Supplementary Course Topic 1:

Quantum Theory

- Evidence for the failure of classical mechanics
- The meaning of the Wave Equation
- Electronic Structure of the Hydrogen Atom

•Wave Equation, Allowed Energies, Wavelengths

•Properties of waves and shapes of electron atomic orbitals

Shapes of Waves

Representations of Orbitals

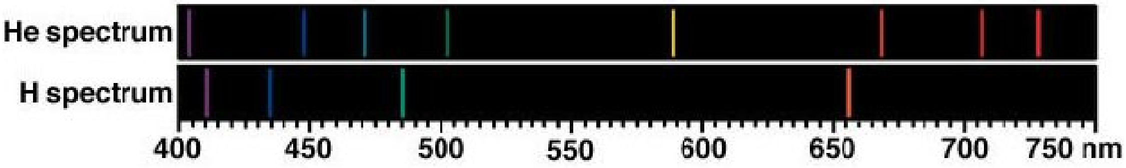
•Energies and Orbitals in Many-electron atoms

Where Does Quantum Mechanics Come From?

Quantum mechanics was developed to explain experimental observations that could not be understood using the prevailing “classical” theories of physics, as well as theoretical inconsistencies with classical electromagnetic theory.

1. Spectroscopic Lines

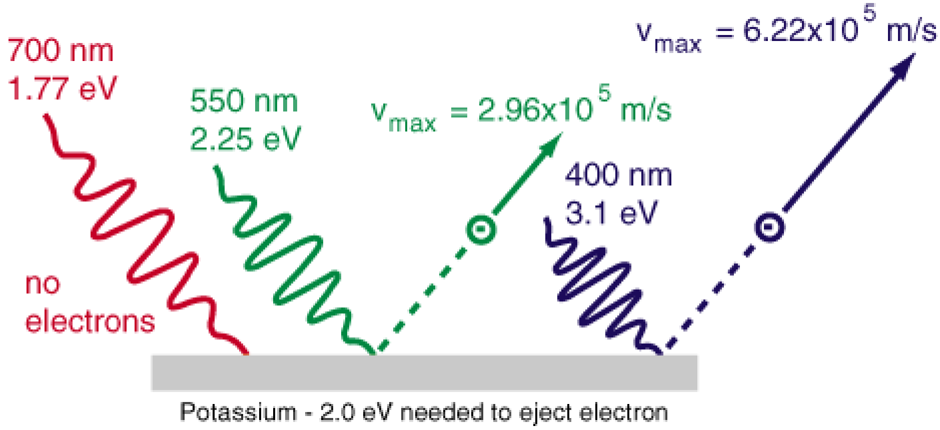
- Moseley: discrete x-ray wavelengths
- Atomic spectra: discrete spectral wavelengths (called “lines”)



Light emitted by an excited atomic gas consists of discrete wavelengths, not a continuous band.

Where Does Quantum Theory Come From?

2. Photoelectric Effect



Photoelectric effect

Light can eject electrons from a metal, but only if its frequency is above a threshold frequency (characteristic for each metal).

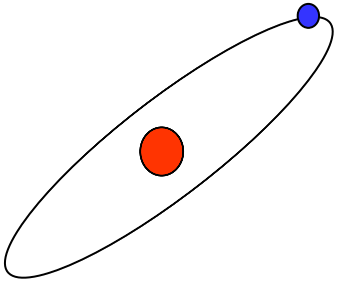
Classically, for light as a wave, its energy is proportional to the square of its *amplitude*.

For particles, energy is proportional to *frequency*.

Einstein (1905) proposed that light has particle nature (as well as wave nature), i.e. light is quantized (photons).

"The Bohr Atom"

3. The Rutherford picture of an atom with electrons orbiting around a central atom *is inconsistent with the laws of classical physics*. Unlike planets orbiting around a star, an orbiting electron is a moving charge and should radiate energy as it spirals towards the nucleus.



Neils Bohr, who had been working in Rutherford's laboratory, developed a quantum model of a single electron near a hydrogen nucleus. His model postulated a set of *circular* orbits for electrons with specific, discrete radii and energies and that electrons could move in each orbit without radiating energy (*even though this violated classical ideas*).

Bohr's theory failed to (i) explain multi-electron atoms (ii) explain bonding and the formation of molecules and liquids and solids (iii) explain the intensities of atomic spectral lines (iv) even explain the "fine structure" in the H spectrum. *Bohr's model did not provide any reason for the discrete orbits or energies* .

Bohr's model proposed discrete or "quantised" allowed energies for the electron for the first time, and provided a rationale for discrete spectral lines.
It even gave the correct formula for the transition wavelengths for one-electron atoms and ions H, He^+, Li^{2+},...

Quantum Theory and Matter Waves

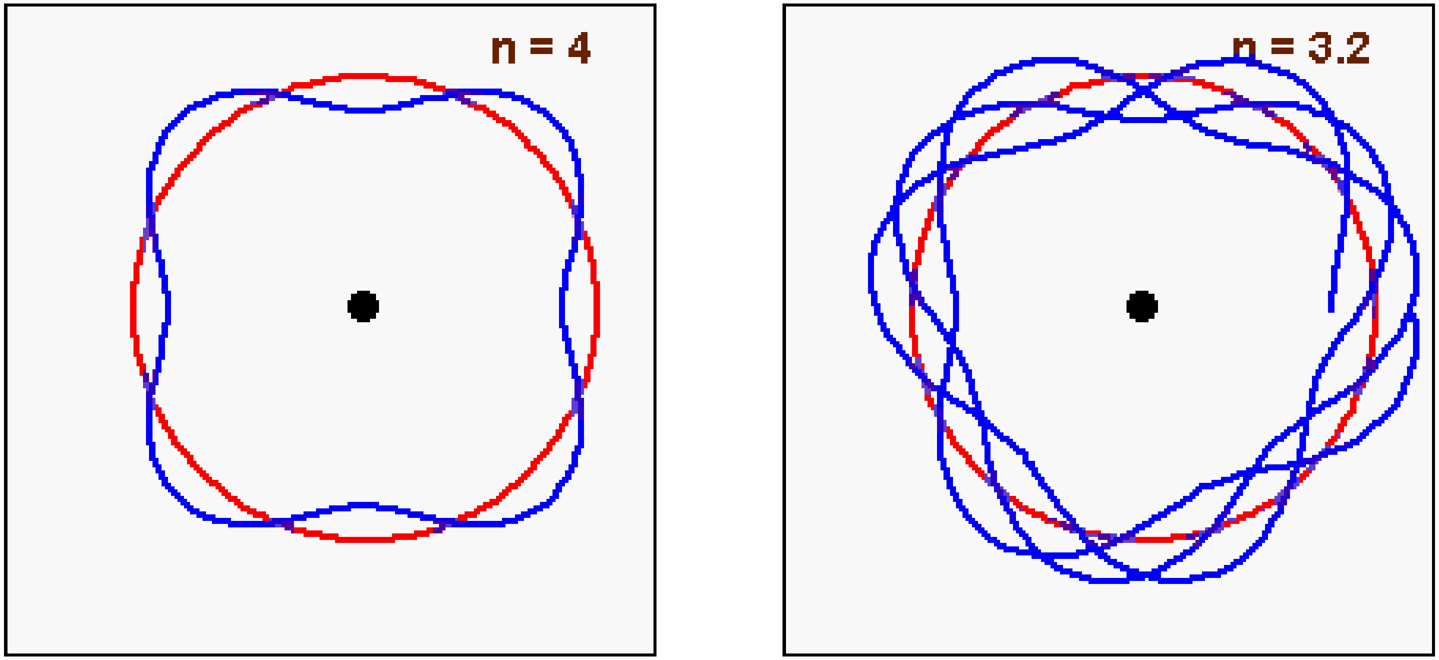
In classical physics, nature consists of matter and energy, which are distinct from one another.

In quantum theory, mass and energy are not distinguished. Matter (electrons, neutrons, atoms, molecules,…) behaves like a wave and energy (= radiation: light, x-rays, γ,...) behaves like a particle.

Quantum theory does not give us an intuitive picture of the fundamental nature of the universe. Very small particles do not behave in a way that is familiar to us based on our (macroscopic) experience.

It began with the radical proposal of Louis de Broglie in 1924 that particles like electrons should exhibit wave-like character, and obey the equations that describe the behaviour of waves, just as light exhibits both particle and wave properties.

Quantum Theory and Matter Waves

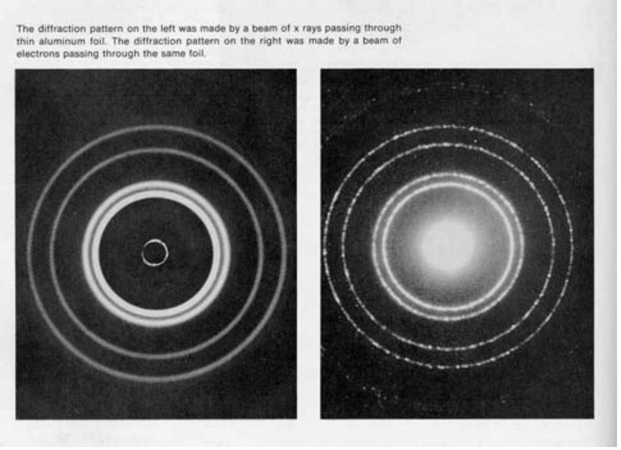


Experimental Evidence for Electron Matter Waves

C.J. Davisson and L.H. Germer; G.P. Thomson (1927) Nobel Prize for Physics 1937

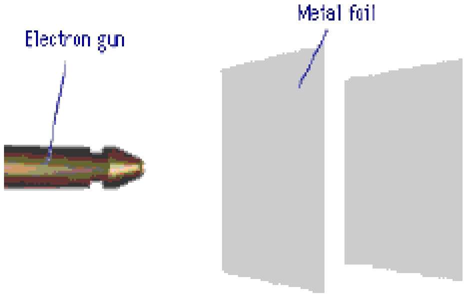
Diffraction patterns produced by a beam of x-rays and electrons passing through Al foil :

X-rays



The diffraction pattern on the left was made by a beam of x rays passing through thin aluminum foil. The diffraction pattern on the right was made by a beam of electrons passing through the same foil.

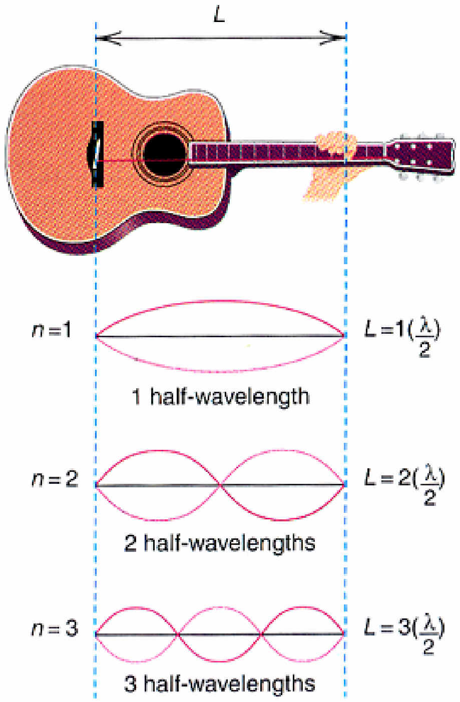
electrons



Application: Electron microscopy

Mechanics of Waves

Waves are common in nature, and we have experience of many kinds of waves on a macroscopic scale.



E.g. Waves on a string

- guitar, violin strings etc. (transverse waves)

E.g. Sound waves.

- Flute (longitudinal waves)

Waves can be two or three dimensional, E.g.

- Bells or chimes; tuning fork; ripples on a pond

The properties or (mechanics) of waves are well-described by the laws of classical physics. The problem of quantum mechanics is how to marry particle and wave character.

Mechanics of Waves

The behaviour of any wave moving in one direction (x) is described by the general wave equation

$$\frac{d^2F}{dx^2} = \frac{1}{v^2}\frac{d^2F}{dt^2}$$

where ***F*** is the “thing that is waving.” i.e.

- the transverse displacement of a string
- the pressure difference in a sound wave
- the magnitude of the electric or magnetic field

and ***v*** is the velocity of the wave. i.e.

- its speed along a string
- the speed of sound
- the speed of light, *c*.

You are not expected to memorise or to use this equation. We will simply use it to establish the historical context for the development of quantum mechanics and the quantum mechanical wave equation.

Electron Wavelengths

The de Broglie relation was first proposed in 1924 to describe the wavelength of a particle, λ.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

where p is the momentum, m the mass and v the velocity. h is the Planck constant 6.626 x 10^{-34} J s.

Although this was just a postulate at the time, subsequent experiments have verified the accuracy of the relationship. E.g. diffraction behaviour of electrons and neutrons of different velocities compared with x-rays of known wavelength.

You are expected to know how to use this equation, which is significant because it relates a classical particle property (mass) to a wavelength, and is generally applicable to all particles.

Electron Wavelengths - Worked Example

What is the wavelength of an electron travelling at 5.0×10^{6} m s^{-1}?

The de Broglie relation $\lambda = \frac{h}{p} = \frac{h}{mv}$

i.e. wavelength, $\lambda = 6.626 \times 10^{-34}/(9.11 \times 10^{-31} \times 5.0 \times 10^{6})$ J s kg^{-1} m^{-1} s

$= 1.5 \times 10^{-10}$ m or 0.15 nm ←

This wavelength is in the same range as an x-ray.

Energy - Electron Volts

The usual (SI) unit of energy is the joule (J). Another convenient unit is the electron volt, eV. This describes the voltage needed to be applied to an electron to accelerate it to a kinetic energy E.

