Review: TDSE in 3D $\quad i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \xrightarrow[\text{w/ } V(\text{space})]{\Psi = \sum c_n \phi_n(t) \psi_n(x)}$ $\quad \phi_n(t) = e^{-i\frac{E_n}{\hbar}t}$

$\hat{H}\psi_n(\text{space}) = E_n(\text{space})$ TISE

$n$ might include several labels due to degeneracy

TISE For central $V(r)$ and in spherical coordinates using s.o.v. $\Psi = R(r)\Theta(\theta)\Phi(\phi)$

I. $\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right) = \ell(\ell+1)$ $\qquad \ell(\ell+1)$ sep. $r$ from $\theta,\phi$

IIa. $\frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Phi$ $\qquad m^2$ sep. $\theta$ from $\phi$

IIb. $\sin\theta \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \Theta}{\partial \theta}\right) + \left[\sin^2\theta \, \ell(\ell+1) - m^2\right]\Theta = 0$ $\qquad m, \ell \in \mathbb{Z}$

Normalized solutions to IIa, IIb: $\underbrace{Y_\ell^m(\theta,\phi)}_{\text{Sph. harmonics orthogonal in } \ell, m} = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}} \; \overbrace{e^{im\phi}}^{\text{IIa}} \; \underbrace{P_\ell^m(\cos\theta)}_{\text{IIb Ass. Leg. functions}}$

Important: a) $\ell \geq 0$ from $\left(\frac{d}{d\cos\theta}\right)^\ell$

b) $|m| > \ell \Rightarrow P_\ell^m = 0$ (so only $|m| \leq \ell$ has $Y_\ell^m \neq 0$)

since $P_\ell^m$ involves $\left(\frac{d}{d\cos\theta}\right)^{|m|}$ on degree $\ell$ poly. $P_\ell$

c) $\epsilon = \begin{cases} (-1)^m & \text{for } m \geq 0 \\ 1 & \text{for } m \leq 0 \end{cases}$

Hydrogen: Solve radial eqn. w/ $V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$ for $R(r)$ and $E$, then tack on $Y_\ell^m(\theta,\phi)$.

Bound states: $E < V(\infty) = 0$

Introduce: $u(r) \equiv r R(r)$ (new radial function)

$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$ (real since $E<0$)

$\rho \equiv \kappa r$ (new radial coordinate) $\Rightarrow u(\rho)$

$\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$ (eliminate constants)

Then radial eqn: $\underbrace{\frac{d^2u(\rho)}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u(\rho)}$

$$\text{for } \rho \to \begin{cases} \infty & \frac{d^2u}{d\rho^2} = u \quad \Rightarrow u(\rho) = Ae^{-\rho} + \cancel{Be^{\rho}} \\ 0 & \frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u \quad \Rightarrow u(\rho) = C\rho^{\ell+1} + \cancel{D\rho^{-\ell}} \end{cases}$$

$=0$ $\infty$ $=0$ $\infty$

Pulling out asymptotics leads to simple recursion solution. Otherwise very difficult!

Introduce $v(\rho)$ via: $u(\rho) = \rho^{\ell+1}e^{-\rho}v(\rho)$ Need to be careful that $v(\rho)$ doesn't dominate at large or small $\rho$!

Then $v(\rho)$ satisfies: $\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0$

Assume $v(\rho) = \sum_{j=-1}^{\infty} c_{j+1}\rho^{j+1}$ power series in $\rho$ (solutions for $v(\rho)$ are coefficients)

$\frac{dv}{d\rho} = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^{j}$ Note sum starts at $j=0$ since $j=-1$ gives $0$.

