Lecture 11

Last time: $\mathcal{H}$-atom : $V(r) \sim -\frac{1}{r}$; $E_n = -\frac{R_y}{n^2}$

E/R_y

$n, l, m_l, m_s = \pm\frac{1}{2}$

0 - - - - - - - - - - -

$-\frac{1}{9}$ — — — — — — — — — — $= \psi_{320} = 3d_{z^2}$

$-\frac{1}{4}$ — $n=2$ — 2s P_x P_y or P_+ P_- P_z : $= \psi_{210}$

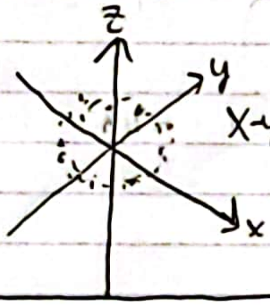
[Note: ψ_{211}, ψ_{21-1} > have the same energy $= E_2$]

this is called "Quantum Superposition", as $\psi_{211} \pm \psi_{21-1}$ is also a solution

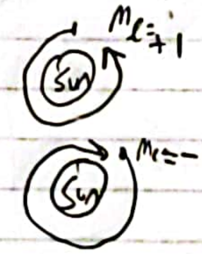
0 — $n=1$ — $E_0 = \psi_{100} = 1S$

More eigenfunction examples: $\psi_{21\pm1} \sim r e^{-r/2a_0} \sin\theta \, e^{\pm i\varphi}$

$P_{21\pm1} \sim r^2 e^{-r/a_0} \cdot \sin^2\theta \cdot 1$



x-y plane vs

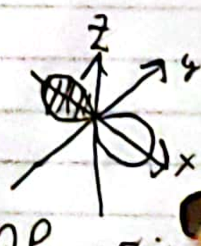


$\mathcal{H}\psi_A = E\psi_A$ and $\mathcal{H}\psi_B = E\psi_B$

$\therefore \mathcal{H}(\psi_A + \psi_B) = E\psi_A + E\psi_B = E(\psi_A + \psi_B)$ — this is a quantum superposition

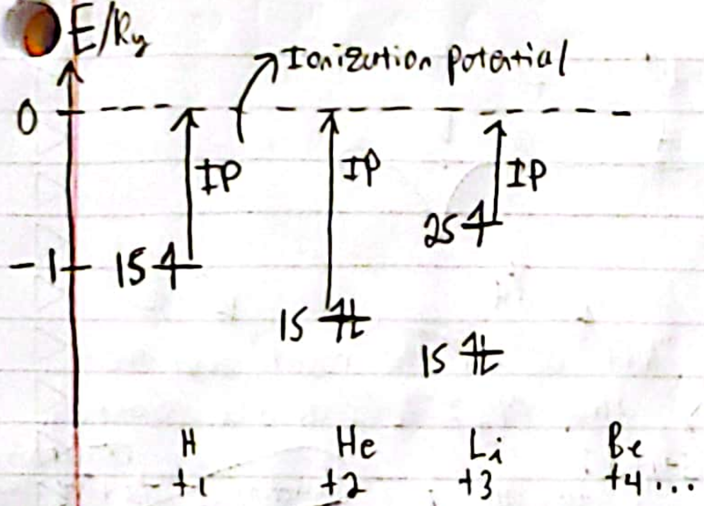
Basically $\mathcal{H}\psi = E\psi$

Sum $\sim r e^{-r/2a_0} \cdot \sin\theta \, (e^{i\varphi} + e^{-i\varphi}) \sim r e^{-r/2a_0} \cdot \sin\theta \cdot \cos\varphi$

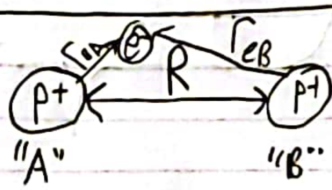


function on x-axis

2Px orbital!



Today: Making molecules: Say H_2^+



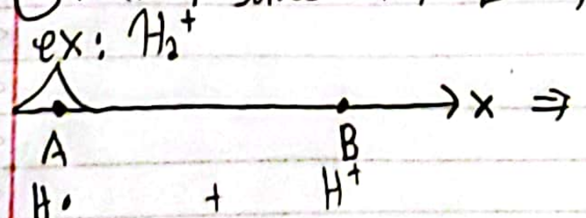
$$\hat{H}\psi = E\psi \Rightarrow \Big\{ \underbrace{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)}_{\text{KE operator}} \underbrace{- \frac{Z_A e^2}{4\pi\varepsilon_0 r_{eA}} - \frac{Z_B e^2}{4\pi\varepsilon_0 r_{eB}} + \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}}_{\text{Potentials}} \Big\} \psi = E\psi$$

Assume (for now) that the nuclei are "frozen" compared to how much the e^- is moving.

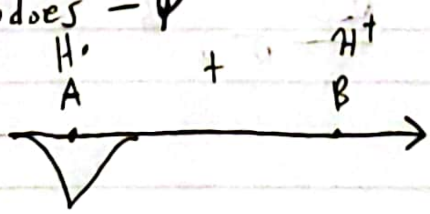
What do solutions look like?

① When ψ solves $\hat{H}\psi = E\psi$, so does $-\psi$

ex: H_2^+



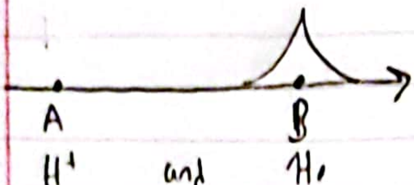
$\Rightarrow$



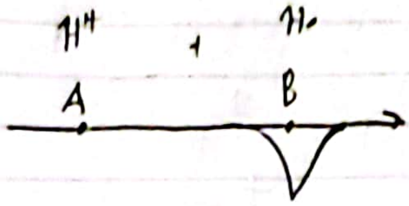
Also a solution

very far apart

Also Solutions:



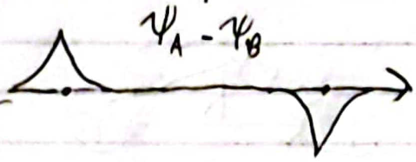
$\Rightarrow$



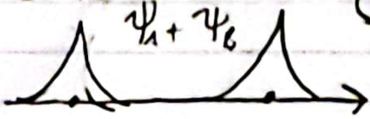
ψ_A ψ_B

If the e^- has a solution on the "left" or on the "right" and the solutions have the same energy, then $\psi_A \pm \psi_B$ is also a solution. This is a quantum superposition state:

ex: $\psi_A - \psi_B$



$\psi_A + \psi_B$

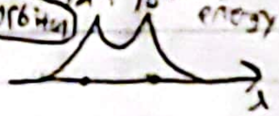


closer together $\rightarrow$

bonding orbital

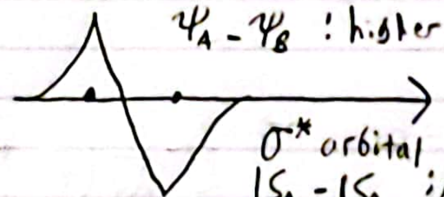
σ orbital

$\psi_A + \psi_B$: lower energy



Bring A and B closer together $\Rightarrow$

$\psi_A - \psi_B$: higher energy



σ^* orbital

$1s_A - 1s_B$: Antibonding orbital

E-level diagram: