Chemical Bond & Spectroscopy I
CHM 6470

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Class: **T R** 2-3 (8:30-10-25 am)
TUR 2341

Lectures 9-10
Hydrogen atom

- Coordinate system
- Bound vs. unbound states
- Complete eigenfunctions
- Radial distribution function
- Orbitals

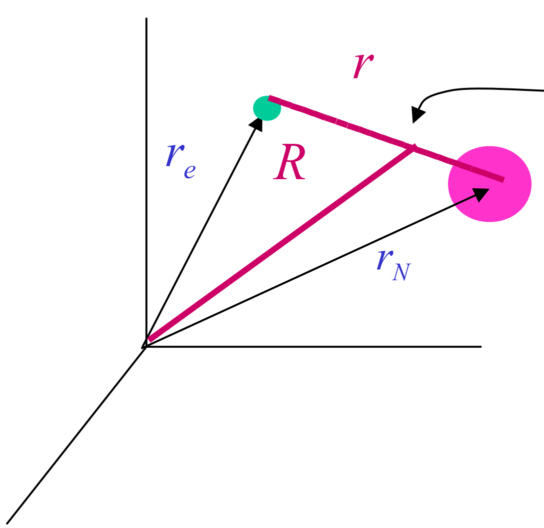
The Hydrogen atom (or ANY 2-particle system with and attractive coulombic potential)

1 nucleus ze^- charge + 1 electron with $1e^-$ charge

$$\Rightarrow \textit{Hamiltonian} \text{ must include } \begin{cases} \hat{T} \text{ electrons} & \dfrac{\hat{p}_e^2}{2m_e} \\ \hat{T} \text{ nucleus} & \dfrac{\hat{p}_N^2}{m_N} \\ \hat{V} \text{ energy for the } \pm \text{ interaction} & -\dfrac{ze^2}{4\pi\varepsilon_o r} \end{cases}$$

$$\hat{H} = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_N^2}{m_N} - \frac{ze^2}{4\pi\varepsilon_o r}$$

$3D$ for e^- x_e, y_e, z_e $+$ 3D for nucleus x_N, y_N, z_N



$$C.M. \Rightarrow \vec{R}M \equiv \sum_i \vec{r}_i m_i = \vec{r}_e m_e + \vec{r}_N m_N \quad \text{and using } \vec{r} = \vec{r}_e - \vec{r}_N$$

$$M = m_e + m_N$$

$$\vec{R} = \frac{\vec{r}_e m_e + (\vec{r}_e - \vec{r})\, m_N}{m_e + m_N} = \frac{\vec{r}_e (m_e + m_N)}{m_e + m_N} - \vec{r}\, \frac{m_N}{m_e + m_N}$$

Internal vs lab coordinates

$$\vec{R} = \vec{r}_e - \vec{r}\,\frac{m_N}{m_e + m_N} \qquad \vec{r}_e = \vec{R} + \vec{r}\,\frac{m_N}{m_e + m_N}$$

and $$\vec{R} = \vec{r}_N + \vec{r}\,\frac{m_e}{m_e + m_N} \qquad \vec{r}_N = \vec{R} - \vec{r}\,\frac{m_e}{m_e + m_N}$$

$$\underbrace{\vec{r}_e \ and\ \vec{r}_N}_{\substack{laboratory\\ coordinates}} = \underbrace{\vec{R}\ and\ \vec{r}}_{\substack{internal\\ coordinates}}$$

we can also write the momenta in *internal coordinates or lab coordinates*

$$p_n = m_N \frac{d\vec{r}_e}{dt} = m_N\left(\frac{d\vec{R}}{dt} - \frac{d\vec{r}}{dt}\,\frac{m_e}{m_e + m_N}\right)$$

$$p_e = m_e \frac{d\vec{r}_e}{dt} = m_e\left(\frac{d\vec{R}}{dt} + \frac{d\vec{r}}{dt}\,\frac{m_N}{m_e + m_N}\right)$$

and we can go back to the $\hat{H}$

$$\hat{H} = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_N^2}{m_N} - \frac{ze^2}{4\pi\varepsilon_o r} \quad \rightarrow \quad \hat{H} = \underbrace{\frac{1}{2} M \left|\frac{d\vec{R}}{dt}\right|^2}_{\substack{motion\ of\ the\\ Center\ of\ Mass}} \underbrace{+ \frac{1}{2}\mu\left|\frac{d\vec{r}}{dt}\right|^2 - \frac{ze^2}{4\pi\varepsilon_o r}}_{\substack{motion\ and\ interaction\\ relative\ to\ each\ other}}$$

