Hydrogen

Assumptions:

① proton is infinitely heavy. Easy to fix

$$m_e \rightarrow \mu = \frac{m_e m_p}{m_e + m_p} \quad \text{reduced mass}$$

same as Kepler problem; e.g. Earth-Moon system

② Electron is non-relativistic - fix with perturbation theory. or use relativistic equation, not Schrödinger

③ Proton has zero size. fix with perturbation

④ proton and electron are spin zero particles.
- add spin by hand.

but really need Dirac Equation (relativistic spin $\frac{1}{2}$)

spin 0 - Klein-Gordon	spin 1 - massive - Proca
$\frac{1}{2}$ massless - Weyl	$\frac{3}{2}$ Rarita - Schwinger
$\frac{1}{2}$ massive - Dirac	massless 2 - Einstein (non-linear)
1 massless - Maxwell	arbitrary - Fierz - Pauli

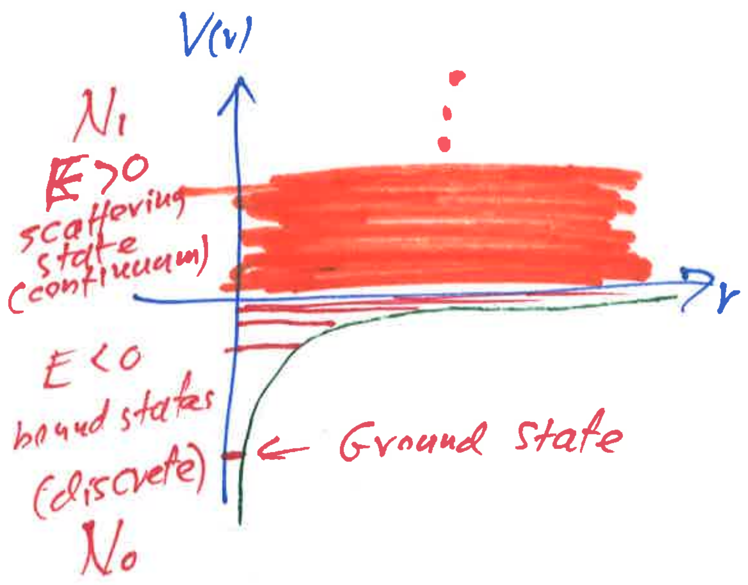
$\boxed{\text{MKS}}$ $\quad V(r) = \dfrac{-e^2}{4\pi\epsilon_0 r}$ ← Remember this is potential energy (in joules), not the electric potential (voltage) in volts.

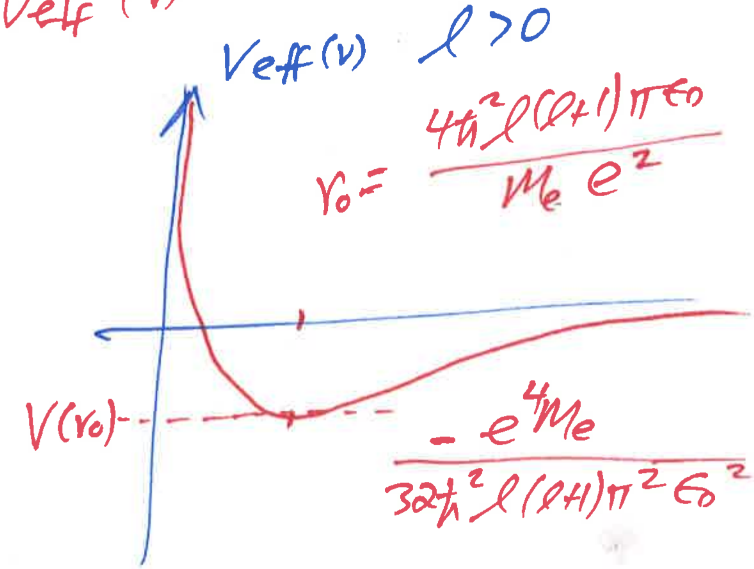
cgs $\quad V(r) = \dfrac{-e^2}{r}$

Radial Equation

$l = 0, 1, 2, 3, \ldots$

$$-\frac{\hbar^2}{2m_e}\frac{d^2u(r)}{dr^2}+\underbrace{\left[-\frac{e^2}{4\pi\epsilon_0 r}+\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]}_{V_{eff}(r)}u(r)=E\,u(r)$$





