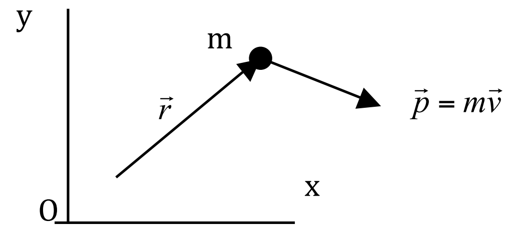
SJP QM 3220 H-Atom 1

Angular Momentum (warm-up for H-atom)
Classically, angular momentum defined as (for a 1-particle system)

$$\vec{L} \equiv \vec{r} \times \vec{p} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$



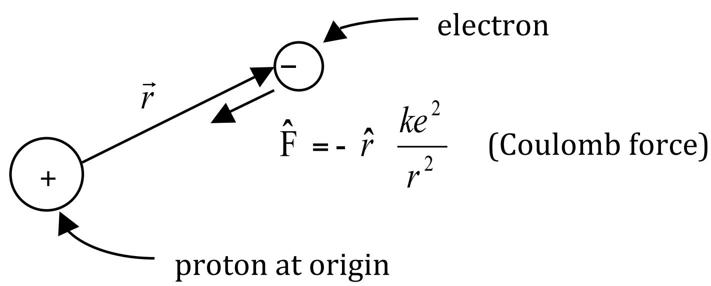
Note: $\vec{L}$ defined w.r.t. an origin of coords.

$$\vec{L} = \hat{x}\,(yp_z - zp_y) + \hat{y}\,(zp_x - xp_z) + \hat{z}\,(xp_y - yp_z)$$

(In QM, the operator corresponding to L_x is $\vec{L}_x = \hat{y}\,\hat{p}_z - \hat{z}\,\hat{p}_y$, $p_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$, etc.)

Classically, torque defined as $\vec{\tau} \equiv \vec{r} \times \vec{F}$, and $\vec{\tau} = \frac{d\vec{L}}{dt}$ (rotational version of $\vec{F} = m\vec{a}$)
If the force is radial (central force), then $\vec{\tau} = \vec{r} \times \vec{F} = 0 \Rightarrow \vec{L} = const.$

H-atom:



In a multi-particle system, total average momentum:

$\vec{L}_{tot} = \sum_i \hat{L}_i$ is conserved for system isolated from external torques.
sum over particles

Internal torques can cause exchange of average momentum among particles, but $\vec{L}_{tot}$ remains constant.

In classical and quantum mechanics, only 4 things are conserved:

- energy
- linear momentum
- angular momentum
- electric charge

Back to QM. Define vector operator $\hat{\vec{L}}$

operator → unit vector

$$\hat{\vec{L}} = \hat{L}_x \hat{x} + \hat{L}_y \hat{y} + \hat{L}_z \hat{z}$$

There is a general theorem in QM (which we have not proven):

$$\frac{d\langle Q\rangle}{dt} = \frac{i}{\hbar}\left\langle \left[\hat{\mathcal{H}},\hat{Q}\right] \right\rangle$$

$$\Rightarrow \quad \underbrace{\frac{d\langle \hat{\vec{L}}\rangle}{dt}}_{} = \frac{i}{\hbar}\left\langle \left[\hat{\mathcal{H}},\hat{\vec{L}}\right] \right\rangle$$

$$\frac{d < L_x >}{dt}\hat{x} + \frac{d < L_y >}{dt}\hat{y} + \ldots$$

Claim: for a <u>central</u> <u>force</u> such as in H-atom

$V = V(r) = -ke^2/r$, then $\left[\hat{\mathcal{H}},\hat{L}\right] = 0$ (will show this later)

This implies $\frac{d\vec{L}}{dt} = 0$ (just like in classical mechanics)

Angular momentum of electron is H-atom is constant, so long as it does not absorb or emit photon. Throughout present discussion, we ignore interaction of H-atom w/photons.

Will show that for H-atom or for any atom, molecule, solid – any collection of atoms – the angular momentum is quantized in units of $\hbar$. $|\vec{L}|$ can only change by integer number of $\hbar$'s.

