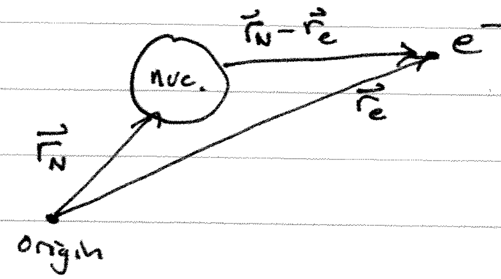
Hydrogen Atom



m_e is much less than even the smallest nucleus

$m_p \approx 1823\ m_e$

$q_e = -1.602 \times 10^{-19} C = -e$

$q_n = {+Ze}$

Z nuclear charge

$$V = \frac{-Ze^2}{4\pi\varepsilon_0 |\vec{r}_N - \vec{r}_e|}$$

$$\hat{H}_{total} = \frac{-\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_N - \vec{r}_e|}$$

This is a problem with 6 degrees of freedom all coupled via the potential term.
However if we use <u>center-of-mass</u> and <u>relative</u> coordinates it becomes 2 less difficult problems.

$$\vec{R} = \frac{m_N \vec{r}_N + m_e \vec{r}_e}{m_N + m_e} \longleftarrow \text{center of mass}$$

$$\vec{r} = \vec{r}_N - \vec{r}_e \longleftarrow \text{relative coordinate}$$

$$\left.\begin{aligned} \vec{r}_N &= \vec{R} + \frac{m_e}{m_N + m_e}\vec{r} \\ \vec{r}_e &= \vec{R} - \frac{m_N}{m_N + m_e}\vec{r} \end{aligned}\right\} \longrightarrow$$

Lets us go back to particle coords.

$$T = \frac{1}{2} m_N |\dot{\vec{r}}_N|^2 + \frac{1}{2} m_e |\dot{\vec{r}}_e|^2$$

Not difficult to prove:

$$= \frac{1}{2}(m_N + m_e)|\dot{\vec{R}}|^2 + \frac{1}{2}\frac{m_N m_e}{m_N + m_e}|\dot{\vec{r}}|^2$$

$$= \frac{1}{2} M |\dot{\vec{R}}|^2 + \frac{1}{2}\mu|\dot{\vec{r}}|^2$$

The kinetic energy, T, is therefore separable into components dealing with center-of-mass <u>translation</u> and <u>relative</u> motion

$r \leftarrow$ distance $\rightarrow$ vibration

$\vec{r} \rightarrow$ direction $\rightarrow$ rotation

$$T = \frac{|\vec{P}|^2}{2M} + \frac{|\vec{p}|^2}{2\mu} \qquad V = \frac{-Ze^2}{4\pi\varepsilon_0 |\vec{r}|}$$

$$\hat{H}_{total} = \underset{\text{3 translations}}{\underset{\Uparrow}{\frac{\hat{P}^2}{2M}}} + \underbrace{\left[\frac{\hat{p}^2}{2\mu} + V(\vec{r})\right]}_{\text{2 rotations + 1 vibration}} = \hat{H}_M + \hat{H}_\mu$$

Overall:

$$(\hat{H}_M + \hat{H}_\mu)\Phi(\vec{R})\psi(\vec{r}) = (E_M + E_\mu)\Phi(\vec{R})\psi(\vec{r})$$

$$E_M = \frac{\hbar^2 |\vec{k}|^2}{2M} \qquad \underbrace{\Phi(\vec{R}) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{R}}}_{\text{Free particle in 3D}}$$

$\vec{k}$ is related to the momentum vector for the atom ($\vec{p} = \hbar\vec{k}$)

$$\left[\frac{\vec{p}}{2\mu} + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \quad \longleftarrow \text{interesting behavior of atoms}$$

(This treatment can be done for 2 particles: as a 2-particle rigid rotator with $V(\vec{r}) = 0$

(Or as $V(r) = \dfrac{-Ze^2}{4\pi\varepsilon_0 |\vec{r}|} \longrightarrow$ H atom)

The relative problem:

$$\hat{H} = \frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r} \quad \Rightarrow \quad \hat{H}\psi = E\psi$$

$$\psi(r,\theta,\phi) = R(r)\,Y_\ell^m(\theta,\phi) \quad \longleftarrow \text{why?}$$

