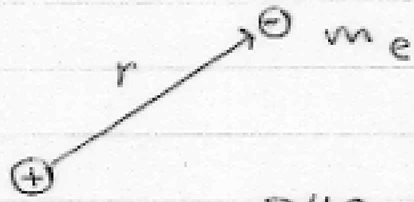
The H-atom

$m_p >> m_e \Rightarrow$

proton (nearly) stationary



$m_p \simeq 1840\, m_e$

Hamiltonian of electron $= \hat{H} = \dfrac{\hat{\vec{p}}^{\,2}}{2m} + V(r)$

$$V(r) = -\frac{ke^2}{r}, \quad k = 1/4\pi\varepsilon_0 \quad \left(\text{or } V(r) = -\frac{kZe^2}{r}\right.$$

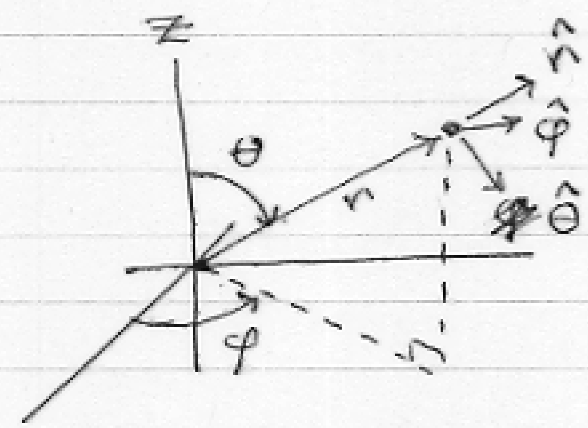
$$\frac{\hat{\vec{p}}^{\,2}}{2m} = \frac{\hat{\vec{p}}\cdot\hat{\vec{p}}}{2m} = -\frac{\hbar^2}{2m}\nabla^2(\;)$$

TISE: $\hat{H}\Psi_n = E_n\Psi_n \Rightarrow$ special sol'ns (stationary states)

$$\Psi_n(x) \Rightarrow \Psi_n(x,t) = \Psi_n(x)\, e^{-iE_nt/\hbar}$$

General sol'n to TDSE: $\Psi(x,t) = \sum_n c_n e^{-iE_nt/\hbar}\,\Psi_n($

Spherical Coordinate system



$$z = r\cos\theta$$
$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$

$\Psi = \Psi(r,\theta,\varphi)$

volume

$$\int dV\,|\Psi|^2 = 1$$

Normalization:

$$\int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi\; r^2\sin\theta\,|\Psi|^2 = 1$$

Need ∇^2 in spherical coordinates

Hard Way: $\nabla^2 f = \nabla \cdot \nabla f = \frac{\partial^2 f}{\partial x^2} + \dots$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial f}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial x} = g$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial g}{\partial x} = \frac{\partial g}{\partial r}\frac{\partial r}{\partial x} + \dots \quad \text{(nightmare!)}$$

Also need 9 derivatives: $\frac{\partial r}{\partial x}, \frac{\partial r}{\partial y} \dots \frac{\partial \theta}{\partial x} \dots$

Easier Way: Curvilinear coordinates (See Boas)

path element:

$$d\vec{s} = \hat{x}\,dx + \hat{y}\,dy + \hat{z}\,dz$$

$$= \hat{r}\,dr + \hat{\theta}\,r\,d\theta + \hat{\varphi}\,r\sin\theta\,d\varphi$$

$$= \hat{e}_1 h_1\,dx_1 + \hat{e}_2 h_2\,dx_2 + \hat{e}_3 h_3\,dx_3$$

$$= \sum_{i=1}^{3} \hat{e}_i h_i\,dx_i \qquad (h_i = \text{"scale factor"})$$

$$\nabla f = \sum_i \hat{e}_i \frac{1}{h_i}\frac{\partial f}{\partial x_i}$$

$$\nabla^2 f = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial x_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial f}{\partial x_1}\right) + \frac{\partial}{\partial x_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial f}{\partial x_2}\right) + \dots\right]$$

Spherical coords: $\{x_i\} = \{r, \theta, \varphi\}$

$$\{h_i\} = \{1, r, r\sin\theta\}$$

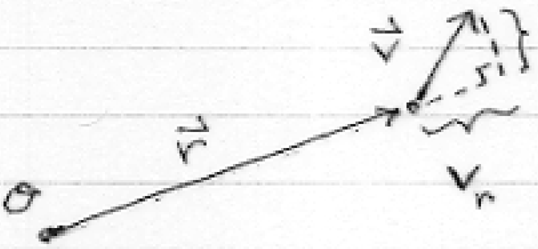
$\Rightarrow \quad \nabla^2 f =$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2 f}{\partial\varphi^2}\right)$$

$$= (\text{radial}) + \frac{1}{r^2}(\text{angular})$$

In Classical Mechanics (CM), $KE = p^2/2m =$

$KE = (\text{radial motion KE}) + (\text{angular, axial motion KE})$



$|\vec{L}| = |\vec{r}\times m\vec{v}| = m r v_\perp$

$(\Rightarrow v_\perp = L/mr)$

$$KE = \frac{1}{2}mv^2 = \frac{m}{2}\left(v_r^2 + v_\perp^2\right) = \underbrace{\frac{p_r^2}{2m}}_{\text{radial}} + \underbrace{\frac{L^2}{2mr^2}}_{\frac{1}{r^2}\times\text{angular}}$$