Units of $L = [L] = [\hbar]$

Note $[L] = [rp]$, $[p] = \left[\frac{\hbar}{r}\right]$ (since $p = \hbar k$)

$$\Rightarrow [\mathrm{L}] = [r] \times [\hbar]/[r] = [\hbar] \quad ✓$$

Claim: $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar \hat{L}_z$

and $\boxed{\left[\hat{L}_i, \hat{L}_j\right] = i\hbar \hat{L}_k}$ (i, j, k cyclic:
x y z or
y z x or
z x y)

To prove, need two very useful identities: $[A+B,C]=[A,C]+[B,C]$
$[AB,C]=A[B,C]+[A,C]B$

Proof: $[L_x,L_y]=[yp_z-zp_y,zp_x-xp_z]=$

$$\underbrace{[yp_z,zp_x]}_{y\underbrace{[p_z,z]}_{-i\hbar}p_x}-\underbrace{[yp_z,xp_z]}_{0}-\underbrace{[zp_y,zp_x]}_{0}+\underbrace{[zp_y,xp_z]}_{x\underbrace{[z,p_z]}_{+i\hbar}p_y}=$$

all other terms like [y, p_x] = 0

$= +i\hbar(xp_y - yp_x) = i\hbar L_z$

(Have used $[x,p_x]=i\hbar,\ [x,y]=0,\ [\mathrm{x},p_y]=0,\ [p_x,p_y]=0,$ etc.

I'm dropping the ˆ over operators when no danger of confusion.

Since [L_x, L_y] ≠ 0, cannot have simultaneous eigenstates of $\hat{L}_x$ and $\hat{L}_y$.

$$\sigma_{L_x}^2\sigma_{L_x}^2 \geq \Big(\frac{1}{2i}\underbrace{\left\langle[\hat{L}_x,\hat{L}_y]\right\rangle}_{i\hbar\langle\hat{L}_z\rangle}\Big)^2 = \left(\frac{\hbar}{2}\right)^2\langle L_z\rangle^2$$

However, $L^2=\vec{L}\cdot\vec{L} = L_x^2 + L_y^2 + L_z^2$ <u>does</u> commute with L_z.

Claim: $[L^2,L_z]=0$

$$\boxed{[L^2,L_i]=0}$$, i = x, y, or z

Proof: $[L^2,L_z]=[L_x^{\ 2},L_z]+[L_y^{\ 2},L_z]+\underbrace{[L_z^{\ 2},L_z]}_{0}$

$$= L_x\underbrace{[L_x,L_z]}_{-i\hbar L_y}+\underbrace{[L_x,L_z]}_{-i\hbar L_y}L_x + L_y\underbrace{[L_y,L_z]}_{+i\hbar L_x}+\underbrace{[L_y,L_z]}_{+i\hbar L_x}L_y$$

= 0 (Note cancellations)

[L^2, L_z] = 0 => can have simultaneous eigenstates of $\hat{L}^2,\hat{L}_z$ (or $\hat{L}^2$, $\hat{L}_i$ any i)

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Looking forward to H-atom:

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

We will show that $\left[\hat{\mathcal{H}}, \hat{L}^2\right] = 0$, $\left[\hat{\mathcal{H}}, \hat{L}_z\right] = 0$

=> simultaneous eigenstates of $\hat{\mathcal{H}}$, $\hat{L}^2$, $\hat{L}_z$

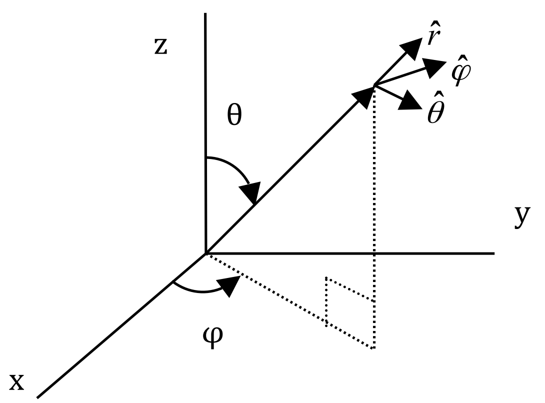
energy q-nbr

$$\psi = \psi_{n\ l\ m}$$

L_z q-number

L^2 q-number

When we solve the TISE $(\nabla^2 + V(r))\psi = E\,\psi$ for the H-atom, the natural coordinates to use will be spherical coordinates: r, θ, φ (not x, y, z)



x = r sin θ cos φ
y = r sin θ sin φ
z = r cos θ

Just rewriting $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ in spherical coordinates is a little ugly.