Separation of variables

$$\hat{H} = \frac{1}{2} M \left| \frac{d\vec{R}}{dt} \right|^2 + \frac{1}{2}\mu \left| \frac{d\vec{r}}{dt} \right|^2 - \frac{ze^2}{4\pi\varepsilon_o r} \quad \xrightarrow{\text{C.M. to Q.M.}} \quad \underbrace{\frac{-\hbar^2}{2M}\nabla_R^2}_{f(R)} - \underbrace{\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{ze^2}{4\pi\varepsilon_o r}}_{f'(r)}$$

we propose $\Psi\left(\vec{R},\vec{r}\right) = \chi\left(\vec{R}\right)\psi\left(\vec{r}\right) \qquad \rightarrow \qquad \varepsilon = W + E$

$$\hat{H}\chi\left(\vec{R}\right)\psi\left(\vec{r}\right) = \frac{-\hbar^2}{2M}\nabla_R^2\chi\left(\vec{R}\right)\psi\left(\vec{r}\right) - \frac{\hbar^2}{2\mu}\nabla_r^2\chi\left(\vec{R}\right)\psi\left(\vec{r}\right) - \frac{ze^2}{4\pi\varepsilon_o r}\chi\left(\vec{R}\right)\psi\left(\vec{r}\right)$$

$$\frac{\psi\left(\vec{r}\right)}{\chi\left(\vec{R}\right)\psi\left(\vec{r}\right)}\frac{-\hbar^2}{2M}\nabla_R^2\chi\left(\vec{R}\right) - \frac{\chi\left(\vec{R}\right)}{\chi\left(\vec{R}\right)\psi\left(\vec{r}\right)}\frac{\hbar^2}{2\mu}\nabla_r^2\psi\left(\vec{r}\right) - \frac{\chi\left(\vec{R}\right)}{\chi\left(\vec{R}\right)\psi\left(\vec{r}\right)}\frac{ze^2}{4\pi\varepsilon_o r}\psi\left(\vec{r}\right)$$

$$\underbrace{\frac{-\hbar^2}{2M}\nabla_R^2\chi\left(\vec{R}\right) = W\chi\left(\vec{R}\right)}_{Schrödinger\ eq.\ of\ the\ CM} \qquad \underbrace{-\frac{\hbar^2}{2\mu}\nabla_r^2\psi\left(\vec{r}\right) - \frac{ze^2}{4\pi\varepsilon_o r}\psi\left(\vec{r}\right) = E\psi\left(\vec{r}\right)}_{Schrödinger\ eq.\ of\ the\ relative\ motion}$$

$\Downarrow$

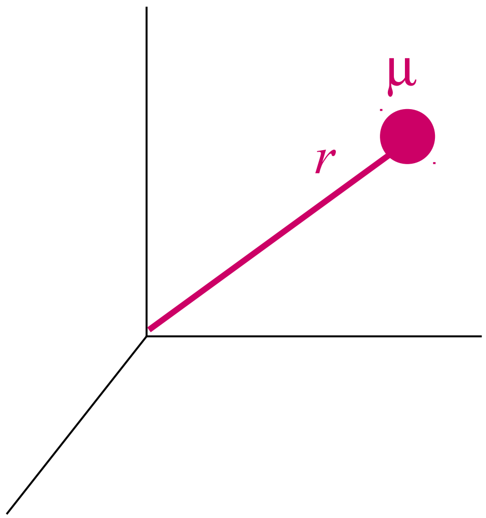
free particle motion

$\Downarrow$

the atom moves freely in space

the $\chi\left(\vec{R}\right) \sim e^{i\vec{k}R}$ $\qquad k^2 = \frac{2MW}{\hbar^2}$ solution only contributes a phase factor to $\Psi\left(R,r\right)$

Particle in a centrosymmetric potential



$$\underbrace{-\frac{\hbar^2}{2\mu}\nabla_r^2\psi(\vec{r}) - \frac{ze^2}{4\pi\varepsilon_o r}\psi(\vec{r}) = E\psi(\vec{r})}_{\textit{Schrödinger eq. of the relative motion}}$$

Since this is a centrosymmetric potential $V(r,\theta,\phi)=V(r)$,

we want to write the equation in spherical coordinates and

propose $\psi(r,\theta,\phi)=R(r)\,Y(\theta,\phi)$

$$\left(\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\Lambda^2\right)-\frac{ze^2}{4\pi\varepsilon_o r}\right)R(r)\,Y(\theta,\phi)=E R(r)\,Y(\theta,\phi)$$

$$\frac{1}{R(r)}\left(r^2\frac{\partial^2}{\partial r^2}+2r\frac{\partial}{\partial r}+\frac{2\mu r z e^2}{4\pi\varepsilon_o\hbar^2}\right)R(r)+\frac{1}{Y(\theta,\phi)}\Lambda^2 Y(\theta,\phi)=\frac{-2\mu E}{\hbar^2}r^2$$