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

Rearrange SE a bit:

$$\underbrace{-\hbar^2\left(\frac{\partial}{\partial r}r^2\frac{\partial\psi}{\partial r}\right)}_{\text{only } r \text{ dependence}} \underbrace{-\hbar^2\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]}_{\text{only } \theta,\phi \text{ dependence}} \underbrace{-2\mu r^2\left[\frac{e^2Z}{4\pi\varepsilon_0 r} - E\right]}_{\text{only } r}$$

$$= 0$$

Also: that middle term is $= \hat{L}^2$

$$-\hbar^2\left(\frac{\partial}{\partial r}r^2\frac{\partial\psi}{\partial r}\right) - \hat{L}^2\psi - 2\mu r^2\left[\frac{e^2Z}{4\pi\varepsilon_0 r} - E\right]\psi = 0$$

We <u>know</u> that if we pick $\psi(r,\theta,\phi) = R(r)Y_\ell^m(\theta,\phi)$

$$\hat{L}^2\psi = R(r)\,\hat{L}^2Y_\ell^m(\theta,\phi) = R(r)\,\ell(\ell+1)\hbar^2\,Y_\ell^m(\theta,\phi)$$

$$\hat{L}\psi = \ell(\ell+1)\hbar^2\psi$$

Likewise, the $\frac{\partial}{\partial r}$ terms leave the angular functions <u>alone</u>, so we can separate these terms

$$-\hbar^2\left(\frac{\partial}{\partial r}r^2\frac{\partial R(r)}{\partial r}\right)Y_\ell^m - \hbar^2\ell(\ell+1)R(r)Y_\ell^m - 2\mu r^2\left(\frac{e^2Z}{4\pi\varepsilon_0 r} - E\right)RY_\ell^m$$

$$= 0$$

If we divide through by Y_l^m, we get an equation for the radial wave function:

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + \frac{\hbar^2 l(l+1)}{2\mu r^2}R - \frac{Ze^2}{4\pi\varepsilon_0 r}R = ER$$

$$a = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2} = \text{Bohr Radius (units of length)} = \begin{cases} 5.29177\times10^{-11}\,\text{m} \\ 0.529177\,\text{Å} \end{cases}$$

(if $\mu = m_e$)

Multiply both sides by $\frac{2(4\pi\varepsilon_0)}{a e^2}$

$$\underbrace{\left(-\frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2 a}\right)}_{=1}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + \underbrace{\frac{\hbar^2(4\pi\varepsilon_0)}{\mu e^2 a}}_{=1}\frac{l(l+1)}{r^2}R$$

$$-\frac{Z\cancel{e^2}}{\cancel{4\pi\varepsilon_0}}\frac{2\cancel{(4\pi\varepsilon_0)}}{a\cancel{e^2}}\frac{1}{r}R = \underbrace{\frac{2(4\pi\varepsilon_0)}{ae^2}E}_{\text{move to other side}} R(r)$$

$$\frac{d^2R(r)}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{2(4\pi\varepsilon_0)}{ae^2}E + \frac{2Z}{ra} - \frac{l(l+1)}{r^2}\right]R(r) = 0$$

Solutions to this equation

$$R_{nl}(r) = \underbrace{-\left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2}\left(\frac{2}{na}\right)^{l+3/2}}_{\text{Normalization}} \underbrace{r^l}_{} \underbrace{e^{-r/na}}_{\text{asymptotic behavior}} \underbrace{L_{n+l}^{2l+1}\left(\frac{2r}{na}\right)}_{\text{associated Laguerre polynomials}}$$

$R(0) \neq 0$ only for $l=0$

$L_{n+l}^{2l+1}\left(\frac{2r}{na}\right)$ = associated Laguerre polynomials

$$L_n^{\alpha}(x) = \frac{x^{-\alpha}e^{x}}{n!}\frac{d^n}{dx^n}e^{-x}x^{n+\alpha}$$

Conditions on n & l:

$n = 1, 2, 3, \ldots$ ($n=0$ is not allowed)

$n \geq l+1$ or ($l = 0, \ldots, n-1$)

n = principal quantum number

$n=1$ $\quad l=0$ $\quad L_1^1(x) = -1$ $\quad x = \frac{2r}{a}$

$n=2$ $\quad l=0$ $\quad L_2^1(x) = -2!(2-x)$ $\quad x = \frac{r}{a}$

$\quad l=1$ $\quad L_3^3(x) = -3!$

$n=3$ $\quad l=0$ $\quad L_3^1(x) = 3!(3-3x+\frac{1}{2}x^2)$ $\quad x = \frac{2r}{3a}$