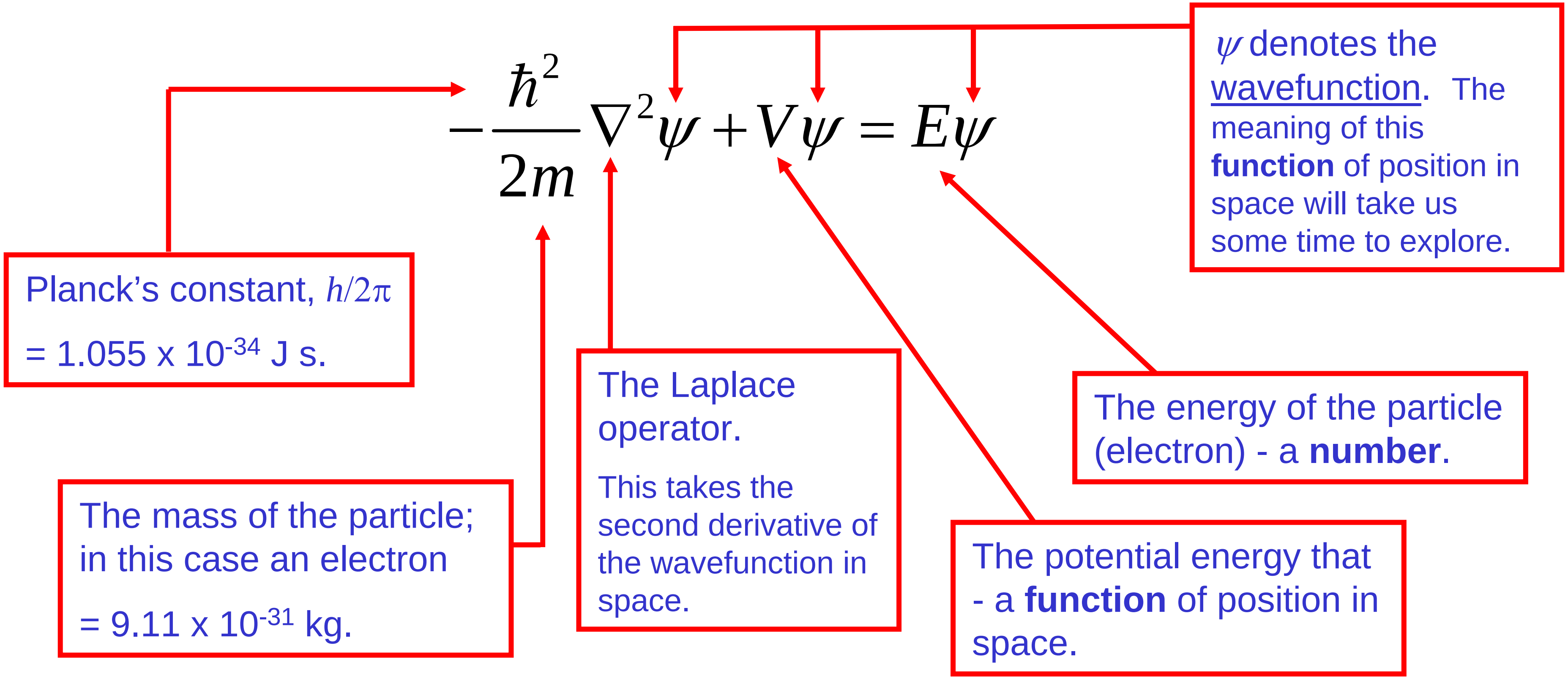
E.g. The electron above has a kinetic energy

$$E = \tfrac{1}{2}mv^{2} = 0.5 \times 9.11 \times 10^{-31} \times (5.0 \times 10^{6})^{2} = 1.1 \times 10^{-17}\,\text{J}$$

or 1.1×10^{-17} J/1.602×10^{-19} J/eV = 71eV.

(Schrödinger's) Wave Equation

In quantum mechanics the wave equation describes the behaviour of all matter. Let's first try to understand the parts of the wave equation.



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

ψ denotes the wavefunction. The meaning of this **function** of position in space will take us some time to explore.

Planck's constant, $h/2\pi$

= 1.055 x 10^{-34} J s.

The Laplace operator.

This takes the second derivative of the wavefunction in space.

The energy of the particle (electron) - a **number**.

The mass of the particle; in this case an electron

= 9.11 x 10^{-31} kg.

The potential energy that - a **function** of position in space.

The wave equation is a *postulate* of quantum mechanics. There is no proof or evidence, except that it successfully describes aspects of the universe. Like the de Broglie relation, it has been repeatedly verified by experiment.

(Schrödinger’s) Wave Equation

The wave equation is often treated in terms of *operators*.

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

The kinetic energy operator (take the 2nd derivative of the wavefunction and multiply by these constants).

The potential energy operator (multiply the potential energy function by the wavefunction)

The energy of the particle (electron) - a **number**.

The wave equation may be viewed as a statement about conservation of energy:

kinetic energy + potential energy = total energy.

(Schrödinger's) Wave Equation

What does the wave equation tell us?

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

Solving the wave equation for a particular potential energy function tells us

1. The wavefunction, ψ.
2. A value for the energy, *E*.

The wave equation is a differential equation which typically has a <u>set</u> of solution functions (eigenfunctions), and a corresponding numerical value for *E* (an eigenvalue).

In this course you are not expected to solve any wave equations. However you will be expected to understand the wavefunction and allowed energies, so we need to go through the use of the wave equation in a bit of detail.

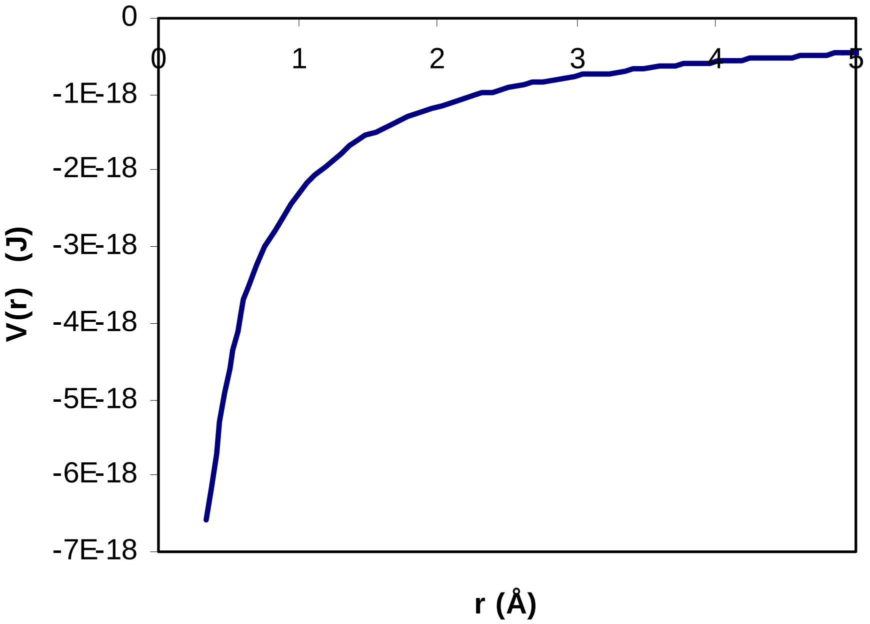
The Potential Energy Function

The potential energy of interaction between a proton and an electron is described by the equation $V(r) = -e^2/4\pi\varepsilon_0 r$

The electron (charge = $-e$) is attracted to the nucleus (charge = $+e$) by an electrostatic force. The potential energy depends on the inverse of the distance between the nucleus and the electron, r, and on the product of the charges of the nucleus and the electron.

$V(r)$ is zero when the proton and electron are an infinite distance apart, but is negative at all values of $r < \infty$. That is, the potential energy of the electron bound to the nucleus is lower than that of a free electron.

We use the term “bound” to describe an electron (or any particle) held in place by an attractive potential energy.



The Wave Equation for the Hydrogen Atom

To solve the wave equation for the hydrogen atom, we substitute the electrostatic potential energy of interaction:- $\boxed{V(r) = -e^2/4\pi\varepsilon_0 r}$

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

For more complex quantum mechanical systems, other potential energy functions are used, as we shall see later.

Solving the wave equation for a particular potential energy function tells us

1. The wavefunction, ψ. (next lecture)
2. A value for the allowed energy, *E*, of each wavefunction

Allowed Energies of the Hydrogen Atom

The solution set of wavefunctions for the hydrogen atom has a set of allowed energies given by the equation

$$E_n = -\frac{me^4}{2\hbar^2 n^2} = -E_R \frac{1}{n^2} \qquad \text{where } n = 1, 2, 3, \ldots$$

The Rydberg constant,

2.18 x 10^{-18} J

Allowed energies in quantum mechanics are often written in terms of a set of quantum numbers such as *n*.

There is one specific energy for each wavefunction, ψ_n.

These values tell us the energies that an electron is allowed to have when it is bound to a hydrogen nucleus. The energies are discrete, or quantized.

That is, only certain specific values of E are allowed. Values between, say $-E_R$ and $-E_R/4$ ($n = 1$ & 2) cannot exist.

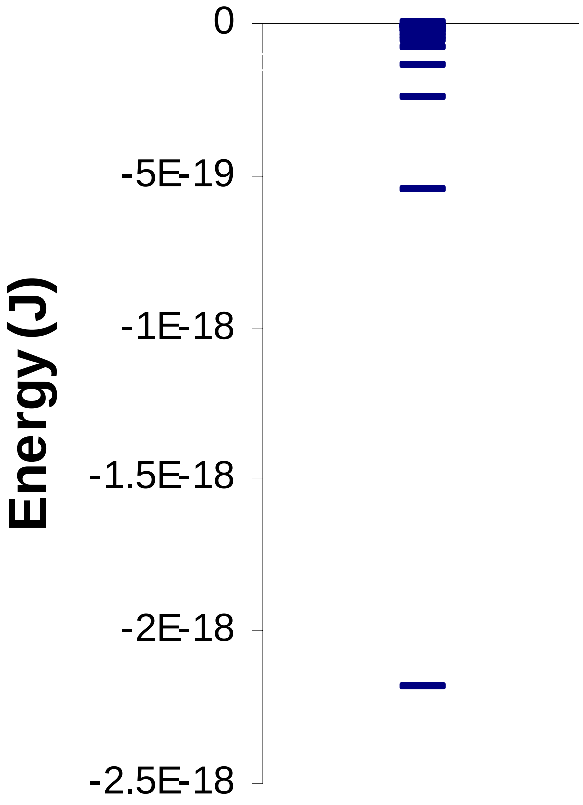
If you want to see the details of the maths, read the Feynmann Lectures on Physics, Lecture 19.

Allowed Energies of the Hydrogen Atom

The lowest allowed energy of the hydrogen atom (n = 1) is E_1 = -2.18 x 10^{-18} J. For n = 2, E_2 = -5.45 x 10^{-19} J; E_3 = -2.42 x 10^{-19} J …

As n increases, E_n approaches the energy of an unbound electron, or 0.

The figure at right shows the allowed electronic energies of the hydrogen atom in their common representation as *energy levels*. (20 levels are shown, but their spacing is too close to be seen on this scale for n > 4.)



Allowed Energies of Hydrogen-Like Atoms

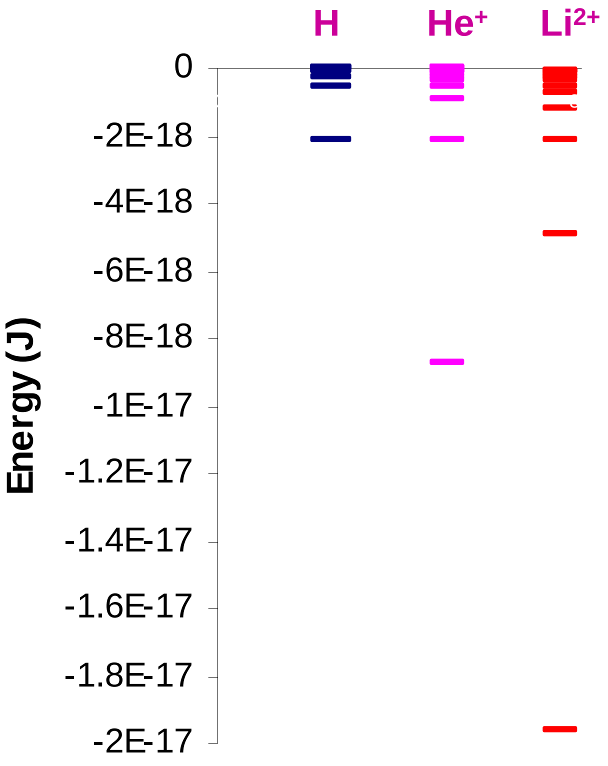
The Schrödinger equation can be solved for an electron bound by a nucleus of any charge. What happens with other “Hydrogen-like” nuclei, e.g. He^{2+}, N^{6+}?

The potential energy function for a nucleus of atomic number (and hence charge) Z is:- $V(r) = -Ze^2/r$.

The allowed energies now become

$$E_n = -\frac{mZ^2e^4}{2\hbar^2n^2} = -E_R\frac{Z^2}{n^2}$$

That is, the energy of the bound states is lowered by the increased attraction of the more highly charged nucleus.



Hydrogen-like atoms have been created in the laboratory and detected in space, and provide experimental verification of these allowed energies.

Spectroscopy and Transitions between States

Spectroscopy is the study of how light interacts with matter. More specifically, it is the study of how photons of light can cause transitions between quantum states of an atom or molecules.

In *electronic spectroscopy*, light causes a change in the quantum state and therefore the energy of a bound electron. This energy change is often diagnostic for the atom or molecule that binds the electron.

Spectroscopy measures the energy difference between between allowed energy levels.