$$\left(r^2\frac{\partial^2}{\partial r^2}+2r\frac{\partial}{\partial r}+\frac{2\mu r z e^2}{4\pi\varepsilon_o\hbar^2}\right)R(r)+\frac{2\mu E}{\hbar^2}r^2 R(r)=\text{constant}\;R(r)$$

$$\Lambda^2 Y(\theta,\phi)=\text{constant}\;Y(\theta,\phi)\quad\Rightarrow\quad\text{constant}=l(l+1)$$

$$\left(r^2\frac{\partial^2}{\partial r^2}+2r\frac{\partial}{\partial r}+\frac{2\mu rze^2}{4\pi\varepsilon_o\hbar^2}\right)R(r)+\frac{2\mu E}{\hbar^2}r^2R(r)=l(l+1)\ R(r)$$

$$\text{x}\ \frac{1}{r^2}\qquad \boxed{\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)R(r)+\left(\frac{2\mu E}{\hbar^2}-\frac{l(l+1)}{r^2}+\frac{2\mu ze^2}{4\pi\varepsilon_o\hbar^2 r}\right)R(r)=0}$$

RADIAL EQUATION for H-like ATOMS

there are solution for $E \lesseqgtr 0$ $\boxed{E<0}$

$$\alpha^2=\frac{-2\mu E}{\hbar^2},\ \lambda=\frac{\mu ze^2}{4\pi\varepsilon_o\hbar^2\alpha}\quad\Rightarrow\quad\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)R(r)+\left(-\alpha^2-\frac{l(l+1)}{r^2}+\frac{2\lambda\alpha}{r}\right)R(r)=0$$

$$\rho=2\alpha r\quad\Rightarrow\qquad 4\alpha^2\left(\frac{\partial^2}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial}{\partial\rho}\right)S(\rho)+4\alpha^2\left(-\frac{1}{4}-\frac{l(l+1)}{\rho^2}+\frac{\lambda}{\rho}\right)S(\rho)=0$$

Boundary conditions $\rho\to\infty$ $\quad S(\rho)\to 0$ $\qquad 0\le\rho\le\infty$

Solution to $S(\rho)$

to solve this equation, we first look for the ASYMPTOTIC solution, and then using a polynomial method, we find ALL solutions

$$\left(\frac{\partial^2}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial}{\partial\rho}\right)S(\rho)+\left(-\frac{1}{4}-\frac{l(l+1)}{\rho^2}+\frac{\lambda}{\rho}\right)S(\rho)=0$$

for $\rho\to\infty$ the term $\frac{2}{\rho}\to 0$ and $\left(\frac{l(l+1)}{\rho^2}+\frac{\lambda}{\rho}\right)\to 0$ $\frac{\partial^2}{\partial\rho^2}S(\rho)-\frac{1}{4}S(\rho)=0$

which has an easy solution!

$S(\rho)=e^{\pm\frac{\rho}{2}}$ the $\oplus$ is not a good solution, because $S(\rho)\to\infty$ for $\rho\to\infty$

the complete solution will be $S(\rho)=e^{-\frac{\rho}{2}}\underbrace{F}_{polinomia}(\rho)$

$$\left(\frac{\partial^2}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial}{\partial\rho}\right)e^{-\frac{\rho}{2}}\underbrace{F}_{polinomia}(\rho)+\left(-\frac{1}{4}-\frac{l(l+1)}{\rho^2}+\frac{\lambda}{\rho}\right)e^{-\frac{\rho}{2}}\underbrace{F}_{polinomia}(\rho)=0$$

$$F''(\rho)+\left(\frac{2}{\rho}-1\right)F'(\rho)+\left(\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}-\frac{1}{\rho}\right)F(\rho)=0$$

this equation has problems for $\rho = 0$. The way to avoid them is by using $F(\rho) = \rho^l L(\rho)$

$$\rho L''(\rho) + \left[2(l+1) - \rho\right] L'(\rho) + (\lambda - l - 1) L(\rho) = 0$$

