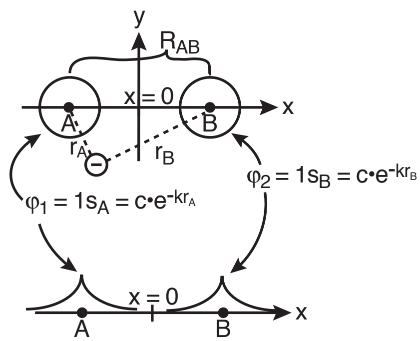
Diagonalizing a matrix to find the energy levels of H_2^+

- -One nucleus is at $x=-R_{AB}$, the other at $x=+R_{AB}$
- -Two basis functions: $\varphi_1(x,y,z) = 1s_A$ and $\varphi_2(x,y,z) = 1s_B$ (**approximation**, leaving out 2s, 2p etc.)
- -Note φ_1 and φ_2 are not quite orthogonal (**approximation**): $\iiint dxdydz\, \varphi_1^* \varphi_2 \neq 0$ [could use Gram-Schmid]



Polar plot

Ψ(x) plot

Hamiltonian for H_2^+:

$$\hat{H} = \frac{\vec{p}^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$$

$$= \frac{-\hbar^2}{2m_e}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} - \frac{e^2}{4\pi\varepsilon_0\sqrt{(x+R_{AB}/2)^2+y^2+z^2}} - \frac{e^2}{4\pi\varepsilon_0\sqrt{(x-R_{AB}/2)^2+y^2+z^2}} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$$

Matrix:

$$\underset{\sim}{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{22} \end{pmatrix} \qquad \text{where} \quad H_{12} = \iiint dx\,dy\,dz\,\varphi_1^*(x,y,z)\hat{H}\varphi_2^*(x,y,z) \qquad \text{etc.}$$

Diagonalizing the Hamiltonian matrix