Chapter 7

The Hydrogen Atom

The only atom that can be solved exactly.
The results become the basis for understanding all other atoms and molecules.
Orbital Angular Momentum – Spherical Harmonics

Nucleus charge $+Ze$ mass m_1
coordinates x_1, y_1, z_1

Electron charge $-e$ mass m_2
coordinates x_2, y_2, z_2

The potential arises from the Coulomb interaction between the charged particles.

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{Ze^2}{4\pi\varepsilon_0\left[(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2\right]^{\frac{1}{2}}}$$

The Schrödinger equation for the hydrogen atom is

$$\frac{1}{m_1}\left(\frac{\partial^2\Psi_T}{\partial x_1^2}+\frac{\partial^2\Psi_T}{\partial y_1^2}+\frac{\partial^2\Psi_T}{\partial z_1^2}\right)+\frac{1}{m_e}\left(\frac{\partial^2\Psi_T}{\partial x_2^2}+\frac{\partial^2\Psi_T}{\partial y_2^2}+\frac{\partial^2\Psi_T}{\partial z_2^2}\right)+\frac{2}{\hbar^2}(E_T-V)\Psi_T=0$$

kinetic energy of nucleus

kinetic energy of electron

potential

energy eigenvalues

Can separate translational motion of the entire atom from relative motion of nucleus and electron.

Introduce new coordinates

x, y, z - center of mass coordinates

r, θ, φ - polar coordinates of second particle relative to the first

$$x = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$y = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2}$$

center of mass coordinates

$$z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

$$r \sin\theta \cos\varphi = x_2 - x_1$$

$$r \sin\theta \sin\varphi = y_2 - y_1$$

relative position – polar coordinates

$$r \cos\theta = z_2 - z_1 .$$

Substituting these into the Schrödinger equation. Change differential operators.

$$\frac{1}{m_1+m_2}\left(\frac{\partial^2\Psi_T}{\partial x^2}+\frac{\partial^2\Psi_T}{\partial y^2}+\frac{\partial^2\Psi_T}{\partial z^2}\right)+$$

This term only depends on center of mass coordinates.
Other terms only on relative coordinates.

$$\frac{1}{\mu}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi_T}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi_T}{\partial\varphi^2}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi_T}{\partial\theta}\right)\right\}+$$

$$\frac{2}{\hbar^2}[E_T-V(r,\theta,\varphi)]\Psi_T=0$$

$$\mu=\frac{m_1 m_2}{m_1+m_2}$$ reduced mass

Try solution

$$\Psi_T(x,y,z,r,\theta,\varphi)=F(x,y,z)\,\Psi(r,\theta,\varphi)$$

Substitute and divide by Ψ_T

Gives two independent equations

$$\frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} + \frac{\partial^2 F}{\partial z^2} + \frac{2(m_1 + m_2)}{\hbar^2} E_{Tr} F = 0$$

Depends only on center of mass coordinates. Translation of entire atom as free particle. Will not treat further.

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

$$+\frac{2\mu}{\hbar^2}[E - V(r,\theta,\varphi)]\Psi = 0$$

With $E_T = E_{Tr} + E$

Relative positions of particles. Internal "structure" of H atom.

In absence of external field $V = V(r)$

Try $\Psi(r,\theta,\varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$

Substitute this into the Ψ equation and dividing by $R\Theta\Phi$ yields

$$\frac{1}{Rr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\Phi r^2\sin^2\theta}\frac{d^2\Phi}{d\varphi^2}+\frac{1}{\Theta r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{8\pi^2\mu}{\hbar^2}[E-V(r)]=0$$

Multiply by $r^2\sin^2\theta$. Then second term only depends φ .

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{8\pi^2\mu r^2\sin^2\theta}{\hbar^2}[E-V(r)]=0$$

Therefore, it must be equal to a constant – call constant $-m^2$.

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m^2$$

and

$$\frac{d^2\Phi}{d\varphi^2}=-m^2\Phi$$

Dividing the remaining equation by $\sin^2\theta$ leaves

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{m^2}{\sin^2\theta}+\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2\mu r^2}{\hbar^2}\left(E-V(r)\right)=0$$

The second and third terms dependent only on *θ*.
The other terms depend only on *r*.

The *θ* terms are equal to a constant. Call it -*β*.