But separation of variables will give special solutions, energy eigenstates, of form

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

The angular part of the solution Y (θ, φ) will turn out to be eigenstates of L^2, L_z and will have form completely independent of the potential V(r).

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Given only $[L^2, L_z] = 0$ and $\hat{L}^2, \hat{L}_z$ hermitean we know there must exist simultaneous eigenstates f (which will turn out to be the Y (θ, φ) mentioned above) such that

$$\hat{L}^2 f = \lambda \cdot f \quad , \quad \hat{L}_z f = \mu \cdot f$$

(λ will be related to *l*, and μ will be related to *m*)

One can show that *f* will depend on quantum-numbers *l, m*, so we write it as f_l^m:

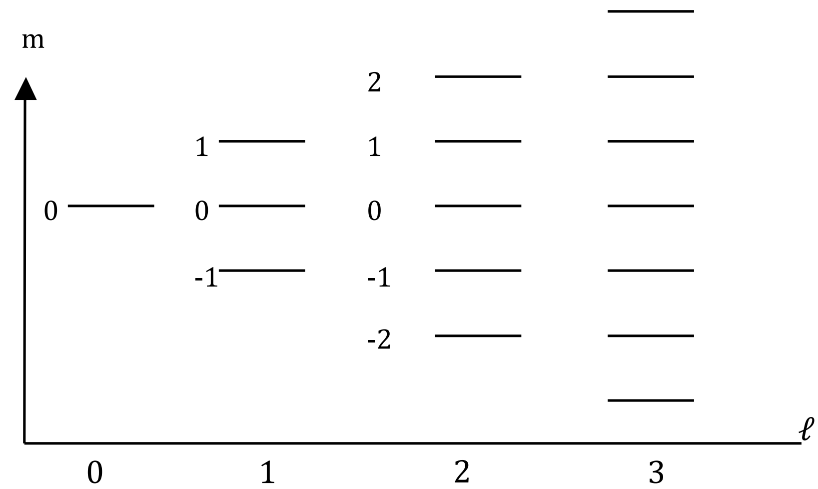
★
$$L^2 f_l^m = \hbar^2 l(l+1) \cdot f_l^m$$
$$L_z f_l^m = \hbar m \cdot f_l^m$$
$$\text{where } l = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots \qquad m = -l, -l+1, \ldots l-1, l$$

$f_l^m = Y_l^m(\theta, \varphi)$ will be determined later.

Notice max eigenvalue of L_z ($= l\hbar$) is smaller than square root of eigenvalue of $L^2 = \hbar\sqrt{l(l+1)}$

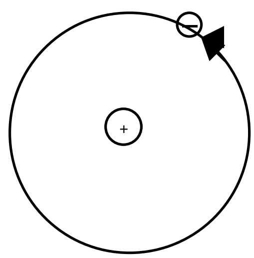
So, in QM, $L_z < |L|$ (Interesting that it's not "or equal to"! The uncertainty principle is lurking in there)

Also notice *l* = 0, *m* = 0 state has <u>zero</u> angular momentum ($L^2 = 0$, $L_z = 0$) so, unlike Bohr model, can have electron in state that is "just sitting there" rather than revolving about proton in H-atom.

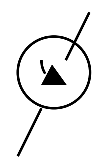


As we know from earlier in the term, there are 2 flavors of angular momentum:

1. Orbital
Ang. Mom.
(integer ℓ <u>only</u>)



2. Spin
Ang. Mom.
(integer <u>or</u> ½ integer OK)

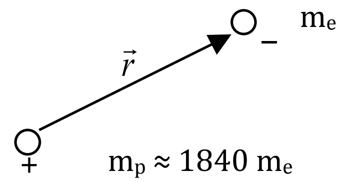


We started focusing on the latter, and now we are paying attention to the former. But, they are basically the same story, and when you write them as a ket $|l, m>$ you can think of that as exactly like $|s,m>$...