$L(\rho)$ is a power series on $\rho \Rightarrow L(\rho) = b_0 + b_1\rho + b_2\rho^2 + b_3\rho^3 + \ldots + b_n\rho^n + \ldots$

$$L'(\rho) = b_1 + 2b_2\rho + b_3 3\rho^2 + \ldots + b_n n\rho^{n-1} + \ldots$$

$$L''(\rho) = 2b_2 + 6b_3\rho + \ldots + b_n n(n-1)\rho^{n-2} + \ldots$$

we replace $L(\rho)$, $L'(\rho)$, and $L''(\rho)$ and obtain a a polynomia on ρ which must be $= 0$

for this to hold, each coefficient must be =0 $\Rightarrow$ $C_0\rho^0 + C_1\rho^1 + C_2\rho^2 + \ldots + C_n\rho^n + \ldots = 0$

$$\left.\begin{array}{l} \{\rho^0\} \rightarrow (\lambda - l - 1) b_o + 2(l+1) b_1 = 0 \\ \{\rho^1\} \rightarrow (\lambda - l - 1 - 1) b_1 + \left[4(l+1) + 2\right] b_2 = 0 \\ \{\rho^2\} \rightarrow (\lambda - l - 1 - 2) b_2 + \left[6(l+1) + 6\right] b_3 = 0 \end{array}\right\}$$

a recursive relation for b_k

$$\boxed{b_{k+1} = f(\lambda, l, k) \times b_k}$$

for $F(\rho)$ not to diverge, the series must be truncated $\Rightarrow (\lambda - \underbrace{l}_{integer} - 1 - \underbrace{k}_{integer}) = 0$

$\Rightarrow \lambda$ must be in *integer*

$$\boxed{R_{n,l}(r) = e^{-\frac{\rho}{2}} \rho^l L(\rho) \quad \text{where} \quad n = k + l + 1}$$

All solutions

$$E < 0$$

BOUND STATES

$$R_{n,l}(r) = e^{-\frac{\rho}{2}} \rho^l L(\rho) \quad \text{where} \quad n = k + l + 1$$

$$\lambda = n = \frac{\mu z e^2}{4\pi\varepsilon_o \hbar^2 \alpha} \Rightarrow \alpha = \frac{\mu z e^2}{4\pi\varepsilon_o \hbar^2 n} \qquad \alpha^2 = \frac{-2\mu E}{\hbar^2} = \left(\frac{\mu z e^2}{4\pi\varepsilon_o \hbar^2 n} \right)^2$$

$$\boxed{E_n = -\frac{1}{2} \frac{\mu}{\hbar^2} \frac{z^2 e^4}{(4\pi\varepsilon_o)^2 n^2}}$$

$$E > 0$$

UNBOUND STATES

$$R(r) \sim e^{\pm i \frac{\sqrt{2\mu E} r}{\hbar}} \qquad (\text{solution for large } r)$$

$$E = 0$$

UNBOUND STATES

attraction between nucleus and electrons = $K.E.$

Ionization Energy?

the energy to remove an electron $\Rightarrow E_\infty - E_1 \qquad \sim \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) = -E_1$

Degeneracy of bound states

$n =$ principal quantum number $\quad 1,2,3,\ldots$

$l =$ spatial angular momentum (magnitude) $\quad 0,1,2,\ldots,n-1$

$m =$ magnetic angular mometum (orientation) $\quad -l,-l+1,\ldots,-1,0,1,\ldots,l-1,l$

$$\text{Since } E_n = -\frac{1}{n^2}\frac{\mu z^2 e^4}{2\hbar^2\left(4\pi\varepsilon_o\right)^2} \Rightarrow \text{there is DEGENERACY}$$

for a given n there are n^2 values of l, and for each value of l there are $2l+1$ values of m

n	1	2		3		
l	$0\left(s\right)$	$0\left(s\right)$	$1\left(p\right)$	$0\left(s\right)$	$1\left(p\right)$	$2\left(d\right)$
m	0	0	-1,0,1	0	-1,0,1	-2,-1,0,1,2
degeneracy	1	4		9		

notation: $\psi_{n,l,m}\left(r,\theta,\phi\right) \Rightarrow \textit{example} \quad \psi_{3,1,-1} = \psi_{3p_{-1}}$

Complete solutions

A complete derivation of the hydrogen atom wavefunctions is given on the following website:
http://physics.gmu.edu/~dmaria/590%20Web%20Page/public_html/qm_topics/hydrogen_atom/hydrogen_atom.htm

$$\Psi_{nlm}(r,\theta,\varphi)=R(r)\,Y(\theta,\varphi)$$

$$\Psi_{nlm}=\left(\frac{2z}{n a_0}\right)^{3/2}\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}\,e^{\frac{-z}{n a_0}r}\left(\frac{2zr}{n a_0}\right)^{l}L_{n-l-1}^{2l+1}\left(\frac{2zr}{n a_0}\right)Y_l^m(\theta,\varphi)$$

$$\rho=\frac{2zr}{n a_0}$$

$$L_{n-l-1}^{2l+1}(\rho)=\sum_{i=0}^{n-l-1}\frac{(-i)^i[(n+l)!]^2\rho^i}{i!(n-l-1-i)!(2l+1+i)!}$$

