So far we have limited our discussion of 3D QM to angular solutions for which we forgo modeling the interactions as they feature in the radial eqn. (1)

We posited solutions that we separable $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$

and we found that the spherical harmonics could fully describe our angular results,

$$Y_\ell^m(\theta,\phi) = \Theta_\ell^m(\theta)\,\Phi_m(\phi)$$

We also found that the separation constant, A, that we introduced was equal to $\ell(\ell+1)$. All of this results in a radial equation given by,

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

b/c the last two terms depend only on r, it's common to refer to their sum as the "effective potential" (like in Classical) 2

$$V_{eff}(r) = V(r) + \ell(\ell+1)\frac{\hbar^2}{2\mu r^2}$$

But to develop a solution we need a particular $V(r)$. In this case, we want to work with Hydrogenic atoms, so

$$\boxed{V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \text{Coulomb Potential}}$$

We can rewrite the DiffyQ,

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right]R = 0$$

$V(r\to\infty)\to 0$ so that we cannot "get rid" of $V(r)$ and we have $E<0$ bound states & $E>0$ unbound states.

"Nondimensionalizing" a Diffy Q

③

It is common practice in theoretical physics to remove the dimensionality in analysis. this leads to find characteristic length, mass, time, energy, etc. scales, but also parameterizes our results in terms of these characteristic scales.

We will do this partially for $R(r)$ by recasting our analysis using a dimensionless variable

$$\rho = r/a \leftarrow \text{as of yet unknown length scale}$$

So that

$$R(r) \rightarrow R(\rho)$$

this is a relatively straight forward process, which we can do via "replacement"

Replace!
$\rho = r/a$ thus $r = \rho a$

and $$\frac{d}{dr} = \frac{d\rho}{dr}\frac{d}{d\rho} = \frac{1}{a}\frac{d}{d\rho}$$

and $$\frac{d^2}{dr^2} = \frac{d}{dr}\left(\frac{1}{a}\frac{d}{d\rho}\right) = \frac{d\rho}{dr}\left(\frac{1}{a}\frac{d^2}{d\rho^2}\right) = \frac{1}{a^2}\frac{d^2}{d\rho^2}$$

This leads to,

$$\frac{1}{a^2}\frac{d^2R}{d\rho^2} + \frac{1}{a^2}\frac{2}{\rho}\frac{dR}{d\rho} + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_0 a\rho} - \frac{\hbar^2 l(l+1)}{2\mu a^2\rho^2}\right]R = 0$$

or,

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \underbrace{\left[\frac{2\mu a^2}{\hbar^2}E + \left(\frac{\mu Z e^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{2a}{\rho} - \frac{l(l+1)}{\rho^2}\right]}R = 0$$

ρ is dimensionless, so is so, the units of $\frac{\mu Z e^2}{4\pi\varepsilon_0\hbar^2}$ are $1/\text{length}$

We identify this as our characteristic length

$$\boxed{a \equiv \frac{4\pi\varepsilon_0\hbar^2}{\mu Z e^2}}$$

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In addition $\frac{2\mu a^2}{\hbar^2}$ has units of $1/\text{energy}$

So we identify $\frac{\hbar^2}{2\mu a^2}$ as a characteristic energy scale and take the ratio,

$E/\left(\hbar^2/2\mu a^2\right)$ as a negative quantity b/c $E<0$ gives bound states

So,

$$\boxed{-\gamma^2 \equiv \frac{E}{\hbar^2/2\mu a^2}}$$

where $\gamma^2 > 0$

Thus,

$$\boxed{\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\gamma^2 + \frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0}$$

is our eigen value eqn.

Solving for $R(\rho)$ (or $R(r)$)

We will bring a new approach to solving this differential equation

$\Rightarrow$ Matching asymptotic solutions ($\rho \to 0$ & $\rho \to \infty$)

This is done in 3 steps,

1. Find Approx Diffy Q for $\rho \to \infty$
2. Find Approx Diffy Q for $\rho \to 0$
3. Match asymptotic solutions with full Diffy Q.

