Particle in a Central potential

a) Review of some classical results:

$$\vec{F} = -\vec{\nabla}V(r) = -\frac{dV}{dr}\hat{r} \quad \text{(directed towards the origin)}$$

$$\vec{L} = \vec{r} \times \vec{p} \quad \text{(angular momentum)}$$

for a central potential:

$$\frac{d\vec{L}}{dt} = 0 \quad \Rightarrow \quad L = \text{const. of motion.}$$

Total Energy

$$E = \underbrace{\frac{1}{2}mv_r^2 + \frac{L^2}{2mr^2}}_{\text{Radial piece + K.E. of rotation abt 0.}} + V(r)$$

Classical Hamiltonian:

$$\mathcal{H} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r)$$

where $p_r = m\frac{dr}{dt}$

If we want to know about the time evolution of r, then we can replace L^2 = const. and obtain an effective potential

$$V_{eff}(r) = V(r) + \frac{L^2}{2mr^2}.$$

} Something analogous happens in quantum mechanics.

Quantum Mechanical Hamiltonian:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\varphi(\vec{r}) = E\,\varphi(\vec{r})$$

∇^2 in spherical polar:

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\underbrace{\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)}_{L^2}$$

$$\therefore H = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2mr^2}L^2 + V(r)$$

L^2: contains the angular dependence of the Hamiltonian.

Therefore:

We need to solve:

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2mr^2}L^2 + V(r)\right]\varphi(r,\theta,\varphi) = E\,\varphi(r,\theta,\varphi)$$

Separation of variables:

$[L^2, H] = 0$ and $[H, \vec{L}] = 0$. Although we have fours constants of motion L^2, L_x, L_y, L_z, then we cannot use all because they do not commute with each other.

The commutation holds since $\vec{L}$ as well as L^2 are functions of θ alone. ~~the~~

We will find the Basis for H, L^2, L_z i.e the basis space ξ_r.

We have:

$$H\varphi(\vec{r}) = E\varphi(\vec{r})$$
$$L^2\varphi(\vec{r}) = l(l+1)\hbar^2\varphi(\vec{r})$$
$$L_z\varphi(\vec{r}) = m\hbar\,\varphi(\vec{r})$$

We already know that we can write:

$$\varphi(\vec{r}) = R_l(r)\, Y_l^m(\theta,\varphi)$$

$\Rightarrow$ Hamiltonian:

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right]R_l(r) = E\,R(r)$$

- We now have to solve a differential Eqn for a fixed value of l, i.e. we solve for ~~the~~ eigenvalues of H_l.

In other words in the state space ξ_r, we work in the subspace ξ_{lm}. corresponding to fixed values of l, m. Since H depends on L^2 and not L_z, the eigenvalues will depend only on l and not on m. Therefore for a fixed l, there will be $(2l+1)$ degenerate eigenvalues. We label these eigenvalues as $E_{k,l}$, where l denotes the subspace $\xi(l,m)$ and k is the solution to the Hamiltonian in that subspace. k could be continuous or discrete. We can interpret k as the the different eigenvalues associated with a given value of l.

i.e. Within a subspace $l = 1$,

$$H_1 = \begin{pmatrix} E_{k_0 1} & & 0 \\ & E_{k_1 1} & \\ 0 & & E_{k_2 1} \end{pmatrix} \qquad H_0 = \left(E_{k_0 0} \right)$$

in this case: $E_{k_0 1} = E_{k_1 1} = E_{k_2 1}$ $(2l+1)$ degeneracies.

The radial fns. $R_{kl}(r)$.

$$\therefore \left[\frac{-\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2mr^2} + V(r) \right] R_{k,l}(r) = E_{k,l} R_{k,l}(r)$$

Let: $R_{k,l} = \dfrac{u_{k,l}(r)}{r}$

$$\text{Then: } \left[-\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} + \frac{l(l+1)}{2mr^3} + \frac{V(r)}{r} \right] u_{k,l}(r) = E_{k,l} \frac{u_{k,l}(r)}{r}$$