For hydrogen-like atoms, the difference between energy levels is given by

$$\Delta E = E_n - E_m = -Z^2 E_R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

but how do we know the energy of light?

Light: Energy, Frequency, Wavelength

Light is an electromagnetic wave. It oscillates with a characteristic frequency or wavelength. Because the speed of light is fixed, the frequency, ν (nu), and wavelength, λ (lambda), are related by

$$\nu = \frac{c}{\lambda}$$

where *c* is the speed of light, 3.0×10^{8} m s^{-1}.

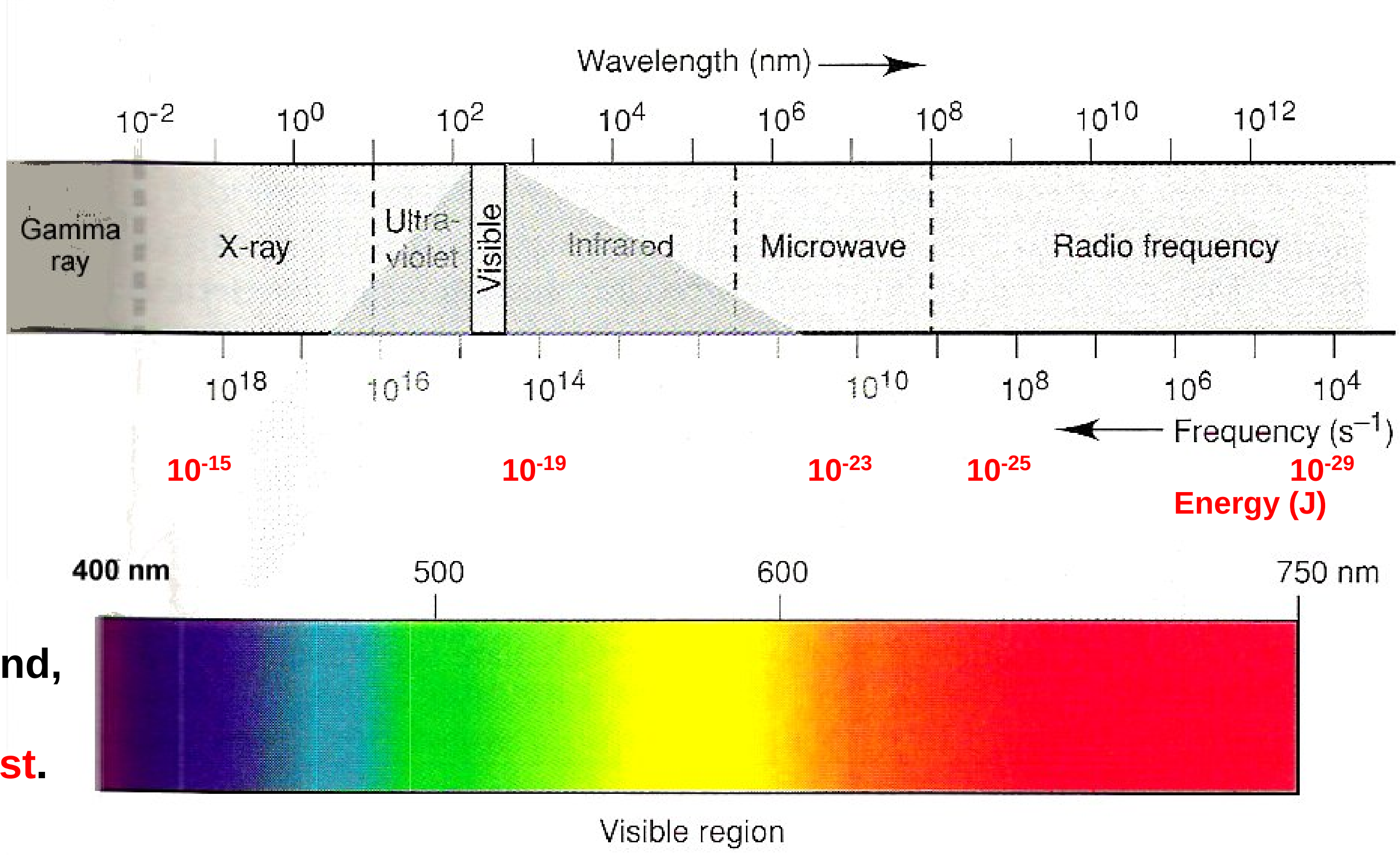
The energy of a light wave is directly proportional to its frequency (and thus inversely proportional to its wavelength),

$$E = h\nu = \frac{hc}{\lambda}$$

Energy, Frequency, Wavelength

Shorter wavelengths equate to higher frequency and higher energy. We broadly classify electromagnetic (EM) radiation into wavelength or frequency bands. In decreasing order of energy these are

γ-rays, x-rays, UV, visible light, infrared, microwaves, radiofrequency



Within the visible band, violet is highest in energy and red lowest.

Energy, Frequency, Wavelength - Worked Example

E.g. Calculate the energy of red light

Referring to the previous diagram, λ = 750nm. The energy is simply

$$E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3.00\times10^{8}}{750\times10^{-9}}\left(\frac{J\ s\ m\ s^{-1}}{m}\right) = 2.65\times10^{-19}\,J$$

E.g. Calculate the energy and wavelength of an x-ray of frequency $10^{18}s^{-1}$.

The energy is $E = h\nu = 6.626\times10^{-34}\times10^{18}(J\ s\ s^{-1}) = 6.63\times10^{-16}\,J$

and the wavelength is $\lambda = \frac{c}{\nu} = \frac{3\times10^{8}}{10^{18}}\left(\frac{m\ s^{-1}}{s^{-1}}\right) = 3\times10^{-10}\,m = 0.3\ nm$

Atomic Spectroscopy - Worked Example

E.g. What wavelength of light will excite an electron in a hydrogen atom from n=1 to n=3?

First, calculate the energy difference for $Z = 1$, $n = 3$, $m = 1$ ← Higher E - Lower E

$$\Delta E = -Z^2 E_R \left(\frac{1}{n^2} - \frac{1}{m^2} \right) = -1 \times 2.18 \times 10^{-18} \times \left(\frac{1}{9} - \frac{1}{1} \right) = 1.94 \times 10^{-18}\, J$$

Now, calculate the wavelength corresponding to that energy

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^{8}}{1.94 \times 10^{-18}} \left(\frac{J\ s\ m\ s^{-1}}{J} \right) = 1.02 \times 10^{-7}\, m$$

or 102 nm. ← This wavelength lies in the ultraviolet range.

This is an example of an atomic spectral line, which was part of the early evidence for quantum effects in nature.
We will examine these in more detail in Lectures 8 & 9.

Atomic Spectroscopy - Alternative Working

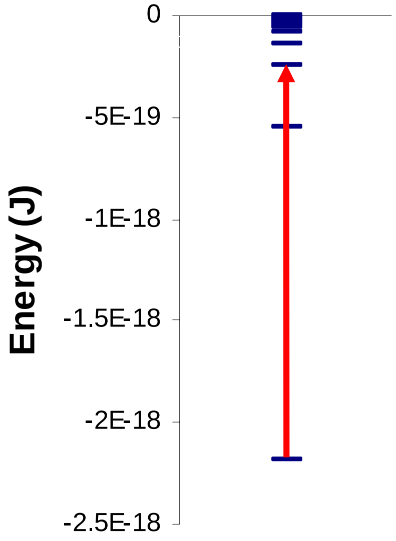
E.g. What wavelength of light will excite an electron in a hydrogen atom from n=1 to n=3?

First, equate the energy difference for *Z* = 1, *n* = 3, *m* = 1 to the photon energy

$$\frac{hc}{\lambda} = -Z^2 E_R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$\Rightarrow \lambda = \frac{hc}{Z^2 E_R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)} = \frac{6.626\times10^{-34}\times3.00\times10^{8}}{2.18\times10^{-18}\times\left(\frac{1}{1} - \frac{1}{9}\right)}$$

$$= 1.02\times10^{-7}\, m$$



This alternative is included because it also shows the form of the equation used (empirically) by Moseley in 1913 to fit his x-ray spectral lines (see lecture 5).

$$\frac{1}{\sqrt{\lambda}} = kZ$$

Atomic Spectrum of Hydrogen

Quantum mechanics can be used to explain atomic line spectra through these two relationships, which had previously been figured out *empirically*. That atomic visible line spectra of hydrogen fall into *series* had been known since Balmer in 1885 showed that they followed the equation

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

where $R = E_R/hc$.

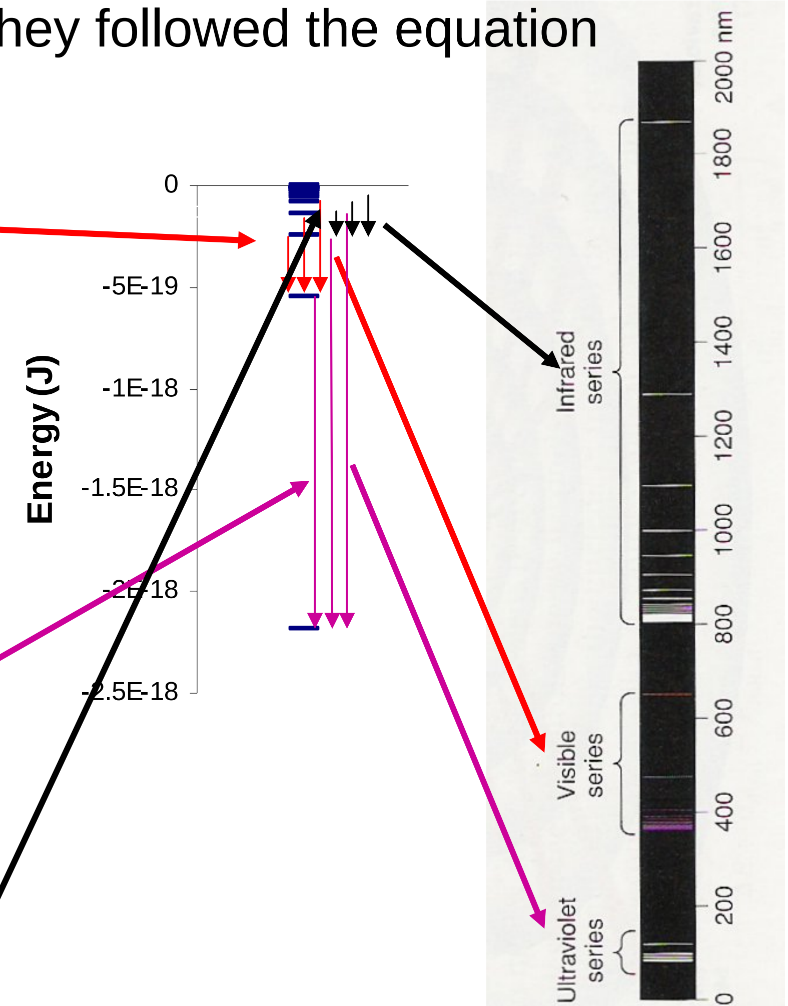
This series describes absorption or emission from hydrogen atoms with electrons in the 3rd, 4th, 5th, etc... energy levels dropping to the 2nd allowed level.

Other series occur at higher (ultraviolet)

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

and at lower energies (infrared)

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{3^2}\right)$$



Atomic Spectroscopy - Worked Example

E.g. What wavelength of light will excite an electron in a hydrogen atom from n=1 to n=3?

First, calculate the energy difference for $Z = 1$, $n = 3$, $m = 1$ ←

Higher E - Lower E

$$\Delta E = -Z^2 E_R \left(\frac{1}{n^2} - \frac{1}{m^2} \right) = -1 \times 2.18 \times 10^{-18} \times \left(\frac{1}{9} - \frac{1}{1} \right) = 1.94 \times 10^{-18}\, J$$

Now, calculate the wavelength corresponding to that energy

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^{8}}{1.94 \times 10^{-18}} \left(\frac{J\ s\ m\ s^{-1}}{J} \right) = 1.02 \times 10^{-7}\, m$$

or 102 nm. ←

This wavelength lies in the ultraviolet range.

This is an example of an atomic spectral line, which was part of the early evidence for quantum effects in nature.
We will examine these in more detail in Lectures 8 & 9.

Mechanics of Waves

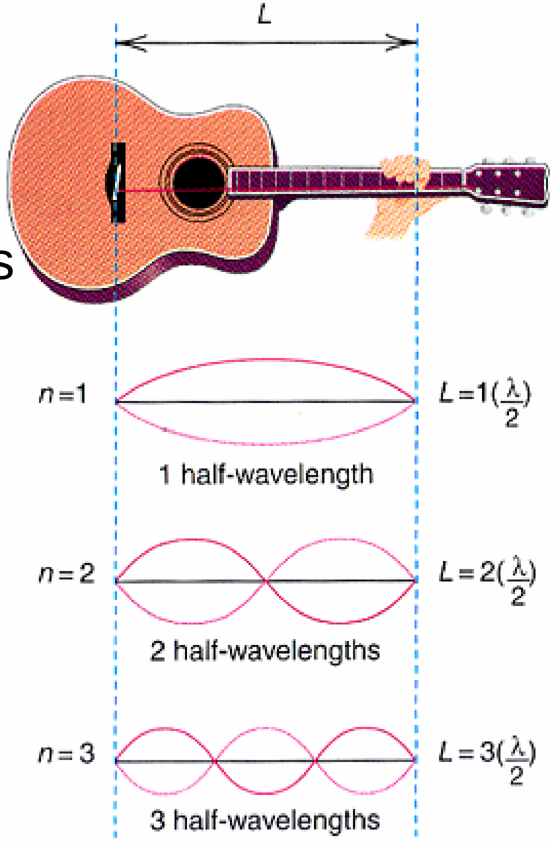
E.g.1. Waves in one dimension: Waves on a (guitar) string

The guitar string is bounded at each end, and oscillates with a particular frequency. The only waves that can be sustained by a string are those with *zero amplitude* at each end. These are called *nodes*.