1. Let $\rho \to \infty$,

$$\frac{d^2R}{d\rho^2} + \underbrace{\frac{2}{\rho}}_{\to 0}\frac{dR}{d\rho} + \left[-\gamma^2 + \underbrace{\frac{2}{\rho}}_{\to 0} - \underbrace{\frac{l(l+1)}{\rho^2}}_{\to 0}\right]R = 0$$

as $\rho \to \infty$

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$$\boxed{\frac{d^2R}{d\rho^2} - \gamma^2 R \approx 0 \qquad \text{Approx Diffy Q for } \rho \to \infty}$$

We thus expect $R(\rho) \sim e^{\pm\gamma\rho}$

But $e^{+\gamma\rho}$ blows up as $\rho \to 0$ so,

$R(\rho) \sim e^{-\gamma\rho}$ is our asymptotic solution. for $\rho \to \infty$

2 Let $\rho \to 0$

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\underbrace{-\gamma^2}_{\text{nominal}} + \underbrace{\frac{2}{\rho}}_{\text{big}} - \underbrace{\frac{l(l+1)}{\rho^2}}_{\text{really big!}}\right]R = 0$$

$$\boxed{\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R \approx 0 \qquad \text{Approx Diffy Q for } \rho \to 0}$$

it looks like a polynomial $R(\rho) = \rho^{q}$

Works as all the terms give ρ^{q-2}

so lets pop that in, (note we could have $C\rho^g$ but the C's cancel) 8

$$\frac{dR}{d\rho} = g\rho^{g-1} \qquad \frac{d^2R}{dg^2} = g(g-1)\rho^{g-2}$$

$$g(g-1)\cancel{\rho^{g-2}} + 2g\cancel{\rho^{g-2}} - \ell(\ell+1)\cancel{\rho^{g-2}} = 0$$

$$g^2 - g + 2g - \ell(\ell+1) = 0$$

$$g(g+1) - \ell(\ell+1) = 0$$

Thus $g = \ell$ or $-\ell-1$

so $R = \rho^\ell$ or $R = \rho^{-(\ell+1)}$ blows up for $\rho \to 0$

So

$R(\rho) \sim \rho^\ell$ for our asymptotic solution as $\rho \to 0$

So we get

$$R(\rho) \sim \rho^\ell e^{-\gamma\rho}$$

This behaves fine as $\rho \to 0$ & $\rho \to \infty$

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(3) Intermediate ρ?

Assume so function $f(\rho)$ as of yet determined. and find the Diffy Q it satisfies,

$$R(\rho) = \rho^{\ell} e^{-\gamma\rho} f(\rho)$$

$$\frac{dR}{d\rho} = \ell\rho^{\ell-1} e^{-\gamma\rho} f(\rho) + \rho^{\ell}(-\gamma e^{-\gamma\rho}) f(\rho) + \rho^{\ell} e^{-\gamma\rho} f'(\rho)$$

$$= \rho^{\ell-1} e^{-\gamma\rho}\left[\ell f(\rho) - \gamma\rho f(\rho) + \rho f'(\rho)\right]$$

$f'(\rho) = df/d\rho$ BTW

$$\frac{d^2R}{d\rho^2} = \rho^{\ell-1} e^{-\gamma\rho}\left[(2-2\gamma-2\gamma\ell) f(\rho) + (2+2\ell-2\gamma\rho) f'(\rho) + \rho f''(\rho)\right]$$

$f''(\rho) = d^2f/d\rho^2$ BTW

Substitution gives,

$$\rho \frac{d^2 f}{d\rho^2} + 2(\ell + 1 - \gamma\rho)\frac{df}{d\rho} + 2(1 - \gamma - \gamma\ell) f(\rho) = 0$$