Associated Laguerre

For m >= 0

$$Y_l^m(\theta,\varphi)=(-1)^{|m|}\sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}\,e^{im\varphi}P_l^{|m|}(\cos\theta)$$

Spherical harmonics

$$P_l^{|m|}(\cos\theta)=(1-\cos^2(\theta))^{\left|\frac{m}{2}\right|}\frac{d^{|m|}P_l(\cos\theta)}{d(\cos\theta)^{|m|}}$$

Associated Legendre

Legendre

$$P_l(\cos\theta)\frac{1}{2^l l!}\frac{d^l(\cos^2\theta-1)^l}{d(\cos\theta)^l}$$

Solutions for hydrogen atom

For z = 1

The Hydrogen Atom:
Wave Functions,
Probability Density "pictures"

Table 1: Wave functions and their components

n	ℓ	m	$R_{n\ell}$	$Y_{\ell m}$	$\psi_{n\ell m} = R_{n\ell}\, Y_{\ell m}$
1	0	0	$2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	0	$\left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0} e^{-r/2a_0}\cos\theta$
2	1	± 1	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0} e^{-r/2a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{8}\sqrt{\frac{1}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0} e^{-r/2a_0}\sin\theta e^{\pm i\phi}$
3	0	0	$2\left(\frac{1}{3a_0}\right)^{3/2}\left(1-\frac{2}{3}\frac{r}{a_0}+\frac{2}{27}(r/a_0)^2\right) e^{-r/3a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(27-18\frac{r}{a_0}+2(r/a_0)^2\right) e^{-r/3a_0}$
3	1	0	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1-\frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\cos\theta$
3	1	± 1	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1-\frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\sin\theta e^{\pm i\phi}$
3	2	0	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\cos^2\theta-1\right)$	$\frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2} e^{-r/3a_0}\left(3\cos^2\theta-1\right)$

Probabilities

Since we know that we cannot *"pinpoint"* the position of the e - with full precision, can we at least predict the *Probability of finding it in a region in space?*

we look at the Probability in a unit volume delimited by $d\tau \begin{cases} r \rightarrow r + dr \\ \theta \rightarrow \theta + d\theta \\ \phi \rightarrow \phi + d\phi \end{cases}$

More important: *Probability of finding the e - at some distance d from the nucleus!*

is the probability of finding the $e-$ in the surface of a sphere of radius r.

$$P(r)\,dr = \int_0^{2\pi}\int_0^{\pi} R_{n,l}^2(r)\,Y_{l,m}^2(\theta,\phi)\,r^2 dr \sin\theta d\theta d\phi$$

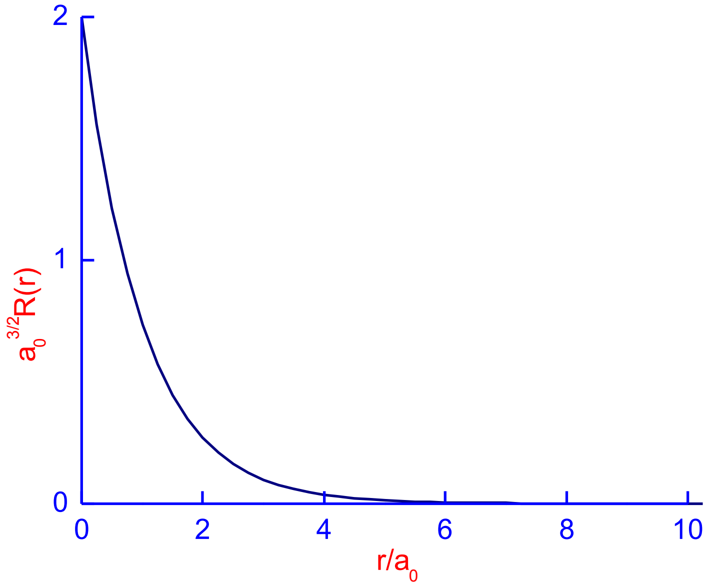
$$= R_{n,l}^2(r)\,r^2 dr \underbrace{\int_0^{2\pi}\int_0^{\pi} Y_{l,m}^2(\theta,\phi)\sin\theta d\theta d\phi}_{normalized\ function=1}$$