Bound Energies $$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \quad n = \cancel{0}, 1, 2, 3 \ldots$$ not (0)

$$= -13.6\,\text{eV}\,\frac{1}{n^2}$$

Wave Functions $$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\,Y_{lm}(\theta,\varphi)$$

spherical harmonics

n - principal quantum number

l - azimuthal (orbital) q.n.

m_l - magnetic q.m.

Later S - spin, $s = \frac{1}{2}(\hbar)$ $\quad |\vec{S}| = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar$

m_s - z component of spin $\quad m_s = \pm\frac{1}{2}(\hbar)$

Orthonormality

$$\int_{\substack{\text{All}\\\text{space}}} \psi^*_{n'\ell'm'}(r,\theta,\varphi)\,\psi_{n\ell m}(r,\theta,\varphi)\, r^2 dr \underbrace{\sin\theta\, d\theta\, d\varphi}_{d^2\Omega} = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}$$

$$\psi_{n\ell m}(r,\theta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\,(n+\ell)!}}\; e^{\frac{-r}{na_0}} \left(\frac{2r}{na_0}\right)^{\ell} L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na_0}\right) Y_{\ell m}(\theta,\varphi)$$

↑ Associated Laguerre polynomial

$$a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 0.529\,\text{Å} \quad \text{Bohr radius}$$

10^{-10} m

$$\boxed{\text{cgs: } a_0 = \frac{\hbar^2}{m_e e^2}}$$

Spectroscopic notation $n \to 1s \leftarrow \ell$, $3p \leftarrow \ell$

$\ell = 0$ s - sharp

1 p - principal

2 d - diffuse

3 f - fundamental

⋮ ⋮

then g, h, i (no j) k, l, m

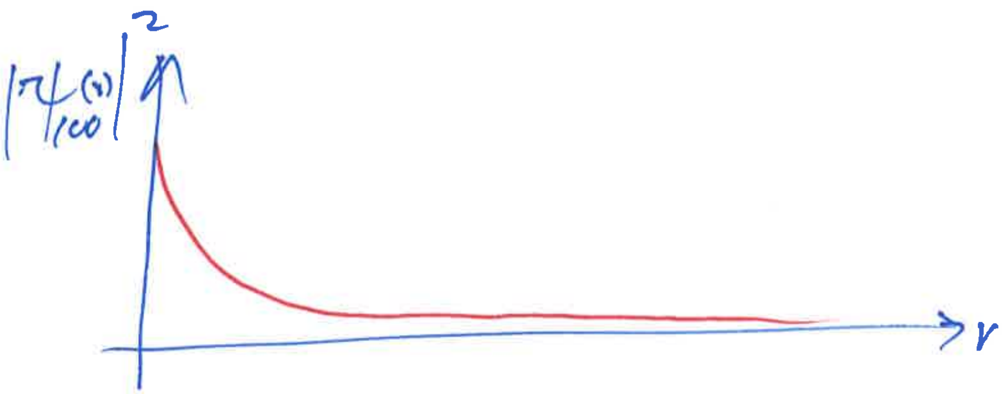
Ground state: $\psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$

Probability Density

$$1 = \langle \psi_{100} | \psi_{100} \rangle = \int_{\substack{\text{All} \\ \text{space}}} dV \, \underbrace{\psi^*_{100}(\vec{r}) \, \psi_{100}(\vec{r})}_{|\psi_{100}(\vec{r})|^2 \, = \text{ Volume probability density}}$$