$\quad l=1$ $\quad L_4^3(x) = 4!(4-x)$

$\quad l=2$ $\quad L_5^5(x) = 5!$

Energy levels depend only on n:

$$E_n = \frac{-\mu e^4 Z^2}{8\varepsilon_0 h^2 n^2} = \frac{-e^2 Z^2}{8\pi\varepsilon_0 a n^2}$$

$$\hat{H}\psi_{nlm}(r,\theta,\phi) = E_n \psi_{nlm}(r,\theta,\phi)$$

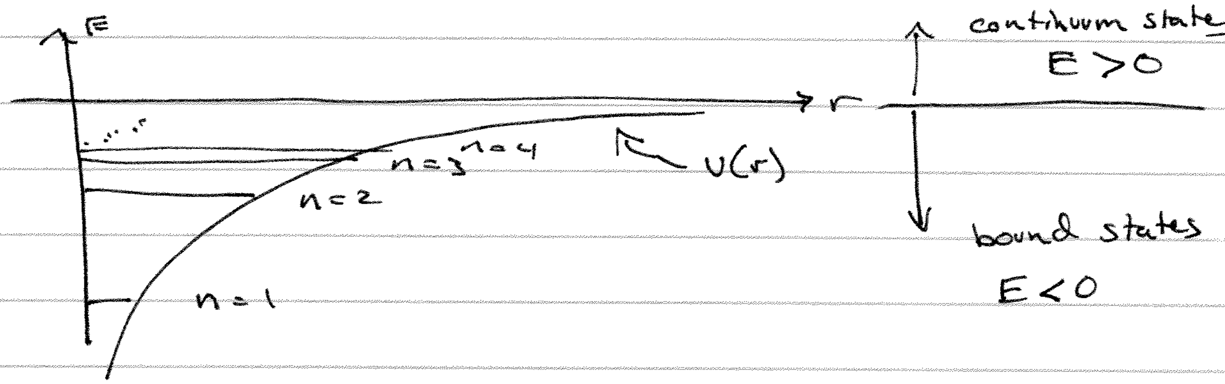
$$\hat{L}^2\psi_{nlm}(r,\theta,\phi) = \hbar^2 l(l+1)\psi_{nlm}(r,\theta,\phi)$$

$$\hat{L}_z\psi_{nlm}(r,\theta,\phi) = \hbar m\,\psi_{nlm}(r,\theta,\phi)$$

$n = 1, 2, \ldots$ principal QN

$l = 0, 1, \ldots, n-1$ angular momentum QN

$m = -l, \ldots 0, \ldots +l$ magnetic QN



Hydrogen Atom is a central force problem

V(r) depends only on r (Distance of particle from origin) V does not depend on θ or ϕ

$$\therefore \frac{\partial V}{\partial \theta} = \frac{\partial V}{\partial \phi} = 0$$

$$\vec{F} = -\vec{\nabla} V(x,y,z) = -\frac{\partial V}{\partial x}\hat{i} - \frac{\partial V}{\partial y}\hat{j} - \frac{\partial V}{\partial z}\hat{k}$$

$$\frac{\partial V}{\partial x} = \frac{\partial V}{\partial r}\frac{\partial r}{\partial x} + \underbrace{\frac{\partial V}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial V}{\partial \phi}\frac{\partial \phi}{\partial x}}_{\text{All of these terms are } 0!}$$

$$= \frac{\partial V}{\partial r}\frac{\partial r}{\partial x}$$

Since $r^2 = x^2 + y^2 + z^2$

$$2r\,dr = 2x\,dx \longrightarrow \frac{dr}{dx} = \frac{x}{r}$$

$\therefore$

$$\frac{\partial V}{\partial x} = \frac{\partial V}{\partial r}\frac{x}{r} \quad \text{likewise} \quad \frac{\partial V}{\partial y} = \frac{\partial V}{\partial r}\frac{y}{r} \quad \text{and} \quad \frac{\partial V}{\partial z} = \frac{\partial V}{\partial r}\frac{z}{r}$$

$$\vec{F} = -\frac{\partial V}{\partial r}\frac{x}{r}\hat{i} - \frac{\partial V}{\partial r}\frac{y}{r}\hat{j} - \frac{\partial V}{\partial r}\frac{z}{r}\hat{k}$$

$$= -\frac{\partial V}{\partial r}\frac{1}{r}\left(x\hat{i} + y\hat{j} + z\hat{k}\right) = -\frac{\partial V}{\partial r}\frac{1}{r}\vec{r}$$

$$= -\frac{\partial V}{\partial r}\hat{r} \leftarrow \text{unit vector pointing along } \vec{r}$$

A central force is radially-directed.

QM of a single particle subjected to a central force.