$P(r) = R_{n,l}^2(r)\,r^2$ *Radial Distribution Function*

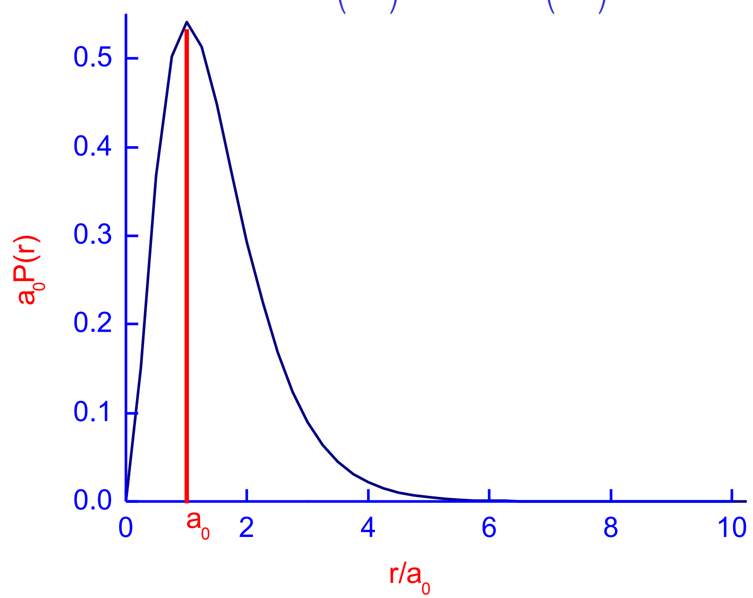
$P(r)\,dr$ corresponds to a shell of the sphere with thickness dr

$R(r)$ and $P(r)$ for $n=1$

$R\left(r\right)$



$P\left(r\right) = R^2\left(r\right) r^2$



Although $R_{1s} \neq 0$,

$P\left(0\right) dr = 0$ because the volume of the sphere is given by $r = 0$

The max of $P(r)$ is for $r = a_o$ (Bohr radius)

For atoms of $\neq$ nucleus charge z, the max. changes to smaller r,
in agreement with a larger attraction of the e - by the higher charge of the nucleus.

Expectation value

We know where the *max Probability* is, but what is the $\langle r \rangle$?

$$\langle r \rangle = \langle \psi_{1s} | r | \psi_{1s} \rangle \quad = \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} R_{1,0} Y_{0,0} \; r \, R_{1,0} Y_{0,0} r^2 \sin\theta dr d\theta d\phi$$

$$= \underbrace{\int_0^{\pi} \int_0^{2\pi} \left| Y_{0,0}{}^2 \right| \sin\theta d\theta d\phi}_{1} \int_0^{\infty} \left| R_{1,0} \right|^2 r^3 dr$$

$$= \int_0^{\infty} 2^2 \left(\frac{z}{a_o} \right)^3 e^{-\frac{z}{a_o} r} r^3 dr \quad = 2^2 \left(\frac{z}{a_o} \right)^3 \frac{3!}{\left(2 \frac{z}{a_o} \right)^4} \quad = \frac{3}{2} \frac{a_o}{z}$$

for H

$$\Rightarrow \langle r \rangle = \frac{3}{2} a_o > a_o = P_{\max}(r)$$

$R(r)$ and $P(r)$ for n=2 and n=3

$$R_{2,0}(r)=\frac{1}{\sqrt{2}}\left(\frac{z}{a_0}\right)^{\frac{3}{2}}\left(1-\frac{zr}{2a_0}\right)e^{\frac{-zr}{2a_0}}$$

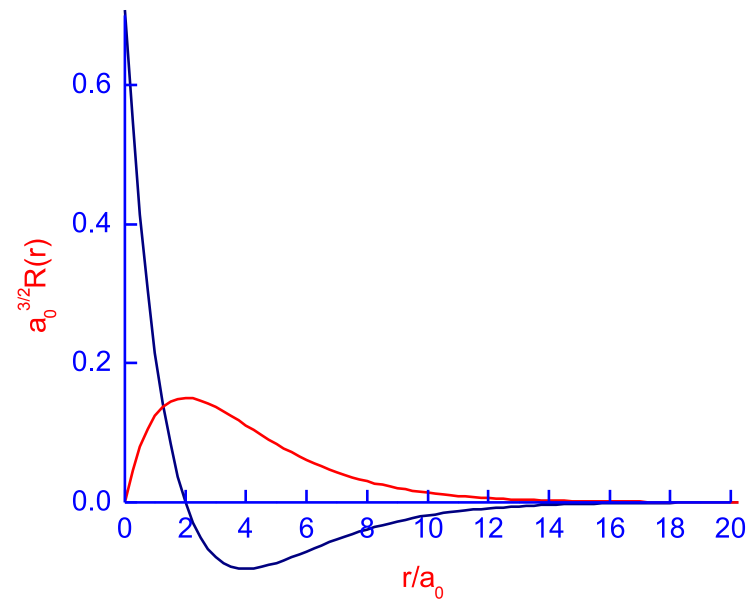
$$P(r)=R_{2,0}^2(r)r^2=\frac{1}{2}\left(\frac{z}{a_0}\right)^3\left(1-\frac{zr}{2a_0}\right)^2 e^{\frac{-zr}{a_0}}r^2$$