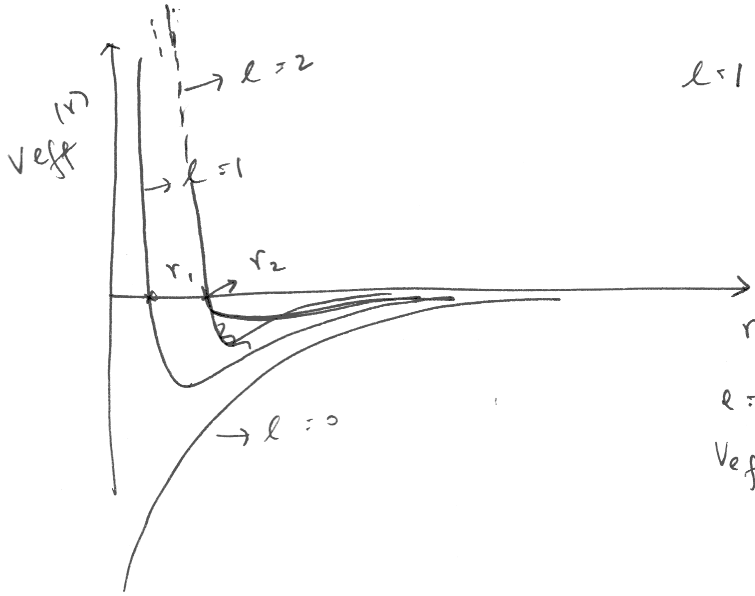
$$\Rightarrow \left[\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + \underbrace{\frac{l(l+1)}{2mr^2} + V(r)}_{V_{eff}(r)} \right] u_{k,l}(r) = E_{k,l} u_{k,l}(r)$$

1D potential $r: 0 \to \infty$.

$\dfrac{l(l+1)}{2mr^2}$ is always positive $\Rightarrow$ the corresp. force < 0 and pointed away from the force center. (Centrifugal Barrier).

Sketch $V_{eff}(r)$ for various l: Assume $V(r) \sim -e^2/r$

$l = 0$ $V_{eff}(r) = V(r) \sim -\frac{e^2}{r}$



$l = 1$ $V_{eff}(r) = \frac{2\hbar^2}{mr^2} - \frac{e^2}{r}$

$l = 2$ $V_{eff}(r) = \frac{6\hbar^2}{2mr^2} - e^2/r$

$l = 1$

$V_{eff}(0) = \frac{2\hbar^2}{mr} = e^2$

~~$r_1 = \frac{me^2}{2\hbar^2}$~~ $r_1 = \frac{2\hbar^2}{me^2}$

$r_2 = \frac{me^2}{6\hbar^2}$ $\frac{6\hbar^2}{me^2}$

$r_2 > r_1$

For higher l's the effect of the attractive piece will eventually decrease and the barrier term will dominate.

Behavior of $R_{kl}(r)$ at the origin:

We need $R_{k,l}(r) \underset{r \to 0}{\sim} C r^s$ (assume) for the wave fn to be well behaved.

Plug this form for the differential eqn:

we get:

$-s(s+1) + l(l+1) = 0$

$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} r^{s+1} + \frac{l(l+1)\hbar^2}{2mr^2} r^s + V(r) r^s = E_{k,l} r^s$$

$$-\frac{\hbar^2}{2m} \frac{1}{r}[s(s+1)] r^{s-1} + \frac{l(l+1)\hbar^2}{2mr^2} r^s + V(r) r^s = E_{k,l} r^s$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left[-s(s+1) + \ell(\ell+1)\right] r^{s-2} + \left[V(r) - E_{k,\ell}\right] r^s = 0$$

for $r \to 0$ $\quad r^{s-2}$ dominates.

$$\Rightarrow \therefore \quad -s(s+1) + \ell(\ell+1) = 0$$

$$\therefore \quad s = \ell \quad \text{or} \quad s = -(\ell+1)$$

$$\Rightarrow R_{k,\ell}(r \to 0) = C r^{\ell} \quad \text{or} \quad C r^{-(\ell+1)}$$

rejected due to bad behavior at the origin.

$$U_{k,\ell} = r R_{k,\ell}$$

$$\Rightarrow U_{k,\ell} \sim C r^{\ell+1} \quad \text{as} \quad r \to 0$$

$$\therefore \quad \varphi_{k,\ell,m} = \frac{U_{k,\ell}(r)}{r} Y_{\ell m}(\theta, \varphi)$$

We need: $\displaystyle\int r^2 dr\, d\Omega \, |\varphi_{k,\ell m}|^2 = 1$

$$\Rightarrow \underbrace{\int d\Omega \, |Y_{\ell m}(\theta,\varphi)|^2}_{1} \int r^2 dr \, \frac{|U_{k,\ell}(r)|^2}{r^2} = 1$$