Same splitting in QM:

$$\hat{L}^2 = \left(\frac{\hbar}{i}\vec{r}\times\nabla\right)^2 = -\hbar^2\left[\frac{1}{s\theta}\frac{\partial}{\partial\theta}\left(s\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{s^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

(Notice $\hat{L}^2$ depends only on θ, φ and not r)

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\cdot\psi = E\cdot\psi$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2}\psi + V(r)\psi = E\psi}$$

Separation of Variables! (as usual)

Seek special solutions of form:

$$\Psi(r,\theta,\varphi) = R(r)\cdot Y(\theta,\varphi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\varphi)$$

Normalization: $\int dV\,|\Psi|^2 =$

$$\underbrace{\int_0^\infty dr\, r^2\,|R|^2}_{1}\cdot\underbrace{\int_0^\pi d\theta\int_0^{2\pi} d\varphi\,\sin\theta\,|Y|^2}_{1} = 1$$

(convention: normalize radial, angular parts individually

Plug $\Psi = R\cdot Y$ into TISE $\Rightarrow$

$$-\frac{\hbar^2}{2m}\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{2mr^2}\hat{L}^2 Y + V\cdot R\cdot Y = E\cdot R\cdot Y$$

Multiply thru by $-\frac{2mr^2}{\hbar^2}\frac{1}{R\cdot Y}$:

$$\underbrace{\left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(V-E)\right\}}_{f(r)} = \underbrace{\frac{1}{\hbar^2 Y}\hat{L}^2 Y}_{g(\theta,\varphi)}$$

$\Rightarrow f(r) = g(\theta,\varphi) = \text{constant } C = l(l+1)$

$$\hat{L}^2 Y = \hbar^2 C\cdot Y = \hbar^2 l(l+1)\,Y \qquad \text{(page H-6)}$$

Have separated TISE into radial part $f(r) = l(l+1)$, involving $V(r)$, and angular part $g(\theta,\varphi) = l(l+1)$ which is independent of $V(r)$

⇨ All problems w/ spherically symmetric potential ($V = V(r)$) ~~~~ , have exactly same angular part of solution: $Y = Y(\theta, \varphi)$ called "spherical harmonics"

We'll look at angular part later. Now, let's examine

Radial SE: $\left(\times - \frac{\hbar^2}{2mr} \cdot R \right)$

$$-\frac{\hbar^2}{2mr} \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + r \cdot R (V - E) = -\frac{\hbar^2 \cdot rR}{2mr^2} \ell(\ell+1)$$

Change of variable: $u(r) = r \cdot R(r)$

$$\left(\int_0^\infty dr\, |u|^2 = 1 \right)$$

Can show that $\frac{1}{r} \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) = \frac{d^2 u}{dr^2}$:

$$\frac{du}{dr} = R + r\frac{dR}{dr}, \quad \frac{d^2u}{dr^2} = \frac{dR}{dr} + \frac{dR}{dr} + r\frac{d^2R}{dr^2}$$

$$\frac{1}{r}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) = \frac{1}{r}\left(2r\frac{dR}{dr} + r^2 \frac{d^2R}{dr^2}\right) = 2\frac{dR}{dr} + r\frac{d^2R}{dr^2}$$

same!

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu}$$

Notice: <u>identical</u> to 1D TISE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V \cdot \psi = E\psi$$ <u>except</u>

$r: 0 \to \infty$ instead of $x: -\infty \to +\infty$ and

$V(x)$ replaced with $\boxed{V_{eff} = V(r) + \frac{\hbar^2}{2mr^2}\ell(\ell+1)}$

