Lecture 11

Friday, September 15, 2023 9:55 AM

Superposition Principle = combining wavefunctions = "orbitals" in atoms & molecules

- If 2 eigenstates have the same (similar) energy, then any linear combination of these eigenstates is also (approx.) eigenstate

Proof: $\mathcal{H}\Psi_A = E\Psi_A \quad \times a$

$+ \quad \mathcal{H}\Psi_B = E\Psi_B \quad \times b$

$$\underbrace{\mathcal{H}(a\Psi_A + b\Psi_B) = E(a\Psi_A + b\Psi_B)}_{\text{satisfies Schrödinger eqn}}$$

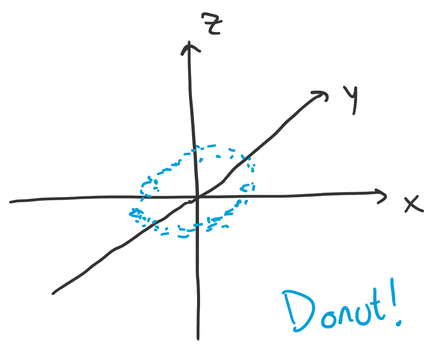
ex. $a=-1,\ b=0 \Rightarrow \mathcal{H}(-\Psi_A) = E(-\Psi_A) \Rightarrow -\Psi_A$ is also soln.

$a=1,\ b=\pm 1 \Rightarrow \Psi_A \pm \Psi_B$ is also soln.

$\frac{1}{\sqrt{2}}(\Psi_A + \Psi_B)$ normalized

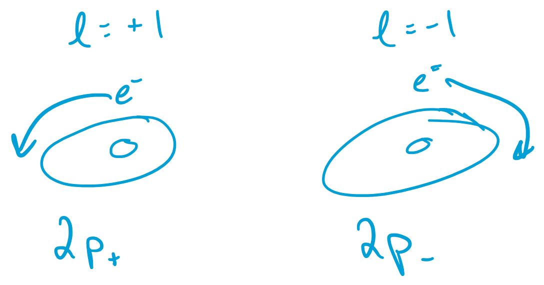
ex. $\Psi_{2,1,\pm1} \sim r \cdot e^{-r/2a_0} \sin\theta\, e^{\pm i\varphi}$

$$P = |\Psi|^2 = r^2 e^{-r/a_0} \underbrace{\sin^2\theta}_{\text{large in xy plane}} (1)$$



Donut!

Orbitals

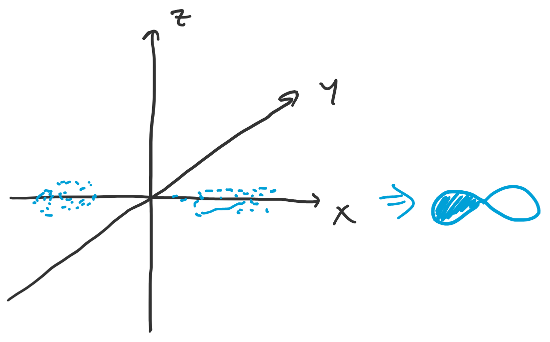


Let's say you are averse to complex numbers,

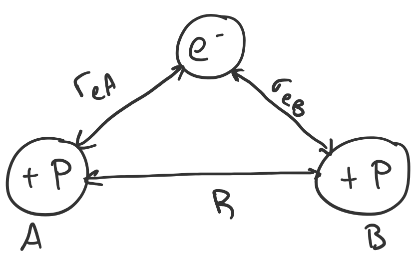
but you realize $e^{i\varphi} + e^{-i\varphi} = 2\cos\varphi$

$\Psi_{2,1,+1} + \Psi_{2,1,-1} \sim r \cdot e^{-r/2a_0} \sin\theta \cos\varphi$

$P \sim r^2 \cdot e^{-r/a_0} \sin^2\theta \cos^2\varphi$

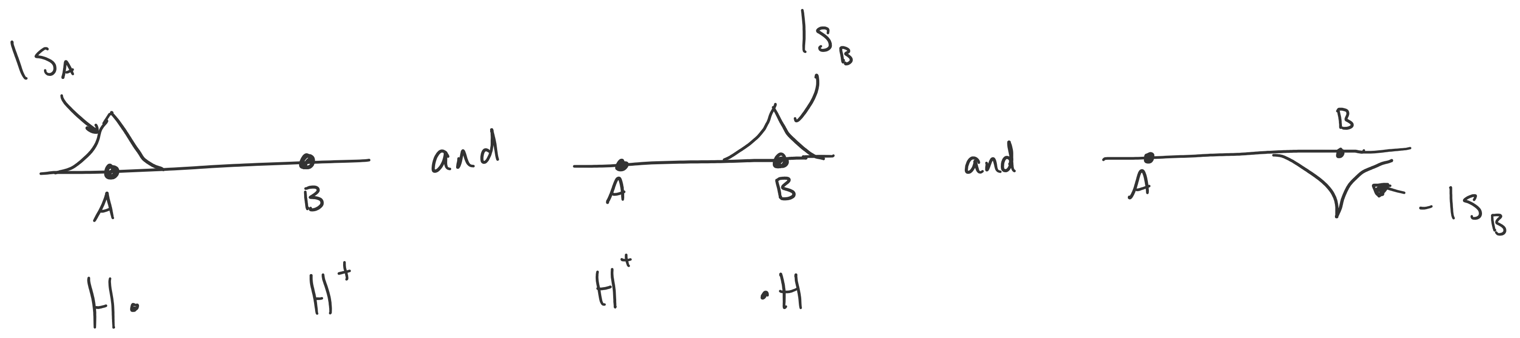


Making Molecules = H_2^+



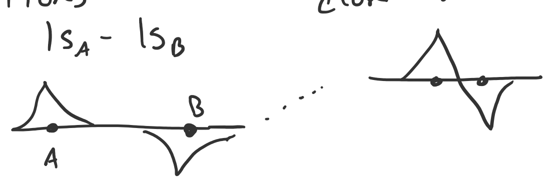
What could a solution to the Schrödinger eqn. looks like?

Let's use superposition

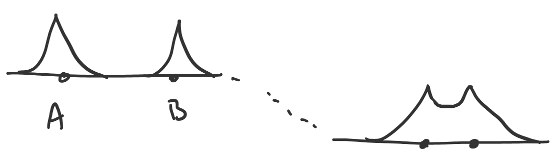


These are all solutions

Superpositions



$\sim 1s_A - 1s_B = \sigma^*$ anti-bonding



$\sim 1s_A + 1s_B = \sigma$ bonding