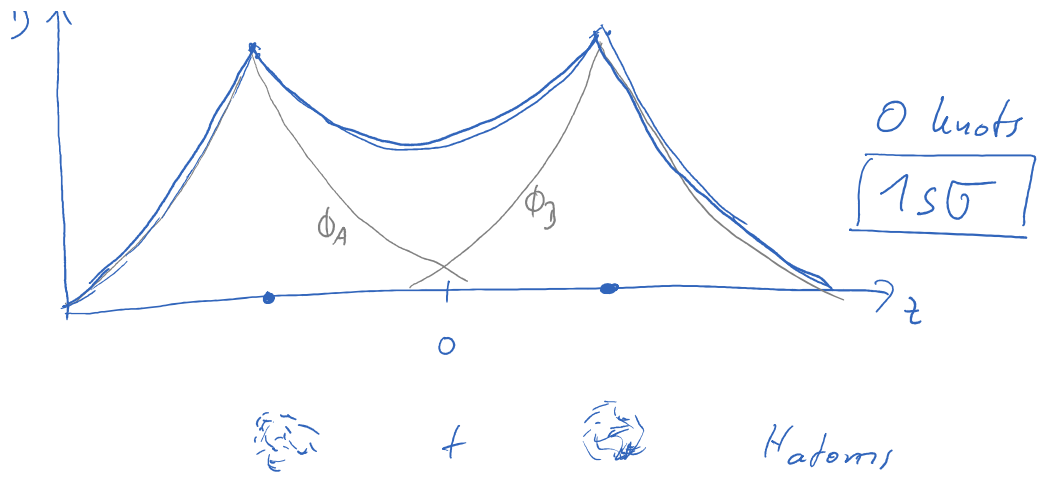
$$\Rightarrow c_1 = \pm c_2$$

$$\Rightarrow \text{Molecular Orbitals: } \psi_s = \frac{1}{\sqrt{2+2S_{AB}}} (\phi_A + \phi_B)$$