Multiplying by Θ and transposing -*β*Θ, yields

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2\Theta}{\sin^2\theta}+\beta\Theta=0$$

Replacing the second and third terms in the top equation by -*β* and multiplying by R/r^2 gives

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{\beta}{r^2}R+\frac{2\mu}{\hbar^2}\left\{E-V(r)\right\}R=0$$

The initial equation in 3 polar coordinates has been separated into three one dimensional equations.

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m^2\Theta}{\sin^2\theta} + \beta\Theta = 0$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\beta}{r^2}R + \frac{2\mu}{\hbar^2}\left\{E - V(r)\right\}R = 0$$

Solve Φ equation. Find it is good for only certain values of *m*.

Solve Θ equation. Find it is good for only certain values of β.

Solve *R* equation. Find it is good for only certain values of *E*.

Solutions of the Φ equation

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi$$

Second derivative equals function times negative constant. Solutions – sin and cos. But can also use

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

Must be single valued (Born conditions).

$\varphi = 0$ **and** $\varphi = 2\pi$ **are same point.**

For arbitrary value of *m*, $e^{im\varphi} \neq 1$ **for** $\varphi = 2\pi$ **but = 1 for** $\varphi = 0$**.**

$$e^{i2\pi} = \cos 2\pi + i \sin 2\pi = 1$$

$e^{in2\pi} = 1$ **if *n* is a positive or negative integer or 0.**

Therefore,

$$e^{im\varphi} = 1 \text{ if } \varphi = 0$$

$$e^{im\varphi} = 1 \text{ if } \varphi = 2\pi$$

and wavefunction is single valued only if *m* is a positive or negative integer or 0.

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

$$m = 0, \pm 1, \pm 2, \pm 3 \cdots$$

m **is called the magnetic quantum number.**

The functions having the same |*m*| can be added and subtracted to obtain real functions.

$$\Phi_0(\varphi) = \frac{1}{\sqrt{2\pi}} \qquad m = 0$$

$$\Phi_{|m|}(\varphi) = \frac{1}{\sqrt{\pi}} \cos|m|\varphi$$

$$|m| = 1, 2, 3 \cdots$$

$$\Phi_{|m|}(\varphi) = \frac{1}{\sqrt{\pi}} \sin|m|\varphi$$

The cos function is used for positive *m*'s and the sin function is used for negative *m*'s.

Solution of the Θ equation.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2\Theta}{\sin^2\theta}+\beta\Theta=0$$

Substitute $z=\cos\theta$ z varies between +1 and –1.

$$P(z)=\Theta(\theta) \quad \text{and} \quad \sin^2\theta=1-z^2$$

$$\frac{d\Theta}{d\theta}=\frac{dP}{dz}\frac{dz}{d\theta}=-\frac{dP}{dz}\sin\theta$$

$$dz=-\sin\theta\, d\theta$$

$$d\theta=-\frac{1}{\sin\theta}dz.$$

Making these substitutions yields

The differential equation in terms of *P*(*z*)

$$\frac{d}{dz}\left\{\left(1-z^2\right)\frac{dP(z)}{dz}\right\}+\left\{\beta-\frac{m^2}{1-z^2}\right\}P(z)=0.$$

This equation has a singularity. Blows up for $z = \pm 1$.

Singularity called Regular Point. Standard method for resolving singularity. The method shows how to find a substitution that eliminates the singularity without changing the final result.

Making the substitution

$$P(z)=(1-z^2)^{\frac{|m|}{2}}G(z)$$

removes the singularity and gives a new equation for *G*(*z*).

$$(1-z^2)G''-2(|m|+1)zG'+\left\{\beta-|m|(|m|+1)\right\}G=0$$

with

$$G'=\frac{dG}{dz} \qquad \text{and} \qquad G''=\frac{d^2G}{dz^2}$$

Use the polynomial method (like in solution to harmonic oscillator).

$$G(z) = a_0 + a_1 z + a_2 z^2 + a_3 z^3 + \cdots$$

G' **and** G'' **are found by term by term differentiation of** $G(z)$**.**

Like in the H. O. problem, the sum of all the terms with different powers of z **equals 0.**

