

Hydrogen Atom

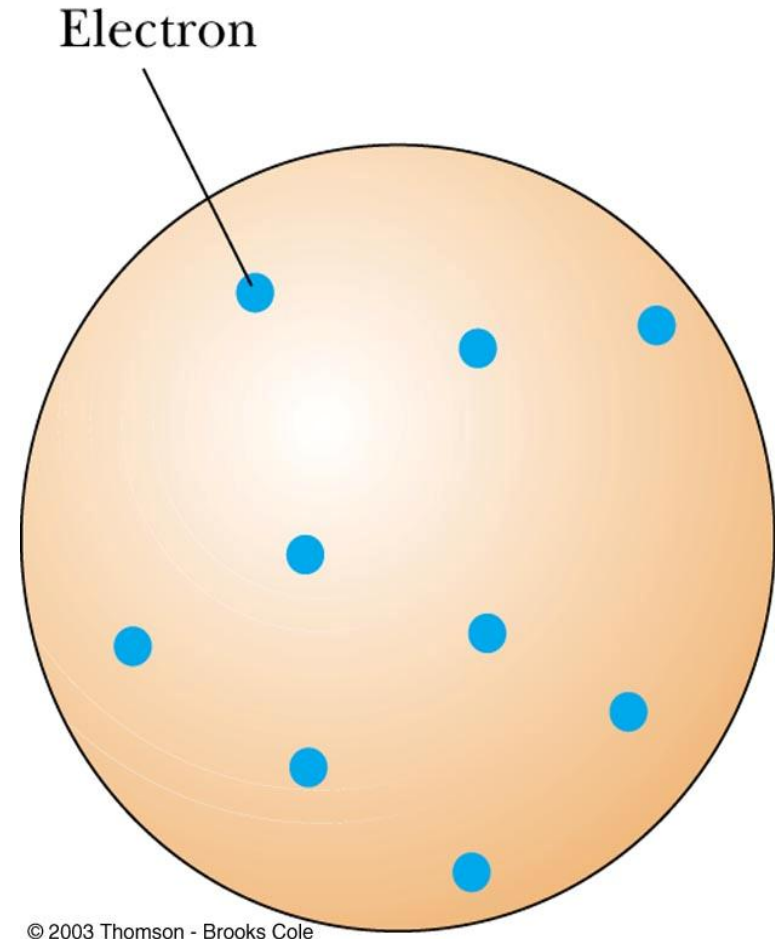
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Importance of Hydrogen Atom

- Hydrogen is the simplest atom
- The quantum numbers used to characterize the allowed states of hydrogen can also be used to describe (approximately) the allowed states of more complex atoms
 - This enables us to understand the periodic table
- The hydrogen atom is an ideal system for performing precise comparisons of theory and experiment
 - Also for improving our understanding of atomic structure
- Much of what we know about the hydrogen atom can be extended to other single-electron ions
 - For example, He^+ and Li^{2+}

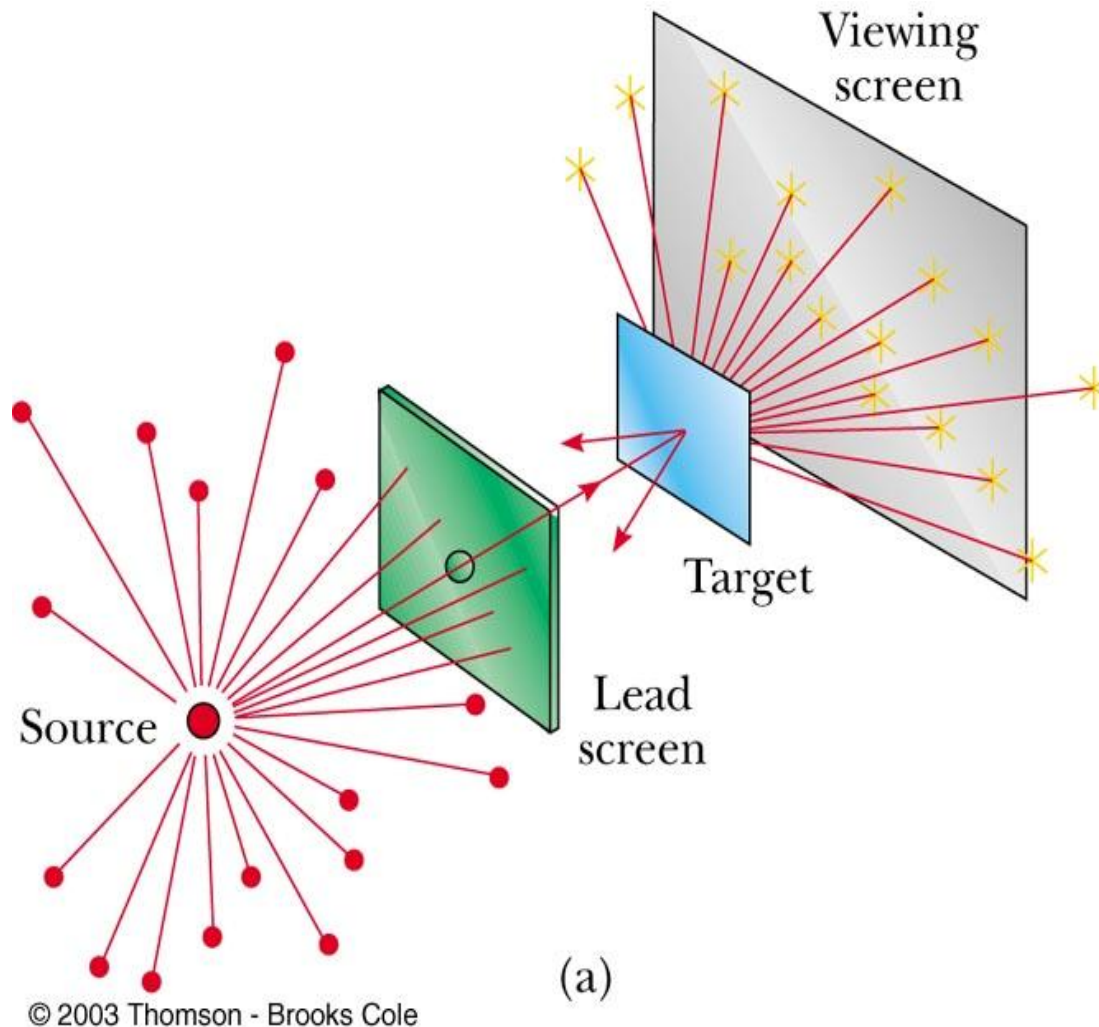
Early Models of the Atom

- J.J. Thomson's model of the atom
 - A volume of positive charge
 - Electrons embedded throughout the volume
- A change from Newton's model of the atom as a tiny, hard, indestructible sphere



“watermelon” model

Experimental tests



Expect:

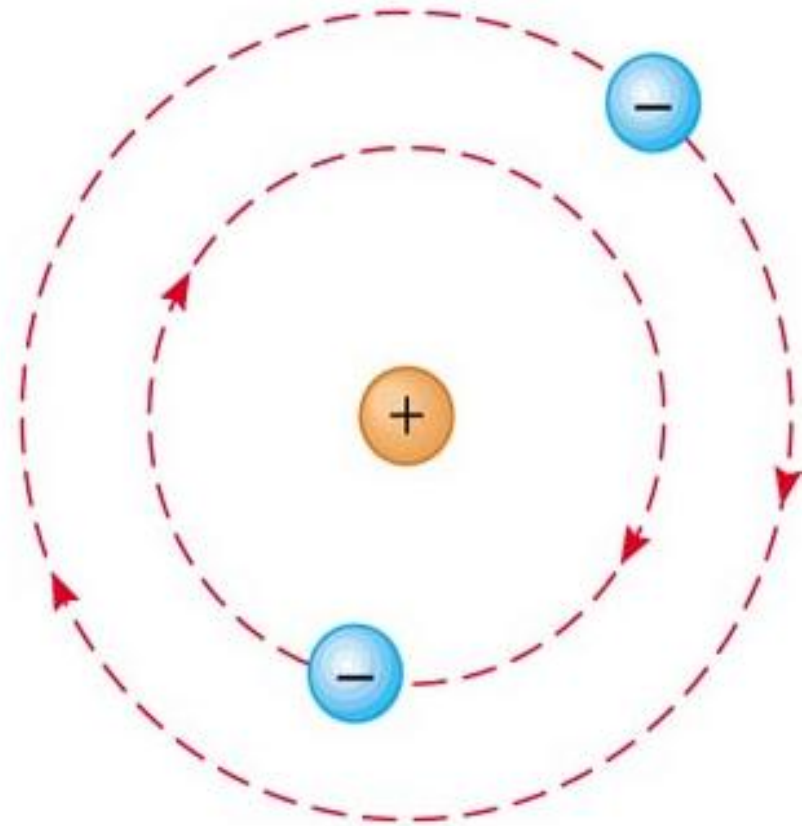
1. Mostly small angle scattering
2. No backward scattering events

Results:

1. Mostly small scattering events
2. Several backward scatterings!!!

Early Models of the Atom

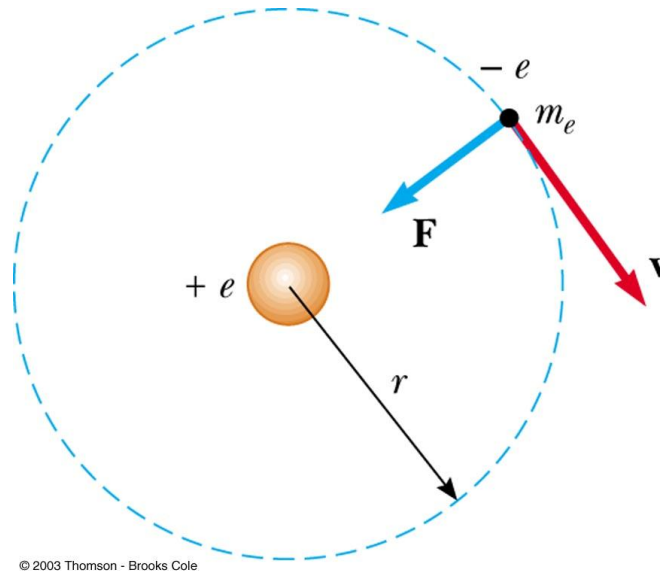
- Rutherford's model
 - Planetary model
 - Based on results of thin foil experiments
 - Positive charge is concentrated in the center of the atom, called the *nucleus*
 - Electrons orbit the nucleus like planets orbit the sun



Problem: Rutherford's model

The “size” of the *atom* in Rutherford's model is about 1.0×10^{-10} m.