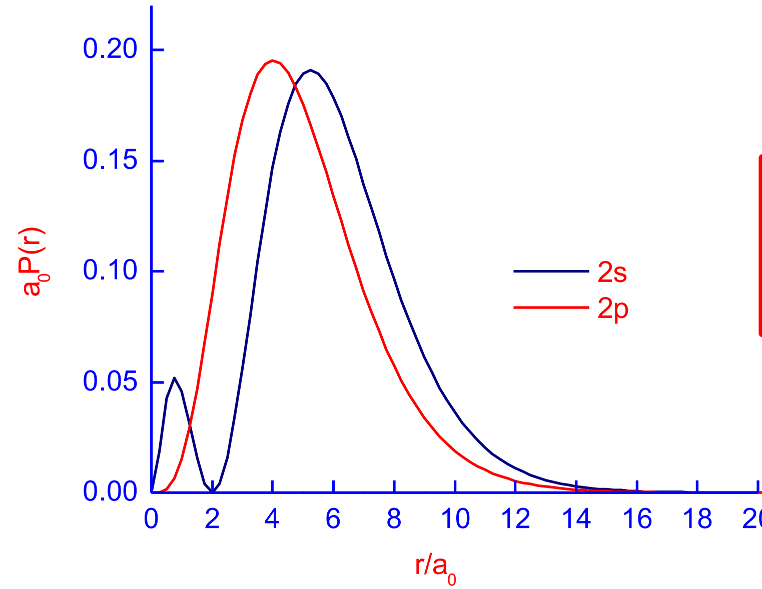
node

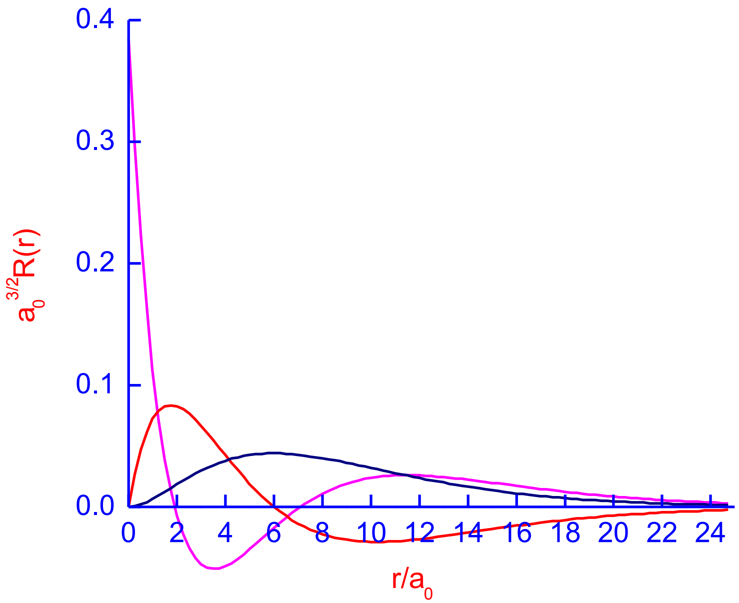
$1-(zr/(2\ a_0)) = 0$

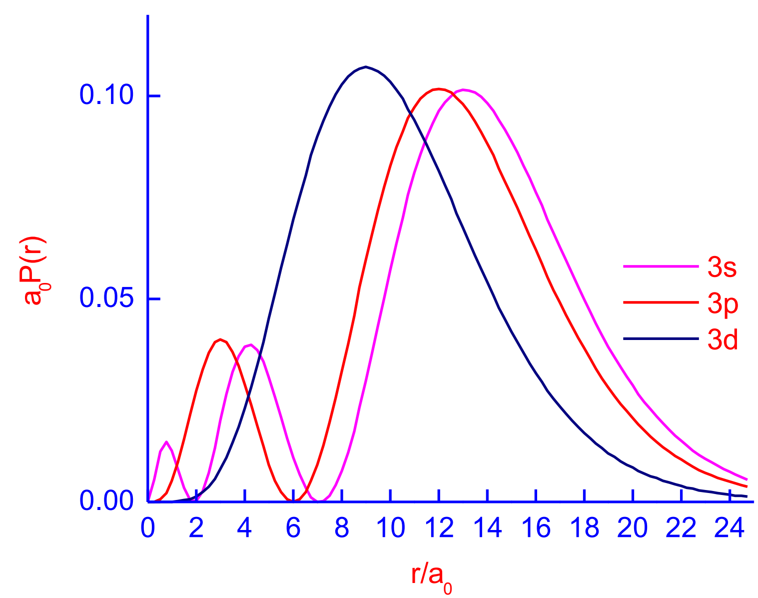
$\rightarrow r = 2\ a_0/r$

$R(r)$









Angular Components $2p$

for $n = 2$

$$H\psi_{2s} = E_{2s}\psi_{2s} \qquad E_{2s} = -R\frac{1}{4} \qquad \psi_{2s} = R_{2,0}Y_{0,0}$$