Therefore, the coefficients of each power of z **must each be equal to 0.**

Let $D = \left\{\beta - |m|(|m|+1)\right\}$

Then

$\{z^0\}$ $2a_2 + Da_0 = 0$

$\{z^1\}$ $6a_3 + (D - 2(|m|+1))a_1 = 0$

$\{z^2\}$ $12a_4 + (D - 4(|m|+1) - 2)a_2 = 0$

$\{z^3\}$ $20a_5 + (D - 6(|m|+1) - 6)a_3 = 0$

$\vdots$ $\vdots$

odd and even series

Pick a_0 ($a_1 = 0$) **– get even terms.**
Pick a_1 ($a_0 = 0$) **– get odd terms.**
a_0 **and** a_1 **determined by normalization.**

The recursion formula is

$$a_{\nu+2} = \frac{(\nu + |m|)(\nu + |m| + 1) - \beta}{(\nu + 1)(\nu + 2)} a_\nu$$

Solution to differential equation, but not good wavefunction if infinite number of terms in series (like H. O.).

To break series off after ν' term

$$\beta = (\nu' + |m|)(\nu' + |m| + 1) \qquad \nu' = 0, 1, 2, \cdots$$

This quantizes β. The series is even or odd as ν' is even or odd.

Let

$$\ell = \nu' + |m| \qquad \ell = 0, 1, 2, 3, \cdots$$

Then

$$\beta = \ell(\ell + 1)$$

s, p, d, f orbitals

$$\Theta(\theta) = \left(1 - z^2\right)^{\frac{|m|}{2}} G(z)$$

$$\beta = \ell(\ell + 1)$$

$G(z)$ are defined by the recursion relation.

$$z = \cos\theta$$

$\Theta(\theta)$ are the associated Legendre functions

Since $\beta = \ell(\ell+1)$, we have

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

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

The potential only enters into the $R(r)$ equation. Z is the charge on the nucleus. One for H atom. Two for He^+, etc.

Make the substitutions

$$\alpha^2 = -\frac{2\mu E}{\hbar^2}$$

$$\lambda = \frac{\mu Z e^2}{4\pi\varepsilon_0 \hbar^2 \alpha}$$

Introduce the new independent variable

$$\rho = 2\alpha r$$

ρ is the the distance variable in units of 2α.

Making the substitutions and
with

$$S(\rho) = R(r)$$

yields

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dS}{d\rho}\right)+\left(-\frac{1}{4}-\frac{\ell(\ell+1)}{\rho^2}+\frac{\lambda}{\rho}\right)S=0 \qquad 0\le\rho\le\infty$$

To solve - look at solution for large ρ, $r\to\infty$ (like H. O.).

Consider the first term in the equation above.

$$\frac{1}{\rho^2}\left(\frac{d}{d\rho}\left(\rho^2\frac{dS}{d\rho}\right)\right)=\frac{1}{\rho^2}\left(\rho^2\frac{d^2S}{d\rho^2}+2\rho\frac{dS}{d\rho}\right)$$

$$=\frac{d^2S}{d\rho^2}+\frac{2}{\rho}\frac{dS}{d\rho}$$

This term goes to zero as $r\to\infty$

The terms in the full equation divided by ρ and ρ^2 also go to zero as $r\to\infty$.

Then, as $r \to \infty$

$$\frac{d^2 S}{d\rho^2} = \frac{1}{4} S.$$

The solutions are

$$S = e^{-\rho/2} \qquad S = e^{+\rho/2}$$

This blows up as $r \to \infty$
Not acceptable wavefunction.

The full solution is

$$S(\rho) = e^{-\rho/2} F(\rho)$$

Substituting in the original equation, dividing by $e^{-\rho/2}$ and rearranging gives

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

The underlined terms blow up at $\rho = 0$. Regular point.

Singularity at $\rho = 0$ - regular point,
to remove, substitute

$$F(\rho) = \rho^{\ell} L(\rho)$$

Gives

$$\rho L'' + (2(\ell + 1) - \rho)L' + (\lambda - \ell - 1)L = 0.$$

Equation for L. **Find L, get F.** **Know F, have $S(\rho) = R(r)$.**

Solve using polynomial method.

$$L(\rho) = \sum_{\nu} a_{\nu} \rho^{\nu} = a_0 + a_1 \rho + a_2 \rho^2 + \cdots$$

Polynomial expansion for *L*. Get *L*' and *L*'' by term by term differentiation.