The H- atom

$m_p >> m_e$ =>

proton (nearly) stationary



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

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

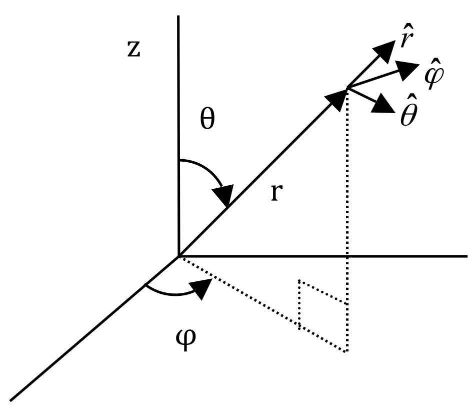
$$\frac{\hat{\vec{p}}^2}{2m} = \frac{\hat{\vec{p}}\cdot\hat{\vec{p}}}{2m} = \frac{-\hbar^2}{2m}\nabla^2(\ )$$

TISE: $\hat{\mathcal{H}}\psi_n = E_n\psi_n \Rightarrow$ special solutions (stationary states).

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

General Solution to TDSE: $\Psi(x,t) = \sum_n c_n e^{-iE_nt/\hbar}\psi_n(x)$

Spherical Coordinate System:



z = r cos θ
x = r sin θ cos φ
y = r sin θ sin φ

ψ = ψ (r, θ, φ)

Normalization: $\int dV|\psi|^2 = 1$ (volume)

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

Need ∇^2 in spherical coordinates. (Work it out!)

$\nabla^2 f =$

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

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

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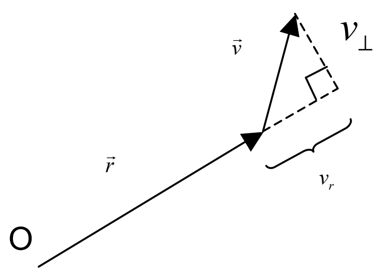
In Classical Mechanics (CM), KE = $p^2/2m$ = KE =
(radial motion KE) + (angular, axial motion KE)

$$\left|\hat{L}\right| = \left|\vec{r}\times m\vec{v}\right| = mrv_\perp$$

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



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

*

Same splitting in QM:

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

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

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

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

Separation of Variables! (as usual) Seek special solution of form:

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

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

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

(Convention: normalize radial, angular parts individually)

Plug ψ = R · Y into TISE =>

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

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

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

=> f(r) = g (θ, φ) = constant C = $\ell(\ell+1)$

$$\hat{L}^2 Y = \hbar^2\, C\cdot Y = \hbar^2\ell(\ell+1)Y$$ (See Page H-5)

Have separated TISE into radial part f(r) = $\ell(\ell+1)$, involving V(r), and angular part g (θ, φ) = $\ell(\ell+1)$ which is independent of V(r).

=> All problems with spherically symmetric potential (V = V(r)) have exactly same angular part of solution: Y = Y(θ, φ) called "spherical harmonics".

Let's focus first on angular equation: $\hat{L}^2 Y_l^m = \hbar^2 \ell(\ell+1) Y_\ell^m$ Want to solve for the Y_ℓ^m's - "spherical harmonics". One CAN start with commutation relations,

and, using operator algebra, solve for the eigenvalues of L^2, L_z. That gives

$$\left.\begin{aligned} L^2 Y_\ell^m &= \hbar^2 \ell(\ell+1) Y_\ell^m \\ L_z Y_\ell^m &= m\hbar Y_\ell^m \end{aligned}\right\} \quad \begin{aligned} &\text{where } \ell = 0, \tfrac{1}{2}, 1, 3/2, \ldots \\ &m = -\ell, -\ell+1 \ldots +\ell \end{aligned}$$

Or, we can use the differential equation version in position space, using $Y_\ell^m = Y_\ell^m(\theta, \varphi)$.

It's easy to find the φ-dependence:

$\hat{L}_z = \dfrac{\hbar}{i}\dfrac{\partial}{\partial\varphi}$ (showed in HW)

$\hat{L}_z Y = \dfrac{\hbar}{i}\dfrac{\partial Y}{\partial\varphi} = \hbar m Y$ (and you can cancel the $\hbar$)

<u>Assume</u> $Y(\theta,\varphi) = \Theta(\theta)\ \Phi(\varphi) \Rightarrow$

$$\frac{d\Phi}{d\varphi} = im\ \Phi \quad \Rightarrow \quad \boxed{\Phi(\varphi) = e^{+im\varphi}}$$

If we assume (postulate) that ψ is <u>single-valued</u> than

$$\Phi(\varphi + \underline{2m}) = \Phi(\varphi) \Rightarrow e^{im2\pi} = 1$$

=> m = 0, ± 1, ± 2, ... But m = - ℓ, ... + ℓ

So for orbital angular momentum, ℓ must be <u>integer</u> <u>only</u>: ℓ = 0, 1, 2, ... (we throw out ½ integer values when dealing with orbital angular momentum, as versus spin!)