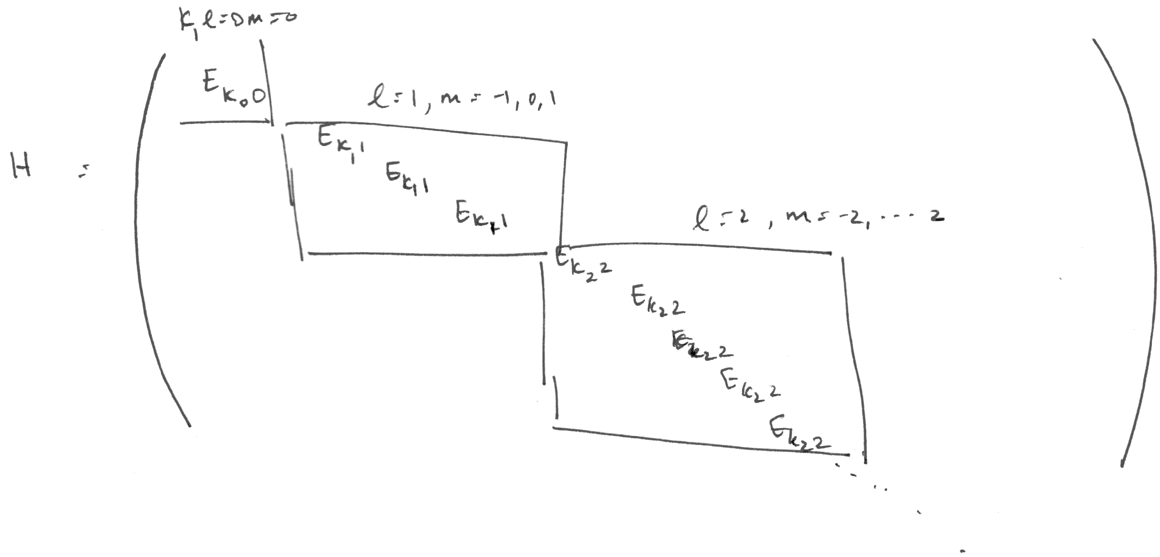
$$\Rightarrow \int dr \, |U_{k,\ell}(r)|^2 = 1$$

Eigenvalues depend on 3 indices: k, ℓ, m

- k: radial q. no.
- ℓ: azimuthal q. no
- m: magnetic q. no

How does the Hamiltonian look like?

$$H\,|k\,l\,m\rangle = E_{kl}\,|k\,l\,m\rangle$$



$\therefore$ For a given k, l. there is atleast $(2l+1)$ degeneracies. In addition: we can have an $E_{kl} = E_{k'l'}$. This is usually a feature of the potential $V(r)$. These are called accidental degeneracies, while the $(2l+1)$ degeneracies are the essential degeneracies.

Motion of Center of Mass and relative Motion

$$\mathcal{L}(\vec{r}_1, \dot{\vec{r}}_1, \vec{r}_2, \dot{\vec{r}}_2) = \frac{1}{2} m_1 \dot{\vec{r}}_1^{\,2} + \frac{1}{2} m_2 \dot{\vec{r}}_2^{\,2} - V(\vec{r}_1 - \vec{r}_2)$$

$$\vec{P}_1 = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_1} = m\dot{\vec{r}}_1 \qquad \Bigg| \qquad \vec{P}_2 = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_2} = m\dot{\vec{r}}_2$$

Define center of mass:

$$\vec{r}_G = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{(m_1+m_2)}$$

and $\vec{r} = \vec{r}_1 - \vec{r}_2$ } 6 co-ordinates.

Then: $\vec{r}_1 = \vec{r}_G + \frac{m_2}{m_1+m_2} \vec{r}$

$$\vec{r}_2 = \vec{r}_G - \frac{m_1}{m_1+m_2} \vec{r}$$

$$\Rightarrow \mathcal{L}(r_G, \dot{r}_G, r \dot{r}) = \frac{1}{2} m_1 \left[\dot{r}_G + \frac{m_2}{m_1+m_2} \dot{r} \right]^2 + \frac{1}{2} m_2 \left[\dot{r}_G - \frac{m_1}{m_1+m_2} \dot{r} \right]^2 - V(r)$$

~~$= \frac{1}{2}(m_1+m_2)\dot{r}_G^2 + \frac{1}{2} \frac{m_1 m_2}{}$~~

$$= \frac{1}{2} m_1 [\dot{r}_G^2) + \frac{1}{2} \frac{m_1 m_2^2}{(m_1+m_2)^2} \dot{r}^2 + \frac{m_1 m_2}{m_1+m_2} \dot{r}_G \dot{r}$$

$$+ \frac{1}{2} m_2 \dot{r}_G^2 + \frac{1}{2} \frac{m_2 m_1^2}{(m_1+m_2)^2} \dot{r}^2 - \frac{m_1 m_2 \dot{r}_G \dot{r}}{m_1+m_2} - V(r)$$

$$= \frac{1}{2}(m_1+m_2) \dot{r}_G^2 + \frac{1}{2} \left(\frac{m_1 m_2}{m_1+m_2} \right) \dot{r}^2 - V(r)$$

Define $M = m_1 + m_2$ (total mass)

$$\mu = \frac{m_1 m_2}{m_1+m_2} \rightarrow \text{Reduced mass.}$$

$$\therefore \mathcal{L} = \frac{1}{2} M \dot{r}_G^2 + \frac{1}{2} \mu \dot{r}^2 - V(r)$$