- (a) Determine the attractive electrical force between an electron and a proton separated by this distance.
- (b) Determine (in eV) the electrical potential energy of the atom.



The “size” of the *atom* in Rutherford’s model is about 1.0×10^{-10} m. (a) Determine the attractive electrical force between an electron and a proton separated by this distance. (b) Determine (in eV) the electrical potential energy of the atom.

Given:

$$r = 1.0 \times 10^{-10} \text{ m}$$

Electron and proton interact via the Coulomb force

$$F = k_e \frac{|q_1 q_2|}{r^2} = \frac{(8.99 \times 10^9 \text{ N} \cdot \text{m}^2 / \text{C}^2)(1.60 \times 10^{-19} \text{ C})^2}{(1.0 \times 10^{-10} \text{ m})^2} = 2.3 \times 10^{-8} \text{ N}$$

Find:

- (a) $F = ?$
- (b) $PE = ?$

Potential energy is

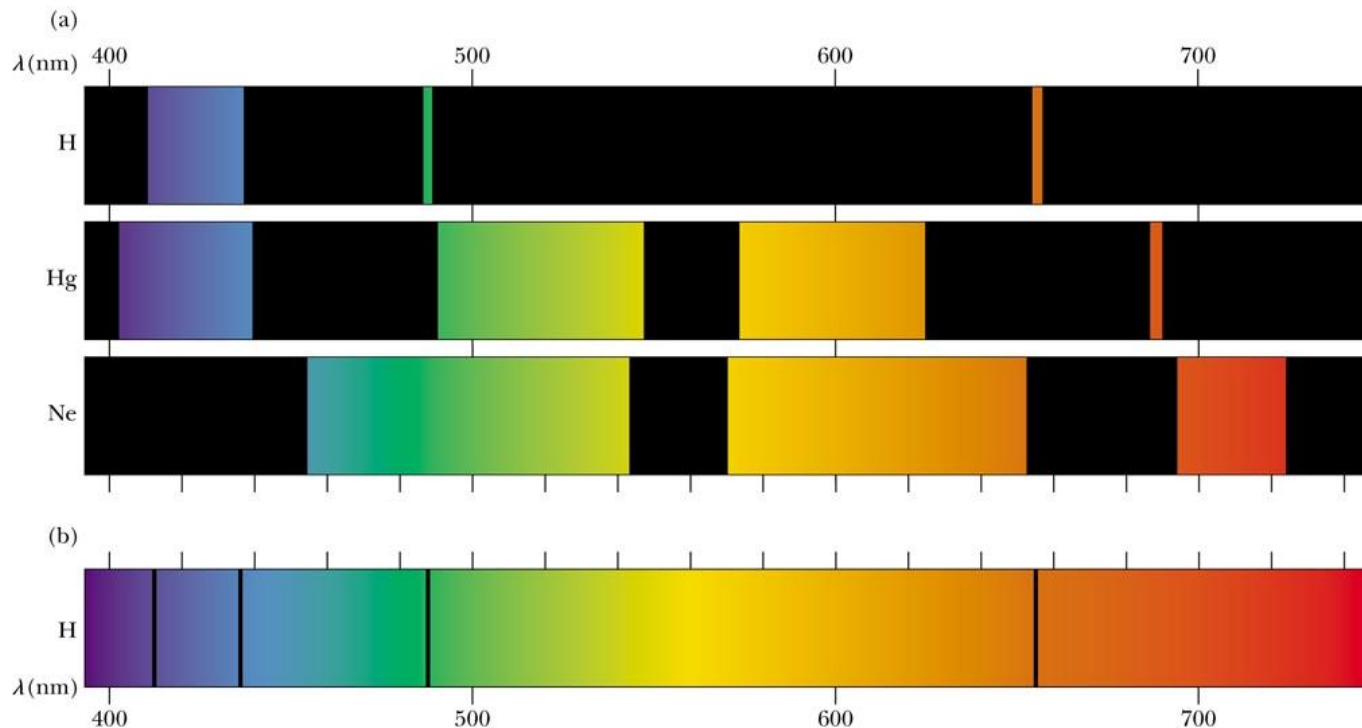
$$PE = k_e \frac{q_1 q_2}{r} = -2.3 \times 10^{-18} \text{ J} \left(\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \right) = -14 \text{ eV}$$

Difficulties with the Rutherford Model

- Atoms emit certain discrete characteristic frequencies of electromagnetic radiation
 - The Rutherford model is unable to explain this phenomena
- Rutherford's electrons are undergoing a centripetal acceleration and so should radiate electromagnetic waves of the same frequency
 - The radius should steadily decrease as this radiation is given off
 - The electron should eventually spiral into the nucleus
 - It doesn't

Emission Spectra

- A gas at low pressure has a voltage applied to it
- A gas emits light characteristic of the gas
- When the emitted light is analyzed with a spectrometer, a series of discrete bright lines is observed
 - Each line has a different wavelength and color
 - This series of lines is called an *emission spectrum*

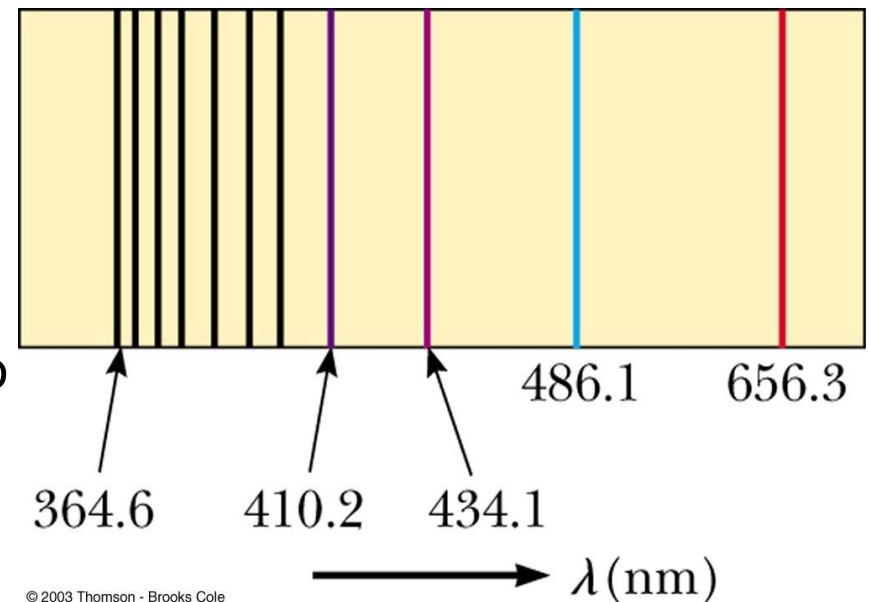


Emission Spectrum of Hydrogen

- The wavelengths of hydrogen's spectral lines can be found from

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

- R_H is the *Rydberg constant*
 - $R_H = 1.0973732 \times 10^7 \text{ m}^{-1}$
- n is an integer, $n = 1, 2, 3, \dots$
- The spectral lines correspond to different values of n
- A.k.a. *Balmer series*
- Examples of spectral lines
 - $n = 3, \lambda = 656.3 \text{ nm}$
 - $n = 4, \lambda = 486.1 \text{ nm}$



Absorption Spectra

- An element can also absorb light at specific wavelengths
- An absorption spectrum can be obtained by passing a continuous radiation spectrum through a vapor of the gas
- The absorption spectrum consists of a series of dark lines superimposed on the otherwise continuous spectrum
 - The dark lines of the absorption spectrum coincide with the bright lines of the emission spectrum

Applications of Absorption Spectrum

- The continuous spectrum emitted by the Sun passes through the cooler gases of the Sun's atmosphere
 - The various absorption lines can be used to identify elements in the solar atmosphere
 - Led to the discovery of helium

Recall Bohr's Assumptions

- Only certain electron orbits are stable. Radiation is emitted by the atom when the electron “jumps” from a more energetic initial state to a lower state

$$E_i - E_f = hf$$

- The size of the allowed electron orbits is determined by a condition imposed on the electron's orbital angular momentum

$$m_e v r = n\hbar, \quad n = 1, 2, 3, \dots$$

Why is that?