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The solution of the polar angle part is somewhat messy, so I just summarize some results:

Normalization from $\int d\theta \int d\varphi \sin\theta \, \left|Y_\ell^m\right|^2$

Notice case $\ell = 0$ $\boxed{Y_0^0 = \text{const} = 1/\sqrt{4\pi}}$:

$$(\text{since } \int_0^\pi d\theta \int_0^{2\pi} d\varphi \sin\theta = \int d\Omega = 4\pi)$$

Example:

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{+i\varphi}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_1^{-1} = +\sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\varphi}$$

Convention on ± sign: $Y_\ell^{-m} = (-1)^m \left(Y_\ell^m\right)^*$

The spherical harmonics form a complete, orthonormal set (since eigenfunctions of hermitean operators)

$$\int d\Omega \; (Y_\ell^m)^* Y_{\ell'}^{m'} = \delta_{\ell\ell'} \delta_{mm'}$$

Completeness:

Any function of angles $f = f(\theta, \varphi)$ can be written as linear combo of Y_ℓ^m's :

$$f(\theta,\varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} Y_\ell^m$$

Likewise (when we get to the radial part): $\int_0^\infty dr\, r^2 (R_{n\ell})^* R_{n'\ell'} = \delta_{nn'}\delta_{\ell\ell'}$

=> H-atom <u>energy</u> <u>eigenstates</u> are

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r) Y_\ell^m(\theta,\varphi) = R_{n\ell}\Theta_{\ell m} e^{im\varphi}$$

n = 1, 2, … ; ℓ = 0, 1 … (n-1) ; m = $-\ell$ … + ℓ

We haven't talked about the radial part yet, so let's go there:

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McIntyre Ch8: The radial part!

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

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

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

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

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

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

same!

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

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

Notice: identical to 1D TISE:

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

r: 0 -> ∞ instead of x: - ∞ -> + ∞ and

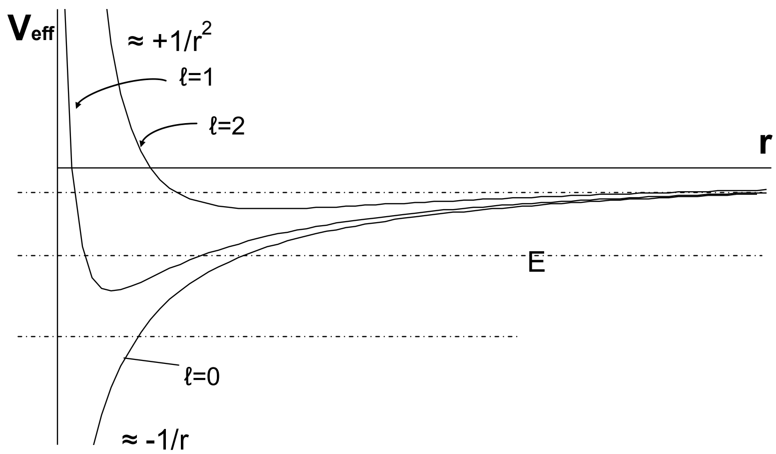
V(x) replaced with $\boxed{V_{eff} = V(r)\ +\ \dfrac{\hbar^2}{2mr^2}\,\ell(\ell+1)}$

V_{eff} = "effective potential"

Boundary conditions: u (r = ∞) = 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 solution to radial equation alone.

Seek bound state solutions E < 0

E > 0 solutions are unbound states, scattering solutions

Full solution of radial SE is <u>very</u> messy, even though it is effectively a 1D problem (different problem for each ℓ)

Power series solution (see text for details). Solutions depend on 2 quantum numbers: n and ℓ (for each effective potential ℓ = 0, 1, 2, ... have a set of solutions labeled by index n.)

Solutions: n = 1, 2, 3, ...   for given n
ℓ = 0, 1, ... (n - 1) ℓ_{max} = (n – 1)

n = "principal quantum number"

energy eigenvalues depend on n only (it turns out)

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

• same as Bohr model, agrees with experiment!