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(r)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

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

In spherical coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

∇^2 can also be expressed in terms of $\hat{L}^2$

$$\frac{-\hat{L}^2}{\hbar^2} = \frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2\hbar^2}\hat{L}^2$$

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

Can we simultaneously measure the energy and angular momentum of a particle subjected to a central force?

$$[\hat{H}, \hat{L}^2] = ?$$

$$= [T, \hat{L}^2] + \cancelto{0}{[\hat{V}, \hat{L}^2]}$$

$\hat{L}^2$ depends only on θ, ϕ

$\hat{V}$ depends only on r

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

$$= \cancelto{0}{\left[\underbrace{\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)}_{\text{depends only on } r}, \underbrace{\hat{L}^2}_{\text{depends only on } \theta,\phi}\right]} + \cancelto{0}{\left[\underbrace{\frac{1}{2mr^2}}_{\text{depends only on } r}\hat{L}^2, \hat{L}^2\right]}$$

and $\hat{L}^2$ commutes with itself

$$= 0$$

Like wise

$$[\hat{H}, \hat{L}_z] = 0 \quad \text{because } \hat{L}_z \text{ depends on } \phi \text{ only}$$
$$\text{and } [\hat{L}^2, \hat{L}_z] = 0$$

$\hat{H}, \hat{L}^2, \hat{L}_z$ share common eigenfunctions, ψ

$$\hat{H}\psi = E\psi$$
$$\hat{L}^2\psi = \hbar^2 l(l+1)\psi \qquad l = 0, 1, 2, \ldots$$
$$\hat{L}_z\psi = m\hbar\psi \qquad m = 0, \pm 1, \pm 2, \ldots \pm l$$

So:

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

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

$$\psi(r,\theta,\phi) = R(r)\overbrace{Y_l^m(\theta,\phi)}^{\text{spherical harmonics}}$$

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)R(r)Y_l^m(\theta,\phi) + \frac{l(l+1)\hbar^2}{2mr^2}R(r)Y_l^m(\theta,\phi)$$
$$+ V(r)R(r)Y_l^m(\theta,\phi) = ER(r)Y_l^m(\theta,\phi)$$

Since none of the remaining operators depend on θ or ϕ we can safely divide both sides by $Y_l^m(\theta,\phi)$

$$\frac{-\hbar^2}{2m}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + \frac{l(l+1)}{2mr^2}R(r) + V(r)R(r) = ER(r)$$

So far $V(r)$ has not been specified, only that it is a <u>central</u> force that depends only on r, (not θ, ϕ).

Before break, we talked about mapping a 2-body problem onto a <u>center-of-mass translational</u> problem and a <u>relative</u> <u>coordinate</u> problem

$$\hat{H} = \hat{T}_1 + \hat{T}_2 + V(|\vec{r}_2 - \vec{r}_1|)$$

$\vec{r}$ is the <u>relative</u> vector between the 2 particles.

$$\hat{H} = \hat{T}_M + \hat{T}_\mu + V(\vec{r})$$

$$= \frac{\hat{P}_M^2}{2M} + \left[\frac{\hat{P}_\mu^2}{2\mu} + V(\vec{r})\right]$$

$$= \hat{H}_M + \hat{H}_\mu$$

relative wavefunction

$$\Psi = \Phi(\vec{R})\,\psi(\vec{r})$$

total center of mass wavefunction

$$\hat{H}_M \Psi = E_M \Psi \qquad \underbrace{E_M = \frac{\hbar^2 |\vec{k}^2|}{2M} \qquad \Phi(\vec{R}) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{R}}}_{\text{free particle in 3D}}$$

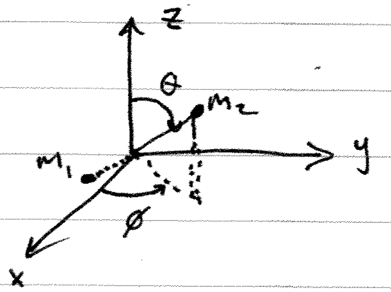
We're <u>really</u> interested in the relative problem,

$$\left[\frac{\hat{P}_\mu^2}{2\mu} + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r})$$

If $V(r) = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r_{12}}$, we've got the H atom

If r is held <u>fixed</u>, we've got the rigid rotator.