Amplitude is the magnitude of the displacement from the average position. It can be positive (up) or negative (down).

In other words, the distance between the nodes (half-wavelength) must divide into the total length of the guitar string an integer number of times.

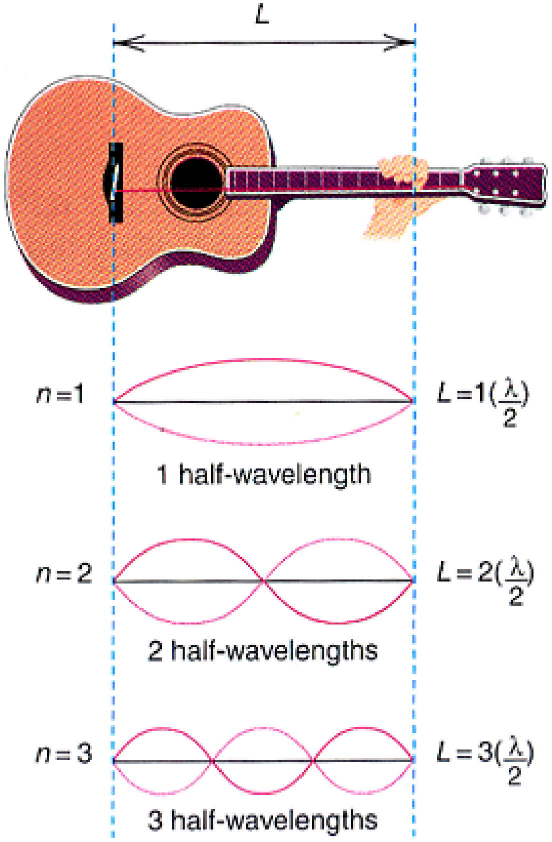
These are known as standing waves or stationary states or normal modes of the string.



More nodes means a shorter wavelength.

Mechanics of Waves - Sound Waves

E.g.1. Waves in one dimension: Waves on a (guitar) string



The lowest frequency mode, L = $\lambda/2$, is called the fundamental frequency, ν, and has nodes only at the ends.

The *first harmonic* is the next lowest frequency, and has one node at the mid-point: L = λ. The *frequency* is twice that of the fundamental, 2ν.

The *second harmonic* has two nodes between the end-points, and its frequency is 3 times the fundamental, 3ν : $\lambda = 2L/3$.

Etc., etc.

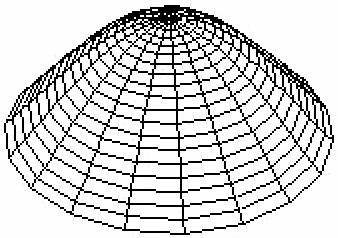
As with all waves, wavelength and frequency are related by $\lambda = \frac{\text{constant}}{\nu}$

Mechanics of Waves on a Surface

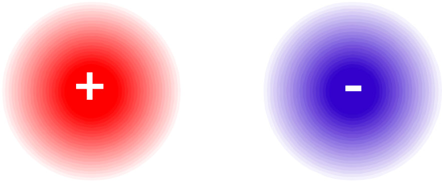
E.g.2. Waves in two dimensions: Modes of a drumhead

Standing waves can also be generated on a surface or thin membrane. A drumhead has a fixed perimeter, and oscillations on this surface lead to more complicated patterns of displacement and nodes

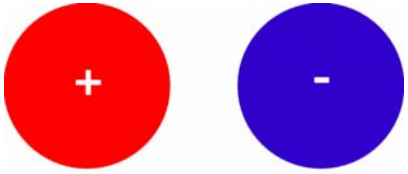
First, consider the *fundamental mode* of the membrane. It is analogous to the fundamental of a vibrating string, and the diameter of the drum is $\lambda/2$. The whole drumhead oscillates above and below the plane with an amplitude defined by the maximum displacement.



These waves can be represented as a *contour plot*, or simply as lobes of positive (above the plane) and negative (below the plane) displacement. The fundamental oscillates between positive and negative with a frequency, ν. The whole drum is either + or -.



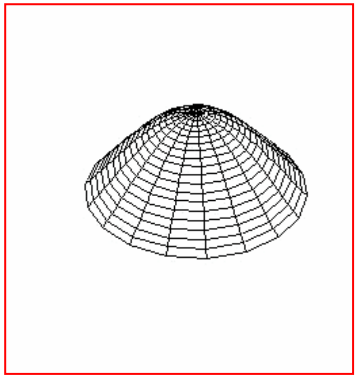
0 nodes



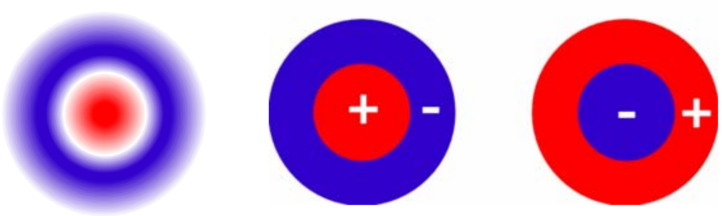
Mechanics of Waves on a Surface

The *fundamental*.

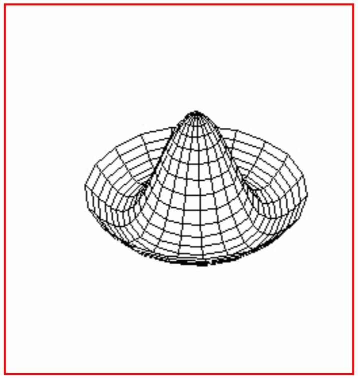
0 nodes



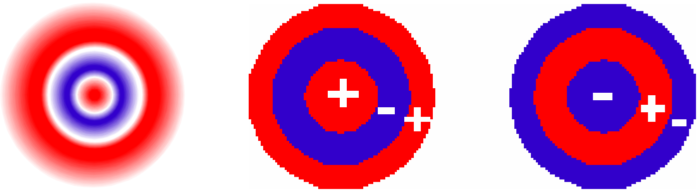
Like 1-D waves, the higher-order harmonic oscillations in higher dimensions also have nodes (lines in 2-D) where the drumhead *never* moves.



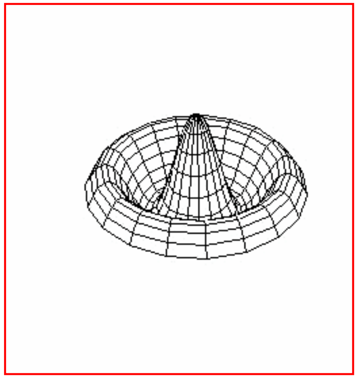
1 circular node



The nodes are lines in the plane of the circumference of the drum.



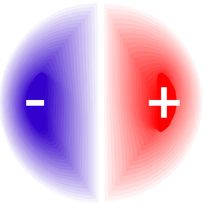
2 circular nodes

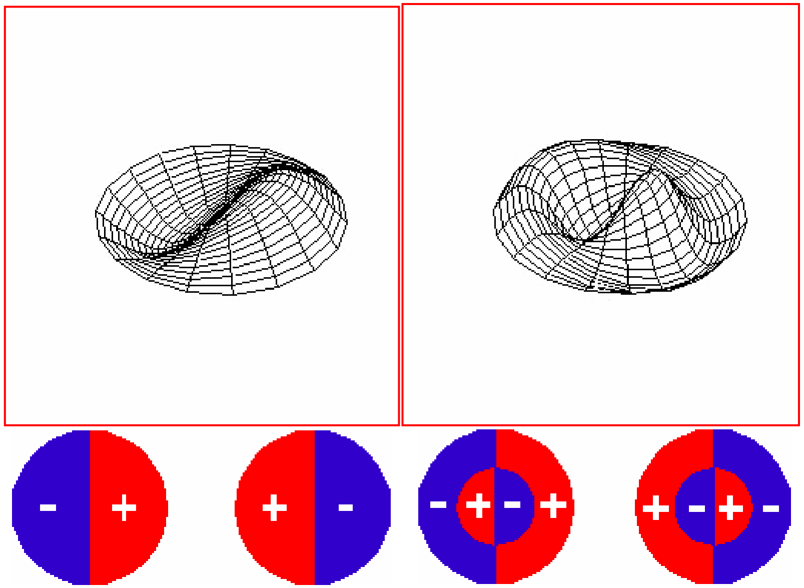


Mechanics of Waves on a Surface

Membranes can also generate <u>asymmetric</u> standing waves of various kinds.

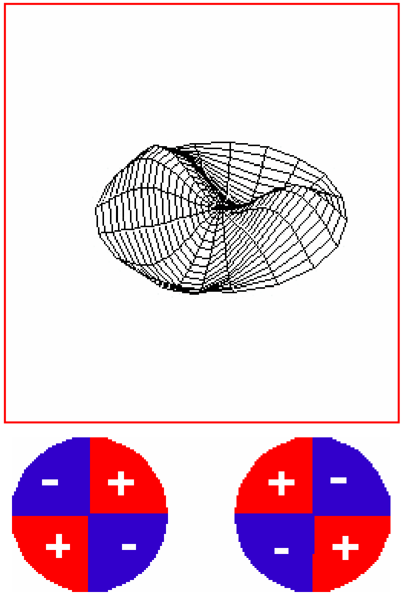
In the simplest kind of harmonic the membrane is halved, making a linear node.





In another, it is quartered, giving two linear nodes at right angles.

These *normal modes* are described mathematically as *orthogonal*. This simply means that you can't create one of them by combining any two or more of the others.



Electrons as Waves in Three Dimensions

The wavefunctions that describe electrons are three-dimensional waves. They have similar properties and features as one- and two-dimensional waves. i.e. Positive and negative lobes, and nodes (which are planes in 3-D).

The quantum description of an electron is simply a standing wave in three dimensions.

Like the modes of a drumhead, standing waves or stationary states in 3-D may be spherically symmetric or asymmetric.

We can use a contour plot or lobe representation to describe an electron wave, but it is need simple representations of 3-D waves.

Spherically Symmetric Wavefunctions

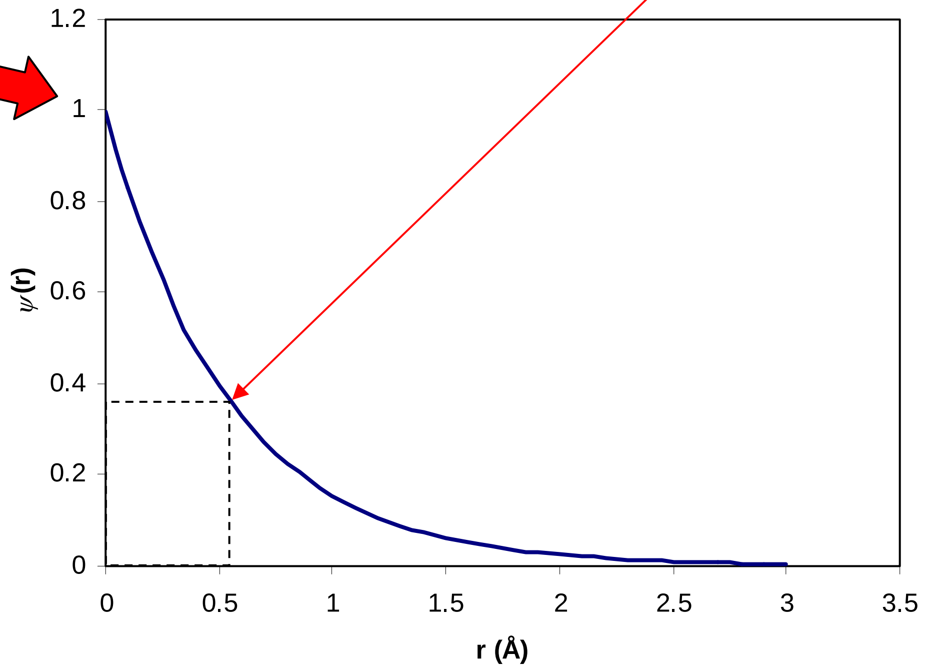
The lowest energy (n=1) solution of the wave equation for the hydrogen atom corresponds to one, spherically symmetric, wavefunction. The shape of the wavefunction is described by the equation

$$\psi(r) = \exp(-r/\rho)$$

The wavefunction only depends on distance from the nucleus, *r*

The Bohr radius, = 0.528Å

ψ is a maximum at the nucleus.



This wavefunction can be represented as a graph of amplitude versus radial distance from the nucleus.