Then:

$$\vec{P}_G = M\dot{r}_G = \vec{p}_1 + \vec{p}_2$$

$$\vec{p} = \mu\dot{\vec{r}} = \mu \frac{m_2 p_1 - m_1 p_2}{m_1 + m_2}$$

$$\Rightarrow \frac{\vec{p}}{\mu} = \frac{p_1}{m_1} - \frac{p_2}{m_2}$$

$\vec{P}_G$: Total momentum of the system

$\vec{p}$: Relative momentum of the 2 particles.

$$\therefore \mathcal{H}(\vec{r}_G \, \vec{P}_G, \vec{r}\, \vec{p}) = \frac{\vec{P}_G^{\,2}}{2M} + \frac{\vec{p}^{\,2}}{2\mu} + V(\vec{r})$$

Hamilton's eqns:

$$\dot{P}_G = 0$$

$$\dot{\vec{p}} = -\nabla V(\vec{r})$$

$\frac{P_G^2}{2M}$: K.E. of a particle of mass M located at the center of mass $\vec{r}_G$, with momentum $\vec{P}_G$.

Does not participate in the dynamics.

Can choose a frame where $\vec{P}_G = 0$ → Center of mass frame

$$\underbrace{\mathcal{H} = \frac{p^2}{2\mu} + V(r)}_{\text{relative motion of the 2 particles.}}$$

} 2 Body problem → 1 Body problem

Separation of Variables in q. Mechanics

Promote: $\vec{r}_1 \to \hat{\vec{R}}_1 \quad \vec{p}_1 \to \hat{\vec{P}}_1, \quad \vec{r}_2 \to \hat{\vec{R}}_2 \quad \vec{p}_2 \to \hat{\vec{P}}_2$

i.e. Vectors $\to$ operators.

then:
$$\left.\begin{aligned} [X_{1i}, P_{1j}] &= i\hbar\,\delta_{ij} \\ [X_{2i}, P_{2j}] &= i\hbar\,\delta_{ij} \end{aligned}\right\}\ \text{Canonical Commutation Relations}$$

of-course all operators corresponding to particle 1, commute with all operators corresponding to particle 2.

Now if we re-difene $\hat{R}_G$ and $\hat{\vec{P}}_G$:

$$\hat{\vec{R}}_G = \frac{m_1\hat{\vec{R}}_1 + m_2\hat{\vec{R}}_2}{m_1+m_2}$$
$$\hat{\vec{R}} = \hat{\vec{R}}_1 - \hat{\vec{R}}_2$$

and

$$\hat{\vec{P}}_G = \hat{\vec{P}}_1 - \hat{\vec{P}}_2$$
$$\hat{\vec{P}} = \frac{m_2\hat{\vec{P}}_1 - m_1\hat{\vec{P}}_2}{m_1+m_2}$$

then once again we see that:

$$[R_{Gi}, P_{Gj}] = i\hbar\,\delta_{ij}$$
$$[R_i, P_j] = i\hbar\,\delta_{ij}$$

and any other commutation relation involving an observable from the set $\{\vec{R}_G, \vec{P}_G\}$ and $\{\vec{R}, \vec{P}\}$ commute.

$\therefore \{\vec{R}, \vec{P}\}$ and $\{\vec{R}_G, \vec{P}_G\}$ are the position and momenta of 2 distinct particles with masses μ and $M = m_1 + m_2$ respectively.

Hamiltonian for the 2 particle system:

$$\hat{H} = \frac{\vec{P}_1^2}{2m_1} + \frac{\vec{P}_2^2}{2m_2} + V(\vec{R}_1 - \vec{R}_2)$$

or:

$$\hat{H} = \frac{\vec{P}_G^2}{2M} + \frac{\hat{\vec{P}}^2}{2\mu} + V(\hat{\vec{R}})$$

$$= H_G + H_r$$

$$\hat{H}_G = \frac{\vec{P}_G^2}{2M}$$

$$\hat{H}_r = \frac{\vec{P}^2}{2\mu} + V(\vec{R})$$

$$[\hat{H}_G, \hat{H}_r] = 0$$

$$\Rightarrow \hat{H}_r |\varphi\rangle = E_r |\varphi\rangle$$

$$\hat{H}_G |\varphi\rangle = E_G |\varphi\rangle$$

Since $\hat{H} = \hat{H}_G + \hat{H}_r$

$$\hat{H} |\varphi\rangle = (E_r + E_G)|\varphi\rangle = E|\varphi\rangle$$

~~Let $|\varphi\rangle = |\vec{r}_a, \vec{r}\rangle$~~

Let us choose a basis $\{|\vec{r}_a, \vec{r}\rangle\}$ to represent the energy eigenvectors $|\varphi\rangle$. In this basis $|\varphi\rangle$ is represented by the wave function: $\langle \vec{r}_G, \vec{r} | \varphi\rangle = \varphi(\vec{r}_a, \vec{r})$.