Looks like a mess, but let's try a series solution,

$$f(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

index shift

note $j=-1$ term $=0$

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

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

maintain ρ^j order

maintain ρ^j order

$$\rho \frac{d^2 f}{d\rho^2} + 2(\ell+1)\frac{df}{d\rho} - 2\gamma\rho \frac{df}{d\rho} + 2(1 - \gamma - \gamma\ell) f = 0$$

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(\ell+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$- 2\gamma \sum_{j=0}^{\infty} j c_j \rho^j + 2(1 - \gamma - \gamma\ell) \sum_{n=0}^{\infty} c_j \rho^j = 0$$

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OK,

$$\sum_{j=0}^{\infty}\left(j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2\gamma j c_j + 2(1-\gamma-\gamma\ell)c_j\right)\rho^j = 0$$

Holds for each j and any ρ so sum vanishes for each j!

$$j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2\gamma j c_j + 2(1-\gamma-\gamma\ell)c_j = 0$$

Thus,

$$c_{j+1}\Big(j(j+1) + 2(\ell+1)(j+1)\Big) - \Big(2\gamma j - 2(1-\gamma-\gamma\ell)\Big)c_j = 0$$

$$c_{j+1} = \frac{2\gamma j - 2 + 2\gamma + 2\gamma\ell}{(j+1)(j+2\ell+2)}\, c_j$$

$$\boxed{c_{j+1} = \frac{2\gamma(j+\ell+1) - 2}{(j+1)(j+2\ell+2)}\, c_j}$$

Recurrence relation

c_0 determines all coeffs

get c_0 from $\langle\psi|\psi\rangle = 1$

$$f(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$ do we have ∞ terms?

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let $j \to \infty$,

$$c_{j+1} \simeq \frac{2\gamma j}{j^2} c_j = \frac{2\gamma}{j} c_j$$

Note

$$e^{\alpha x} = 1 + \frac{a}{1!} x + \frac{a^2}{2!} x^2 + \frac{a^3}{3!} x^3 + \dots$$

here, $c_j = \frac{\alpha}{j+1} c_j$ which is $c_{j+1} \simeq \frac{\alpha}{j} c_j$ for $j \to \infty$

In the large j limit,

$$f(\rho) \simeq e^{2\gamma\rho}$$ like this exponential

So,

$$R(\rho) \simeq \rho^{l} e^{-\gamma\rho} e^{2\gamma\rho} = \rho^{l} e^{\gamma\rho}$$

Oh no! that grows as $\rho \to \infty$!

To get a well behaved $R(\rho)$, j must terminate (like w/ Legendre Polys)

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Assume a j_{max} such that,

$$2\gamma(j_{max}+l+1) - 2 = 0$$ (numerator of recurrence relationship)

j_{max}, l are integers

so $j_{max}+l+1$ is an integer, n

$$\boxed{n \equiv j_{max}+l+1}$$

Principal Quantum Number, n

j and l start @ 0 so

$$\boxed{n = 1, 2, 3, \ldots \infty}$$

$2\gamma n - 2 = 0$ so $\boxed{\gamma = 1/n}$

energy is quantized (by n!)

Energy Quantization

With $\gamma = 1/n$ we get,

$$-\gamma^2 = -\frac{1}{n^2} = \frac{E}{\hbar^2/2\mu a^2} = \frac{E}{\frac{\hbar^2}{2\mu}}\left(\frac{4\pi\varepsilon_0\hbar^2}{\mu Z e^2}\right)^2$$

So that,

$$\boxed{E_n = -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{\mu}{\hbar^2} \quad n = 1, 2, 3, \ldots}$$

For a given n,

$$l = n - j_{max} - 1$$

And thus we have 3 quantum numbers

$n = 1, 2, 3, \ldots, \infty$ "shell"/"orbital" number

$l = 0, 1, 2, \ldots, n-1$ ang. mom. #

$m = -l, -l+1, \ldots, 0, l-1, l$ mag. quantum #