$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1}$

Inserting and equating coefficients of like power of $\rho$:

[Do not write] $j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(\ell+1)]c_j = 0$

or $c_{j+1} = \left[\frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}\right]c_j$ Recursion formula for $c_{j+1}$ in terms of $c_j$

For large $\rho$ ( large j since $\rho^{j+1}$ will be dominated by $\rho^{\text{large}}$ for $\rho \sim$ large):

$$c_{j+1} \cong \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j \Rightarrow \left.\begin{aligned} c_1 &= 2 c_0 \\ c_2 &= 1\, c_1 \\ c_3 &= \tfrac{2}{3} c_2 \\ c_4 &= \tfrac{1}{2} c_3 \end{aligned}\right\} c_j = \frac{2^j}{j!} c_0$$

If $v(\rho) = c_0 e^{2\rho} \Rightarrow v(\rho) = c_0 \underbrace{\sum_{j=0}^{\infty} \frac{2^j}{j!}}_{\text{right behavior for } c_j} \rho^j$

But then $u(\rho) = \rho^{l+1} c_0 e^{\rho} \rightarrow \infty$ for $\rho \to \infty$ which we wanted to avoid.

2 possibilities: i) don't use large j to evaluate $v(\rho)$ [back to square one]

ii) terminate large j at some $j_{max}$ (for $j > j_{max}$ $c_j = 0$).

Note the recursion relation is exact so as long as we use it w/ $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$ we have exact solutions.

Let's check:

~~Suppose $j_{max} = 0$ $\Rightarrow$ $v(\rho) = c_0$ $\Rightarrow$ $u(\rho) = c_0 \rho^{l+1} e^{-\rho}$~~ ~~what is $l$?~~

To terminate at $j_{max}$ : $c_{j_{max}+1} = \left[ \underline{2(j_{max}+l+1) - \rho_0} \right] c_{j_{max}} = 0$

$$\Downarrow$$

$$2(j_{max}+l+1) - \rho_0 = 0 \Rightarrow l = \frac{\rho_0}{2} - j_{max} - 1$$

Example

$j_{max} = 0 \Rightarrow v(\rho) = c_0 \Rightarrow u(\rho) = c_0 \rho^{l+1} e^{-\rho} \Rightarrow \frac{d^2u}{d\rho^2} = \left[ \frac{l(l+1)}{\rho^2} - \underbrace{\frac{2(l+1)}{\rho}}_{-\frac{\rho_0}{\rho} \text{ for } j_{max}=0} + 1 \right] u$

$\Rightarrow R(r) = \frac{u(r)}{r} = \frac{u(\rho = kr)}{r} = c_0 k^{l+1} r^{l} e^{-kr}$ $\boxed{\text{what is } l = ?}$

Consider $E$: $E = -\frac{\hbar^2 k^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$

Recall: $\rho_0 = 2(\underset{\substack{\uparrow \\ \text{integer}}}{j_{max}} + \overset{\substack{\text{integer} \\ \downarrow}}{l} + 1) \equiv 2n$ So $E_n$ will be same for $j_{max} + l$ = constant

$\hookrightarrow E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} \quad n = 1, 2, \cdots$

So let's re-order our thinking:

higher $n$, higher $E$

Lowest energy: $n = 1$ only works for $j_{max} = 0 = l$

$n = 2$ works for $\begin{cases} j_{max} = 0 & l = 1 \\ j_{max} = 1 & l = 0 \end{cases}$

$n = 3$ works for $\begin{cases} j_{max} = 0 & l = 2 \\ j_{max} = 1 & l = 1 \\ j_{max} = 2 & l = 0 \end{cases}$

clearly for a given $n$ we can have $l = 0, \cdots, n-1$ but for each choice of $l$ we have to go back and get a new $u(\rho)$ since $j_{max}$ changes.

But this is good!!

The value of $l$ changes $R(r)$ and hence labels degenerate solutions!

$R_{nl}(r)$

Back to question what is $l$ when $j_{max} = 0$?

Take $l = 0 \Rightarrow E_1 \Rightarrow R_{10}$

$l = 1 \Rightarrow E_2 \Rightarrow R_{11}$

$l = 2 \Rightarrow E_3 \Rightarrow R_{12}$

etc.