$\therefore$ The Hamiltonian in the basis of $\{|\vec{r}_a, \vec{r}\rangle\}$.

$$\langle \vec{r}_G, \vec{r} | \hat{H} | \varphi\rangle = \langle \vec{r}_G, \vec{r} | E | \varphi\rangle$$

or:
$$-\frac{\hbar^2}{2M} \vec{\nabla}_G^2 \varphi(\vec{r}_a, \vec{r}) - \frac{\hbar^2}{2\mu} \nabla_r^2 \varphi(\vec{r}_a, \vec{r}) + V(\vec{r}) \varphi_G(\vec{r}_a, \vec{r})$$

$$= E\, \varphi(\vec{r}_a, \vec{r})$$

Let $\varphi(\vec{r}_a, \vec{r}) = \chi_G(\vec{r}_a)\, \omega_r(\vec{r})$ (This is possible because $|\varphi\rangle = |\varphi_a\rangle \otimes |\varphi_r\rangle$ since $\xi = \xi_a \otimes \xi_r$)

Then:

$$-\frac{\hbar^2}{2M} \left[\nabla_G^2 \right] \chi_G(\vec{r}_a) = E_G\, \chi_G(\vec{r}_a) \quad \text{— I}$$

and
$$-\frac{\hbar^2}{2\mu} \nabla_r^2\, \omega_r(\vec{r}) + V(\vec{r})\, \omega_r(\vec{r}) = E_r\, \omega_r(\vec{r}) \quad \text{— II}$$

Take eqn: I: Can separate into $X(x)\, Y(y)\, Z(z)$ and solve. Each is a plane wave. So that finally:

$$\chi_G(\vec{r}_a) = \frac{1}{(2\pi\hbar)^{3/2}}\, e^{i \vec{P}_a \cdot \vec{r}_a/\hbar}$$

and
$$E_G = P_a^2/2M$$

$E_G \geq 0$ and is the K.E. corresponding to a translation of the system as a whole.

The second eqn. (Eq. II) is the interesting piece that describes the behavior of the system of 2 interacting particle in the center of mass frame. If

$$V(\vec{r}) = V(|\vec{r}|) = V(|\vec{r}_1 - \vec{r}_2|)$$ we have a central potential.

What happens to the angular momentum of the 2 particles?

If $\vec{L} = \vec{L}_1 + \vec{L}_2$ (Total Orbital angular Momentum)

where $\vec{L}_1 = \vec{R}_1 \times \vec{P}_1$

$\vec{L}_2 = \vec{R}_2 \times \vec{P}_2$

then one can show that under the transformation to $(\vec{R}_G, \vec{R})$ and $(\vec{P}_G, \vec{P})$

$$\vec{L} = \vec{L}_G + \vec{L}$$

where

$\vec{L}_G = \vec{R}_G \times \vec{P}_G$ and $\vec{L} = \vec{R} \times \vec{P}$ → SHOW THIS!

Quantum Mechanical Theory of the hydrogen Atom:

Hamiltonian:

$$H_r \varphi(\vec{r}) = E\varphi(r) \Rightarrow \left[-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r} \right] \varphi(\vec{r}) = E\varphi(\vec{r})$$

This Hamiltonian describes the relative motion of the proton and the $\bar{e}$ in the center of mass frame. The potential is central.

$$\Rightarrow \quad \varphi(\vec{r}) \equiv \varphi_{k\ell m}(\vec{r}) = \frac{u_{k,\ell}(r)}{r} Y_{\ell m}(\theta,\varphi)$$

$$\therefore \left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} \right] \varphi_{k\ell m}(\vec{r}) = E_{k\ell}\, \varphi_{k\ell m}(\vec{r})$$

becomes:

$$\underbrace{\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r} \right] u_{k,\ell}(r) = E_{k,\ell}\, u_{k\ell}(r)}$$

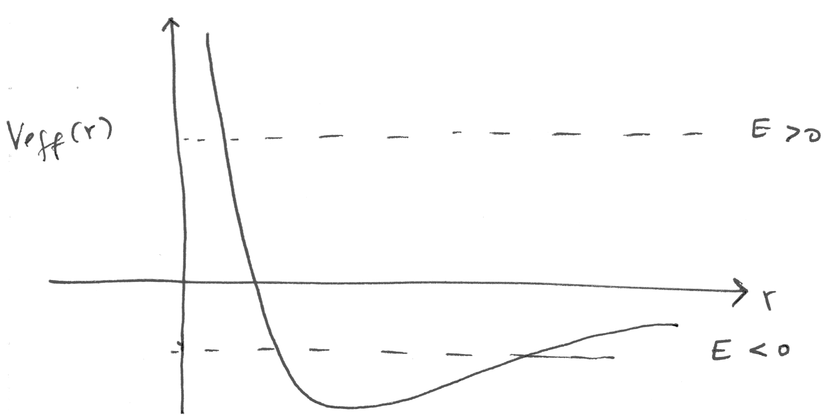
Radial Eqn.

and we have: $u_{k,\ell}(0) = 0$

What sort of states can the potential have? Consider the effective potential:

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

for any $\ell > 0$



$E > 0$ unbounded motion $\Rightarrow$ spectrum is continuous and wave fn is not square integrable.

