

Huge scale difference between electronic & nuclear degrees of freedom (mass!)

B.O 1927: keep nuclei fixed

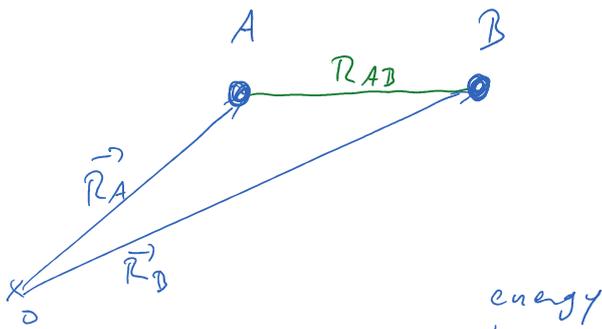
ansatz for wf: product of electronic & nuclear wf.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2) = \Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \cdot \psi(\vec{R})$$

$$= \Phi(\vec{r}) \cdot \psi(\vec{R})$$

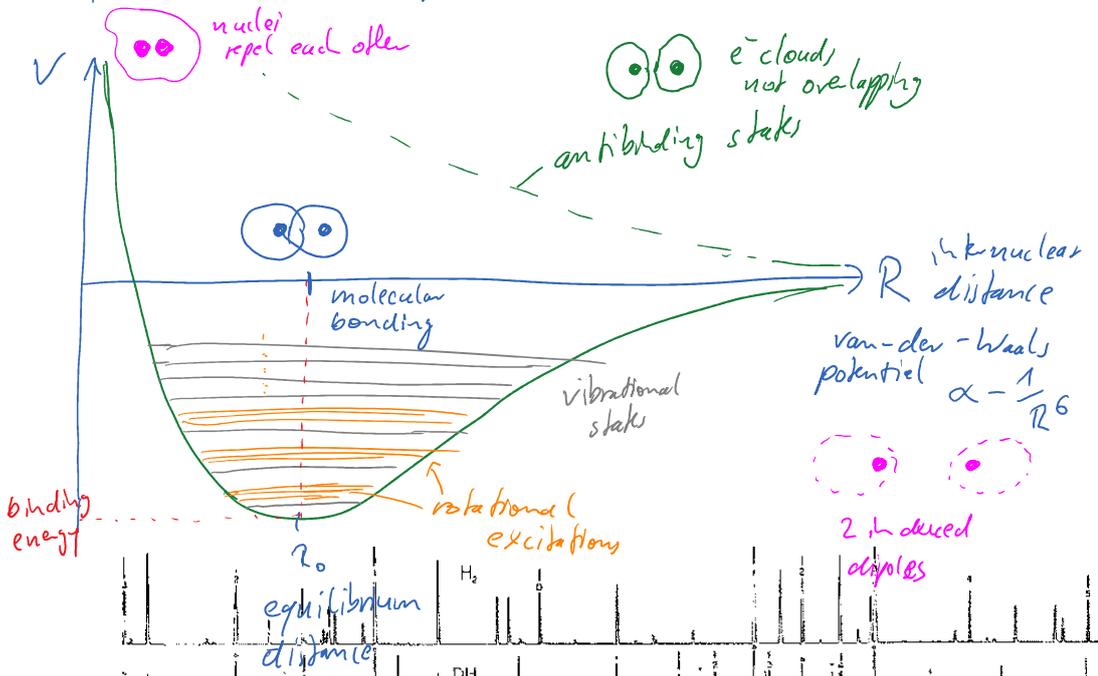
↑ all electrons ↑ all nuclei

e.g. diatomic molecules $\vec{R} \Rightarrow R_{AB} \leftarrow$ parameter $\{\vec{R}_A, \vec{R}_B\}$