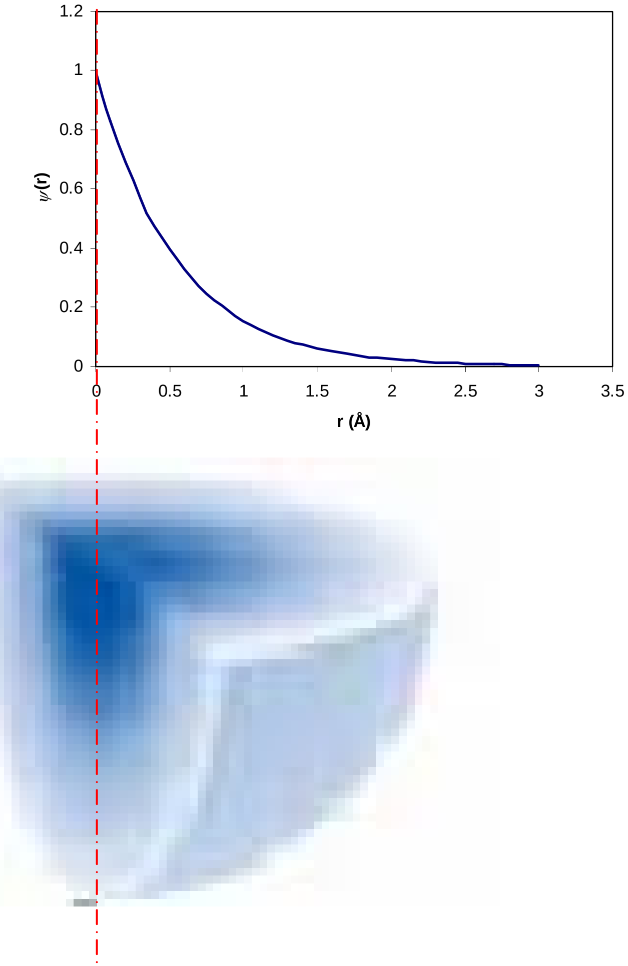
This wavefunction is called the 1s orbital and corresponds to an energy

$$E_1 = -E_R = -2.18 \times 10^{-18}\ \text{J}$$

The 1s Orbital

This orbital can be represented as a radial function,

This plot shows the amplitude of the 1s wavefunction, plotted as a function of distance, *r*, away from the nucleus.
The maximum amplitude is <u>at the nucleus</u>.



or as gradient or contour

The intensity of the shading indicates the amplitude of the wavefunction, which is a maximum at the nucleus and decreases with increasing *r*.
Only 1/4 of the wavefunction is represented here.

or simply as a lobe.

The spherical lobe indicates the *sign* of the wavefunction, and its radius is an indication of how far the electron extends from the nucleus. (This will be quantified later.)

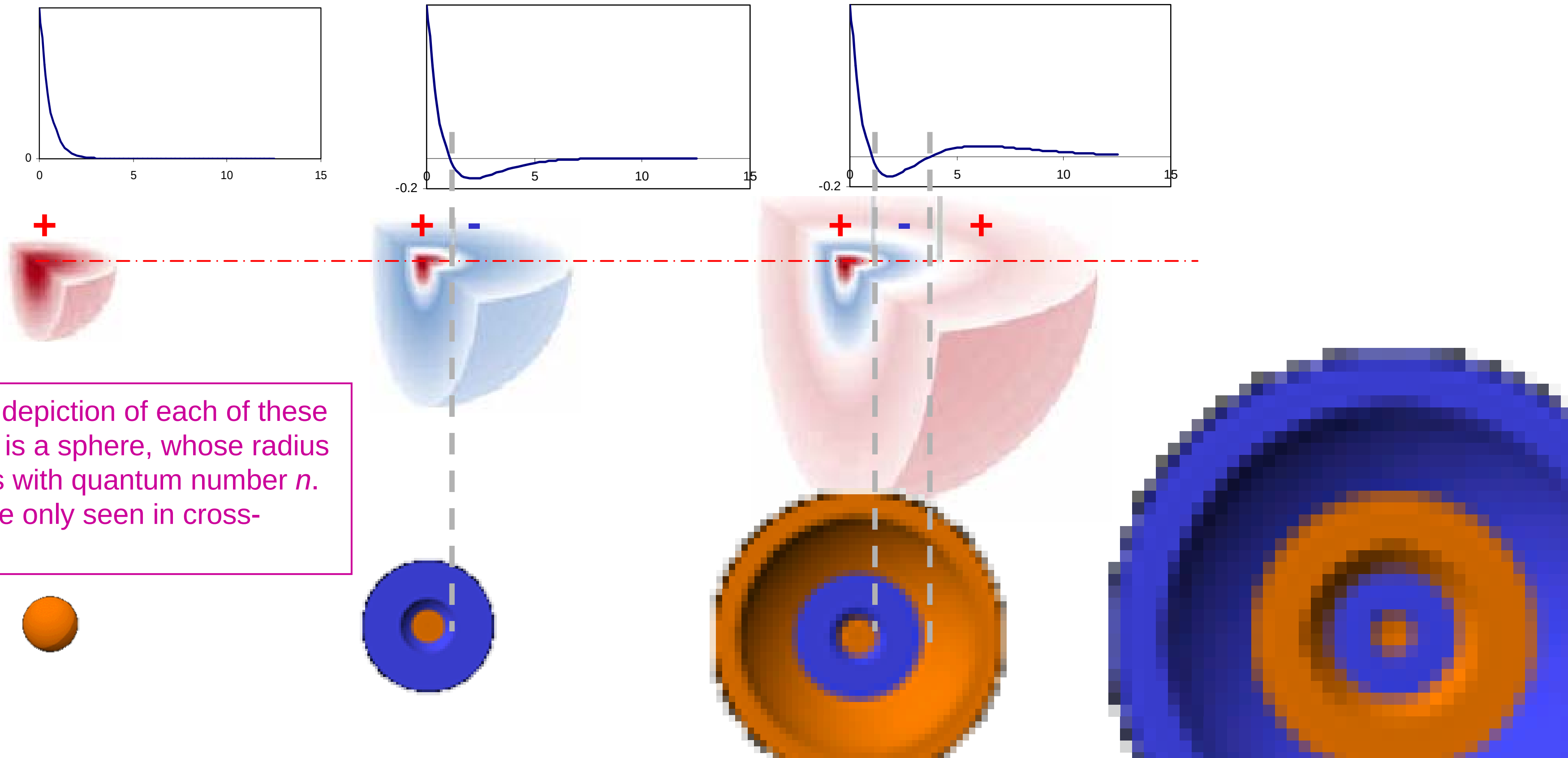
Note that there are no nodes in the 1s orbital.

Spherically Symmetric Orbitals

Higher energy solutions to the wave equation have more than one wavefunction. Like drums in 2-D, these can be radially symmetrical or not.

Higher energy wavefunctions have more nodes (and shorter wavelengths). The nodes of the radially symmetric wavefunctions are the surfaces of spheres.

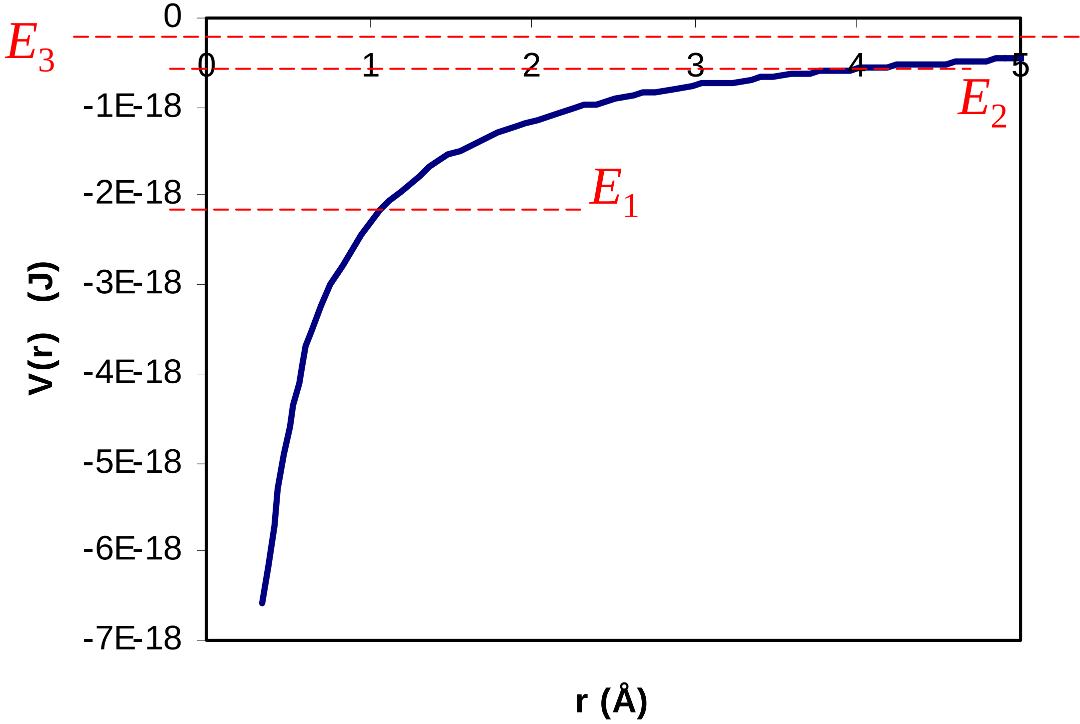
n=1 1s *n*=2 2s *n*=3 3s *n*=4 4s



The lobe depiction of each of these *s* orbitals is a sphere, whose radius increases with quantum number *n*. *Nodes* are only seen in cross-section.

Boundary Conditions

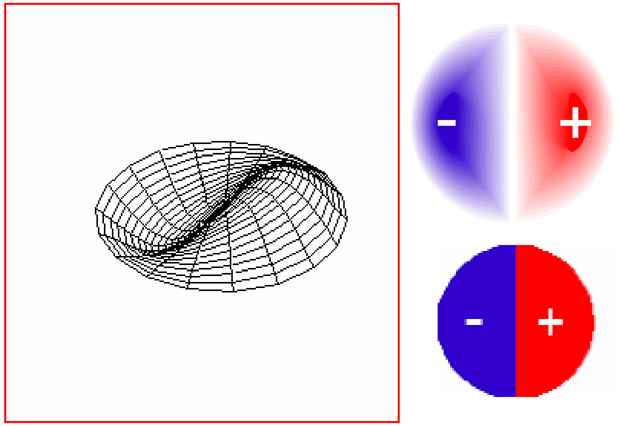
Unlike a drumhead or a string, an electron is not fixed at its perimeter or ends by a mechanical device. An electron wave is bounded by the potential energy function which is not an abrupt step, but a smooth function. For the hydrogen atom this bounding potential is $V(r) = -e^2/r$.

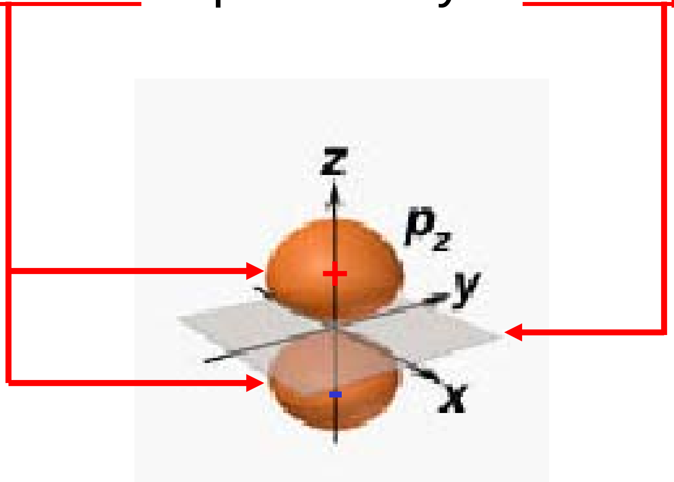


Higher energy (and higher quantum number) electron wavefunctions extend farther from the nucleus.

Non-spherical orbitals

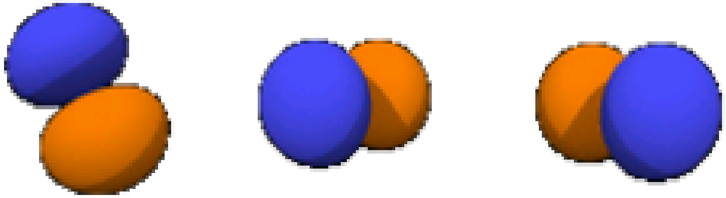
The Schrödinger equation for the hydrogen atom also has solution wavefunctions that are *not spherically symmetrical*. These are easily seen to be analogous to the asymmetric drumhead modes.
The simplest form consists of two lobes separated by a nodal plane, and is denoted a a p-orbital.





The lobe representating the angular dependence of the wavefunctions are described by functions known as *spherical harmonics*.

There are three (orthogonal) p-orbitals, one with lobes oriented along each of the x-, y-, and z-axes.



Orbital Angular Momentum

As we have seen from the de Broglie relation, electrons have both wavelength and momentum. Electrons bound in orbitals also have *angular momentum*, and this is described by two additional quantum numbers.

Like energy, angular momentum is *quantised* into discrete values.

- Spherically symmetric (s) orbitals have 0 angular momentum.
- Other orbitals have angular momenta that are integer multiples of $h/2\pi$. This integer is the orbital angular momentum quantum number, l.
- l may take on any value between 0 and n-1;

For $n = 1$, $l = 0$ - Only an s orbital.
For $n = 2$, $l = 0$ (s orbital) or 1 (p orbitals)

Orbital Angular Momentum

The *number* of orbitals with angular momentum $l \times h/2\pi$ is determined by their shape. This also determines the number of orthogonal wavefunctions - such as p_x, p_y, and p_z.

This is characterised by the *magnetic quantum number*, m or m_l. m_l can take any integer value between $-l$ and l, and describes the *orientation* of the orbital.

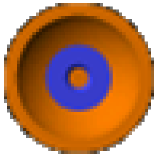
For $l = 0$, $m_l = 0$ (one s orbital)
For $l = 1$, $m_l = -1, 0, +1$ (three p orbitals)
For a given l, there are always $2l+1$ orbitals

In hydrogen-like (one electron) atoms, the energy of the wavefunction depends only on the principal quantum number, n. Thus for $n = 1$, there is one wavefunction (1s), for $n = 2$ there are four degenerate wavefunctions - 2s, $2p_x$, $2p_y$, $2p_z$.

Quantum states or wavefunctions of equal energy are referred to as *degenerate*.