$E < 0$ bounded motion spectrum is discrete and wave fn is sq. integrable.

Therefore we look for the B. states of the radial eqn.

<u>What do we know abt the Hydrogen atom:</u>

- Consists of a proton and an e^-.

  $m_p \sim 1.7 \times 10^{-27}$ kg ~ 1 GeV

  $m_e \simeq 0.91 \times 10^{-30}$ kg ~ 0.5 MeV

  $q \sim 1.6 \times 10^{-19}$ C.

- Interaction is electrostatic:

$$V(r) = -\frac{q^2}{4\pi\varepsilon_0 r} \sim -\frac{e^2}{r} \qquad \text{where } e^2 = \frac{q^2}{4\pi\varepsilon_0}$$

We can transform the 2 body problem into an equivalent 1 body problem: (in Center of mass frame) described by the Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2\mu} - \frac{e^2}{r}$$

$$\mu = \frac{m_e m_p}{m_e + m_p} \sim m_e\left(1 - \frac{m_e}{m_p}\right)$$ therefore since $\frac{m_e}{m_p}$ is small,

$$\mu \simeq m_e .$$

<u>Bohr Model:</u> Semi-classical model where the e^- orbits a heavy nucleus (proton). The total energy

$$E = \frac{1}{2}\mu v^2 - \frac{e^2}{r}$$

such that $\frac{\mu v^2}{r} = \frac{e^2}{r}$ $\Big\}$ → classical

and $\underbrace{\mu v r = n\hbar}_{\text{quantization (empirical)}}$ $\qquad$ n: positive integer.

With a little bit of algebra:

$$E_n = -\frac{E_I}{n^2} \qquad E_I : \text{Ionization energy.}$$

$$r_n = n^2 a_0 \qquad a_0 : \text{Bohr radius}$$

$$v_n = \frac{v_0}{n}.$$

$$E_I = \frac{\mu e^4}{2\hbar^2} \sim 13.6\ eV \qquad \text{(experimentally verified).}$$

$$a_0 = \frac{\hbar^2}{\mu e^2} \sim 0.52\ \mathring{A}$$

Going back to the quantum theory: Let us switch to dimensionless variables:

$$\rho = r/a_0$$

$$\lambda_{k,l} = \sqrt{-E_{k,l}/E_0} \qquad \text{(-ve sign because we are interested in b. states).}$$

Using this:

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \lambda^2_{k,l}\right] u_{k,l}(\rho) = 0$$

We need to solve for $u_{k,l}(\rho)$. We do this by series expansion (a very standard method of solving differential eqns).

Asymptotic Behavior:

In the limit $\rho \to \infty$ $1/\rho^2$ and $1/\rho$ become negligible.

$$\Rightarrow \left[\frac{d^2}{d\rho^2} - \lambda_{k,\ell}^2\right] u_{k,\ell}(\rho) = 0$$

$$\Rightarrow u_{k,\ell}(\rho) \sim e^{\pm \rho \lambda_{k,\ell}} \Big|_{\rho \to \infty}$$

Since we require bounded solutions, we need

$$u_{k,\ell}(\rho)\Big|_{\rho \to \infty} \sim e^{-\rho \lambda_{k,\ell}}.$$

Now for any ρ, let us assume

$$u_{k,\ell}(\rho) = e^{-\rho \lambda_{k,\ell}} \underbrace{y_{k,\ell}(\rho)}_{\text{Polynomial}}$$

Then:

$$\left\{\frac{d^2}{d\rho^2} - 2\lambda_{k,\ell}\frac{d}{d\rho} + \left[\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]\right\} y_{k,\ell}(\rho) = 0$$

and we need $y_{k,\ell}(0) = 0$ so that $u_{k,\ell}(0) = 0$.