2 particle rigid rotator:



$$\vec{r} = |\vec{r}_1 - \vec{r}_2| = d = \text{fixed}$$

$$V(r, \theta, \phi) = 0$$

$$\hat{H} = \frac{\hat{p}_\mu^{\,2}}{2\mu} = \frac{-\hbar^2}{2\mu}\nabla^2$$

$$= \frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2}$$

r is held fixed at d, so we can ignore all $\frac{\partial}{\partial r}$ terms in the Hamiltonian:

$$\hat{H} = \frac{1}{2\mu d^2}\hat{L}^2$$

$$\hat{H}\psi = E\psi$$

$$\frac{1}{2\mu d^2}\hat{L}^2\psi = E\psi$$

$$\hat{L}^2\psi = 2\mu d^2 E\psi$$

$$\psi = Y_J^m(\theta, \phi)$$

typical to use J instead of l to describe rigid rotor.

$$\hat{L}^2 Y_J^m(\theta,\phi) = \hbar^2 J(J+1)\, Y_J^m(\theta,\phi)$$

$$= 2\mu d^2 E\, Y_J^m(\theta,\phi)$$

$$\therefore \quad 2\mu d^2 E = \hbar^2 J(J+1)$$

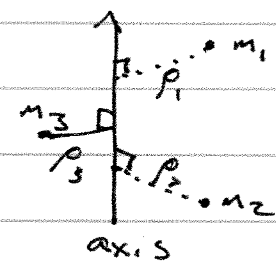
$$E_J = \frac{\hbar^2 J(J+1)}{2\mu d^2} \qquad J = 0, 1, 2, \ldots$$

Energies don't depend on m

each level is $2J+1$ degenerate

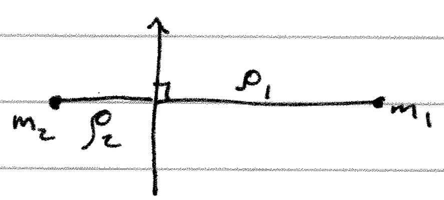
Moment of inertia.

$$I = \sum_{i=1}^{N} m_i \rho_i^2$$



$\rho_i = \perp$ distance from m_1 to the axis

for a diatomic molecule: (center of mass at origin)



$$-m_1\rho_1 + m_2\rho_2 = 0$$

$$m_1\rho_1 = m_2\rho_2$$

$$I = m_1\rho_1^2 + m_2\rho_2^2 = \mu d^2$$

$$\mu d^2 = \frac{m_1 m_2}{m_1+m_2}(\rho_1+\rho_2)^2 = \frac{m_1 m_2}{m_1+m_2}\left(\rho_1^2 + 2\rho_1\rho_2 + \rho_2^2\right)$$

$$\rho_1\rho_2 = \frac{m_2}{m_1}\rho_2^2 \quad \text{or} \quad \rho_1\rho_2 = \frac{m_1}{m_2}\rho_1^2$$

$$2\rho_1\rho_2 = \frac{m_2}{m_1}\rho_2^2 + \frac{m_1}{m_2}\rho_1^2$$

$$\therefore \mu d^2 = \frac{m_1 m_2}{m_1+m_2}\left(\rho_1^2 + \frac{m_1}{m_2}\rho_1^2 + \rho_2^2 + \frac{m_2}{m_1}\rho_2^2\right)$$

$$= \frac{m_1 m_2}{m_1+m_2}\left(\frac{m_1+m_2}{m_2}\rho_1^2 + \frac{m_1+m_2}{m_1}\rho_2^2\right)$$

$$= m_1\rho_1^2 + m_2\rho_2^2$$

So:

$$\boxed{E_J = \frac{J(J+1)\hbar^2}{2I}}$$

$E_2 = 3\hbar^2/I$

$E_1 = \hbar^2/I$

$E_0 = 0$ no zero point energy (the molecule can be in a non-rotating state)

Selection Rules for pure rotational transitions

pure rotational transitions are typically in the microwave region of the spectrum (microwave ovens excite the rotations of H_2O which then collides & dissipates the rotational energy as heat)

$$\vec{M} = \langle Y_{J'}^{M'} | \hat{\mu} | Y_J^M \rangle$$

dipole operator

transition dipole moment; final rotational state; initial rotational state

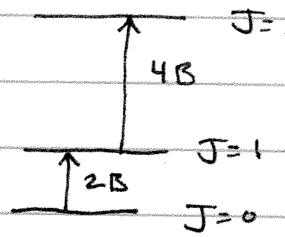
$$= \int Y_{J'}^{M'}(\theta,\phi)\, \hat{\mu}\, Y_J^M(\theta,\phi)\, d\theta\, d\phi$$

$$\hat{\mu} = \mu_x \hat{i} + \mu_y \hat{j} + \mu_z \hat{k} = \mu_0(\sin\theta\cos\phi\, \hat{i} + \sin\theta\sin\phi\, \hat{j} + \cos\theta\, \hat{k})$$