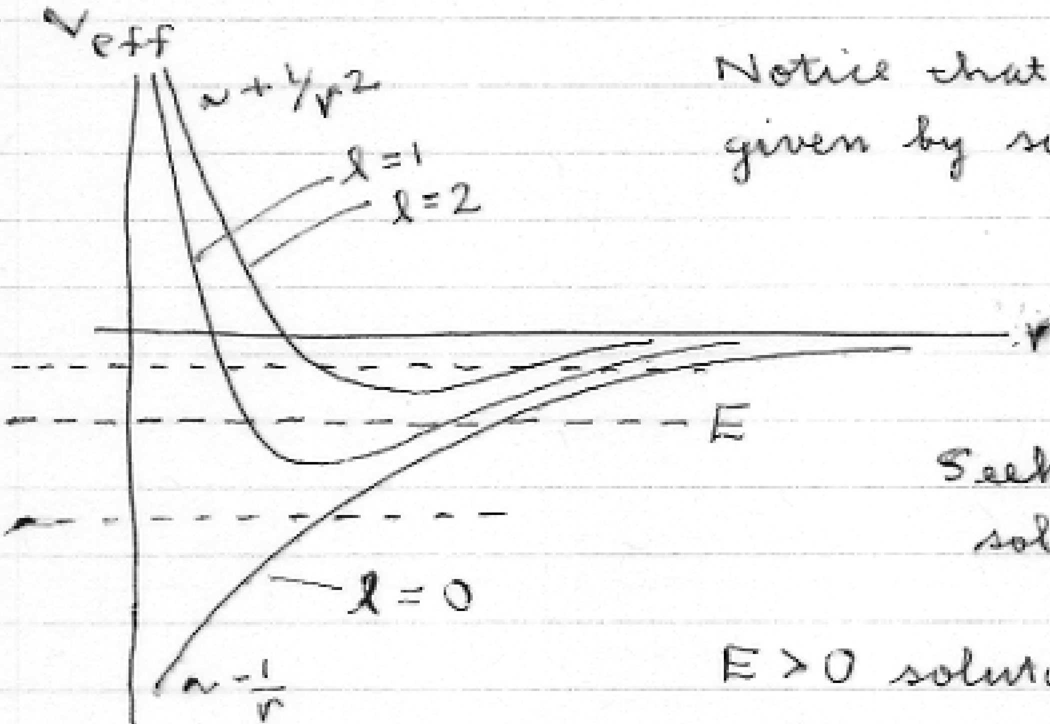
V_{eff} = "effective potential"

Boundary conditions:

$u(r=\infty) = 0$ from normalization $\int dr\, |u|^2 = 1$

$u(r=0) = 0$, otherwise $R = \frac{u}{r}$ blows up at $r=0$ (subtle!)

$V(r) = -\frac{A}{r}$, $V_{eff} = -\frac{A}{r} + \frac{B}{r^2}$



Notice that energy eigenvalues given by sol'n to radial eq'n alone.

Seek bound state solutions $E < 0$

$E > 0$ solutions are unbound states, scattering solutions

Full sol'n of radial SE is very messy, even though it is effectively a 1D problem (different problem for each l)

Power series sol'n (see text for details)

Sol'ns depend on 2 quantum numbers: n and l (for each eff. potential $l = 0, 1, 2 \ldots$ have a set of solutions labeled by index n.)

Solutions: $\left.\begin{array}{l} n = 1, 2, 3, \ldots \\ l = 0, 1, \ldots (n-1) \end{array}\right\}$ for given n $l_{max} = (n-1)$

n = "princip~~le~~al quantum number"

energy eigenvalues depend on n only (it turns out)

$$E_n = \frac{E_1}{n^2}, \quad E_1 = -\frac{m(ke^2)^2}{2\hbar^2} \quad \text{(independent of } l\text{)}$$

• same as Bohr model, agrees w/ expt!

First few sol'ns: $R_{nl}(r)$ "Bohr radius"

normalization

$$R_{10} = A_{10}\, e^{-r/a_0}, \quad a_0 = \hbar^2/kme^2 = 4\pi\varepsilon_0 \hbar^2/me^2$$

$$R_{20} = A_{20}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

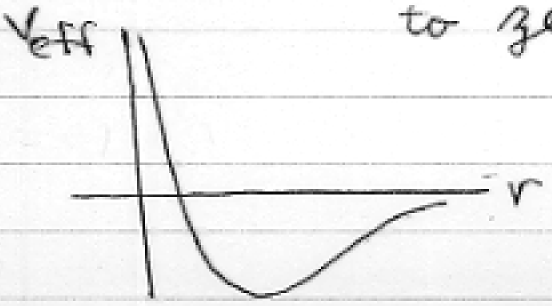
$$R_{21} = A_{21}\left(\frac{r}{a_0}\right) e^{-r/2a_0}$$

NOTE:

- for $l = 0$ (s states), $R(r=0) \neq 0 \Rightarrow$ wavefcn Ψ "touches" nucleus
- for $l \neq 0$, $R(r=0) = 0 \Rightarrow \Psi$ does not touch nucleus

$l \neq 0 \Rightarrow$ electron has angular momentum.
Same as classical behavior, ~~system~~ particle with non-zero L cannot pass thru origin ($\vec{L} = \vec{r} \times \vec{p}$: $r = 0 \Rightarrow p = \infty$)

Can also see this in QM: for $l \neq 0$, V_{eff} has infinite barrier at origin $\Rightarrow u(r)$ must decay to zero at $r = 0$ exponentially.



$\Rightarrow$ exponential decay ~~is~~ in

$$R(r) = \frac{u(r)}{r} \text{ as well.}$$