S.E. $\hat{H} \psi = E \psi$ is then solved for many values of $R = R_{AB}$

typical molecular potential



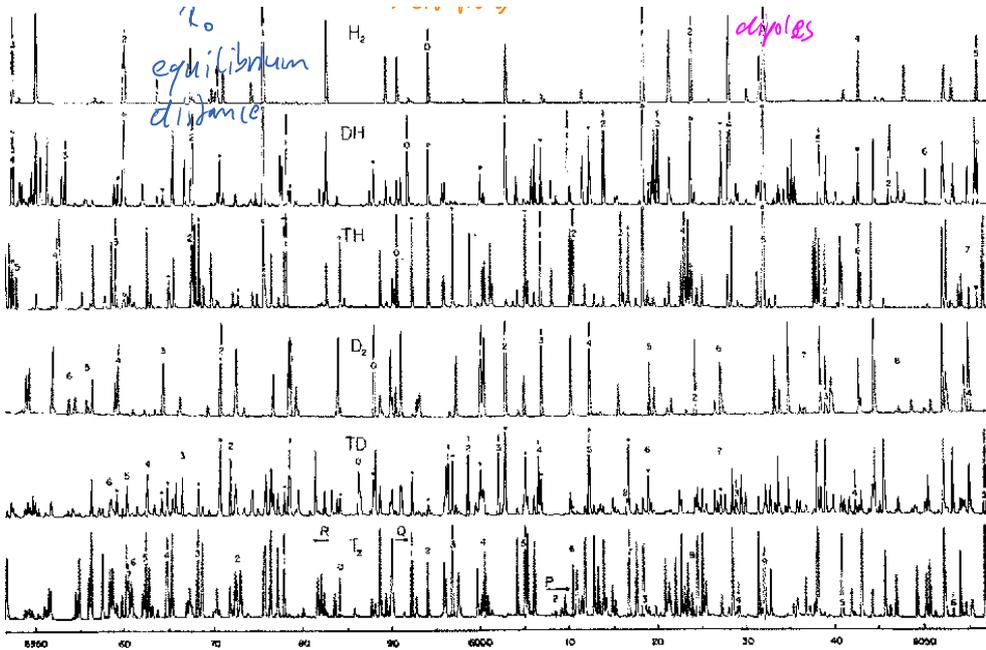
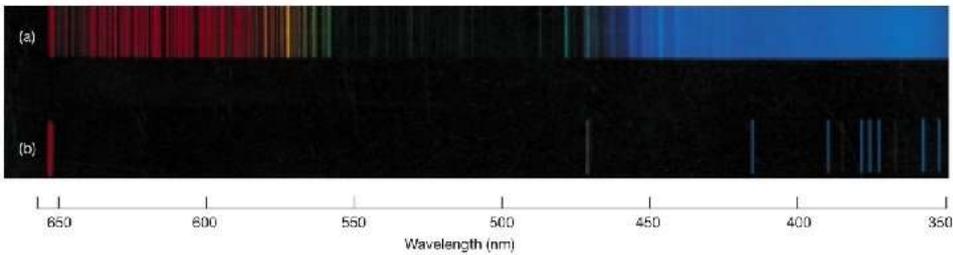


FIG. 1. Comparison of the spectrum near 6000Å of the six isotonic species of molecular

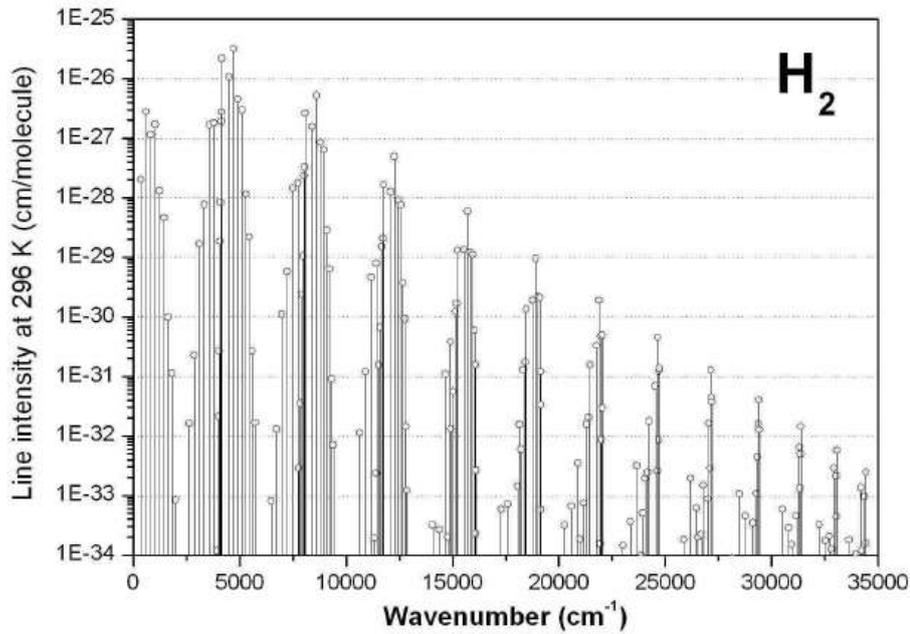
Molecules

Molecular spectra are much more complex than atomic spectra, even for hydrogen:

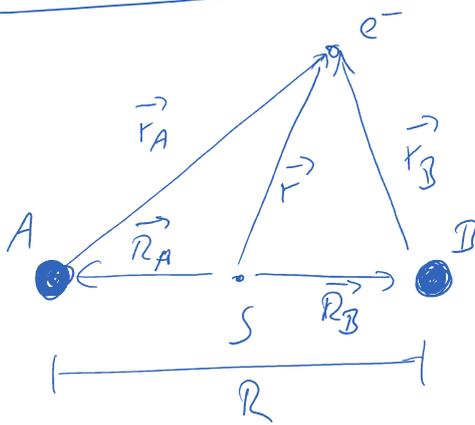
(a) Molecular hydrogen (b) Atomic hydrogen



Copyright © 2005 Pearson Prentice Hall, Inc.



H₂⁺ molecular ion

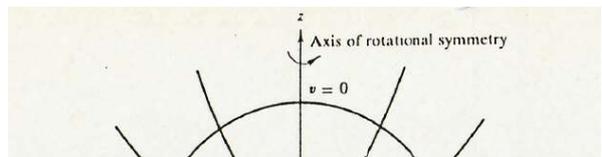
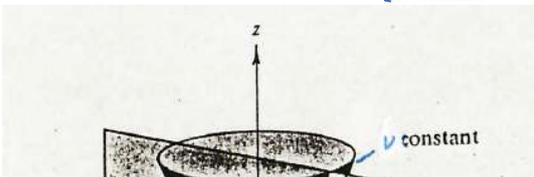


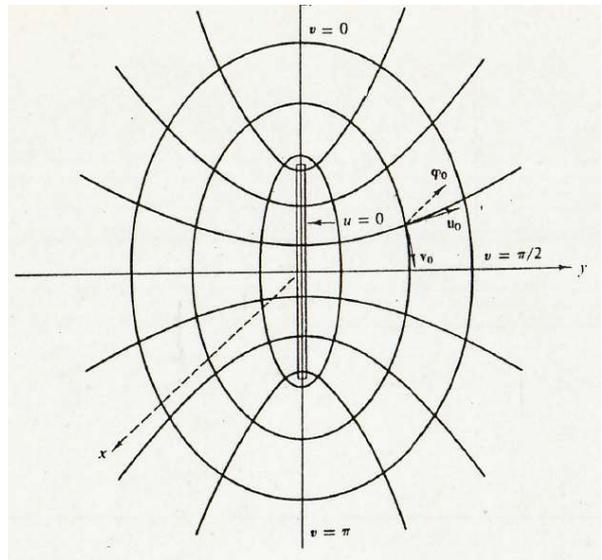
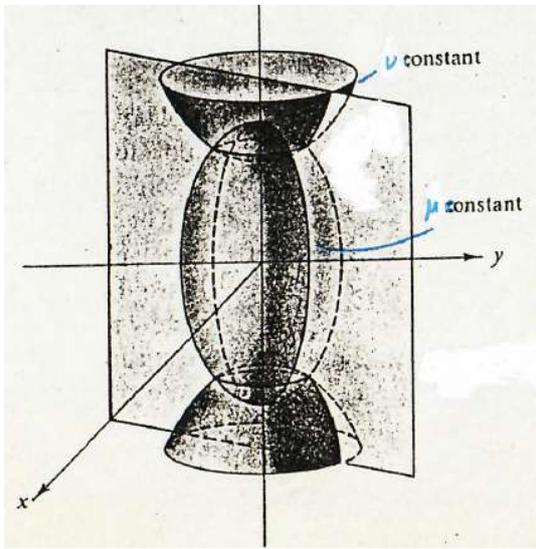
$$SE: \left[-\frac{\hbar^2}{2M} (\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2me} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R} \right) \right] \psi = E\psi$$

gradient² along \vec{R}_A, \vec{R}_B
 e^-
Coulomb interaction

nuclear part, neglected in BO
→ fixed nuclei

This can be solved analytically in elliptic coordinates





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

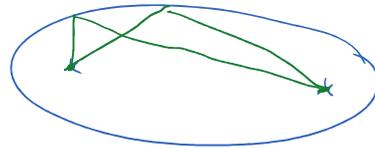
$$v = \frac{r_A - r_B}{2}$$

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

$\mu = \text{const.} \hat{=} \text{ellipsoids}$
 $v = \text{const.} \hat{=} \text{hyperboloids}$