Cartesian components of molecular permanent dipole

<u>Rules for rotational transitions:</u>

1. Molecule must have permanent dipole ($\mu_0 \neq 0$)
2. $\Delta J = \pm 1$
3. $\Delta M = 0, \pm 1$



$$h\nu = E_{J+1} - E_J$$

$$= \frac{\hbar^2}{2I}\left((J+1)(J+2) - J(J+1)\right)$$

$$= \frac{h^2}{8\pi^2 I}\left[J^2 + 3J + 2 - J^2 - J\right]$$

$B = \frac{h}{8\pi^2 I}$ = rotational constant

$$\nu = \underbrace{\frac{h}{8\pi^2 I}}_{B}\left[2(J+1)\right] = 2(J+1)B$$

B is usually reported in frequency units [Hz or MHz] or sometimes in cm^{-1}

$$B\,[Hz] = \frac{h}{8\pi^2 I}$$

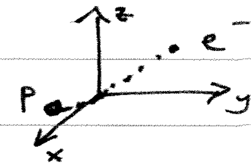
$$B\,[MHz] = \frac{h}{8\pi^2 I} \times 10^{-6}$$

$$B\,[cm^{-1}] = \frac{h}{8\pi^2 c I}$$

rotational spectra give us <u>structural</u> information:

$$B \rightarrow I \rightarrow d$$

Back to Hydrogenlike atoms:



$$\hat{H} = \underbrace{\frac{-\hbar^2}{2\mu}\nabla^2}_{\text{Kinetic part for relative motion of electron \& proton}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}}_{\text{potential energy}}$$

We solved this by using separation of variables:

$$\psi(r,\theta,\phi) = R(r)\,Y_\ell^m(\theta,\phi)$$

acts only on Y_ℓ^m

$$\hat{H}\psi = \left[\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\right] R(r)\,Y_\ell^m(\theta,\phi)$$

$$= \left[\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\right] R(r)\,Y_\ell^m(\theta,\phi) = E\psi$$

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

$$a_0 \equiv \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = \text{Bohr radius (units of length)} = 5.29177\times10^{-10}\,\text{m}$$

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{2(4\pi\varepsilon_0)}{a_0 e^2}E + \frac{2Z}{ra_0} - \frac{\ell(\ell+1)}{r^2}\right]R = 0$$

Solutions are associated Laguerre polynomials:

$$R_{n\ell}(r) = \underbrace{-\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2}}_{\text{normalization}} r^\ell \underbrace{e^{-r/na_0}}_{\text{asymptotic behavior}} \underbrace{L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right)}_{\text{associated Laguerre polynomials}}$$

only $\ell=0$ allows $R\neq0$ at origin!

$$L_n^{\alpha}(x) = \frac{x^{-\alpha}e^{x}}{n!}\frac{d^n}{dx^n}e^{-x}x^{n+\alpha}$$

Conditions on n & l:

$n = 1, 2, \ldots$ (positive integers, $n=0$ not allowed)

$n \geq l+1$ (or $l = 0, \ldots, n-1$)

n is principal quantum number

$n=1$ $\quad l=0 \quad L_1^1(x) = -1 \quad x = \frac{2r}{a_0}$

$n=2$ $\quad l=0 \quad L_2^1(x) = -2!(2-x) \quad x = \frac{r}{a_0}$

$\quad l=1 \quad L_3^3(x) = -3!$

$n=3$ $\quad l=0 \quad L_3^1(x) = 3!(3-3x+\frac{1}{2}x^2) \quad x = \frac{2r}{3a_0}$

$\quad l=1 \quad L_4^3(x) = 4!(4-x)$

$\quad l=2 \quad L_5^5(x) = 5!$

Energy levels $\sim -\frac{1}{n^2}$ and depend <u>only</u> on n

$$E_n = \frac{-\mu e^4 Z^2}{8\varepsilon_0 h^2 n^2} = \frac{-e^2Z^2}{8\pi\varepsilon_0 a_0 n^2}$$