First few solutions: $R_{n\ell}(r)$

normalization ↓   "Bohr radius" ↙

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

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

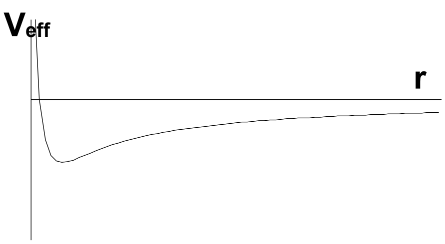
$$R_{21} = A_{21}\left(\frac{r}{a_0}\right) e^{-r/2a_0}$$

NOTE:

- for $\ell = 0$ (s states), $R(r = 0) \neq 0$ => wavefunction ψ "touches" nucleus.
- for $\ell \neq 0$, $R(r = 0) = 0$ => ψ does not touch nucleus.

$\ell \neq 0$ => electron has angular momentum. Same as classical behavior, 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 $\ell \neq 0$, V_{eff} has infinite barrier at origin = > u(r) must decay to zero at r=0 <u>exponentially</u>.



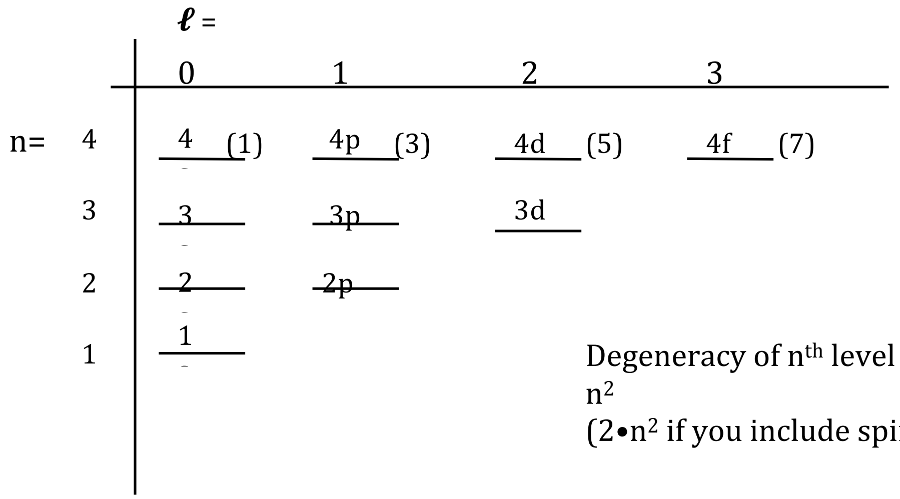
=> exponential decay in $R(r) = \frac{u(r)}{r}$ as well.

Completeness: any arbitrary (bound) state is

$$\psi = \sum_{n,\ell,m} c_{n\ell m} \cdot \psi_{n\ell m} \qquad \text{(c's are any complex constants)}$$

energy of state (n, ℓ, m) depends only on n.

$E_n = -\text{constant}/n^2$ (states ℓ, m with same n are <u>degenerate</u>)



Degeneracy of n^{th} level is n^2
($2 \bullet n^2$ if you include spin)

Radial Probability Density

$$\int dV |\psi|^2 = 1$$

Prob (find particle in dV about $\vec{r}$) = $|\psi(\vec{r})|^2 dV$

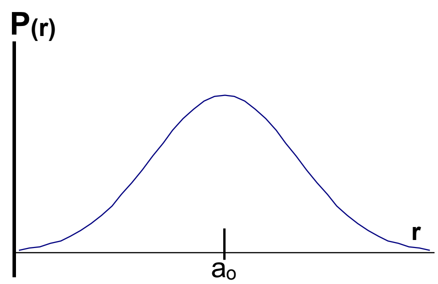
If $\ell = 0$, ψ = ψ(r) then $\int dV|\psi|^2 = \int dr 4\pi r^2 |\psi(r)|^2$