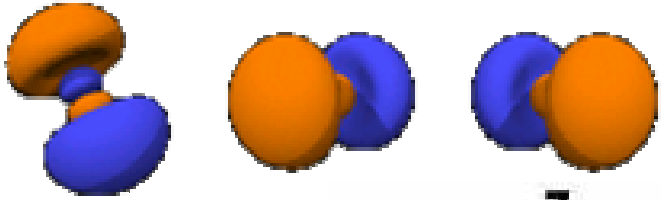
3p and 3d Orbitals

When $n = 3$, then l can be 0 (one 3s orbital),



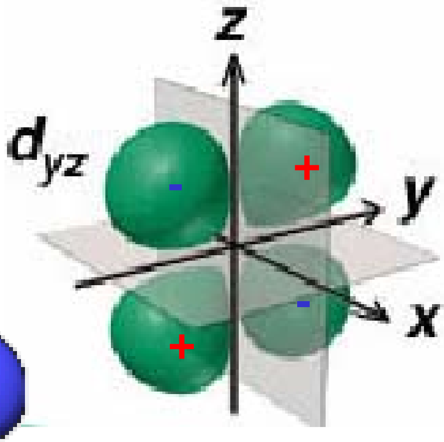
Higher quantum number *n* leads to more nodes in all orbitals.

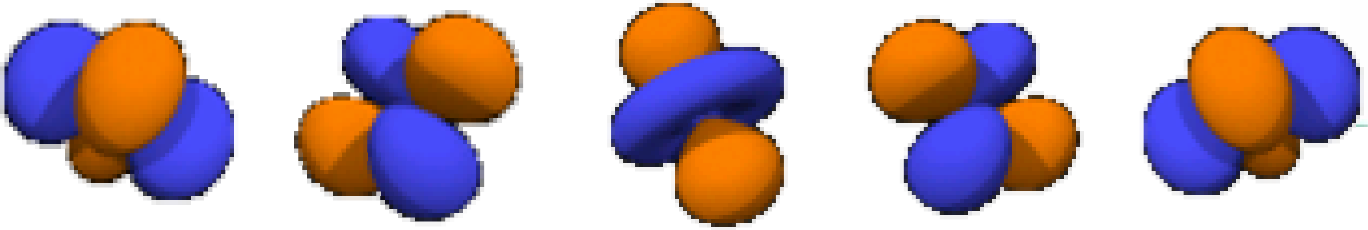
$l = 1$ (three 3p orbitals)



3p orbitals have the same shape and designation as 2p orbitals ($3p_X$, $3p_Y$, $3p_Z$), but have an extra spherical node.

or $l = 2$ (d-orbitals). 3d orbitals have more lobes than 2p orbitals, and their shape is obviously different. For d-orbitals, m may take on five values:





3d orbitals have four lobes. The lobes point along pair of axes ($d_{x^2-y^2}$), or between axes (d_{xy}, d_{xz}, d_{yz}) or along the z axis (d_{z^2}).

Higher n and l...

Higher principal quantum numbers and higher orbital angular momentum quantum numbers lead to *more nodes* and *more lobes*.

As l increases, the orbitals are denoted s, p, d, f, g, h,...

s, p, d & f are named for historical reasons - g, h,… just continue the alphabet

The Born Hypothesis - Electron Density

Charge (electron) density is proportional to the square of the wavefunction ψ. This means that ψ^2 is equivalent to *the probability* of finding an electron at a particular point in space.

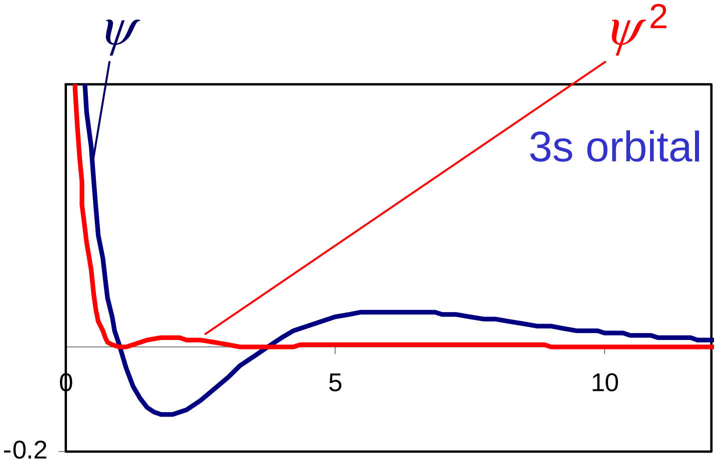
ψ^2 is always positive, so this removes the complication of the sign of the amplitude of the wave.

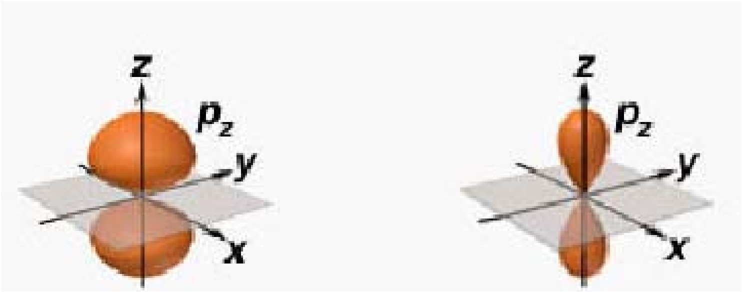
Squaring ψ changes lobe shape slightly, but the general features are the same.

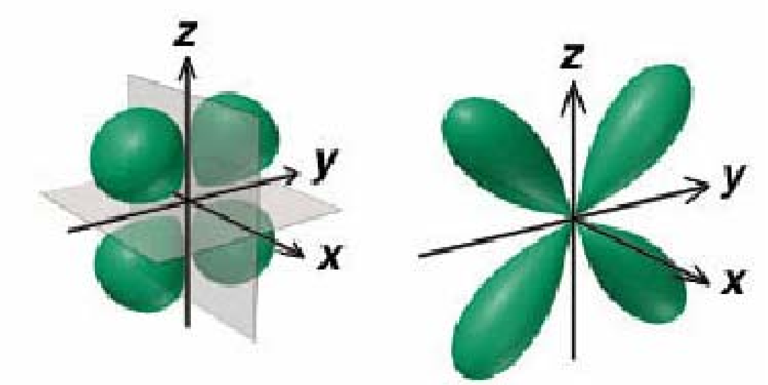
E.g.

$2p_z$ orbital - same number of lobes and nodes

$3d_{yz}$ - same number of lobes and nodes







Meaning of the Lobes Representation

Because electrons are not bound within a perimeter, the radial part of all wavefunctions decays *exponentially* towards 0 as $r \to \infty$.

This means the electron density *also decays exponentially towards 0*, so that there is a finite charge density even at a very large distance from the nucleus. (There is a finite probability of finding an electron at a large distance from the nucleus.)

Lobes are commonly drawn to represent surfaces of constant probability. E.g. The surface within which the probability of finding an electron is 95%; Alternatively the surface that contains 95% of the electronic charge density.

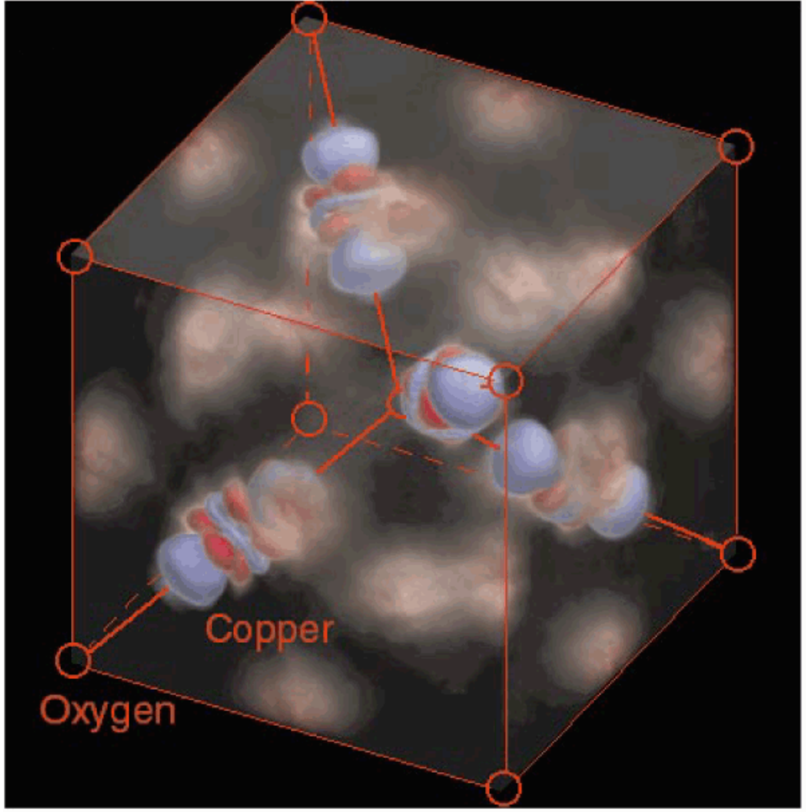
For s orbitals the probability is a function of radial distance only, so the size or extent of the lobes varies with probability but not the shape.

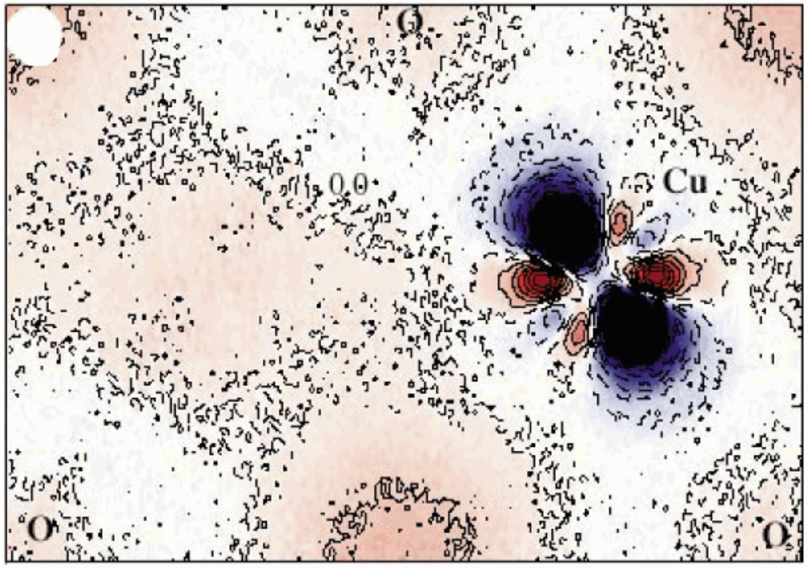
Experimental Observation

Orbital shapes are one of the unexpected predictions of quantum theory. The experimental observable is electron density, which can be obtained from x-ray diffraction experiments on crystals.

The electron density in the $3d_{z^2}$ orbital of Cu in Cu_2O has been measured in this way, with the lobes clearly visible in the results. This provides a powerful confirmation of the predictions of quantum theory. [*Nature* **401**, 49 - 52 (1999)]

http://www.nature.com/cgi-taf/DynaPage.taf?file=/nature/journal/v401/n6748/full/401049a0_r.html





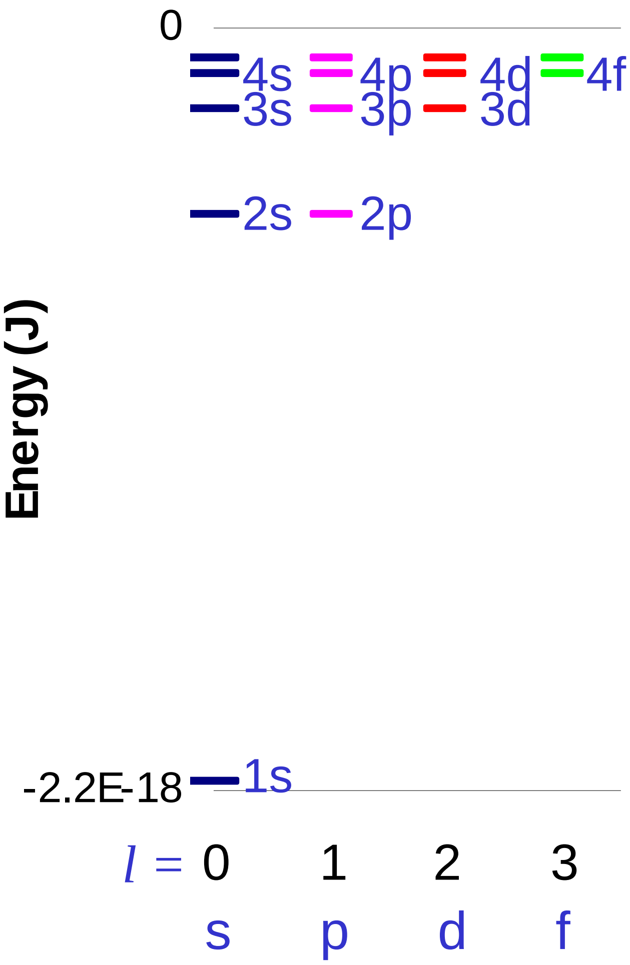
Wavefunctions for the Hydrogen Atom

Solving the wave equation for a single electron bound to a proton (H)

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

tells us the allowed energies, E_n, and orbital wavefunctions (shapes or electron densities) for different *quantum numbers*, n and l.

These may be represented as shown at right:



For hydrogen-like atoms, energy depends only on n, shape is described by l, and orientation is described by m.

How does quantum theory deal with more complex atoms and molecules?

Quantum Theory of Atoms and Molecules

The wave equation describes the properties of all matter, but practically it can only be solved *analytically* (to give an equation for the wavefunction) in a small number of cases. Quantum theory can be used in two broad ways when dealing with realistic chemical systems.