Following substitution, the sum of all the terms in all powers of ρ equal 0. The coefficient of each power must equal 0.

$$\{\rho^0\} \qquad (\lambda - \ell - 1)a_0 + 2(\ell + 1)a_1 = 0$$

$$\{\rho^1\} \qquad (\lambda - \ell - 1 - 1)a_1 + \left[4(\ell + 1) + 2\right]a_2 = 0$$

$$\{\rho^2\} \qquad (\lambda - \ell - 1 - 2)a_2 + \left[6(\ell + 1) + 6\right]a_3 = 0$$

$$\vdots \qquad \qquad \vdots$$

Note not separate odd and even series.

Recursion formula

$$a_{\nu+1} = \frac{-(\lambda - \ell - 1 - \nu)a_{\nu}}{[2(\nu + 1)(\ell + 1) + \nu(\nu + 1)]}$$

Given a_0, all other terms coefficients determined. a_0 determined by normalization condition.

$$a_{\nu+1} = \frac{-(\lambda - \ell - 1 - \nu)a_\nu}{[2(\nu+1)(\ell+1) + \nu(\nu+1)]}$$

Provides solution to differential equation, but not good wavefunction if infinite number of terms.

Need to break off after the $\nu = n'$ term by taking

$$\lambda - \ell - 1 - n' = 0$$

or

integers

$\lambda = n$ **with** $n = n' + \ell + 1$ $\qquad$ n **is an integer.**

n' ⇒ **radial quantum number**

n ⇒ **total quantum number**

$n = 1$	**s orbital**	$n' = 0, l = 0$
$n = 2$	**s, p orbitals**	$n' = 1, l = 0$ **or** $n' = 0, l = 1$
$n = 3$	**s, p, d orbitals**	$n' = 2, l = 0$ **or** $n' = 1, l = 1$ **or** $n' = 0, l = 2$

Thus,

$$R(r) = e^{-\rho/2} \rho^{\ell} L(\rho)$$

with

$$L(\rho)$$

defined by the recursion relation,

and

$$\lambda = n$$

$$n = n' + \ell + 1$$

integers

$$n = \lambda \quad n = 1, 2, 3, \cdots$$

$$\lambda = \frac{\mu Z e^2}{4\pi\varepsilon_0 \hbar^2 \alpha}$$

$$\alpha^2 = -\frac{2\mu E}{\hbar^2}$$

$$n^2 = \lambda^2 = -\frac{\mu Z^2 e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 E}$$

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

Energy levels of the hydrogen atom.

Z **is the nuclear charge. 1 for H; 2 for** $\mathbf{He^+}$**, etc.**

$$a_0 = \frac{\varepsilon_0 h^2}{\pi \mu e^2} \qquad a_0 = 5.29 \times 10^{-11}\, m$$

Bohr radius - characteristic length in H atom problem.

In terms of Bohr radius

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

Lowest energy, 1s, ground state energy, -13.6 eV.

Rydberg constant

$$R_H = 109{,}677\ \text{cm}^{-1}$$

$$E_n = -\frac{Z^2}{n^2} R_H hc$$

$$R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c}$$

Rydberg constant if proton had infinite mass.
Replace μ with m_e. R_∞ = 109,737 cm^{-1}.

Have solved three one-dimensional equations to get

$$\Phi_m(\varphi) \qquad \Theta_{\ell m}(\theta) \qquad R_{n\ell}(r)$$

The total wavefunction is

$$\Psi_{n\ell m}(\varphi,\theta,r) = \Phi_m(\varphi)\Theta_{\ell m}(\theta)R_{n\ell}(r)$$

$$n = 1,\ 2,\ 3\cdots$$

$$\ell = n-1, n-2,\cdots 0$$

$$m = \ell, \ell-1\cdots -\ell$$

$\Phi_m(\varphi)$ **is given by the expressions in exponential form or in terms of sin and cos.**

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

$$\Phi_0(\varphi) = \frac{1}{\sqrt{2\pi}} \qquad m = 0$$

$$\Phi_{|m|}(\varphi) = \begin{cases} \dfrac{1}{\sqrt{\pi}} \cos|m|\varphi \\ \dfrac{1}{\sqrt{\pi}} \sin|m|\varphi \end{cases} \qquad |m| = 1, 2, 3 \cdots$$

$\Theta_{\ell m}(\theta)$ **and** $R_{n\ell}(r)$

can be obtained from generating functions (like H. O.).
See book.