$$\psi_a = \frac{1}{\sqrt{2-2S_{AB}}} (\phi_A - \phi_B)$$

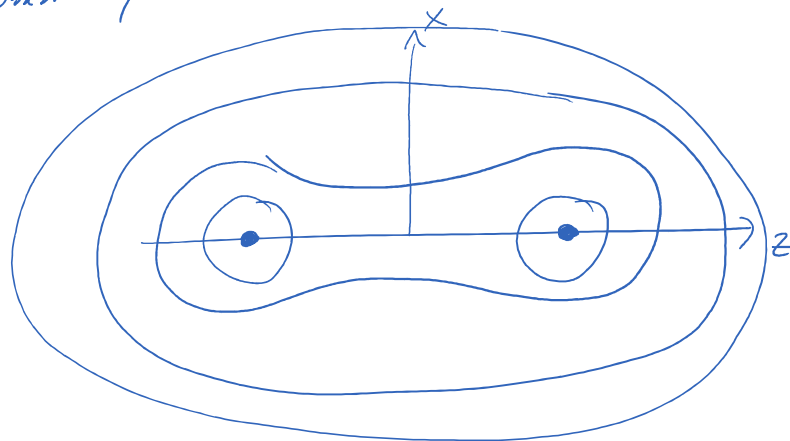
$\psi_s \uparrow$



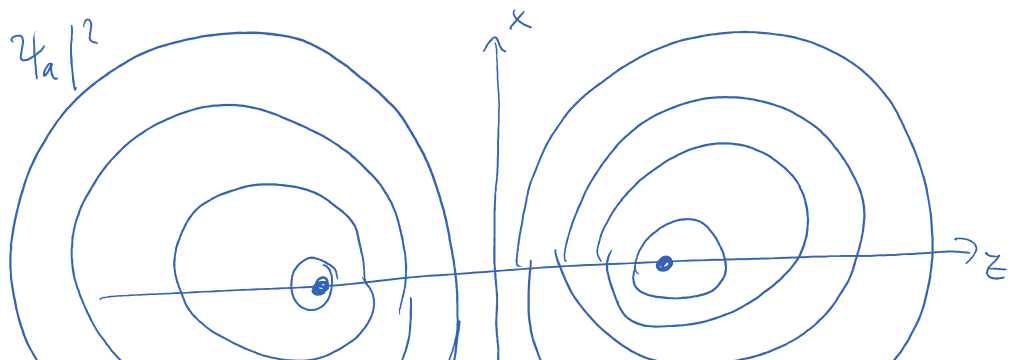


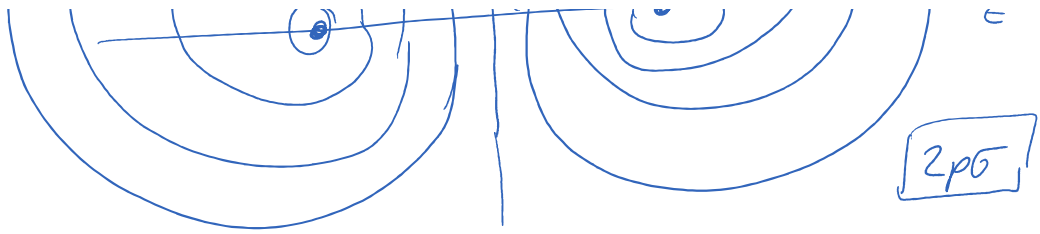
e^- probability

$$|\psi_s|^2$$



$$|\psi_a|^2$$

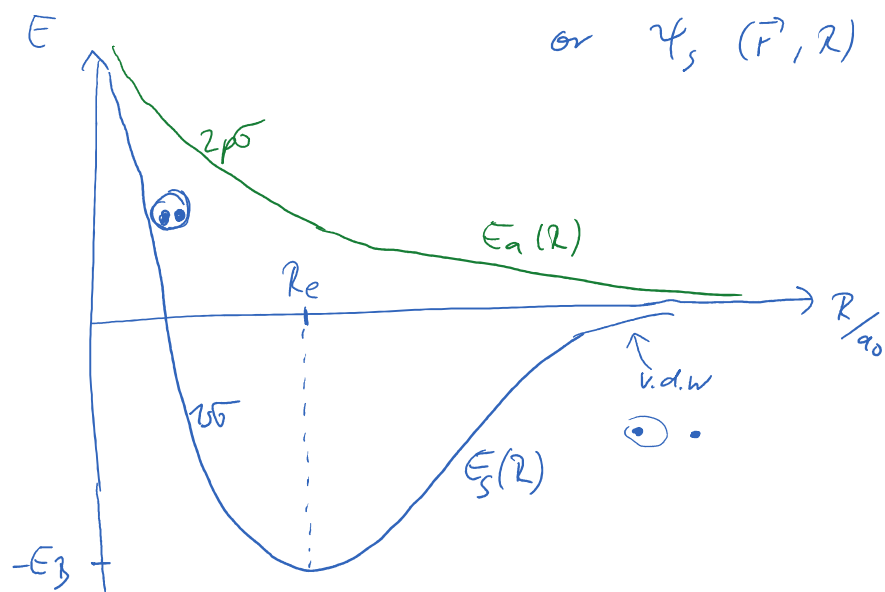




Expectation value of energy

$$E(R) = \langle E \rangle = \int \psi^* H \psi d^3r$$

with $\psi_a(\vec{r}, R)$
or $\psi_s(\vec{r}, R)$



Bonding energy

equilibrium distance

LCAO

1.76 eV @ 2.5 a_0

exact

2.79 eV @ 2.0 a_0

ψ_s = bonding

electron density between repelling protons
= "glue"

ψ_a = antibonding

no electron density $\Rightarrow$ protons repel each other

also a blinding effect in h.h. energy term of e^-

"more space" in $\psi_s \rightarrow$ smaller momentum / h.h. energy
 $\hookrightarrow$ good