$1e^- \rightarrow$ multi-$e^- \rightarrow$ Molecule $\rightarrow$ spectroscopy

$\downarrow$ S.E.

$\psi_{n l m_l}$ $\quad$ $1e^-$ Wave f^n $\rightarrow$ "ORBITAL"

1s

RDF = $r^2 R^2(r)$

"n" for H-atom

$\downarrow$ Ignore $e^- - e^-$ repulsion i.e. $\left(\frac{1}{r_{12}}\right)$ term in $\hat{H}$

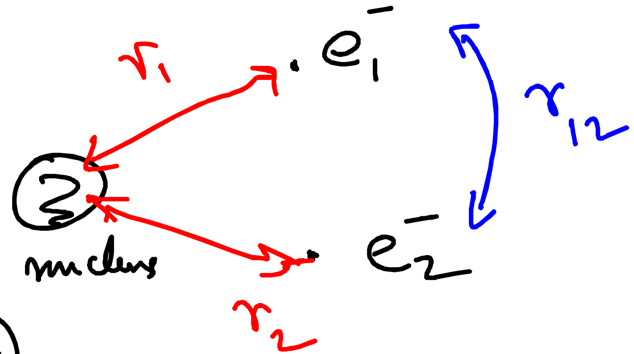
H-like wave f^n $(1e^-)$

n, l, m_l

He atom $\rightarrow 2e^-$

$1s^2$ $\rightarrow \psi_{1s}(1)$, $\psi_{1s}(2)$

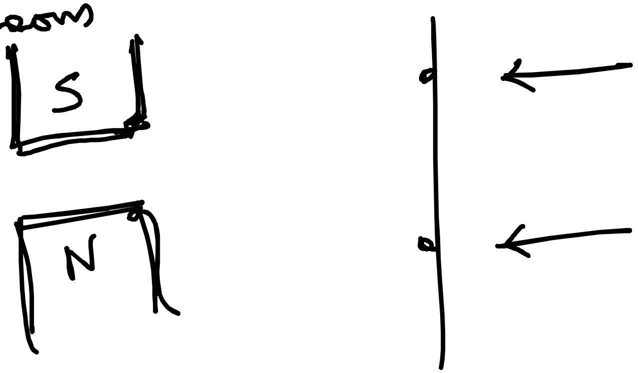
1s(1) . 1s(2)



Stern Garlach Expt proved e^- spin

Inhomogeneous B-field

Ag ions

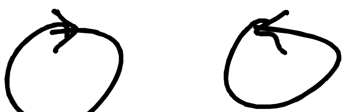


Pauli spin of e^-

Exclusion principle → wave f^n. is Antisymmetric to e^- exchange

$$\psi(1,2) = -\psi(2,1)$$

2 possibility of spin



m_s

e^- are Fermions → No $2e^-$ are going to have the same set of quantum #s.

$$\psi_{Total}(1,2) = \underbrace{\psi_{Space}(1,2)}_{n,\, l,\, m_l} \cdot \underbrace{\psi_{spin}(1,2)}_{\alpha,\, \beta}$$

α, β → Pauli

$$\Psi_{space}(1,2) = 1s(1)\cdot 1s(2) \xleftarrow{\text{Short hand}} \Psi_{1s}(1)\,\Psi_{1s}(2)$$

$$\Psi_{Total}(1,2) = \underbrace{1s(1)\cdot 1s(2)}_{space}\ \underbrace{\left[\alpha(1)\cdot\beta(2) - \alpha(2)\cdot\beta(1)\right]}_{spin}$$

He atom $\longrightarrow 1s^2$

Li $\quad \underline{n = 2}$

$2s \qquad 2p$

$-5.44\,eV \qquad -3.64\,eV$

$1.8\,eV$

$1s^2\,2s^1 \longleftarrow \Psi(1,2,3)$ is antisymmetric

multi-e^- systems

Shielding of nuclear charge (shielding effect)