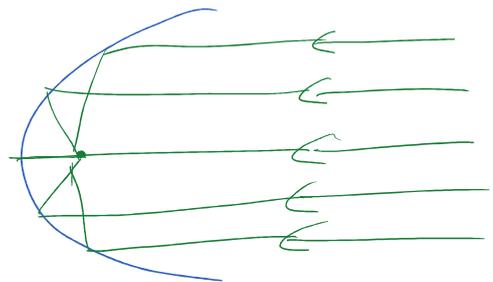
\Rightarrow Separation $\Psi(\vec{r}_A, \vec{r}_B, R) = M(\mu) \cdot N(v) \cdot \Phi(\varphi)$

protons are in the foci of (nuclei) ell. + hyp.



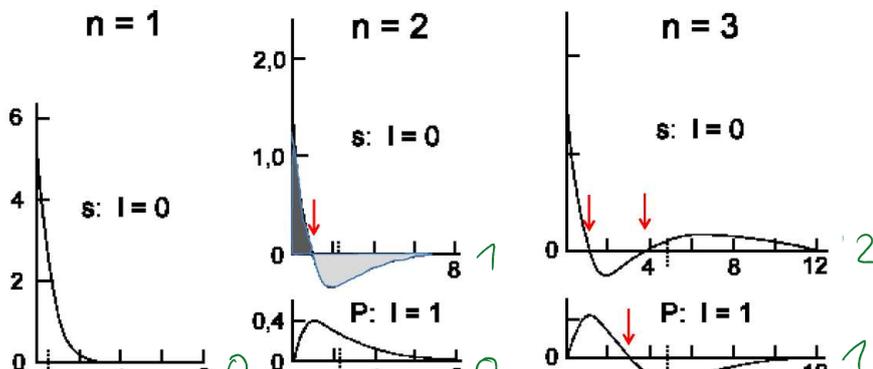
quantum numbers:

$n_\mu =$ number of knots of wf. $M(\mu)$
 (elliptical part)

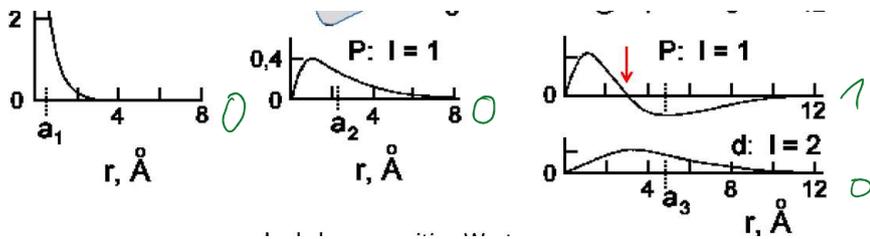


$n_\nu = -1 -$ $N(v)$
 (hyperbolic part)

See H atom



of knots
 $= n - l - 1$



LCAO in H_2^+

Linear
Combination of
Atomic
Orbitals

H_2^+ molecular ion $\hat{=}$ 1 Hydrogen in ground state
+ 1 proton

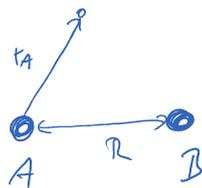
e^- can be either at proton A or B

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

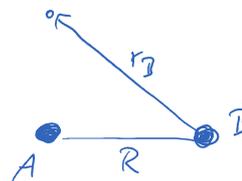
with
$$\phi_A(\vec{r}_A) = \phi(r_A) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_A}{a_0}}$$