1. Solve complicated potential energies numerically (computer solution)

Even for the next simplest system, the 2-electron helium atom, the wave equation must be solved numerically. Here is what it looks like.

$$\boxed{-\frac{\hbar^2}{2m}\left(\nabla^2\psi_1+\nabla^2\psi_2\right)}+\boxed{\left(-\frac{2e^2}{r_1}-\frac{2e^2}{r_1}+\frac{e^2}{r_{12}}\right)}\psi=E\psi$$

Kinetic energies of *both* electrons.

Potential energies for interactions between *both* electrons & the nucleus.

This approach is used for both qualitative (understanding) and quantitative (calculation) chemistry, and you will see examples later in this course.

2. Develop approximations and principles or “rules” that we can carry about and use.

This approach is used to give us a toolkit and to develop intuition about the quantum world.

Many-Electron Atoms: The First Two Rules

The *quantum state* of an electron is specified by the orbital quantum numbers, n, l, and m_l, *plus* an electron spin quantum number s. So far we have neglected this property of electrons, and we will not say any more about it at this stage except to note that s can have one of two values, +½ or -½.

The **Pauli Exclusion Principle** says that no two electrons in an atom may have be in the same *quantum state*.

- That is, no two electrons can have the same four quantum numbers, n, l, m_l, and s.
- This is equivalent to saying that no orbital (specified by n, l, and m_l) can be occupied by more than two electrons.

The second rule is that electrons in atoms (and molecules) generally exist in their lowest possible energy state. This is called the *ground state*.

This is enough to begin to handle multi-electron atoms, at least He.

Worked Example: The Ground State Electronic Configuration of He

Using the atomic orbitals obtained for the hydrogen atom, we fill orbitals beginning with the lowest energy. (To do this we are pretty much ignoring the interactions between electrons, and treating them as two independent waves bound to the same (2+) nucleus.)

Electron 1 goes into the 1s orbital (n=1, l=0, m=0) with s = +½

Electron 2 goes into the 1s orbital (n=1, l=0, m=0) with s = -½

The ground state electron configuration of He is written as $1s^2$. (For H it is written $1s^1$.)

What happens to the next electron?

What is the ground state configuration of Li?

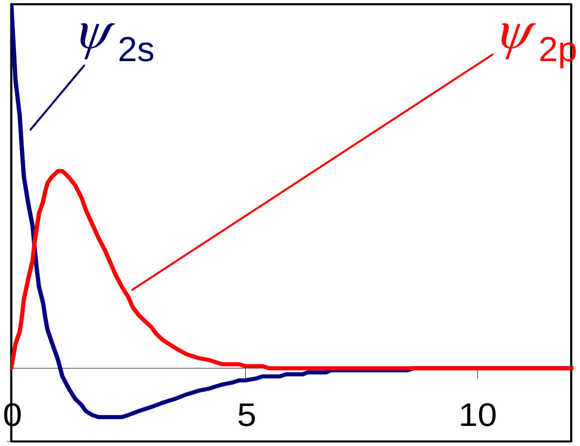
Filling the *n* = 2 orbitals: Rule 3

After He, the *n* =1 (1s) orbital is full. According to the wave equation for the hydrogen atom, the 2s and three 2p orbitals all have the same energy, so the next electron could go into any of the four *n* =2 orbitals.

However we have already seen that the wavefunctions for the s and p orbitals are different.

- s orbitals have their maximum amplitude at the nucleus. This means that electrons in s orbitals are bound by the true nuclear charge (3+ for Li, etc.)

- p orbitals have a node at the nucleus. Their interaction with the nucleus is *screened* by electrons closer in, so electrons in 2p orbitals are bound by a lower effective charge.



The different effective nuclear charges lower the energy of the *ns* orbital relative to *np*, so the s orbital fills first with up to 2 electrons. The ground state configuration of Li is $1s^2\ 2s^1$, and for Be it is $1s^2\ 2s^2$.

Filling the *n* = 2 orbitals: Rule 4

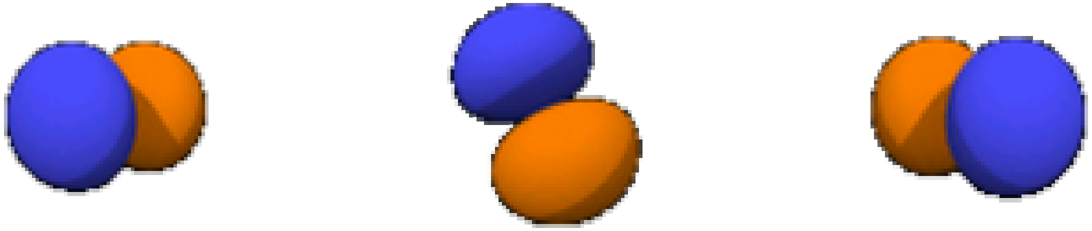
After Be, the 1s and 2s orbitals are full. The 2p orbitals are next to fill.

Three 2p orbitals can accommodate a total of six electrons, which gives the configurations of elements B through to Ne.

B	$1s^2\ 2s^2\ 2p^1$
C	$1s^2\ 2s^2\ 2p^2$
N	$1s^2\ 2s^2\ 2p^3$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
Ne	$1s^2\ 2s^2\ 2p^6$

In what order are the degenerate p-orbitals filled?

If we remember the shapes of p-orbitals, then putting one electron into *each* p-orbital will keep the electrons as far from each other as possible. This is a way of accounting for the repulsive potential energy between electrons without actually solving the wave equation.

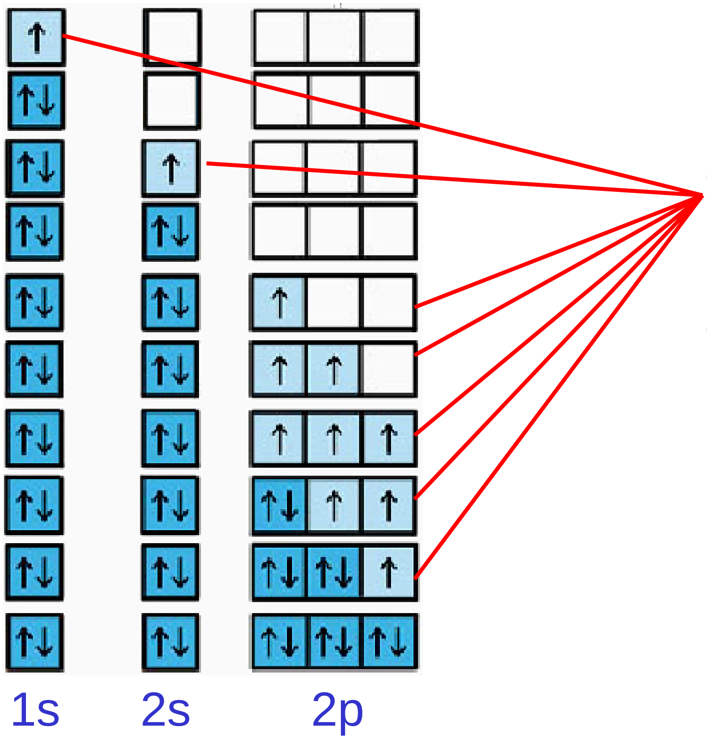


This is summarised in *Hund's Rule*, that the lowest energy electron configuration in orbitals of equal energy is the one with the maximum number of unpaired electrons with parallel spins.

Hund’s Rule

Electron configurations are often represented in an *orbital diagram*, which explicitly shows the number and spin of electrons in various atomic orbitals.

H	$1s^1$
He	$1s^2$
Li	$1s^2\ 2s^1$
Be	$1s^2\ 2s^2$
B	$1s^2\ 2s^2\ 2p^1$
C	$1s^2\ 2s^2\ 2p^2$
N	$1s^2\ 2s^2\ 2p^3$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
Ne	$1s^2\ 2s^2\ 2p^6$



These orbitals contain unpaired electrons.

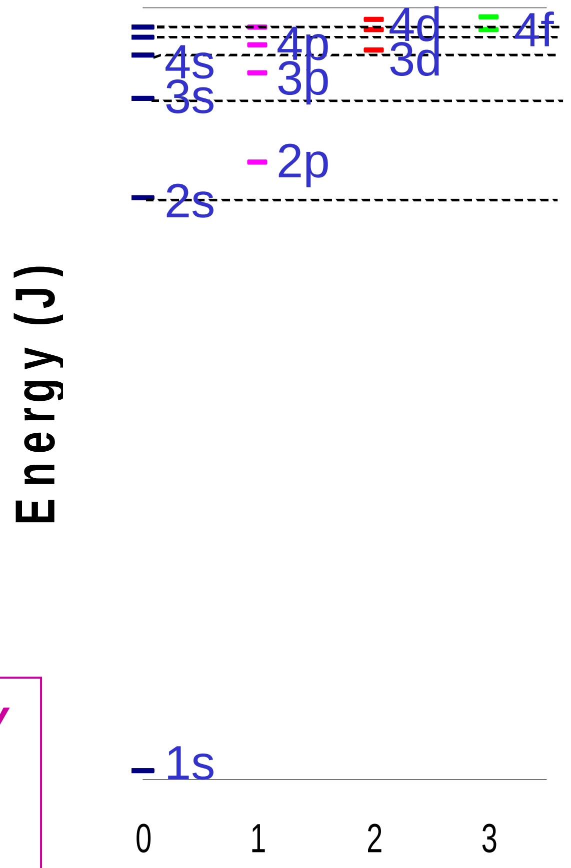
The number of unpaired electrons in degenerate orbitals is maximised.

Filling higher orbitals

The same rules apply for the order of orbital filling as we deduced for n =2. First the 3s orbitals fill (Na & Mg), and then 3p (Al-Ar).

As the angular momentum quantum number, l, increases, the orbitals extend further from the nucleus, and all orbitals except s have nodes at the nucleus. This means that the energy of an orbital *increases with l for a given n*.

This effect is big enough that the energy of the 4s orbital is lower than 3d. The order of increasing energies and of filling is shown in the diagram at right.



An important consequence of this is in atomic spectroscopy (next lecture). The energy level spacings or differences ΔE are unique to each atom, which means that we can identify atoms by their atomic absorbance or emission spectra.

Multi-Electron Configurations

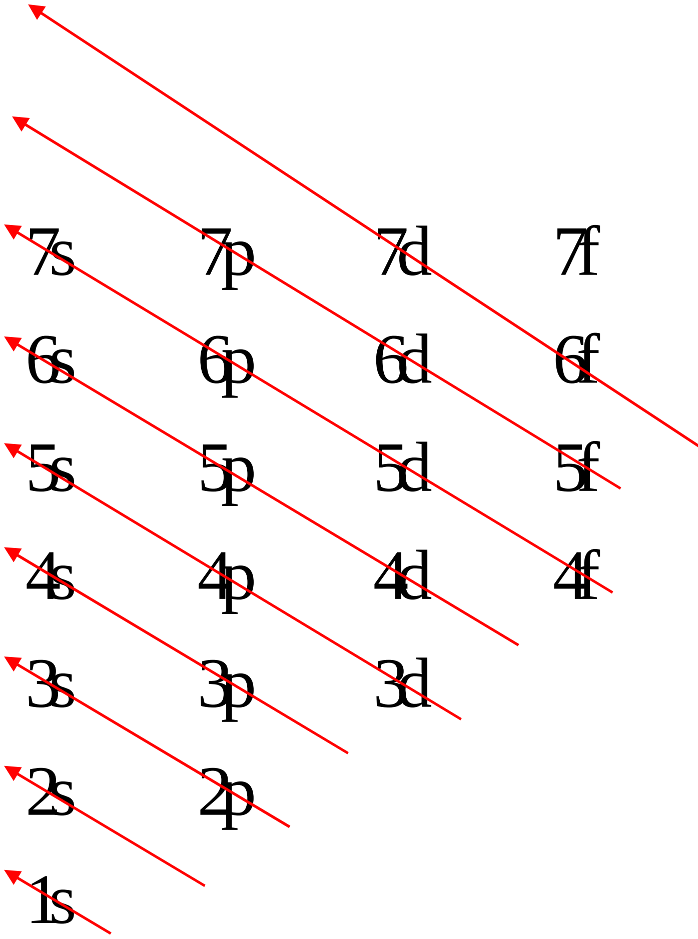
The order of filling orbitals can easily be remembered using a diagonal pattern:-

The rules for generating electron configurations can be summarised as

1. **Pauli Exclusion Principle**. No two electrons in an atom may be in the same quantum state $\{n, l, m, s\}$
2. **Aufbau Principle**. Electrons adopt the lowest possible energy configuration.
3. **Penetration**. Orbitals of equal n nearest the nucleus have lowest energy:

$$s < p < d < f...$$

4. **Hund's Rule**. Maximise unpaired electron spins in degenerate orbitals.

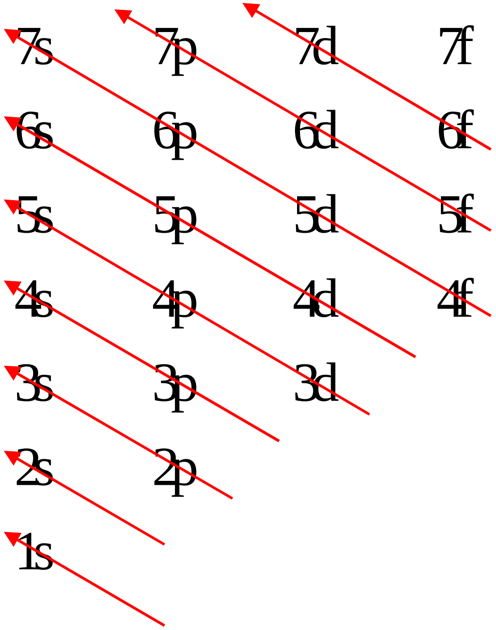


7s	7p	7d	7f
6s	6p	6d	6f
5s	5p	5d	5f
4s	4p	4d	4f
3s	3p	3d	
2s	2p		
1s			

Multi-Electron Configurations - Worked example

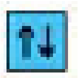
What are the electron configurations of atomic Ca and Ge?