$$\hat{H}\psi_{nlm}(r,\theta,\phi) = E_n\psi_{nlm}(r,\theta,\phi)$$

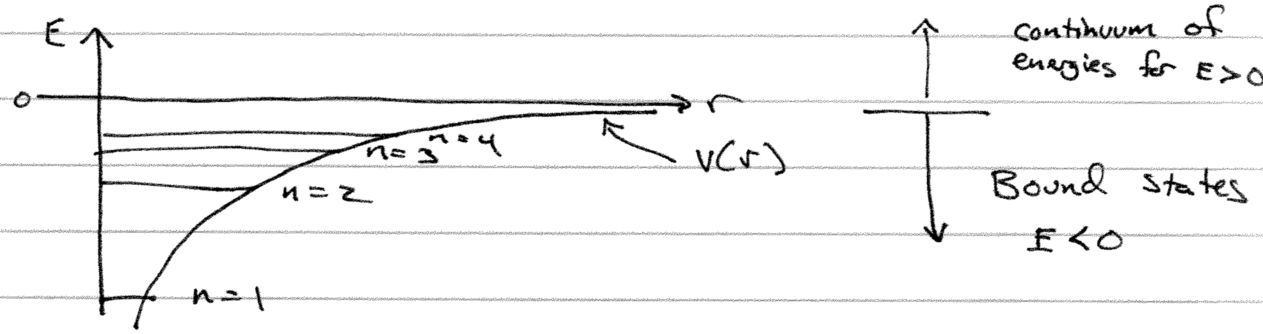
$$\hat{L}^2\psi_{nlm}(r,\theta,\phi) = \hbar^2 l(l+1)\psi_{nlm}(r,\theta,\phi)$$

$$\hat{L}_z\psi_{nlm}(r,\theta,\phi) = \hbar m\,\psi_{nlm}(r,\theta,\phi)$$

$n = 1, 2, \ldots$ principal Quantum number

$l = 0, 1, \ldots, n-1$ angular momentum Quantum number

$m = -l, \ldots, 0, \ldots l$ magnetic Quantum number



The complete wavefunctions: $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$

Suppose I was interested in the average distance between electron & nucleus: How would I calculate that?

$$\langle r \rangle_{nlm} = \int_{\substack{\text{all} \\ \text{space}}} \psi^*_{nlm}(r,\theta,\phi)\, r\, \psi_{nlm}(r,\theta,\phi)$$

$$= \int_0^\infty r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\ \psi^*_{nlm}(r,\theta,\phi)\, r\, \psi_{nlm}(r,\theta,\phi)$$

$$= \int_0^\infty r^3 R^*_{nl}(r) R_{nl}(r) dr \underbrace{\int_0^\pi \sin\theta \int_0^{2\pi} Y_l^m(\theta,\phi)^* Y_l^m(\theta,\phi) d\theta d\phi}_{Y_l^m \text{ are normalized already!}}$$

So:

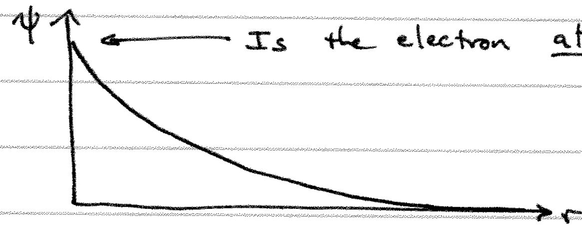
$$\langle r \rangle_{nlm} = \int_0^\infty r^3 |R_{nl}(r)|^2 dr$$

For 1s orbital: $R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$

$$\langle r \rangle_{100} = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} \, dr$$

$$= \frac{4}{a_0^3} \frac{3!}{(2/a_0)^4} = \frac{24 a_0^4}{16 a_0^3} = \frac{3}{2} a_0$$

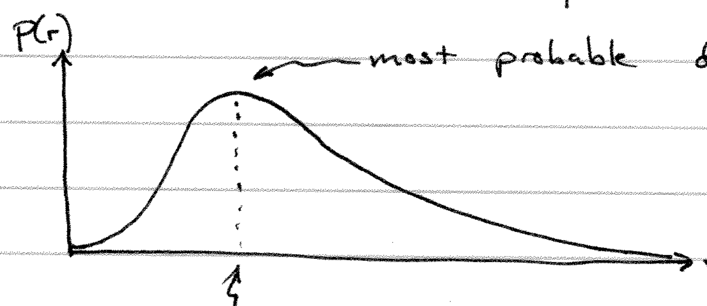
$$\psi_{1s}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0}$$ ← complete with Y_0^0



← Is the electron at the nucleus?