$$H\psi_{2p} = E\psi_{2p} \qquad E_{2s} = -R\frac{1}{4} \qquad \begin{cases} \psi_{2p} = R_{2,1}Y_{1,0} \\ \psi_{2p} = R_{2,1}Y_{1,-1} \\ \psi_{2p} = R_{2,1}Y_{1,+1} \end{cases}$$

if $\hat{A}\varphi_1 = a_1\varphi_1$ and $\hat{A}\varphi_2 = a_2\varphi_2$ and $a_1 = a_2$ $\Rightarrow c_1\varphi_1 + c_2\varphi_2$ is also an eigenfunction with the same eigenvalue a

$$\underbrace{H\psi_{2p-1} = -R\frac{1}{4}\psi_{2p-1} \qquad H\psi_{2p+1} = -R\frac{1}{4}\psi_{2p+1}}$$

$$H\varphi = H\left(c_1\psi_{2p-1} + c_2\psi_{2p+1}\right) = -R\frac{1}{4}\varphi$$

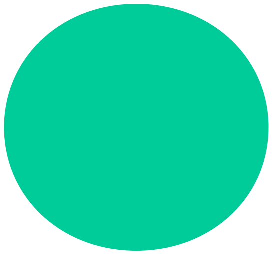
$$Y_{1,+1} = A\sin\theta e^{+i\phi} \qquad Y_{1,-1} = A\sin\theta e^{-i\phi}$$

$$\psi_{2px} = A're^{-\frac{z}{a_o}r}\sin\theta\left(e^{+i\phi} + e^{-i\phi}\right) = A'e^{-\frac{z}{a_o}r}\underbrace{r\sin\theta\cos\phi}_{x}$$

$$\psi_{2py} = A're^{-\frac{z}{a_o}r}\sin\theta\,(-i)\left(e^{+i\phi} - e^{-i\phi}\right) = A'e^{-\frac{z}{a_o}r}\underbrace{r\sin\theta\sin\phi}_{y}$$

Contour plots

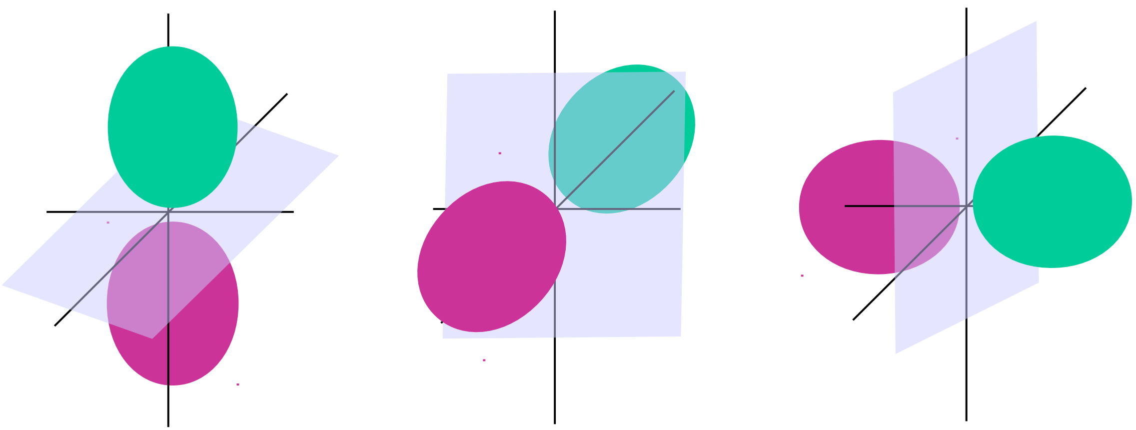
we plot constant $|\psi|^2$, and we choose all values of r such that $\int_0^r |\psi|^2 = 0.95$



$1s$ is a sphere

$2s$ is also a sphere but the wavefunction changes sign inside (1 node)

$3s$ is also a sphere but the wavefunction changes sign inside twice (2 nodes)



p_x, *node in yz plane*

p_y, *node in xz plane*

p_z, *node in xy plane*

$d_{x^2-y^2}$, *x and y axes*

d_{xy}, *xy plane*

d_{yz}, *yz plane*

d_{xz}, *xz plane*

d_{z^2} *z axes xy plane*