Prob (find in r → r + dr) = $\boxed{P(r)dr \;=\; 4\pi r^2 |\psi(r)|^2 dr}$

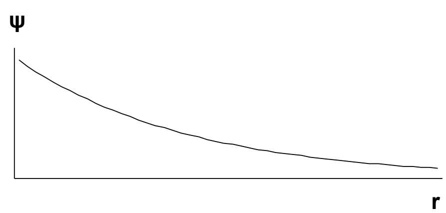
P(r) = radial probability density

Ground state: $\psi_{100} \;=\; Ae^{-r/a_0}$

$P(\mathrm{r}) = \; |A|^2 \, 4\pi r^2 e^{-2r/a_0}$



Notice P(r) very different from ψ(r):



If $\ell \neq 0$, ψ = ψ (r, θ, φ) = R(r) Y(θ, φ), then

"solid angle"

$$\int dV|\psi|^2 \;=\; \underbrace{\int dr\, r^2 \,|R|^2}_{1} \;\; \underbrace{\int d\Omega |Y|^2}_{1} = 1$$

Prob (find in r → r + dr) = r^2 $|R|^2$ dr

$\boxed{P(r) = r^2 \; |R|^2}$ even if $\ell \neq 0$

Note: $\psi = \psi(r) = R \cdot Y = R \cdot \dfrac{1}{\sqrt{4\pi}} \Rightarrow |R|^2 = 4\pi|\psi|^2$ if

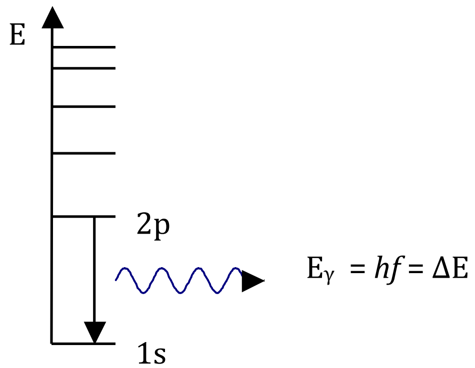
so $P(r) = r^2 |R|^2 = 4\pi \, r^2 |\psi|^2$

H-atom and emission/absorption of radiation:

If H-atom is in excited state (n = 2, ℓ = 1, m = 0) then it is in energy eigenstate = stationary state. If atom is isolated, then atom should remain in state ψ_{210} forever, since stationary state has simple time dependence:

$$\Psi(\vec{r},t) = \psi_{210}(r)\cdot e^{-eE_2t/\hbar}$$

But, experimentally, we find that H-atom emits photon and de-excites: $\psi_{210} \to \psi_{100}$ in ≈ 10^{-7} s -> 10^{-9} s



The reason that the atom does not remain in stationary state is that it is not truly isolated. The atom feels a fluctuating EM field due to "vacuum fluctuations". Quantum Electrodynamics is a relativistic theory of the QM interaction of matter and light. It predicts that the "vacuum" is not "empty" or "nothing" as previously supposed, but is instead a seething foam of virtual photons and other particles. These vacuum fluctuations interact with the electron in the H-atom and slightly alter the potential V(r). So eigenstates of the coulomb potential are not eigenstates of the actual potential: $V_{coulomb} + V_{vacuum}$

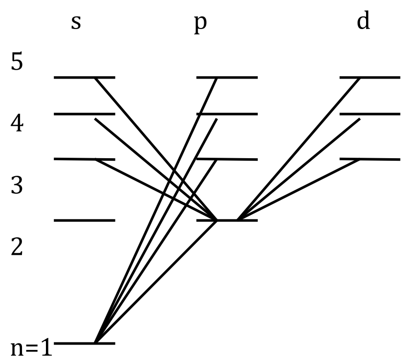
Photons possess an intrinsic angular momentum (spin) of 1 $\hbar$, meaning

$$\ell = 1 \Rightarrow \left|\vec{L}\right| = \hbar\sqrt{\ell(\ell+1)} = \sqrt{2}\hbar$$

$$\text{and } L_{z_{\max}} = \hbar$$

So when an atom absorbs or emits a single photon, its angular momentum must change by 1 $\hbar$, by Conservation of Angular Momentum, so the orbital angular momentum quantum number ℓ must change by 1.

"Selection Rule": $\Delta\ell = \pm 1$ in any process involving emission or absorption of 1 photon => allowed transitions are:



If an H-atom is in state 2s (n = 2, ℓ = 0) then it cannot de-excite to ground state by emission of a photon. (since this would violate the selection rule). It can only lose its energy (de-excite) by collision with another atom or via a rare 2-photon process.