With normalization constants

Associate Legendre Polynomials

$$\Theta(\theta) = \sqrt{\frac{(2\ell+1)}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}}P_\ell^{|m|}(\cos\theta).$$

Associate Laguerre Polynomials

$$R_{n\ell}(r) = -\sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}e^{-\rho/2}\rho^\ell L_{n+\ell}^{2\ell+1}(\rho)$$

$$\rho = 2\alpha r = \frac{2Z}{a_0 n}r$$

Total Wavefunction

$$\Psi_{n\ell m}(\varphi,\theta,r) = \Phi_m(\varphi)\Theta_{\ell m}(\theta)R_{n\ell}(r)$$

1s function

$$\Psi_{1s}(\varphi,\theta,r) = \Psi_{100} = \Phi_0\Theta_{00}R_{10} = \left(\frac{1}{\sqrt{2\pi}}\right)\left(\frac{\sqrt{2}}{2}\right)\left(2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\rho/2}\right)$$

$$\Psi_{1s} = \frac{1}{\sqrt{\pi a_0^{\,3}}} e^{-r/a_0}$$

for $Z = 1$

No nodes.

2s function

$$\Psi_{2s}(\varphi,\theta,r) = \Psi_{200} = \Phi_0\Theta_{00}R_{20} = \frac{1}{4\sqrt{2\pi a_0^3}}(2 - r/a_0)e^{-r/2a_0}$$

Node at $r = 2a_0$.

H atom wavefunction - orbital

1*s* orbital

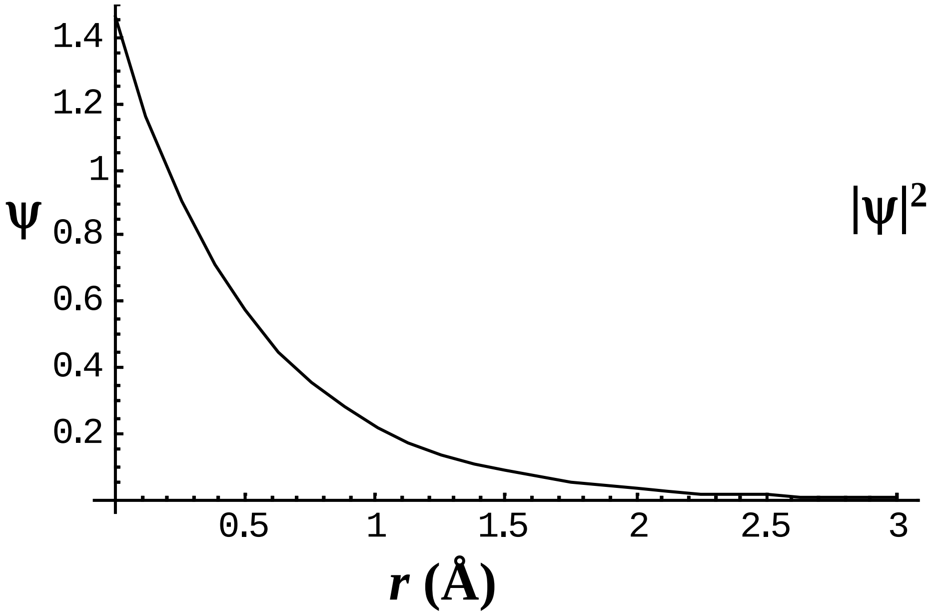
$$\psi_{1s} = A e^{-r/a_0} \qquad A = \frac{1}{\sqrt{\pi a_0^3}}$$