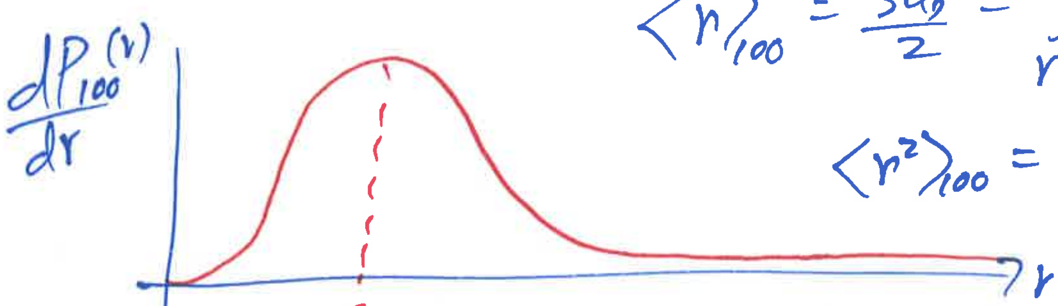
Radial Probability Density

$$1 = \int_{r=0}^{\infty} \underbrace{\psi^*_{100}(r) \, \psi_{100}(r) \, r^2 \, \overset{\int d^2\Omega}{4\pi}}_{\frac{dP}{dr} \text{ radial prob. density}} \, dr$$



$$\langle r \rangle_{100} = \frac{3a_0}{2} = \int_{r=0}^{\infty} r \left(\frac{dP}{dr} \right) dr$$

$$\langle r^2 \rangle_{100} = 3a_0^2, \quad r_{rms} = \sqrt{3}\, a_0$$



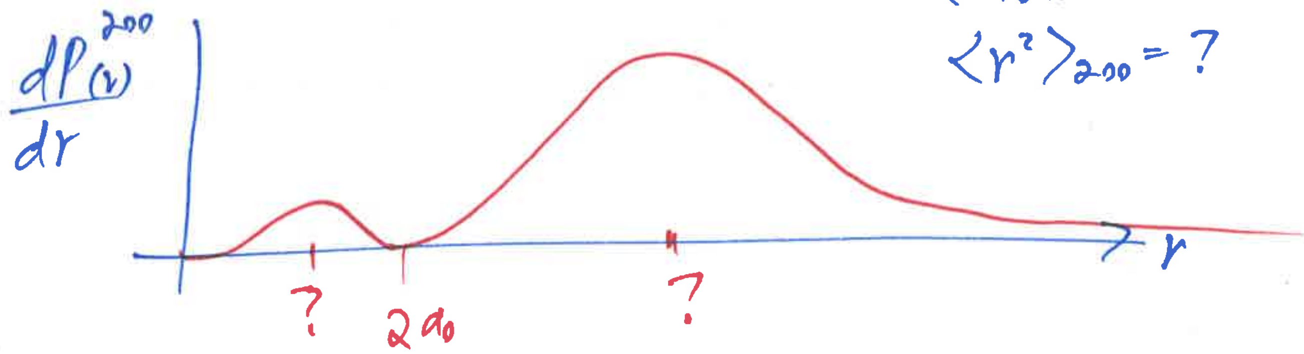
a_0 – most probable radius

First excited state   4-fold degenerate

$2s$ $\quad \psi_{200}(r) = \dfrac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \dfrac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$

$\langle r \rangle_{200} = ?$

$\langle r^2 \rangle_{200} = ?$



$2p$ $\quad \psi_{210}(r,\theta,\varphi) = \dfrac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(\dfrac{r}{a}\right) e^{-\frac{r}{2a_0}} \cos\theta$

$\psi_{21\pm1}(r,\theta,\varphi) = \dfrac{1}{8\sqrt{\pi}\, a_0^{3/2}} \left(\dfrac{r}{a}\right) e^{-\frac{r}{2a_0}} \sin\theta\, e^{\pm i\varphi}$