Aufbau Principle

$3s < 3p < 3d$

1s

2s

3s 3p 3d

4s 4p 4d 4f

Spin multiplicity

Hund's rule

$3e \rightarrow$ $\uparrow$ $\uparrow$ $\uparrow$

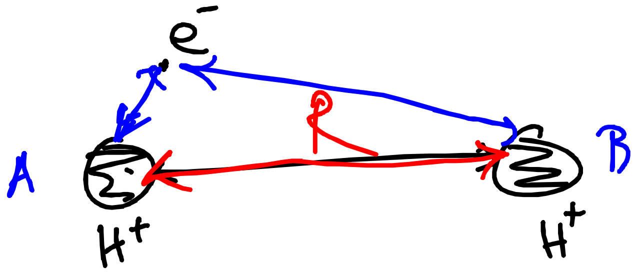
p_x p_y p_z

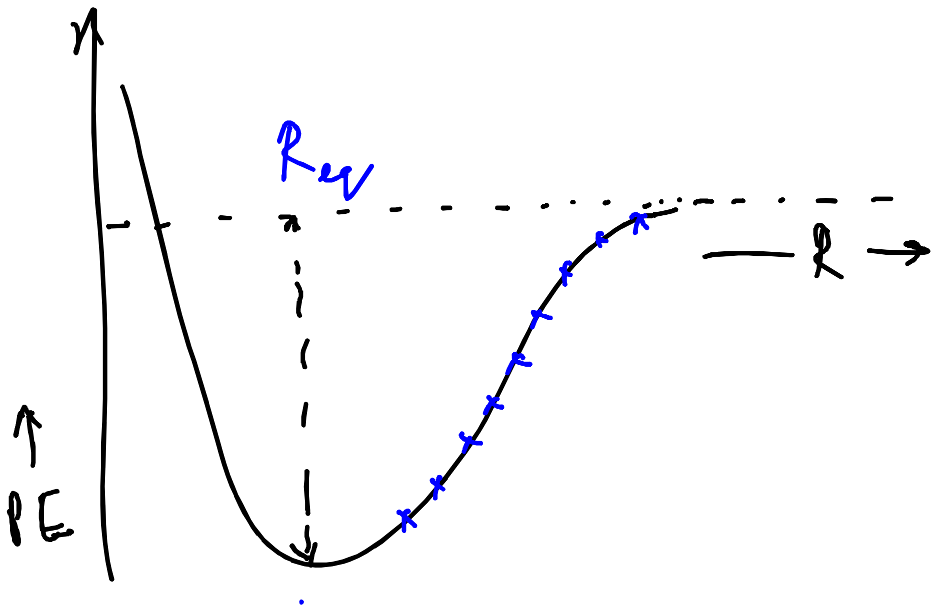
Molecules

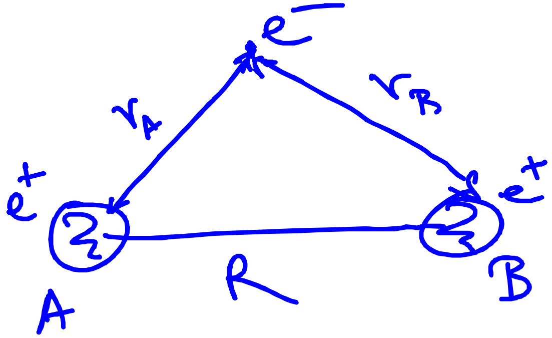
Combining of Atomic Orbitals $\longrightarrow$ Molecular Orbitals.

$1e^-$ Molecule H_2^+ ion

$H \longleftarrow H^+$







$$\hat{H} = (KE)_A + (KE)_B + (KE)_{e^-} + PE$$

$$-\underbrace{\frac{e^2}{r_A} - \frac{e^2}{r_B}}_{\text{solving}} + \underbrace{\frac{e^2}{R}}$$

for every fixed value of R

Born-Oppenheimer Approximation

$E = E(R)$

Vary R, solve $\hat{H}\Psi = E\Psi$

& construct $E(R)$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \underbrace{\frac{e^2}{R}}_{\text{Const.}}$$

$E = E(R)$ at $R \to \infty$ E_{1s} $\downarrow$ as $R \to R_{eq}$

H_2^+ Molecular ion

$\cdot e^-$

A B

$\psi \sim 1s_A \sim e^{-r_A/a_0}$

H_2^+

2.8 eV.

A B $\cdot e^-$

$\psi \sim 1s_B \sim e^{-r_B/a_0}$

Linear Combination or Superposition

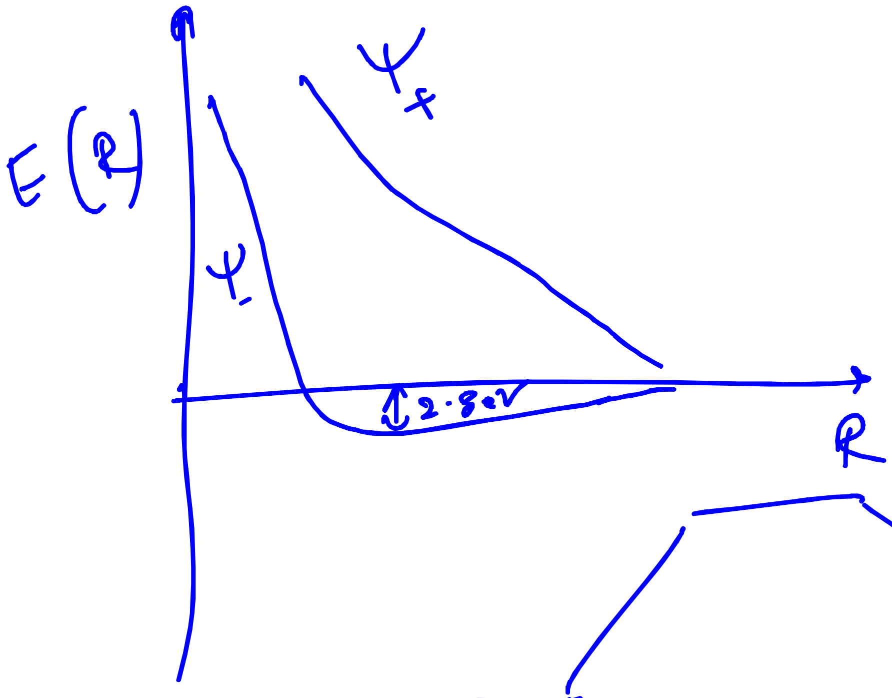
"LCAO"

$\psi_{1,2} \sim 1s_A \pm 1s_B$

$\boxed{1\ e^- \text{ Molecular orbital.}}$

$|\psi(A,B)|^2 = |\psi(B,A)|^2$

$|\psi_\pm|^2 \simeq 1s_A^2 + 1s_B^2 \pm 2\, 1s_A \cdot 1s_B$



$H + H^+$