Let us expand

$$y_{k,\ell}(\rho) = \rho^s \sum_{q=0}^{\infty} c_q \rho^q$$

$c_0 \neq 0$ so we need to multiply by ρ^s so that $y_{k,\ell}(\rho)\Big|_{\rho=0} = 0$.

also we know from the condition at $\rho = 0$ that $s > 0$

Then:
$$\frac{d}{d\rho} y_{k,l}(\rho) = \sum_{q=0}^{\infty}{}' (q+s)\, c_q\, \rho^{q+s-1}$$

$$\frac{d^2}{d\rho^2} y_{kl}(\rho) = \sum_{q=0}^{\infty}{}' (q+s)(q+s-1)\, c_q\, \rho^{q+s-2}$$

$$\Rightarrow \sum_{q=0}^{\infty}{}' \Big[(q+s)(q+s-1) c_q \rho^{q+s-2} - 2\lambda_{kl} (q+s) c_q \rho^{q+s-1}$$
$$+ 2 c_q \rho^{q+s-1} - l(l+1) c_q \rho^{q+s-2} \Big] = 0$$

or:
$$\sum_{q=0} \Big[\big[(q+s)(q+s-1) - l(l+1)\big] c_q \rho^{q+s-2} - \big(2\lambda_{kl}(q+s) - 2\big) c_q \rho^{q+s-1} \Big] = 0$$

All coeffns must be identically zero.

set $q = 0$ coeffn to 0:

$$\Rightarrow \big[s(s-1) - l(l+1) \big] c_0 = 0$$

since $c_0 \neq 0$

$$\boxed{s = \begin{cases} l+1 \\ -l \end{cases}}$$

Setting the coeffn of a general $q \neq 0$ term to zero: we get:

$$q(q+2l+1)\, c_q = 2\big[(q+l)\lambda_{k,l} - 1\big] c_{q-1} \qquad (\text{using } s = l+1)$$

If we know c_0, then we can determine $c_1, c_2 \ldots$ etc using the above recurrence relation.

Also we know: $\frac{c_q}{c_{q-1}} \to 0$ as $q \to \infty$ (should be a convergent series)

– otherwise the condition at $\rho \to \infty$ will be violated.

$$\frac{c_q}{c_{q-1}} = \frac{2((q+l)\lambda_{k,l} - 1)}{q(q+2l+1)}$$

$$\therefore \left.\frac{c_q}{c_{q-1}}\right|_{q \to \infty} \sim \frac{2\lambda_{k,l}}{q}$$

Consider the power series expansion of a fn:

$$e^{2\rho\lambda_{k,l}} = \sum_{q=0}^{\infty} d_q \rho^q$$

where $d_q = \frac{(2\lambda_{k,l})^q}{q!}$

then: $\frac{d_q}{d_{q-1}} = \frac{2\lambda_{kl}}{q!}$

Therefore we see that if the ratio of coeffns become $\frac{2\lambda_{k,l}}{q}$,

then the series is ~~is~~ an exponential of the form $e^{2\lambda_{k,l}\rho}$.

~~Therefore~~ Not acceptable as $u_{k,l}(\rho)\Big|_{\rho \to \infty}$ is not bounded.

(then: $u_{k,l}(\rho) = e^{\lambda_{kl}\rho}\Big|_{\rho \to \infty} \to \infty$.

$\therefore$ The series:

$$y_{k,l}(\rho) = \rho^s \sum_{q=0}^{\infty} c_q \rho^q$$ cannot have infinite terms.

$\Rightarrow y_{k,l}(\rho)$ is a polynomial!

Therefore we need to find an integer k such that:

$$\frac{c_q}{c_{q-1}} = 0 \quad \text{when} \quad q = k.$$

Then all other c_q for $q > k$ $= 0$.

$$\Rightarrow (q+l)\,\lambda_{k,l} - 1 = 0$$

$$\Rightarrow \lambda_{k,l} = \frac{1}{q+l} = \frac{1}{k+l} \quad \text{for } q = k.$$

We know that

$$\lambda_{k,l} = \sqrt{-\frac{E_{k,l}}{E_I}}$$

$$\Rightarrow \lambda_{k,l}^2 = \frac{1}{(k+l)^2} = -\frac{E_{k,l}}{E_I}$$

$$\Rightarrow \boxed{E_{k,l} = -\frac{E_I}{(k+l)^2}} \quad \text{and} \quad k = 1, 2, 3 \ldots$$

Discrete solutions!

$y_{k,l}(\rho)$ is a polynomial in ρ. The lowest order term is ρ^{l+1} and highest order term is ρ^{l+k}.

We know that:

$$c_q = -\frac{2(k-q)}{q(q+2l+1)(k+l)}\,c_{q-1} \quad \left(\text{where we have used } \lambda_{k,l} = \frac{1}{k+l}\right).$$

$$= (-1)^q \left(\frac{2}{k+l}\right)^q \frac{(k-1)!}{(k-q-1)!} \frac{(2l+1)!}{q!\,(q+2l+1)!}\, c_0$$

Then c_0 can be determined using normalization condition of the wave fn. $u_{kl}(\rho)$.