Modifications of the Bohr Theory – Elliptical Orbits

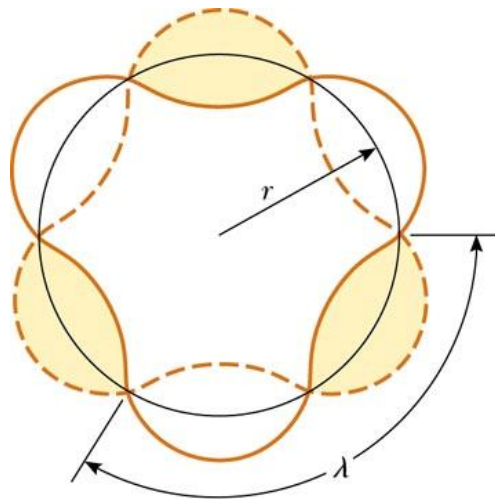
- Sommerfeld extended the results to include elliptical orbits
 - Retained the *principle quantum number*, n
 - Added the *orbital quantum number*, ℓ
 - ℓ ranges from 0 to $n-1$ in integer steps
 - All states with the same principle quantum number are said to form a *shell*
 - The states with given values of n and ℓ are said to form a *subshell*

Modifications of the Bohr Theory – Zeeman Effect and fine structure

- Another modification was needed to account for the *Zeeman effect*
 - The Zeeman effect is the splitting of spectral lines in a strong magnetic field
 - This indicates that the energy of an electron is slightly modified when the atom is immersed in a magnetic field
 - A new quantum number, m_ℓ , called the *orbital magnetic quantum number*, had to be introduced
 - m_ℓ can vary from $-\ell$ to $+\ell$ in integer steps
- High resolution spectrometers show that spectral lines are, in fact, two very closely spaced lines, even in the absence of a magnetic field
 - This splitting is called *fine structure*
 - Another quantum number, m_s , called the *spin magnetic quantum number*, was introduced to explain the fine structure

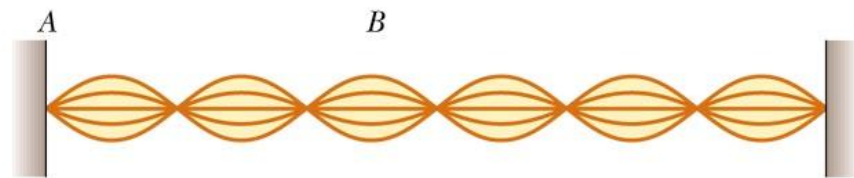
de Broglie Waves

- One of Bohr's postulates was the angular momentum of the electron is quantized, but there was no explanation why the restriction occurred
- de Broglie assumed that the electron orbit would be stable only if it contained an integral number of electron wavelengths



(a)

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(b)

de Broglie Waves in the Hydrogen Atom

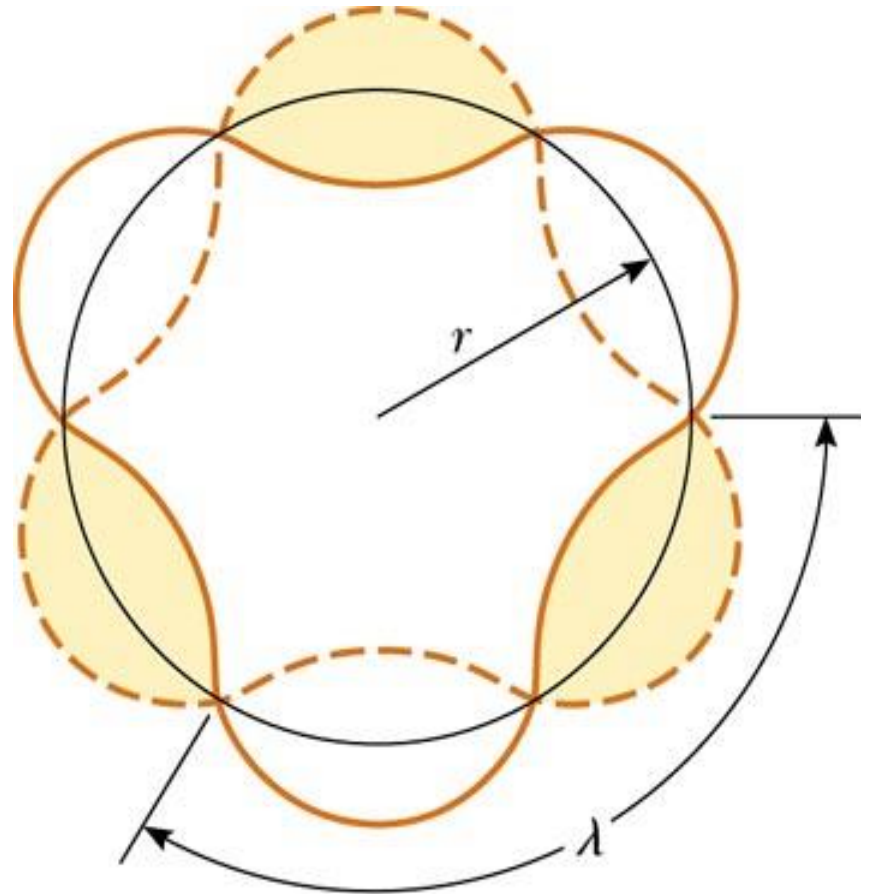
- In this example, three complete wavelengths are contained in the circumference of the orbit
- In general, the circumference must equal some integer number of wavelengths

$$2\pi r = n\lambda, \quad \lambda = 1, 2, 3, \dots$$

$$\lambda = \frac{h}{m_e v}$$

$$m_e v r = n\hbar, \quad n = 1, 2, 3, \dots$$

This was the first convincing argument that the wave nature of matter was at the heart of the behavior of atomic systems

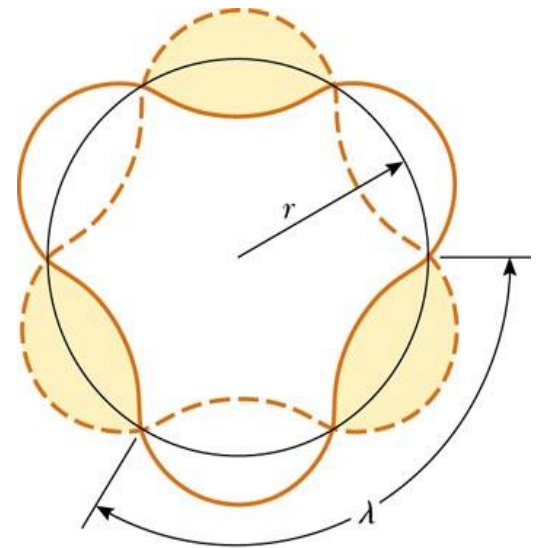


Quantum Mechanics and the Hydrogen Atom

- One of the first great achievements of quantum mechanics was the solution of the wave equation for the hydrogen atom
- The significance of quantum mechanics is that the quantum numbers and the restrictions placed on their values arise directly from the mathematics and not from any assumptions made to make the theory agree with experiments

Problem: wavelength of the electron

Determine the wavelength of an electron in the third excited orbit of the hydrogen atom, with $n = 4$.



Determine the wavelength of an electron in the third excited orbit of the hydrogen atom, with $n = 4$.

Given:

$$n = 4$$

Recall that de Broglie's wavelength of electron depends on its momentum, $\lambda = h/(m_e v)$. Let us find it,

$$m_e v r_n = n\hbar, \quad \text{so} \quad m_e v = \frac{n\hbar}{r_n}$$

Recall that $r_n = n^2 a_0$, so $m_e v = \frac{h}{(2\pi a_0)n}$

Find:

$$\lambda_e = ?$$

Thus, $\lambda = \frac{h}{m_e v} = (2\pi a_0)n = 8\pi(0.0529\text{nm}) = 1.33\text{nm}$

Quantum Number Summary

TABLE 28.2 Three Quantum Numbers for the Hydrogen Atom

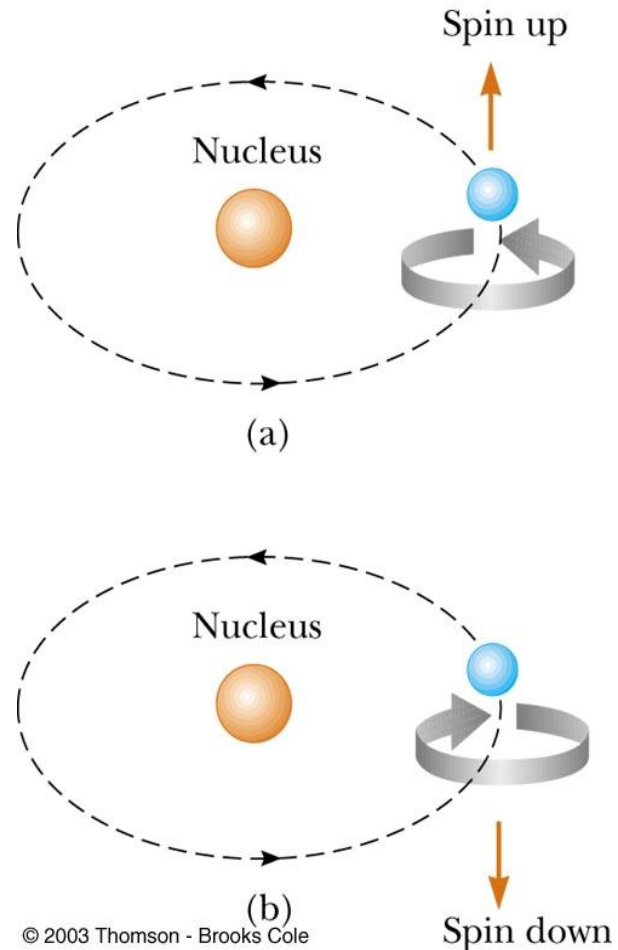
Quantum Number	Name	Allowed Values	Number of Allowed States
n	Principal quantum number	$1, 2, 3, \dots$	Any number
ℓ	Orbital quantum number	$0, 1, 2, \dots, n - 1$	n
m_ℓ	Orbital magnetic quantum number	$-\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell$	$2\ell + 1$

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- The values of n can increase from 1 in integer steps
- The values of ℓ can range from 0 to $n-1$ in integer steps
- The values of m_ℓ can range from $-\ell$ to ℓ in integer steps