We can define a probability density for finding the electron between r & $r + dr$

$$P(r)dr = \underbrace{r^2}_{\text{why is this here?}} |R_{n\ell}(r)|^2 dr$$



← most probable distance

at this point $\frac{d}{dr} P(r) = 0$

For 1s:

$$P(r)dr = \frac{4}{a_0^3} r^2 e^{-2r/a_0} dr$$

$$\frac{d}{dr} P(r) = \left(\frac{8r}{a_0^3} - \frac{8r^2}{a_0^4} \right) \underbrace{e^{-2r/a_0}}_{\text{only 0 when } r \to \infty} = 0$$

$$\frac{8r}{a_0^3} - \frac{8r^2}{a_0^4} = 0 \longrightarrow r - \frac{r^2}{a_0} = 0$$

$$r^2 - a_0 r = 0$$

Roots are $r = 0, a_0$ ← maximum in $P(r)$

$r=0$ ← minimum in $P(r)$

So the **most** probable radius for $\psi_{1s} = a_0$

the *average* radius for $\psi_{1s} = \frac{3}{2} a_0$

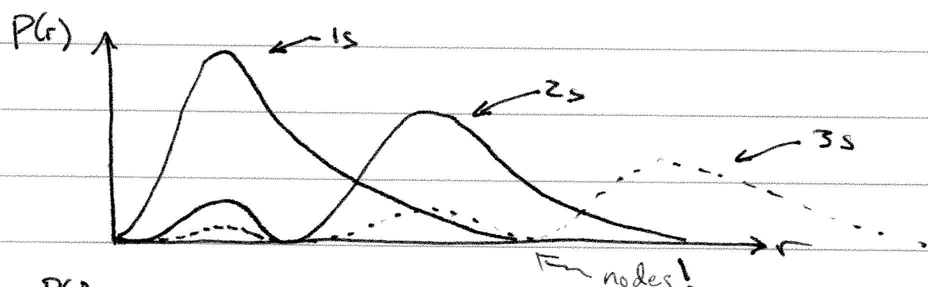
How would we find the probability for observing electron *inside* a_0?

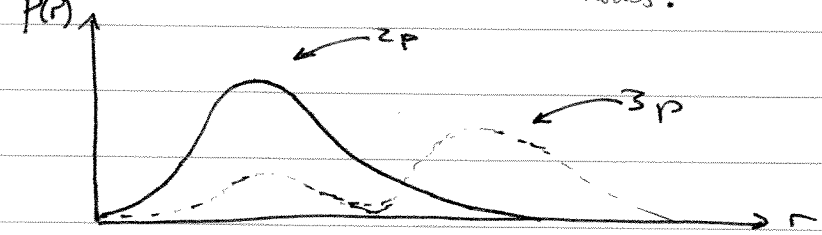
$$\int_0^{a_0} P(r)\,dr = \int_0^{a_0} \frac{4}{a_0^3} r^2 e^{-2r/a_0}\,dr$$

$$= 4 \int_0^1 x^2 e^{-2x}\,dx$$

$$= 1 - 5e^{-2} = 0.323$$

Other $P(r)$ functions are more complicated





So.... $\langle r \rangle_{2s} = \ ? = \int_0^{\infty} r^2 \int_0^{\pi} \sin\theta \int_0^{2\pi} \psi_{2s}^*(r,\theta,\phi)\, r\, \psi_{2s}(r,\theta,\phi)\, d\phi\, d\theta\, dr$

$$\psi_{2s} = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\langle r \rangle_{2s} = \frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3 \int_0^\infty r^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0} \underbrace{\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi}_{4\pi}$$

$$\langle r \rangle_{2s} = \frac{1}{8}\left(\frac{1}{a_0}\right)^3 \int_0^\infty r^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}\, dr = 6a_0$$

This <u>is</u> one of your problems!

Hybridization:

$$2p_0 = R_{20}(r)\, Y_1^0(\theta,\phi)$$

$$3p_0 = \underbrace{R_{31}(r)}_{\text{shell}}\ \underbrace{Y_1^0(\theta,\phi)}_{\text{orbital "shape"}}$$

"shape" of $p_1 = Y_1^1(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} \Rightarrow |Y_1^1|^2 = \frac{3}{8\pi}\sin^2\theta$

"shape" of $p_{-1} = Y_1^{-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} \Rightarrow \underbrace{|Y_1^{-1}|^2 = \frac{3}{8\pi}\sin^2\theta}_{\text{Fundamental p-orbital angular distribution.}}$

$$p_x = \frac{1}{\sqrt{2}}\left(p_1 + p_{-1}\right) = \sqrt{\frac{3}{8\pi}}\sin\theta\cos\phi$$

$$p_y = \frac{1}{i\sqrt{2}}\left(p_1 - p_{-1}\right) = \sqrt{\frac{3}{8}}\sin\theta\sin\phi$$