Now switching back to r, ~~which is~~ ~~r = a~~ ~~ρ~~ the first few radial wave fns:

$$R_{k=1,\ell=0}(r) = 2(a_0)^{-3/2} e^{-r/a_0}$$

$$R_{k=2\ \ell=0}(r) = 2(a_0)^{-3/2}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

etc.

$$R_{k\ell}(r) = \frac{e^{-r/(k+\ell)a_0}}{r}\left[c_0\left(\frac{r}{a_0}\right)^{\ell+1} + c_1\left(\frac{r}{a_0}\right)^{\ell+2} + \cdots + c_k\left(\frac{r}{a_0}\right)^{\ell+k}\right]$$

Possible values of the q. nos: degeneracies:

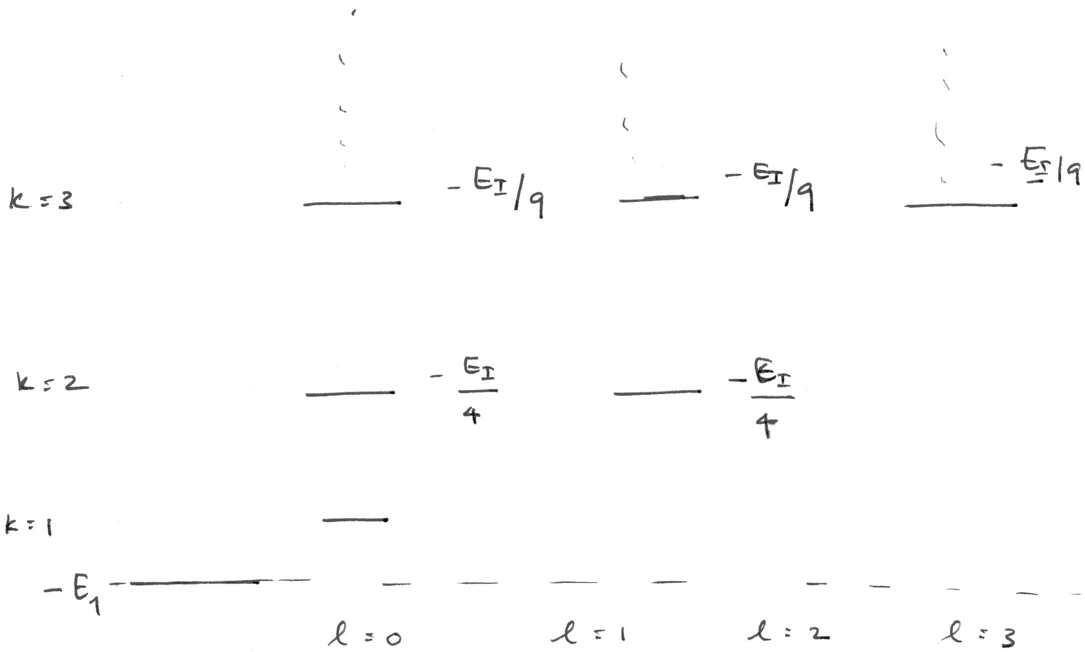
For a fixed ℓ, there exists an infinite no. of possible energy values corresponding to $k = 1, 2, 3 \ldots$. Each of them is atleast $(2\ell+1)$ fold degenerate (essential degeneracy).

In addition there exists accidental degeneracies:

$$E_{k\ell} = -\frac{E_I}{(k+\ell)^2}$$

$\Rightarrow E_{k\ell} = E_{k'\ell'}$ (for distinct ℓ values ie $\ell \neq \ell'$)

if $k+\ell = k'+\ell'$



In the case of Hydrogen atom $k+l = n$ and Energy depends on the sum i.e. n.

$$E_n = -\frac{E_I}{n} \qquad n = 1, 2, 3 \ldots\ldots$$

Since $k + l = n \Rightarrow l = n - k$

~~and the smallest~~

∴ largest value l can take given a fixed n is when k takes its smallest value 1

∴ $l_{max} = n - 1$.

Smallest value l can take is 0

so that $\boxed{k = n}$.

$\therefore$ $l = 0, 1, 2 \ldots n-1$ for a given n.

$\therefore$ for each n contains n subshells and each sub-shell has $(2l+1)$ distinct states:

$\Rightarrow$ total of degeneracies $= \sum_{l=0}^{n-1} (2l+1) = n^2$

Take spin into account this number is multiplied by (2).

Spectroscopic Notation:

$l = 0 \longleftrightarrow s$

$l = 1 \longleftrightarrow p$

$l = 2 \longleftrightarrow d$

etc:

$k = 1$	$n = 1$,	$l = 0$	1s	$-E_I$
$k = 2$	$n = 2$	$l = 0$	2s	$-E_I/4$
$k = 1$	$n = 2$	$l = 1$	2p	$-E_I/4$
$k = 3$	$n = 3$	$l = 0$	3s	$-E_I/9$
$k = 2$	$n = 3$	$l = 1$	3p	$-E_I/9$
$k = 1$	$n = 3$	$l = 2$	3d	$-E_I/9$
	etc.			

$l = 0$ spherically symm.