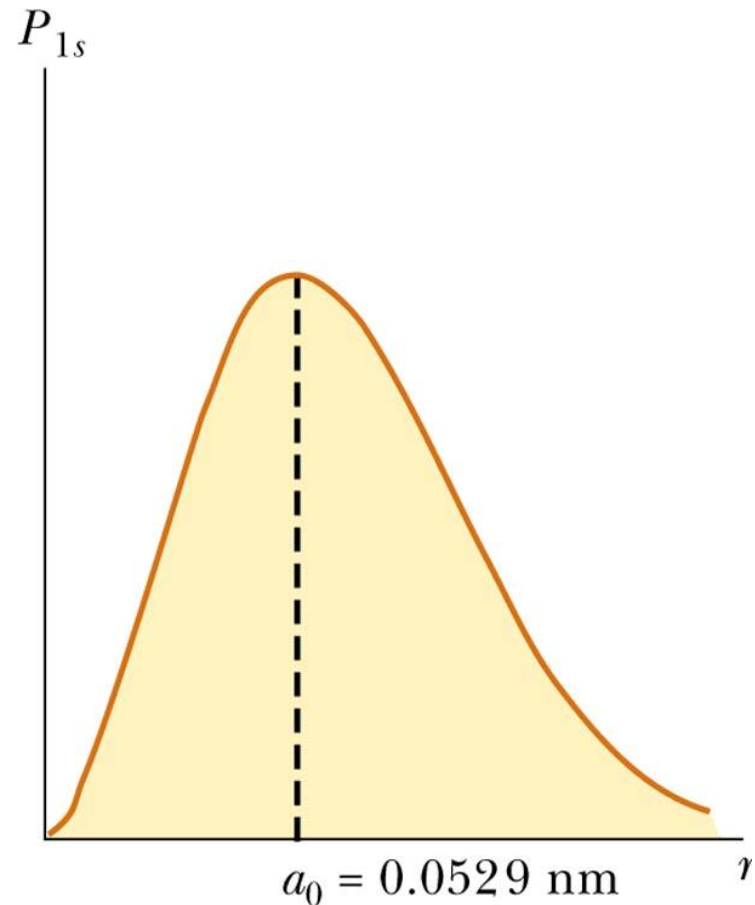
Spin Magnetic Quantum Number

- It is convenient to think of the electron as spinning on its axis
 - The electron is *not* physically spinning
- There are two directions for the spin
 - Spin up, $m_s = \frac{1}{2}$
 - Spin down, $m_s = -\frac{1}{2}$
- There is a slight energy difference between the two spins and this accounts for the Zeeman effect



Electron Clouds

- The graph shows the solution to the wave equation for hydrogen in the ground state
 - The curve peaks at the Bohr radius
 - The electron is not confined to a particular orbital distance from the nucleus
- The *probability* of finding the electron at the Bohr radius is a maximum



Electron Clouds

- The wave function for hydrogen in the ground state is symmetric
 - The electron can be found in a spherical region surrounding the nucleus
- The result is interpreted by viewing the electron as a cloud surrounding the nucleus
 - The densest regions of the cloud represent the highest probability for finding the electron

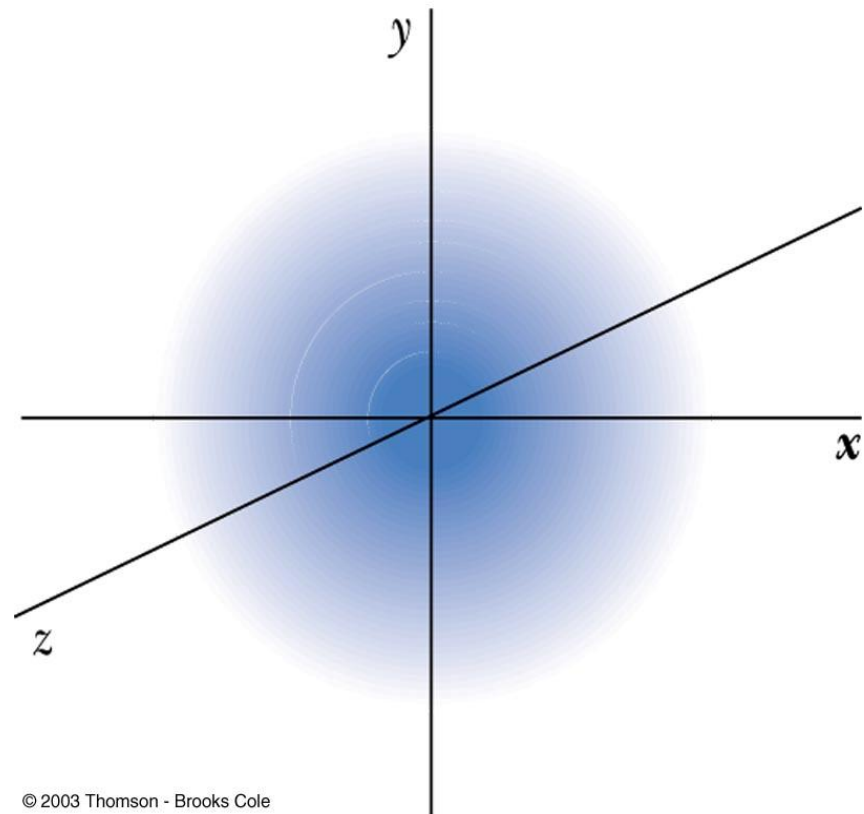


TABLE 28.3**Number of Electrons in Filled Subshells and Shells**

Shell	Subshell	Number of Electrons in Filled Subshell	Number of Electrons in Filled Shell
K ($n = 1$)	$s(\ell = 0)$	2	2
L ($n = 2$)	$s(\ell = 0)$	2	8
	$p(\ell = 1)$	6	
M ($n = 3$)	$s(\ell = 0)$	2	18
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
N ($n = 4$)	$s(\ell = 0)$	2	32
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
	$f(\ell = 3)$	14	

Mathematical Details

Roadmap for solution of Hydrogen-like atoms

- Start from 3D TISE for electron in Coulomb potential of nucleus
- Separate variables to give 1D radial problem and angular problem
Solution of angular part already known
in terms of spherical harmonics.
- Simplify 1D radial problem using substitutions and atomic units
- Solve radial problem
Extract asymptotic solution at large r
Use Frobenius method
Find eigenvalues by requiring normalizable solutions

Reminder: SE in three dimensions

H-atom is our first example of the 3D Schrödinger equation

Wavefunction and potential energy are now functions of *three* spatial coordinates:

$$\begin{aligned}\psi(x) &\rightarrow \psi(\mathbf{r}) = \psi(x, y, z) \\ V(x) &\rightarrow V(\mathbf{r}) = V(x, y, z)\end{aligned}$$

Kinetic energy involves *three* components of momentum

$$\begin{aligned}\frac{p_x^2}{2m} &\rightarrow \frac{\mathbf{p}^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \\ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} &\rightarrow -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]\end{aligned}$$

Interpretation of wavefunction:

$$d^3\mathbf{r} |\psi(\mathbf{r}, t)|^2$$

probability of finding particle in a volume element centred on \mathbf{r}

$$|\psi(\mathbf{r}, t)|^2$$

probability density at \mathbf{r}
(probability *per unit volume*)

Time-independent Schrödinger equation

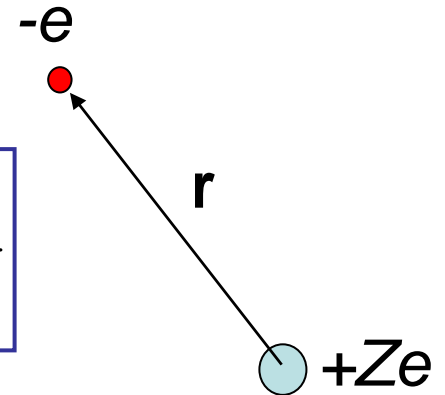
$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The Hamiltonian for a hydrogenic atom

In a hydrogenic atom or ion with nuclear charge $+Ze$ there is the Coulomb attraction between electron and nucleus. This has spherical symmetry – potential only depends on r . This is known as a **CENTRAL POTENTIAL**

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$



The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

NB: for greater accuracy we should use the reduced mass not the electron mass here. This accounts for the relative motion of the electron and the nucleus (since the nucleus does not remain precisely fixed):

$$m_e \rightarrow \mu = \frac{m_e m_N}{m_e + m_N}; \quad m_e = \text{electron mass}, m_N = \text{nuclear mass}$$

Hamiltonian for hydrogenic atoms

The natural coordinate system is spherical polars. In this case the Laplacian operator becomes (see 2B72):

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{L^2}{\hbar^2 r^2}$$

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

So the Hamiltonian is

$$\hat{H}(\mathbf{r}) = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

TISE for H-like atom is
($m = m_e$ from now on)

$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

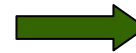
$$-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(\mathbf{r})}{\partial r} \right) + \frac{\hat{L}^2 \psi(\mathbf{r})}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Angular momentum and the H atom

$$\hat{H}(\mathbf{r}) = -\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Reminder:
Ehrenfest's theorem

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



$$\begin{aligned} [\hat{H}, \hat{L}^2] = 0 &\Leftrightarrow \frac{d\langle \hat{L}^2 \rangle}{dt} = 0 \\ [\hat{H}, \hat{L}_z] = 0 &\Leftrightarrow \frac{d\langle \hat{L}_z \rangle}{dt} = 0 \end{aligned}$$

CONCLUSIONS

- The angular momentum about any axis and the total angular momentum commute with the Hamiltonian
- They are therefore both conserved quantities
- We can have simultaneous eigenfunctions of these operators and the Hamiltonian
- We can have well-defined values of these quantities and the energy at the same time

The angular wavefunction

This suggests we look for separated solutions of the form

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$$

The angular part are the eigenfunctions of the total angular momentum operator L^2 . These are the spherical harmonics, so we already know the corresponding eigenvalues and eigenfunctions (see §5):

$$\begin{aligned}\hat{L}_z Y_{lm}(\theta, \phi) &= m\hbar Y_{lm}(\theta, \phi) \\ \hat{L}^2 Y_{lm}(\theta, \phi) &= l(l+1)\hbar^2 Y_{lm}(\theta, \phi)\end{aligned}$$

Eigenvalues of \hat{L}^2 are $l(l+1)\hbar^2$, with $l = 0, 1, 2, \dots$

Eigenvalues of \hat{L}_z are $m\hbar$, with $-l \leq m \leq l$

l = principal angular momentum quantum number.

m = magnetic quantum number ($2l+1$ possible values).

$$\begin{aligned}Y_{00}(\theta, \phi) &= \frac{1}{\sqrt{4\pi}} \\ Y_{11}(\theta, \phi) &= -\sqrt{\frac{3}{8\pi}} \sin \theta \exp(i\phi) \\ Y_{10}(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos \theta \\ Y_{1-1}(\theta, \phi) &= \sqrt{\frac{3}{8\pi}} \sin \theta \exp(-i\phi)\end{aligned}$$

Note: this argument works for *any* spherically-symmetric potential $V(r)$, not just the Coulomb potential.