and same

$$\phi(r_B) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_B}{a_0}}$$



+



Normalization of the wf. ψ

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

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

↑
all electron coordinates

overlap integral

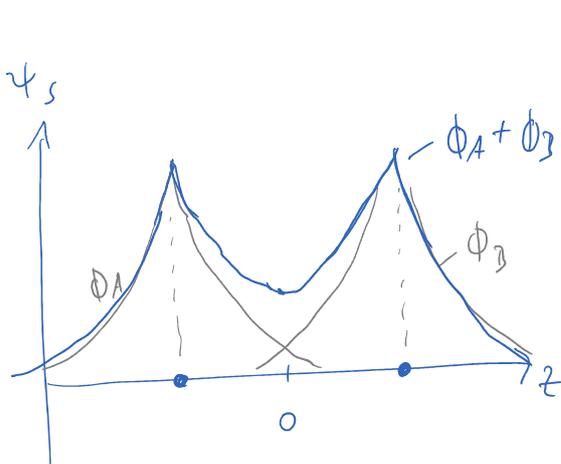
Symmetry H_2^+ (but (maybe) not H_2^{2+} !)

$$\hookrightarrow |c_1|^2 = |c_2|^2$$

$$\Rightarrow c_1 = \pm c_2$$

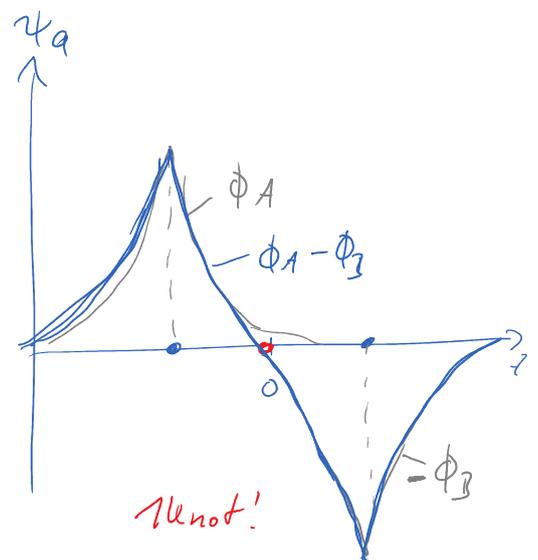
$$\Rightarrow \text{Molecular orbital } \psi_s = \frac{1}{\sqrt{2 + 2S_{AB}}} (\phi_A + \phi_B)$$

