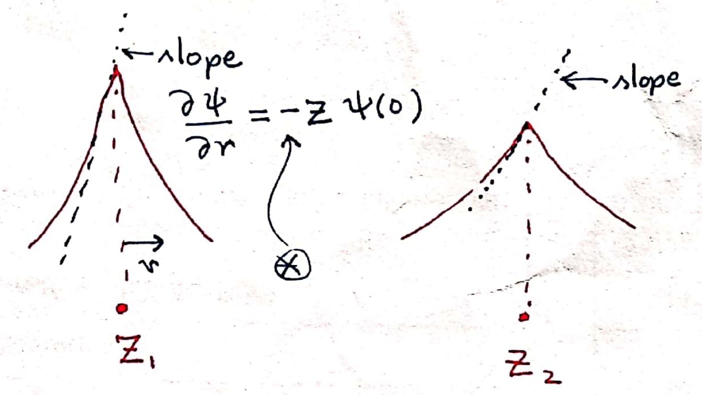
Electron - nuclear cusp



more generally:

$$\left\langle \frac{\partial \psi}{\partial r} \right\rangle_{\substack{\text{spherical}\\ \text{average}}} \Bigg|_{r=0} = -Z \left\langle \psi(0) \right\rangle_{\substack{\text{spherical}\\ \text{average}}}$$

Proof of $\left.\frac{\partial \psi}{\partial r}\right|_{r\to 0} = -Z\,\psi(0)$

- Assume : 1 e^- system in an s-state i.e. $l = 0$.

$$\hat{H} = -\frac{1}{2}\nabla^2 + V(\bar{r}) = -\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\hat{l}^2}{r^2}\right) - \frac{Z}{r}$$

Atomic Units.

$$\hat{H}\psi = E\psi \quad , \quad \boxed{E \text{ is finite}}$$

$$\underbrace{E\psi}_{\boxed{\text{finite}}} = \hat{H}\psi$$

$$= -\frac{1}{2}\frac{\partial^2\psi}{\partial r^2} \underbrace{-\frac{1}{r}\frac{\partial\psi}{\partial r} \underbrace{- \frac{\hat{l}^2\psi}{r^2}}_{=0 \text{ as } l=0 \text{ (s-state)}} - \frac{Z}{r}\psi}_{\text{these terms diverge as } r\to 0}$$

these terms diverge as $r \to 0$

$\therefore$ for RHS to remain finite :

$$-\frac{1}{r}\frac{\partial\psi}{\partial r} - \frac{Z}{r}\psi = 0$$

or $\left.\frac{\partial\psi}{\partial r}\right|_{r\to 0} = -Z\,\psi(0)$

$\rho(r)$?

$\rho(\bar{r})$ also contains cusps.

$$\left.\frac{\partial \rho}{\partial r}\right|_{r\to 0} \to -2Z|\psi(0)|^2$$

Show it starting from $\rho(\bar{r}) = |\psi|^2$