The radial equation

Substitute separated solution into the time-independent Schrödinger equation

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$$

$$-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{\hat{L}^2 \psi}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Get radial equation

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} R - \frac{Ze^2}{4\pi\epsilon_0 r} R = ER$$

Note that this depends on l but not on m : $R(r)$ and E therefore involve the **magnitude** of the angular momentum but not its **orientation**.

The radial equation (2)

Define a new radial function $\chi(r)$ by:

$$R(r) = \frac{\chi(r)}{r}$$

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} R - \frac{Ze^2}{4\pi\epsilon_0 r} R = ER$$

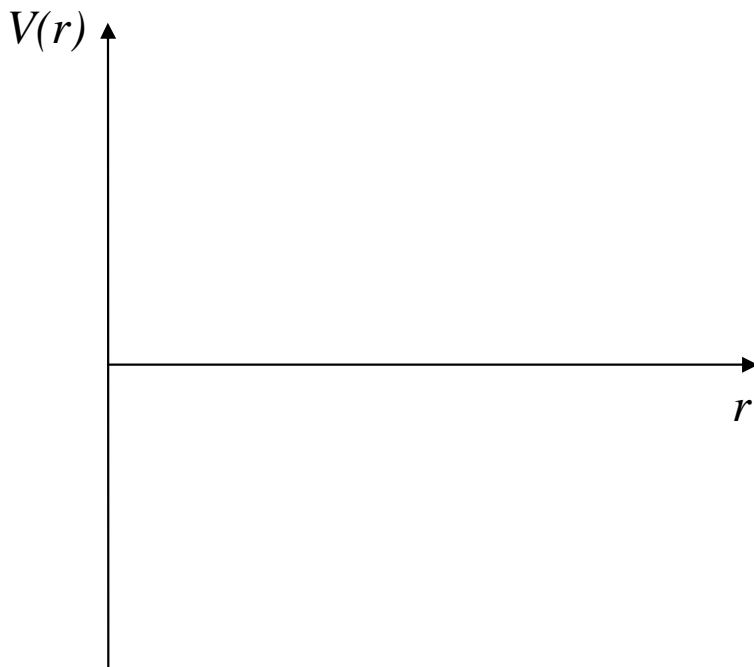
Get radial equation for $\chi(r)$

$$-\frac{\hbar^2}{2m} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \chi = E \chi$$

The effective potential

New radial equation looks like the 1D Schrödinger equation with an **effective potential**

$$V_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$



$$-\frac{\hbar^2}{2m} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \chi = E \chi$$

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dr^2} + V_{\text{eff}}(r) \psi = E \psi$$

1D TISE

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi$$

$$\frac{l(l+1)\hbar^2}{2mr^2}$$

is known as the centrifugal barrier potential

The centrifugal barrier

Where does the centrifugal barrier come from?

$$V_{cb}(r) = \frac{l(l+1)\hbar^2}{2mr^2}$$

CLASSICAL ARGUMENT

Fixed l corresponds to fixed angular momentum for the electron. $L = mv_{\perp}r$ so as r becomes small, v_{\perp} must increase in order to maintain L . This causes an increase in the apparent outward force (the 'centrifugal' force).

For circular motion

$$F = \frac{mv_{\perp}^2}{r} = \frac{L^2}{mr^3}$$

$$L = mv_{\perp}r$$

$$F = -\frac{dV}{dr} \Rightarrow V = \frac{L^2}{2mr^2}$$

Alternatively, we can say that the energy required to supply the extra angular speed must come from the radial motion so this decreases as if a corresponding outward force was being applied.

Roadmap for solution of radial equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \chi = E \chi$$

$$\psi_{nlm}(\mathbf{r}) = R(r)Y_{lm}(\theta, \phi)$$
$$R(r) = \frac{\chi(r)}{r}$$

- Simplify equation using atomic units
- Solve equation in the asymptotic limit (large r)
Gives a decaying exponential solution

$$\chi(r) \xrightarrow{r \rightarrow \infty} \exp(-\kappa r)$$

- Define new radial function by factoring out asymptotic solution

$$\chi(r) = F(r) \exp(-\kappa r)$$

- Solve equation for F(r) using the series (Frobenius) method

$$F(r) = \sum_p a_p r^{p+s}$$

- Find that solution is not normalizable unless series terminates.
This only happens if the eigenvalues have certain special values.
Hence we find the eigenvalues and eigenstates of the H-atom.

Atomic units

There are a lot of physical constants in these expressions. It makes atomic problems simpler to adopt a system of units in which as many as possible of these constants are one. In **atomic units** we set:

Planck constant $\hbar = 1$ (dimensions $[ML^2T^{-1}]$)

Electron mass $m_e = 1$ (dimensions $[M]$)

Constant appearing in Coulomb's law $\frac{e^2}{4\pi\epsilon_0} = 1$ (dimensions $[ML^3T^{-2}]$)

It follows that:

$$\text{Unit of length} = \left(\frac{4\pi\epsilon_0}{e^2} \right) \frac{\hbar^2}{m_e} = 5.29177 \times 10^{-11} \text{ m} = \text{Bohr radius, } a_0$$

$$\text{Unit of energy} = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m_e}{\hbar^2} = 4.35974 \times 10^{-18} \text{ J} = 27.21159 \text{ eV} = \text{Hartree, } E_h$$

In these units the radial equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \chi = E \chi \rightarrow -\frac{1}{2} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] \chi = E \chi$$

Asymptotic solution of radial equation (large r)

Consider the radial equation at very large distances from the nucleus, when both terms in the effective potential can be neglected. We are looking for **bound states** of the atom where the electron does not have enough energy to escape to infinity (i.e. $E < 0$):

$$-\frac{1}{2} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] \chi = E \chi$$

$$\text{Put } E = -\frac{\kappa^2}{2}$$

This gives

$$\frac{d^2 \chi}{dr^2} = \kappa^2 \chi \Rightarrow \chi(r) = \exp(\pm \kappa r)$$

For normalizable solutions we must take the decaying solution

Inspired by this, rewrite the solution in terms of yet another unknown function, $F(r)$:

$$\chi(r) = F(r) \exp(-\kappa r)$$

Differential equation for F

Derive equation for F

$$-\frac{1}{2} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] \chi = E \chi$$

$$\chi(r) = F(r) \exp(-\kappa r)$$

Differential equation for F :

$$\left[\frac{d^2}{dr^2} - 2\kappa \frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} \right] F(r) = 0$$

Series solution (1)

Look for a power-series solution (Frobenius method). The point $r = 0$ is a regular singular point of the equation so at least one well-behaved series solution should exist (see 2B72).

Substitute

$$F(r) = \sum_p a_p r^{p+s}$$

$$\left[\frac{d^2}{dr^2} - 2\kappa \frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} \right] F(r) = 0$$

$$\sum_{p=0}^{\infty} a_p r^{p+s-2} \left[(p+s)(p+s-1) - l(l+1) \right] + \sum_{p=0}^{\infty} a_p r^{p+s-1} \left[-2\kappa(p+s) + 2Z \right] = 0$$

Series solution (2)

The **indicial equation** that fixes s comes from equating coefficients of the lowest power of r which is $s - 2$

$$\sum_{p=0}^{\infty} a_p r^{p+s-2} \left[(p+s)(p+s-1) - l(l+1) \right] + \sum_{p=0}^{\infty} a_p r^{p+s-1} \left[-2\kappa(p+s) + 2Z \right] = 0$$

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

$$\Rightarrow s^2 - s - l(l+1) = 0$$

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

$$s = -l, \quad \text{or} \quad s = l+1$$

We need the **regular solution** that will be well-behaved as $r \rightarrow 0$, so take

$$s = l+1$$

Series solution (3)

General recursion relation comes from equating coefficients of r to the power $p+l$

$$\sum_{p=0}^{\infty} a_p r^{p+l-1} \left[(p+l+1)(p+l) - l(l+1) \right] + \sum_{p=0}^{\infty} a_p r^{p+l} \left[-2\kappa(p+l+1) + 2Z \right] = 0$$

$$\frac{a_{p+1}}{a_p} = \frac{2 \left[\kappa(p+l+1) - Z \right]}{(p+l+2)(p+l+1) - l(l+1)}$$

Series solution (4)

For $p \rightarrow \infty$ we find:

$$\frac{a_{p+1}}{a_p} \xrightarrow{p \rightarrow \infty} \frac{2\kappa}{p}$$

$$\frac{a_{p+1}}{a_p} = \frac{2[\kappa(p+l+1) - Z]}{(p+l+2)(p+l+1) - l(l+1)}$$

Compare with:

(remember a_p is coefficient of r^{p+l+1} in the expansion)

$$\exp(2\kappa r) = \sum_{n=0}^{\infty} \frac{(2\kappa r)^n}{n!} = \sum_{n=0}^{\infty} b_n r^n \quad \text{with } b_n = \frac{(2\kappa)^n}{n!}.$$

Coefficient of r^{p+l+1} would be b_{p+l+1} .

$$\frac{\text{Coefft. of } r^{p+l+2}}{\text{Coefft. of } r^{p+l+1}} = \frac{b_{p+l+2}}{b_{p+l+1}} = \frac{(2\kappa)^{p+l+2}}{(2\kappa)^{p+l+1}} \times \frac{(p+l+1)!}{(p+l+2)!} = \frac{2\kappa}{(p+l+2)} \xrightarrow{p \rightarrow \infty} \frac{2\kappa}{p}$$

So, our series behaves for large p just like $\exp(2\kappa r)$.