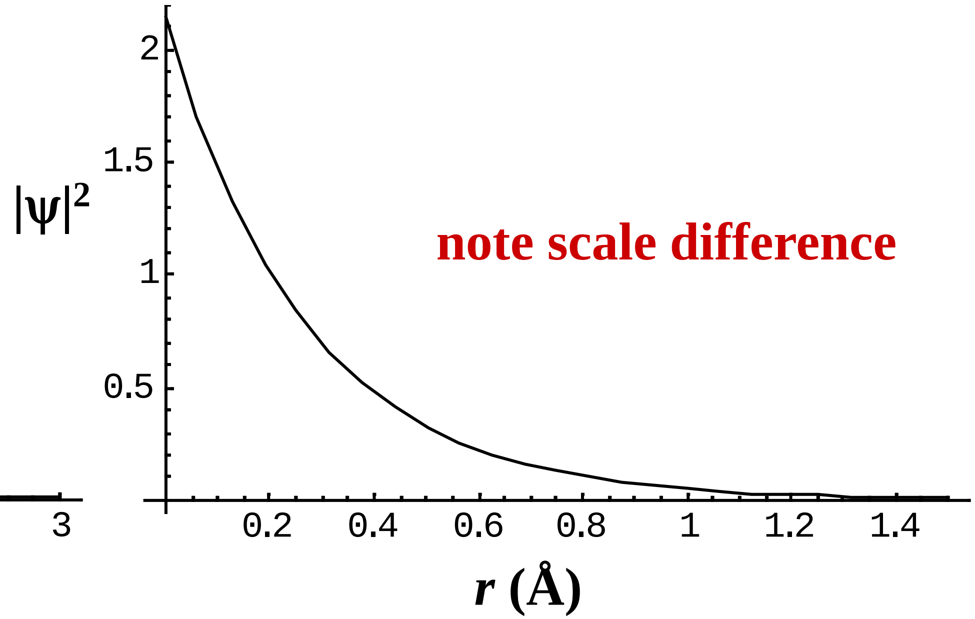
$a_0 = 0.529$ Å the Bohr radius

The wavefunction is the probability amplitude. The probability is the absolute valued squared of the wavefunction.

$$\left|\psi_{1s}\right|^2 = A^2 e^{-2r/a_0}$$

This is the probability of finding the electron a distance *r* from the nucleus on a line where the nucleus is at *r* = 0.