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



0 knots

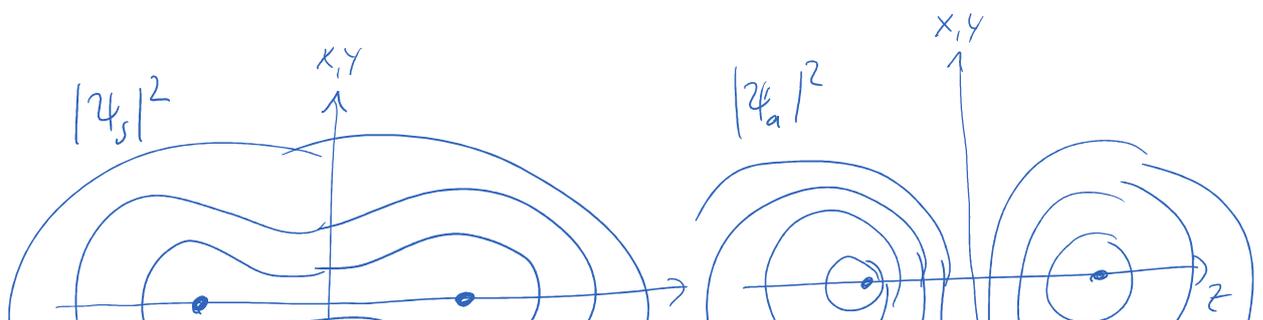
1s σ

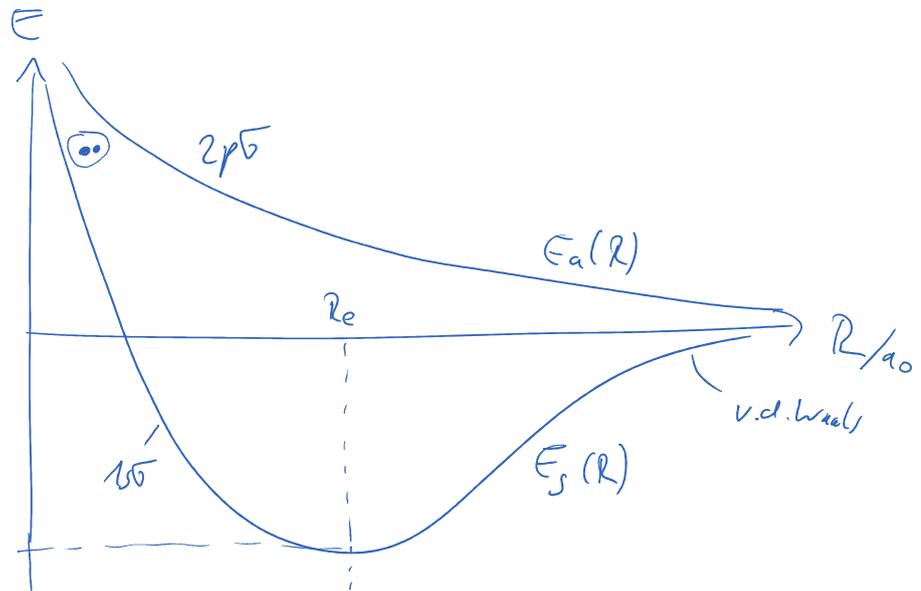
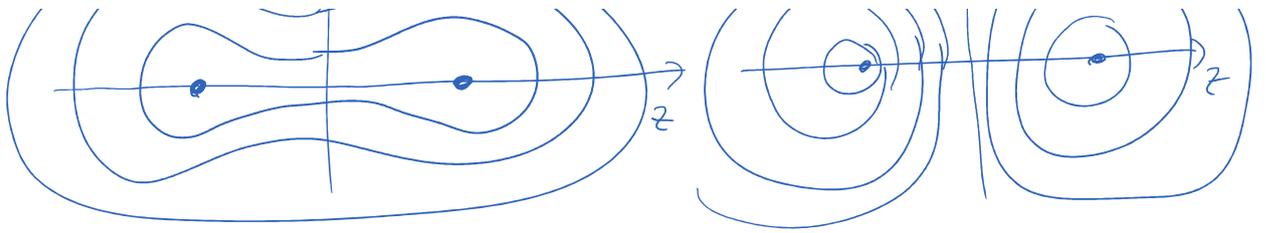


1 knot!

2p σ

square of wf. = probability for e^-





	binding energy	equilibrium distance
exact	2.79 eV	2.0 a_0
LCAO	1.76 eV	2.5 a_0

$\psi_s = \text{bonding}$ electron density between (repelling) protons
 \rightarrow "glue"

$\psi_a = \text{antibonding}$ no electron density between protons
 \rightarrow repel

H₂ molecule

$2e^- \rightarrow e-e$ interaction

separation of S.E. is not possible any more

\Rightarrow approximate, numerical methods

take Pauli Principle into account (like He atom)

Heitler-London approximation

$e^- \#1$ is close to proton A
and $\#2$ " " B vice versa

$$\psi = \underbrace{\chi^+(1)\chi^+(2)}_{\text{symmetric spin wf.}} \left[\underbrace{\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) - \phi_A(\vec{r}_2)\phi_B(\vec{r}_1)}_{\text{antisymmetric spatial wf.}} \right] \cdot \mathcal{N}$$

normaliz.

↳ "ungerade"

$$\text{or } = (\chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1)) \left[\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) + \phi_A(\vec{r}_2)\phi_B(\vec{r}_1) \right] \cdot \mathcal{N}$$

symmetric spatial

↳ "gerade"

or ansatz

$$\psi = \psi_s(\vec{r}_1)\psi_s(\vec{r}_2) \cdot \left[\chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1) \right] \cdot \mathcal{N}$$

↑
symmetric H_2^+
wf.
for $1e^-$

anti-symmetric
spin wf.

gives you states $\phi_A(\vec{r}_1)\phi_A(\vec{r}_2) + \phi_B(\vec{r}_1)\phi_B(\vec{r}_2)$

≙ both electrons are at the same proton

$$\hat{=} H_2 = H^- + H^+ \quad \text{2 ionic states}$$



these ionic states are missing in Heitler-London, but they are also not very probable

These ionic states are missing in ...
but they are also not very probable

Recipe: Perturbation theory

- ① ignore ionic states,
- ② find equilibrium distance in Hitle-London
- ③ treat ionic states as perturbation