Series solution (5)

So, if the series continues to arbitrarily large p , the overall solution becomes

$$\chi(r) = F(r) \exp(-\kappa r)$$

$$\chi(r) \propto \exp(2\kappa r) \times \exp(-\kappa r) = \exp(\kappa r)$$

(not normalizable)

To prevent this **the series must terminate** after a finite number of terms. This only happens if

$$\begin{aligned} \frac{Z}{\kappa} &= (p + l + 1) \text{ for some integer } p = 0, 1, 2, \dots \\ &= n \text{ where } n \text{ is a positive integer } > l : n = l + 1, l + 2, \dots \end{aligned}$$

So finally the energy is

$$E = -\frac{\kappa^2}{2} = -\frac{Z^2}{2n^2}$$

with $n > l$

n is known as the **principal quantum number**. It defines the “shell structure” of the atom.

Summary of solution so far

Each solution of the time-independent Schrödinger equation is defined by three quantum numbers n, l, m

The radial solution depends on n and l but not m

$$\begin{aligned}\psi_{nlm}(\mathbf{r}) &= R_{nl}(r)Y_{lm}(\theta, \phi) \\ &= \frac{\chi_{nl}(r)}{r}Y_{lm}(\theta, \phi) \\ &= \frac{F_{nl}(r)e^{-Zr/n}}{r}Y_{lm}(\theta, \phi)\end{aligned}$$

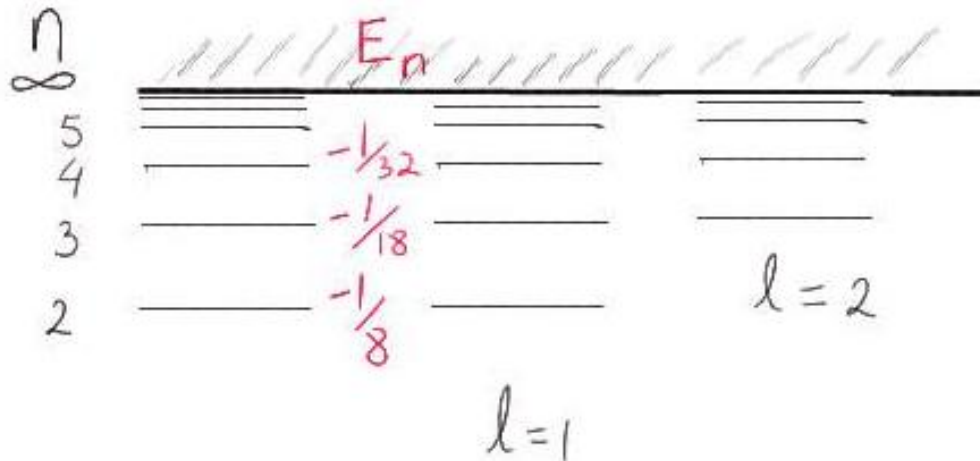
$$F_{nl}(r) = r^{l+1} \sum_{p=0}^{\infty} a_p r^p$$

$$\frac{a_{p+1}}{a_p} = \frac{2Z[(p+l+1)-n]}{n[(p+l+2)(p+l+1)-l(l+1)]}$$

The energy only depends on the principal quantum number n which is bigger than l

$$E_n = -\frac{Z^2}{2n^2}, \quad n = 1, 2, 3, \dots \quad (n > l)$$

The hydrogen energy spectrum



$$E_n = -\frac{1}{2n^2}$$

In Hartrees ($E_h = 27.2\text{eV}$)

In eV ground state energy

= -13.6eV

= - ionisation energy

This simple formula agrees with observed spectral line frequencies to within 6 parts in ten thousand

Hand-drawn diagram showing the energy level for $n=1$ and $l=0$. The energy value is given as $-1/2$ Hartrees.

$n > l$ so

$n = 1$	$l = 0$
$n = 2$	$l = 0, 1$
$n = 3$	$l = 0, 1, 2$

Traditional spectroscopic nomenclature:
 $l = 0$: s states (from “sharp” spectral lines)
 $l = 1$: p states (“principal”)
 $l = 2$: d states (“diffuse”)
 $l = 3$: f states (“fine”)
 ...and so on alphabetically (g,h,i... etc)

The energy spectrum: degeneracy

For each value of $n = 1, 2, 3, \dots$ we have a definite energy:

$$E_n = -\frac{Z^2}{2n^2} \text{ (in atomic units)}$$

For each value of n , we can have n possible values of the total angular momentum quantum number l :

$$l = 0, 1, 2, \dots, n-1$$

For each value of l and n we can have $2l+1$ values of the magnetic quantum number m :

$$m = -l, -(l-1), \dots, 0, \dots, (l-1), l$$

The total number of states (statistical weight) associated with a given energy E_n is therefore: (This neglects electron spin. See Section 7.)

$$\sum_{l=0}^{n-1} (2l+1) = n^2.$$

The fact that the energy is independent of m is a feature of all spherically symmetric systems and hence of all atoms. The independence on l is a special feature of the Coulomb potential, and hence just of hydrogenic atoms. This is known as accidental degeneracy.

The radial wavefunctions

$R_{nl}(r)$ depends on n and l but not on m

$$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0)$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right) \exp\left(\frac{-Zr}{2a_0} \right)$$

$$R_{20}(r) = 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) \exp\left(\frac{-Zr}{2a_0} \right)$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right)^2 \exp\left(\frac{-Zr}{3a_0} \right)$$

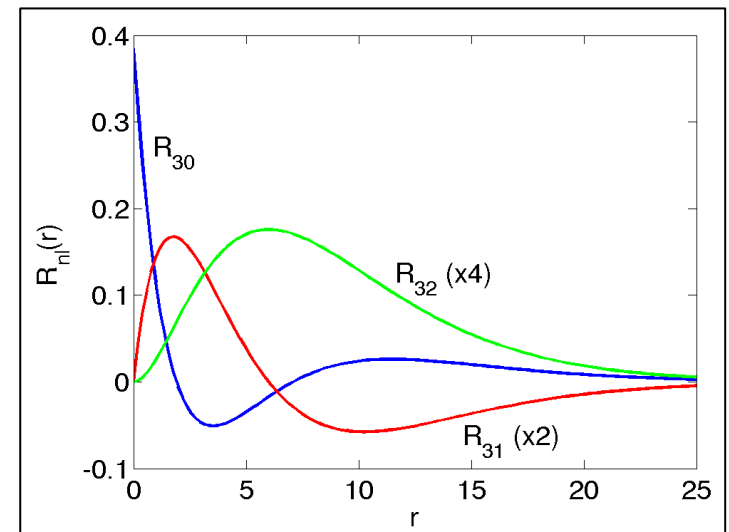
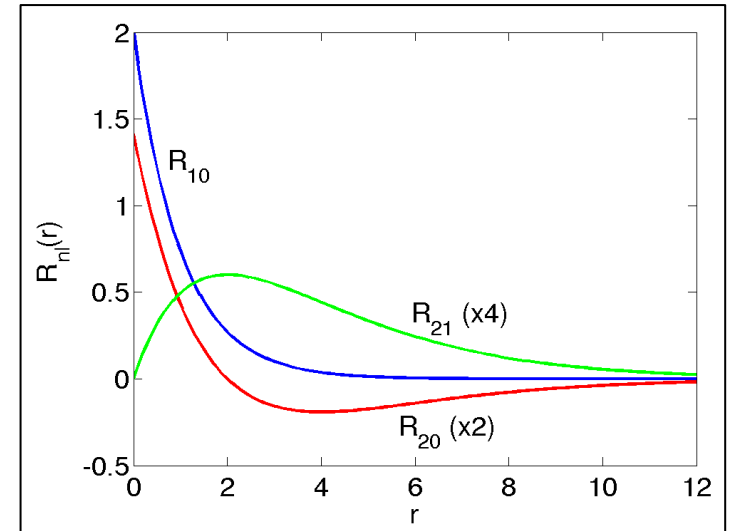
$$R_{31}(r) = \frac{4\sqrt{2}}{9} \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{Zr}{6a_0} \right) \left(\frac{Zr}{a_0} \right) \exp\left(\frac{-Zr}{3a_0} \right)$$

$$R_{30}(r) = 2 \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2 r^2}{27a_0^2} \right) \exp\left(\frac{-Zr}{3a_0} \right)$$

For atomic units set $a_0 = 1$

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

$$R_{nl}(r) = \frac{\chi_{nl}(r)}{r} = \frac{F_{nl}(r)e^{-Zr/n}}{r}$$



The radial wavefunctions (2)

$$\begin{aligned}
 R_{10}(r) &= 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0) \\
 R_{21}(r) &= \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right) \exp\left(\frac{-Zr}{2a_0} \right) \\
 R_{20}(r) &= 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) \exp\left(\frac{-Zr}{2a_0} \right) \\
 R_{32}(r) &= \frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right)^2 \exp\left(\frac{-Zr}{3a_0} \right) \\
 R_{31}(r) &= \frac{4\sqrt{2}}{9} \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{Zr}{6a_0} \right) \left(\frac{Zr}{a_0} \right) \exp\left(\frac{-Zr}{3a_0} \right) \\
 R_{30}(r) &= 2 \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2 r^2}{27a_0^2} \right) \exp\left(\frac{-Zr}{3a_0} \right)
 \end{aligned}$$

Full wavefunctions are:

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

Normalization chosen so that:

$$\int_0^\infty dr r^2 R_{nl}^2(r) = 1$$

Asymptotic solution

$$R_{nl}(r) \xrightarrow{r \rightarrow \infty} \propto r^{n-1} \exp(-Zr/n)$$

Solution near $r = 0$

$$R_{nl}(r) \xrightarrow{r \rightarrow 0} \propto r^l$$

Only s states ($l = 0$) are finite at the origin.