note scale difference

The 2s Hydrogen orbital

$$\psi_{2s} = B(2 - r/a_0)e^{-r/2a_0} \qquad B = \frac{1}{4\sqrt{2\pi a_0^3}}$$

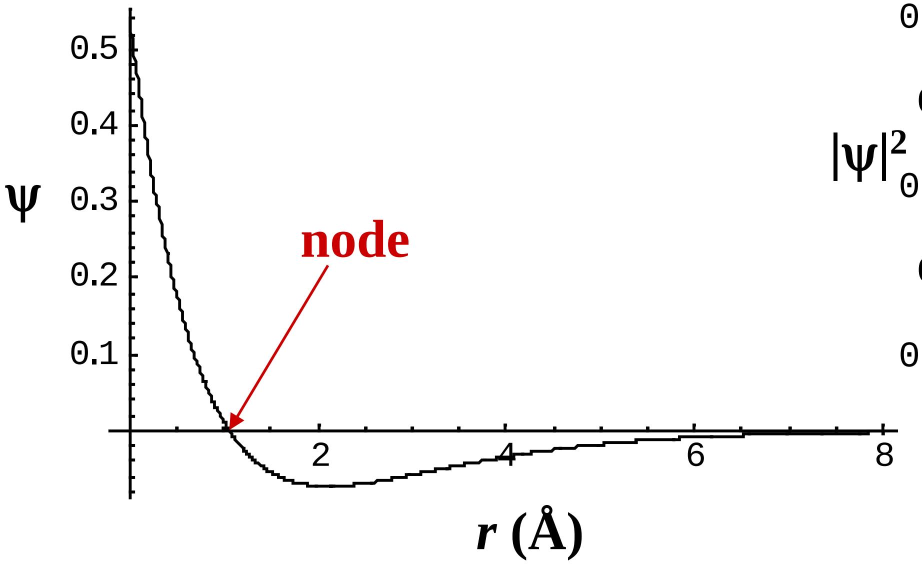
Probability amplitude

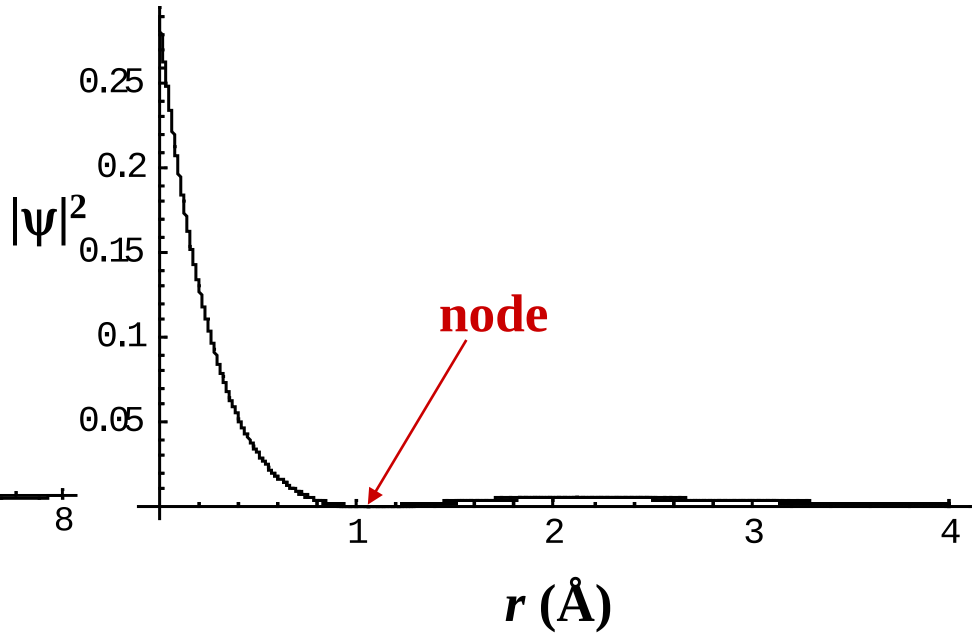
When r = 2a_0, this term goes to zero.
There is a “node” in the wave function.

a_0 = 0.529, the Bohr radius

$$|\psi_{2s}|^2 = \left[B(2 - r/a_0)e^{-r/2a_0}\right]^2$$

Absolute value of the wavefunction squared – probability distribution.



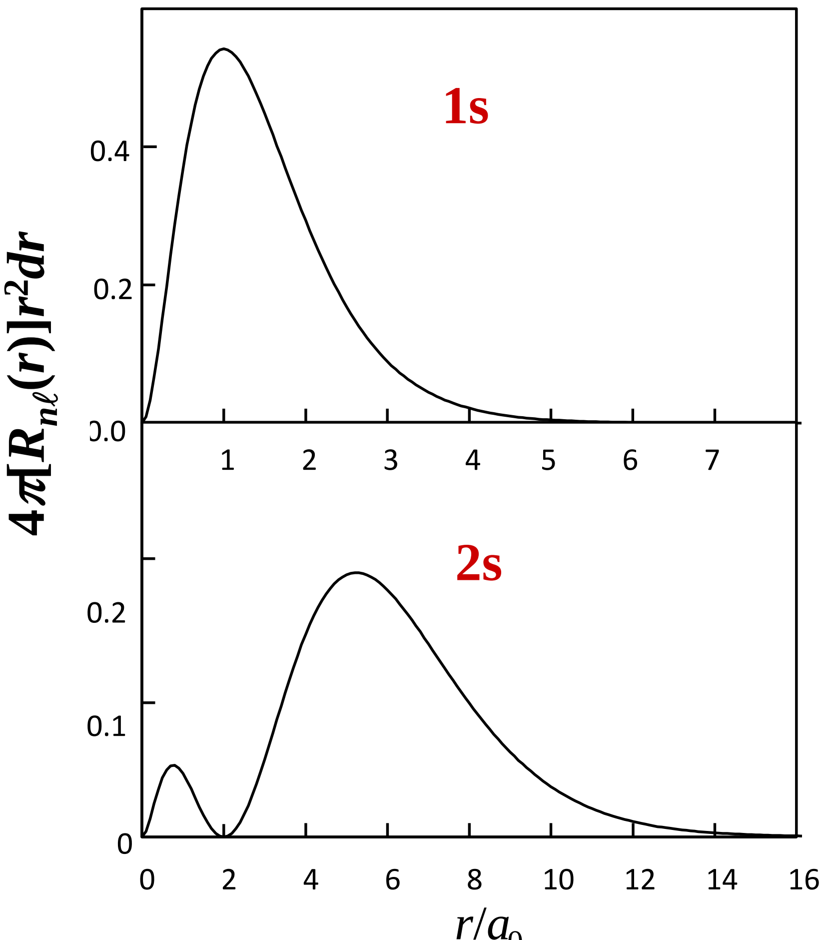


Radial distribution function

Probability of finding electron distance *r* from the nucleus in a thin spherical shell.