Radial functions have $(n-l-1)$ zeros (excluding $r = 0$).

Radial probability density

Total probability density

$$|\psi_{nlm}(\mathbf{r})|^2 = R_{nl}^2(r) |Y_{lm}(\theta, \phi)|^2 \quad (R_{nl} \text{ is real})$$

$$|\psi_{nlm}(\mathbf{r})|^2 d^3\mathbf{r} = \text{probability of finding particle in a volume element centred on } (r, \theta, \phi)$$

Integrate over all angles using normalization of spherical harmonics

$$d^3\mathbf{r} = r^2 dr d\Omega$$

$$d\Omega = \sin \theta d\theta d\phi \quad (\text{solid angle element})$$

Radial probability density

$$r^2 R_{nl}^2(r) dr = \int_{\theta, \phi} R_{nl}^2(r) |Y_{lm}(\theta, \phi)|^2 r^2 dr d\Omega$$

$$r^2 R_{nl}^2(r) dr = \text{probability of finding the particle in a spherical shell centred on } r, \text{ i.e. at any angle}$$

$$r^2 R_{nl}^2(r) dr = \chi_{nl}^2(r) dr \quad \text{so this is analogous to the 1D case}$$

Angular probability density

Solid angle probability density

$|Y_{lm}(\theta, \phi)|^2$ = probability density of finding particle in a solid angle element

$$d\Omega = \sin \theta d\theta d\phi$$

$$|Y_{lm}(\theta, \phi)|^2 d\Omega =$$

$$|Y_{lm}(\theta, \phi)|^2 \sin \theta d\theta d\phi$$

= probability of finding particle between θ and $\theta + d\theta$ and ϕ and $\phi + d\phi$

Total probability density

$$|\psi_{nlm}(\mathbf{r})|^2 d^3\mathbf{r} = \left(r^2 R_{nl}^2(r) dr \right) \cdot \left(|Y_{lm}(\theta, \phi)|^2 \sin \theta d\theta d\phi \right)$$

= (Radial probability) x (Angular probability)

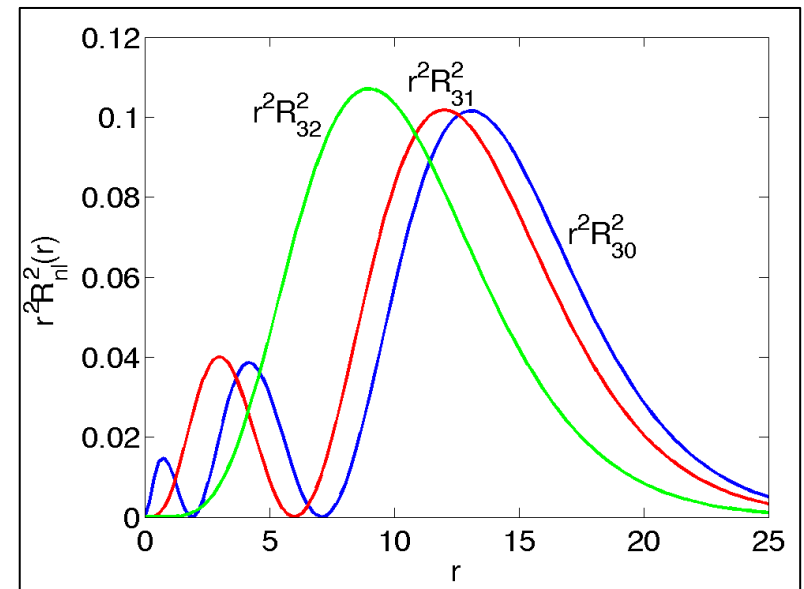
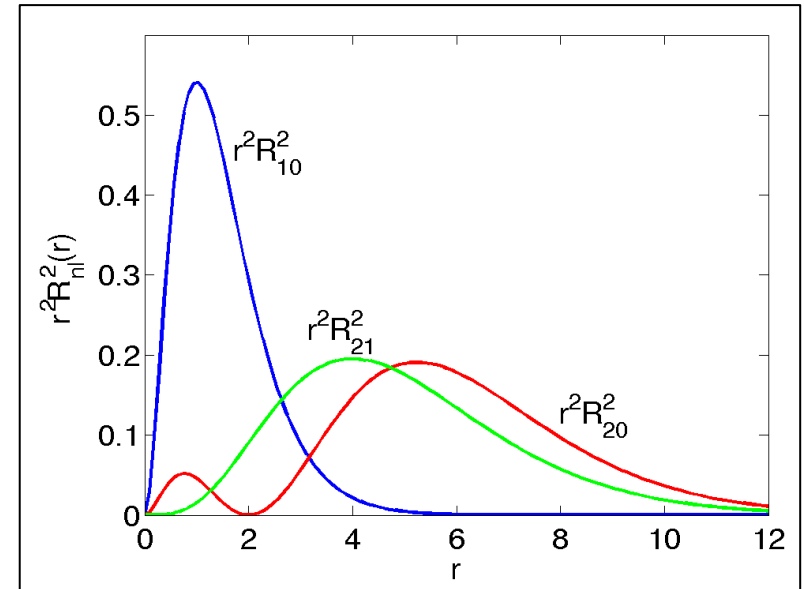
Radial probability density

Radial probability density

$$r^2 R_{nl}^2(r)$$

Orbital	n l	$\langle r \rangle$ (au)
1s	1 0	1.5
2s	2 0	6.0
2p	2 1	5.0
3s	3 0	13.5

$$\begin{aligned} \langle r \rangle &= \int d^3\mathbf{r} \psi_{nlm}^*(\mathbf{r}) r \psi_{nlm}(\mathbf{r}) \\ &= \int_0^\infty dr r^3 |R_{nl}(r)|^2 \end{aligned}$$



Comparison with Bohr model

Bohr model

Angular momentum (about any axis) *assumed* to be quantized in units of Planck's constant:

$$L_z = n\hbar, n = 1, 2, 3, \dots$$

Electron otherwise moves according to classical mechanics and has a single well-defined orbit with radius

$$r_n = \frac{n^2 a_0}{Z}, a_0 = \text{Bohr radius}$$

Energy quantized and determined solely by angular momentum:

$$E_n = -\frac{Z^2}{2n^2} E_h, E_h = \text{Hartree}$$

Quantum mechanics

Angular momentum (about any axis) *shown* to be quantized in units of Planck's constant:

$$L_z = m\hbar, m = -l, \dots, l$$

Electron wavefunction spread over all radii. Can show that the quantum mechanical expectation value of $1/r$ satisfies

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2 a_0} = \frac{1}{r_n}, a_0 = \text{Bohr radius}$$

Energy quantized, but determined solely by principal quantum number n , not by angular momentum:

$$E_n = -\frac{Z^2}{2n^2} E_h, E_h = \text{Hartree}$$

The remaining approximations

These results are not exact because we have made several approximations.

- We have neglected the motion of the nucleus. To fix this we should replace m_e by the **reduced mass** μ . This improves agreement with experiment by an order of magnitude (simple formula gives spectral lines to within 4 parts in 100 thousand!)

$$m_e \rightarrow \mu = \frac{m_e m_p}{m_e + m_p} \quad \text{and} \quad E(n) \propto m_e$$
$$\Rightarrow E(n) \rightarrow \frac{1}{1 + m_e / m_p} E(n) = - \left(\frac{1}{1 + m_e / m_p} \right) \frac{Z^2}{2n^2} E_h$$

- We have used a non-relativistic treatment of the electron and in particular have neglected its spin (see §7). Including these effects give rise to

“**fine structure**”

(from the interaction of the electron’s orbital motion with its spin)

“**hyperfine structure**”

(from the interaction of the electron’s spin with the nuclear spin)

- We have neglected the fact that the EM field between the nucleus and the electron is itself a quantum object. This leads to “quantum electrodynamic” (QED) corrections, and in particular to a small “Lamb shift” of the energy levels.

Summary

Energy levels in au

$$E_n = -\frac{Z^2}{2n^2}, \quad n = 1, 2, 3 \dots \quad (n > l)$$

In Hartrees ($E_h = 27.2\text{eV}$)

Ground state energy = $-1/2 \text{ au} = -13.6\text{eV} = -$ ionisation energy

Statistical weight

$$g = \sum_{l=0}^{n-1} (2l + 1) = n^2$$

Wavefunction

$$\begin{aligned} \psi_{nlm}(\mathbf{r}) &= R_{nl}(r) Y_{lm}(\theta, \phi) \\ &= \frac{F_{nl}(r) e^{-Zr/n}}{r} Y_{lm}(\theta, \phi) \end{aligned}$$

$$F_{nl}(r) = r^{l+1} \sum_{p=0}^{\infty} a_p r^p$$

$$\frac{a_{p+1}}{a_p} = \frac{2Z[(p+l+1)-n]}{n[(p+l+2)(p+l+1)-l(l+1)]}$$

Radial probability density

$$r^2 R_{nl}^2(r)$$

Permissible Quantum States

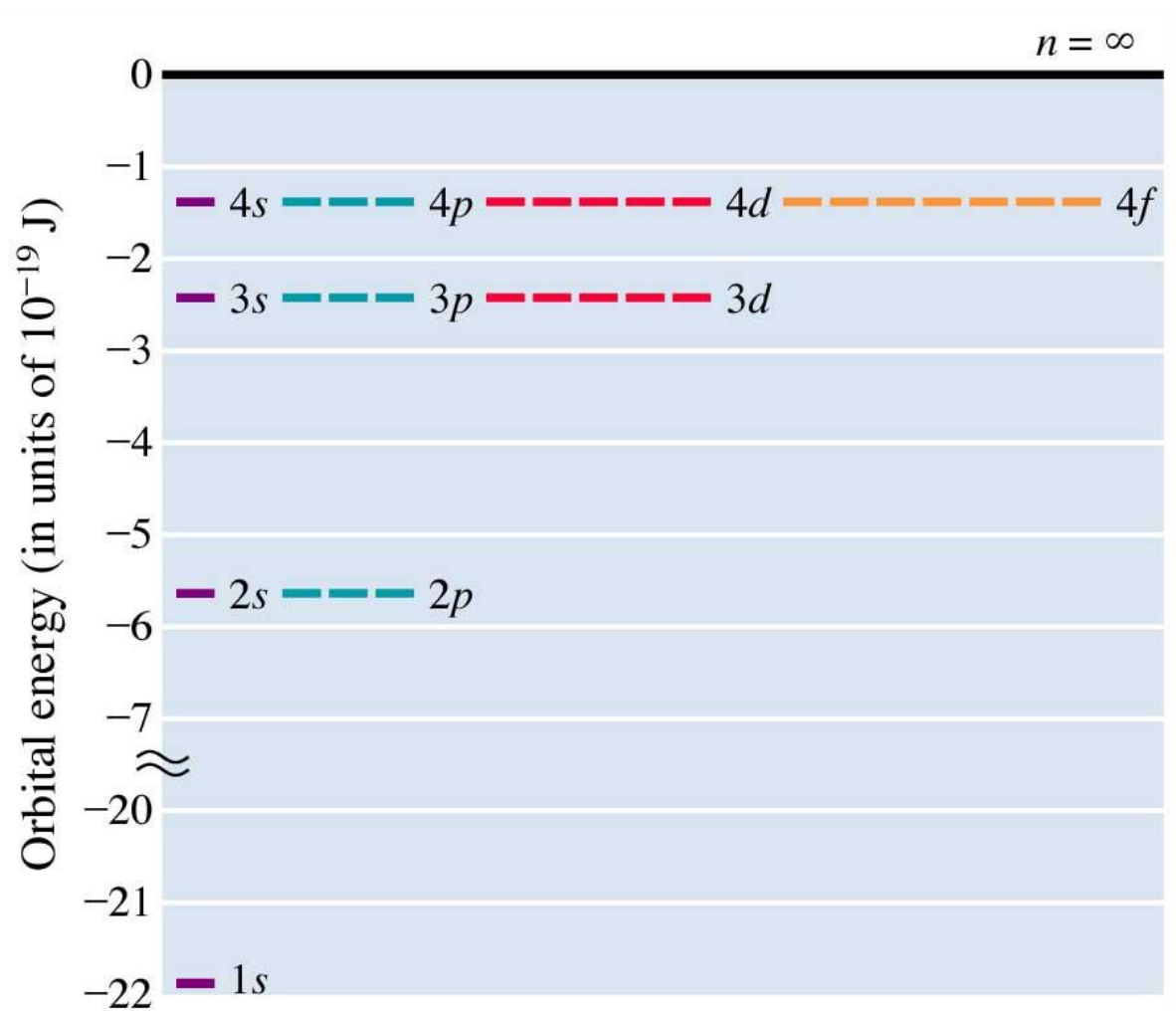
Table 7.1

Permissible Values of Quantum Numbers for Atomic Orbitals

n	l	m_l^*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	-1, 0, +1	2p	3
3	0	0	3s	1
3	1	-1, 0, +1	3p	3
3	2	-2, -1, 0, +1, +2	3d	5
4	0	0	4s	1
4	1	-1, 0, +1	4p	3
4	2	-2, -1, 0, +1, +2	4d	5
4	3	-3, -2, -1, 0, +1, +2, +3	4f	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.

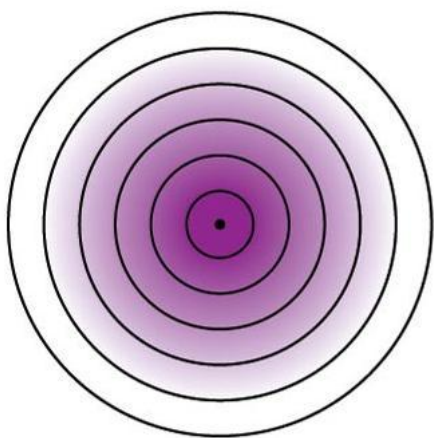
Orbital energies of the hydrogen atom.



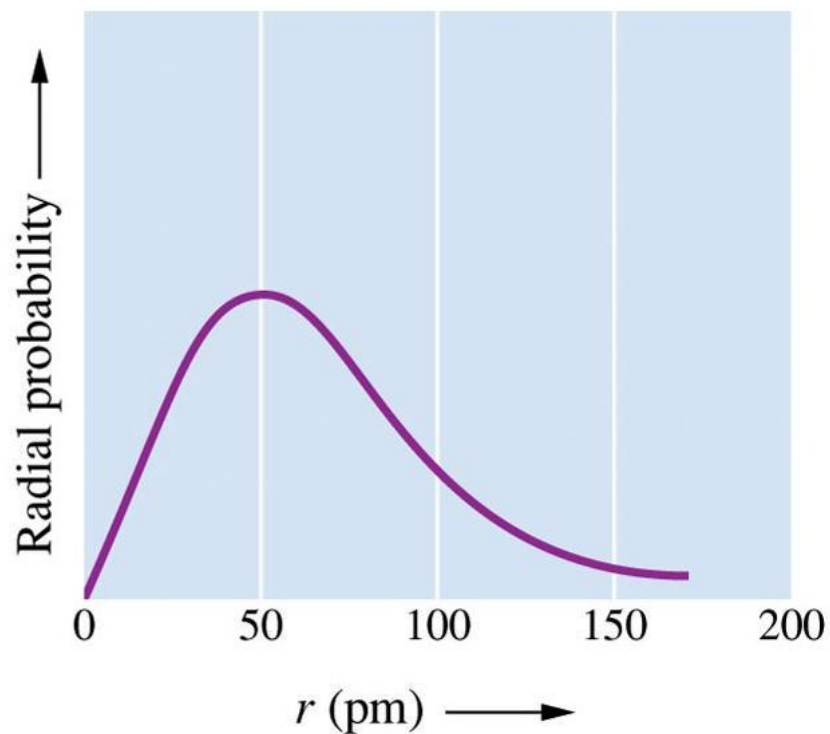
Orbital Energies of Multielectron Atoms

- All elements have the same number of orbitals (s,p, d, and etc.).
- In hydrogen these orbitals all have the same energy.
- In other elements there are slight orbital energy differences as a result of the presence of other electrons in the atom.
- The presence of more than one electron changes the energy of the electron orbitals ([click here](#))

Shape of 1s Orbital

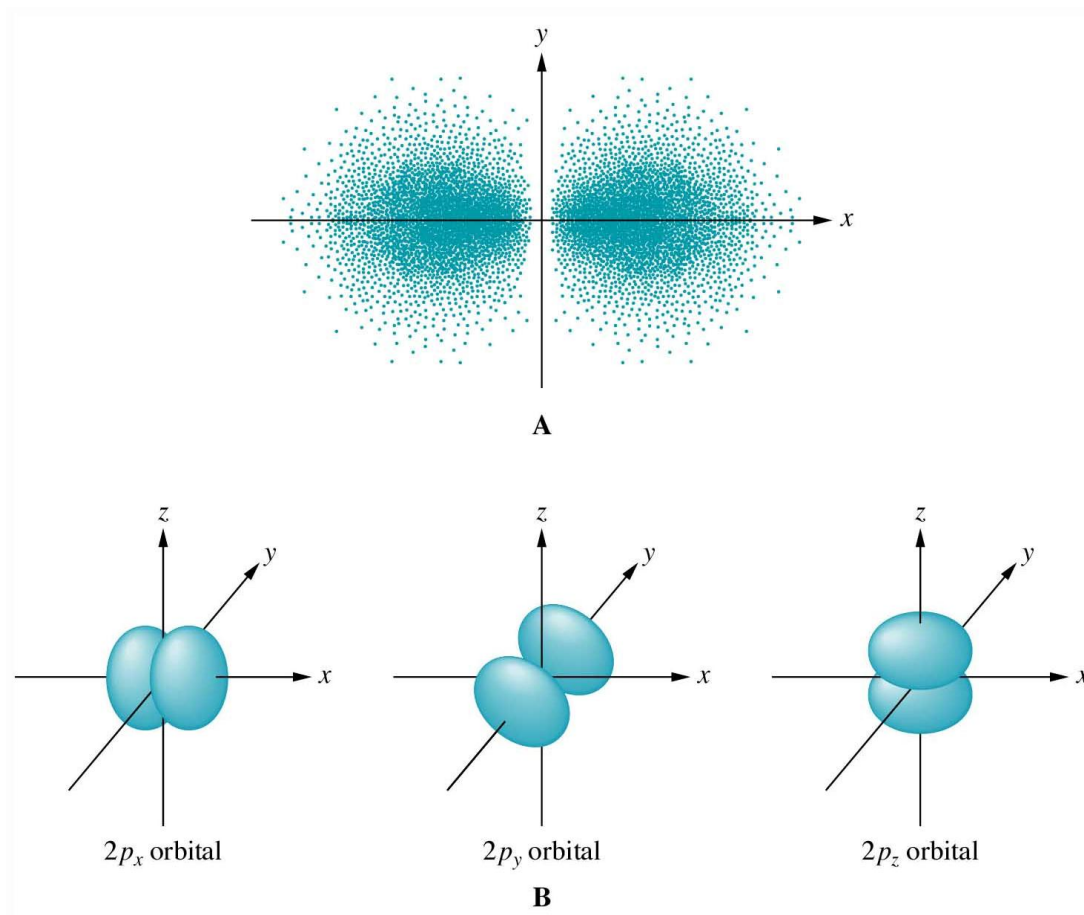


A



B

Shape of 2p Orbital



Shape of 3d Orbitals