$$D_{nl}(r) = 4\pi\left[R_{n\ell}(r)\right]^2 r^2 dr$$

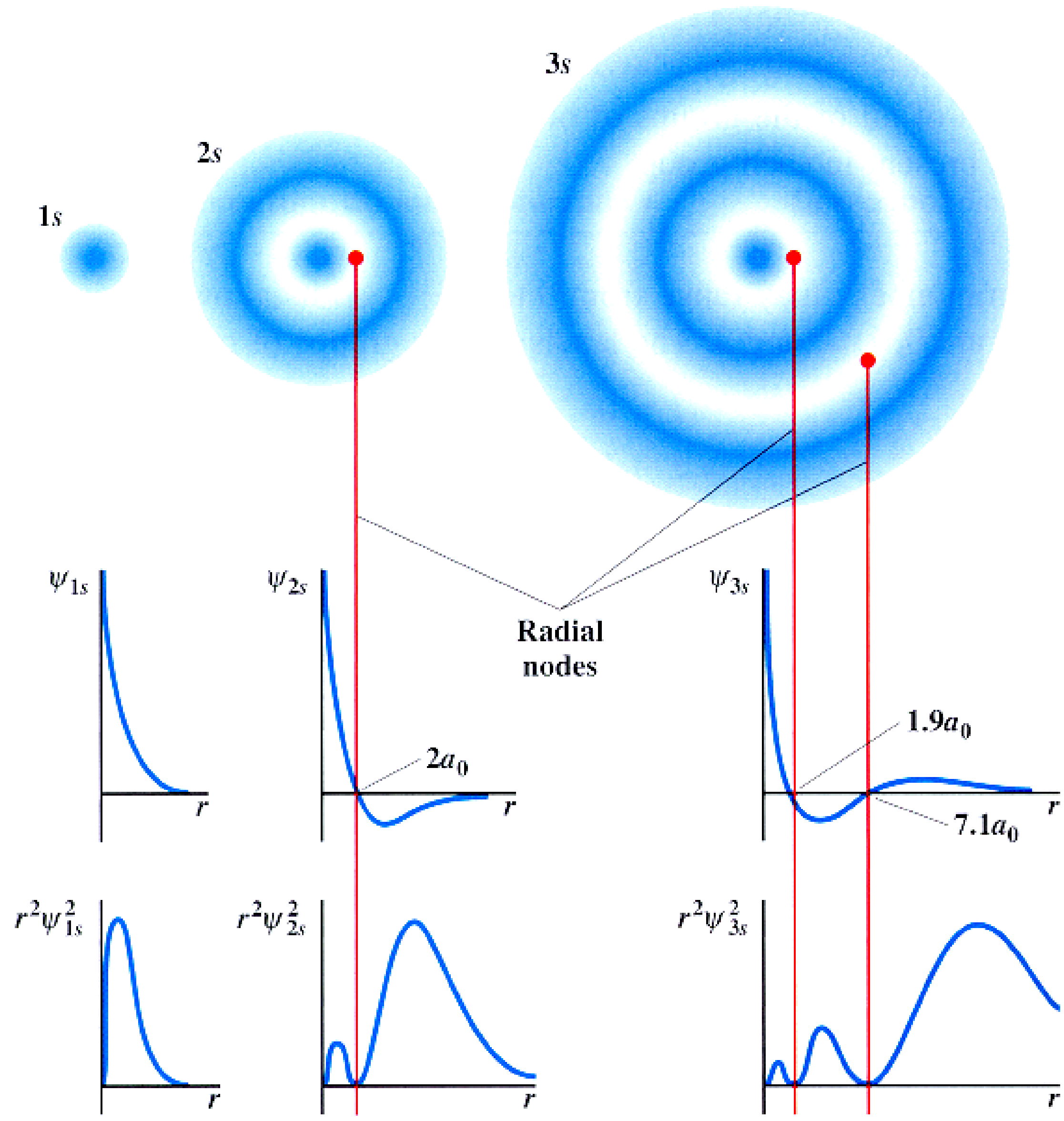
For s orbital there is no angular dependence.
Still must integrate over angles with the differential operator sin*θdθdφ* = 4π



s orbitals - $\ell = 0$

1s – no nodes
2s – 1 node
3s – 2 nodes

The nodes are radial nodes.



Oxtoby, Freeman, Block