Using the pattern at right as a guide, we fill the orbitals from the lowest energy.



Ca has 20 electrons, which we fill as follows

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ or $[Ar]4s^2$

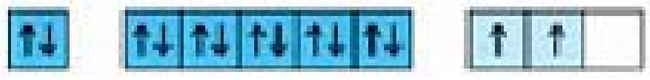
or [Ar] 

No unpaired electrons.

Ge has 32 electrons, which we fill as follows

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$

or $[Ar]4s^2\ 3d^{10}\ 4p^2$

or [Ar] 

Two unpaired electrons in p-orbitals.

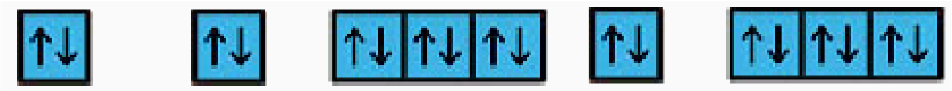
Orbitals and Electron Shells

Periodic trends are related to electron configurations. The classical model of the atom included the concept of electron “shells” derived from the row lengths in the periodic table.

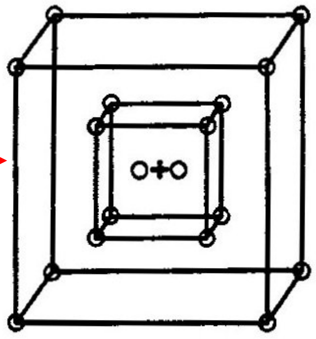
Noble gases are unreactive because they contain filled electron shells. This emerges from quantum theory as a natural consequence of the allowed orbital structure.

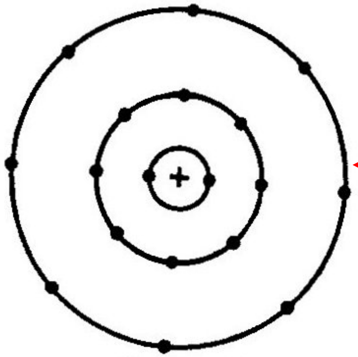
E.g. The electron configuration of argon

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ or [Ne] $3s^2\ 3p^6$



Regular shapes were thought to underlie bonding, crystal structure, and other properties.


Lewis, 1916



Kossel, 1916

Classical orbit model with “shells” of 2, 8, 8…

Structure of the Periodic Table

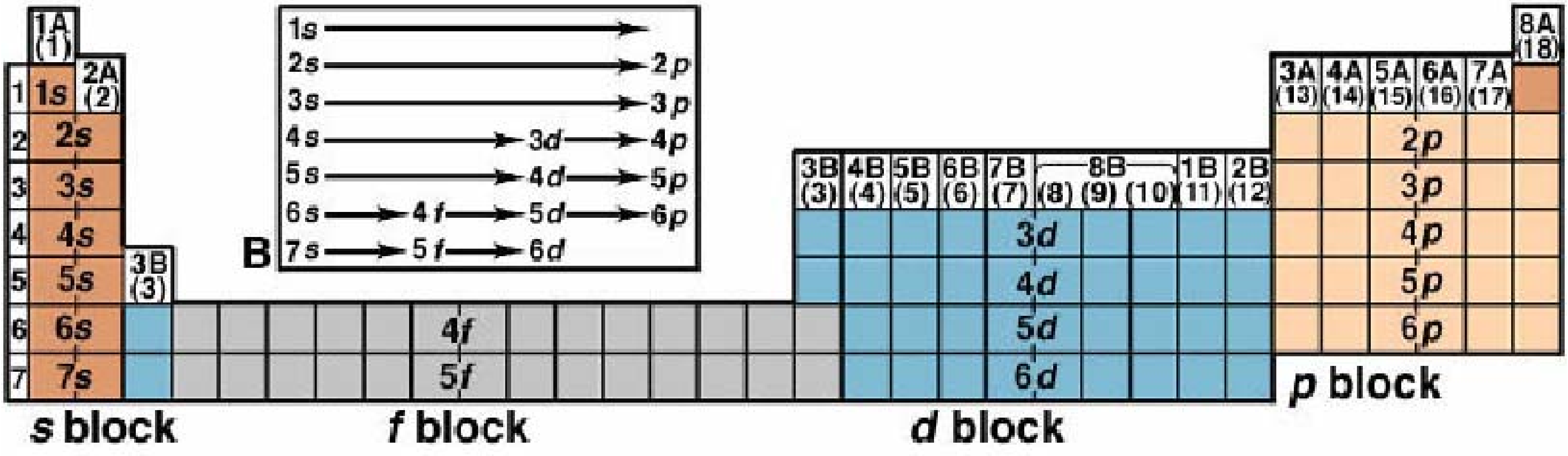
Atoms with the same *outer shell configuration* are expected to have similar chemical properties. Outer shell or *valence* electrons are important in the formation of chemical bonds (as we shall see later) They will lie in the same group in the periodic table, and form compounds with the same stoichiometry.

E.g.		Oxide	Hydride
C	[He] $2s^2\ 2p^2$	CO_2	CH_4
Si	[Ne] $3s^2\ 3p^2$	SiO_2	SiH_4
Ge	[Ar] $4s^2\ 3d^{10}\ 4p^2$	GeO_2	GeH_4
Sn	[Kr] $5s^2\ 4d^{10}\ 5p^2$	SnO_2	SnH_4

Structure of the Periodic Table

The periodic table can be regarded in terms of electron configurations, denoted by orbital angular momentum quantum number. The periodic table may thus be divided into *s*, *p*, *d*, and *f* blocks according to which orbital is being filled.

The *s*-block is 2 electrons "wide", *p*-block is 6 (3 p-orbitals x 2 electron/orbital), *d*-block is 10 (5x2), and the *f*-block is 14 (2x7).



Electron Configurations of d- and f-block Atoms

What you need to know

- How to write electron configurations of s- and p-block elements.
- Where the d- and f-block are on the periodic table, but

What you don’t need to know

...NOT individual configurations is the d- and f-blocks.

Why not? The orbital energies of ns and $(n\text{-}1)$d orbitals are affected by addition of electrons, and by electron-electron interactions. This leads to some unusual effects like

V is $[Ar]4s^23d^3$ Cr is $[Ar]4s^{\mathbf{1}}3d^5$ Mn is $[Ar]4s^23d^5$
Nb is $[Kr]5s^{\mathbf{1}}4d^4$ Mo is $[Kr]5s^{\mathbf{1}}4d^5$ Tc is $[Kr]5s^{\mathbf{1}}4d^6$

As there are no simple rules for writing configurations of d- and f-block elements, you are not required to learn them. Some will be dealt with later in the context of transition metal chemistry.

Periodic Atomic Properties and Quantum Theory

1. Atomic Radius

The atomic radius is determined by the electronic configuration, and particularly by how far the electron density extends from the nucleus. The wavefunctions and potential energy help make sense of the observed trends.

Down a group	the radius increases as an entire new shell of electrons is added each new row. This effect is especially noticeable in going up one atomic number from group 8 (noble gas) to the group 1 (alkali metal). The one additional electron goes into the next s-orbital, increasing the radius markedly.
Across a row	the radius decreases as the nuclear charge increases. Electrons are added to orbitals in the same shell (same n), so orbital contraction arises mainly from the increased attraction of the nucleus. E.g. the radius shrinks from group 1 to group 2, where both outer shell electrons are in the same ns orbital.

Periodic Atomic Properties and Quantum Theory

1. Atomic Radius

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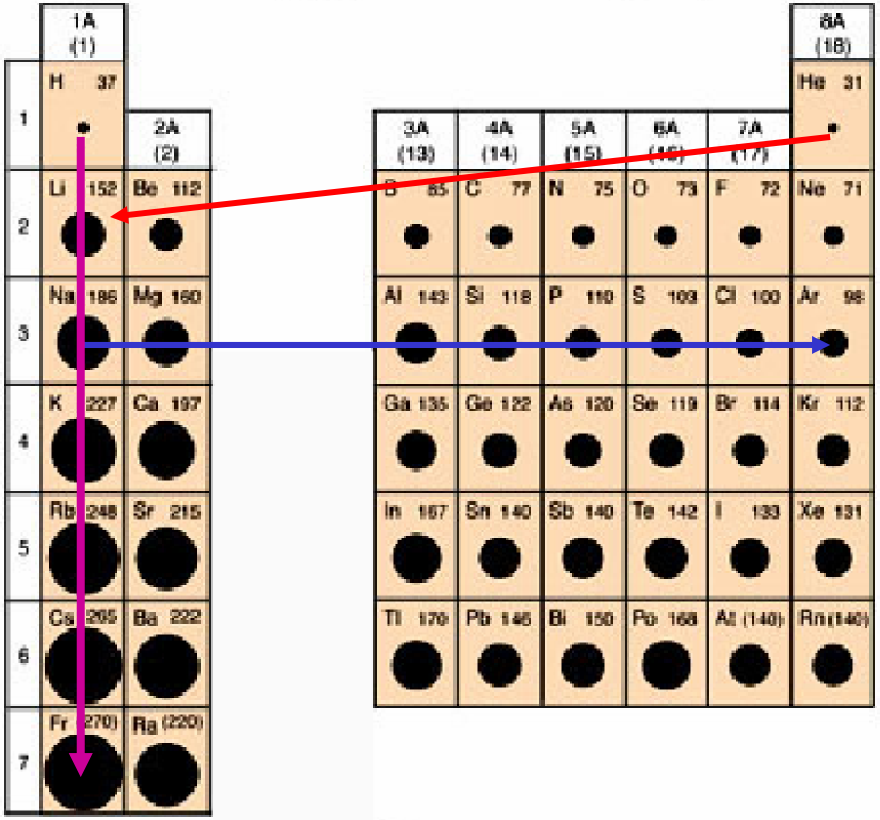


	1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	H 37							He 31
2	Li 152	Be 112	B 85	C 77	N 75	O 73	F 72	Ne 71
3	Na 186	Mg 160	Al 143	Si 118	P 110	S 103	Cl 100	Ar 98
4	K 227	Ca 197	Ga 135	Ge 122	As 120	Se 119	Br 114	Kr 112
5	Rb 248	Sr 215	In 167	Sn 140	Sb 140	Te 142	I 133	Xe 131
6	Cs 265	Ba 222	Tl 170	Pb 146	Bi 150	Po 168	At (140)	Rn (140)
7	Fr (270)	Ra (220)						

Radii of the s- and p-block elements

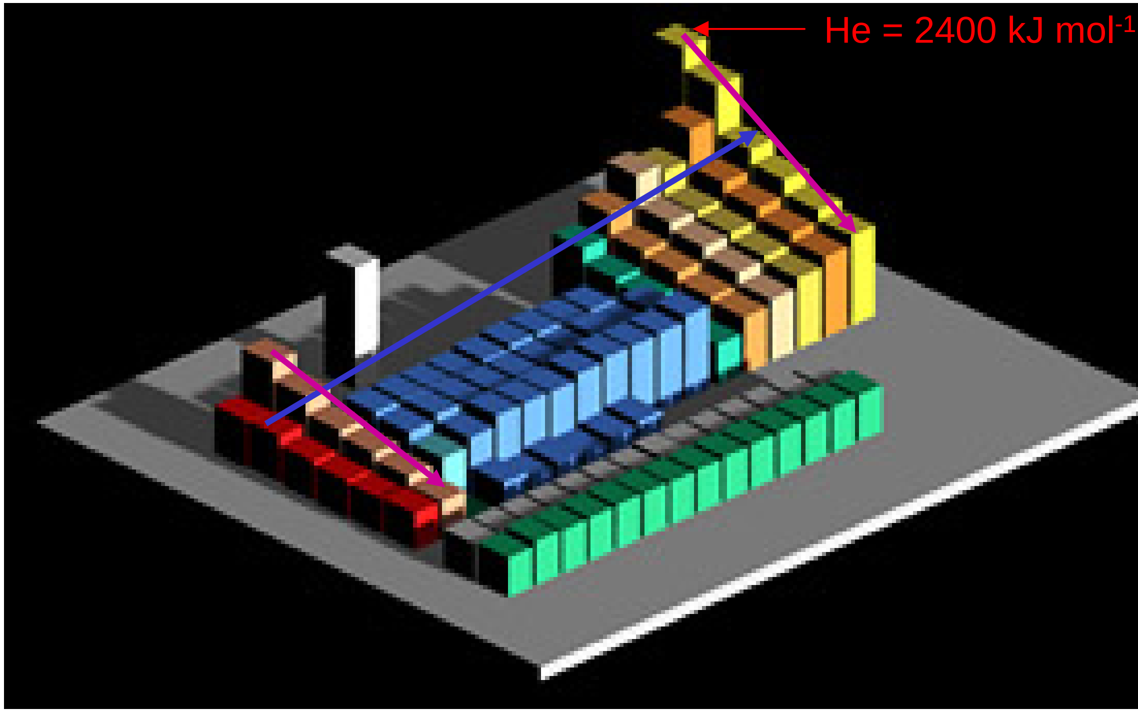
Periodic Atomic Properties and Quantum Theory

2. Ionization Energy

Quantum theory also helps make sense of ionization energy trends.

Stepping down a group, the outer electrons of each element is another shell further away from the nucleus. Inner electrons screen the nuclear attraction that binds the electron, so ionization becomes easier.

Across a row, electrons are added to the same shell. The increase in nuclear charge without additional screening holds the electrons more tightly to the nucleus.



Periodic Atomic Properties and Quantum Theory

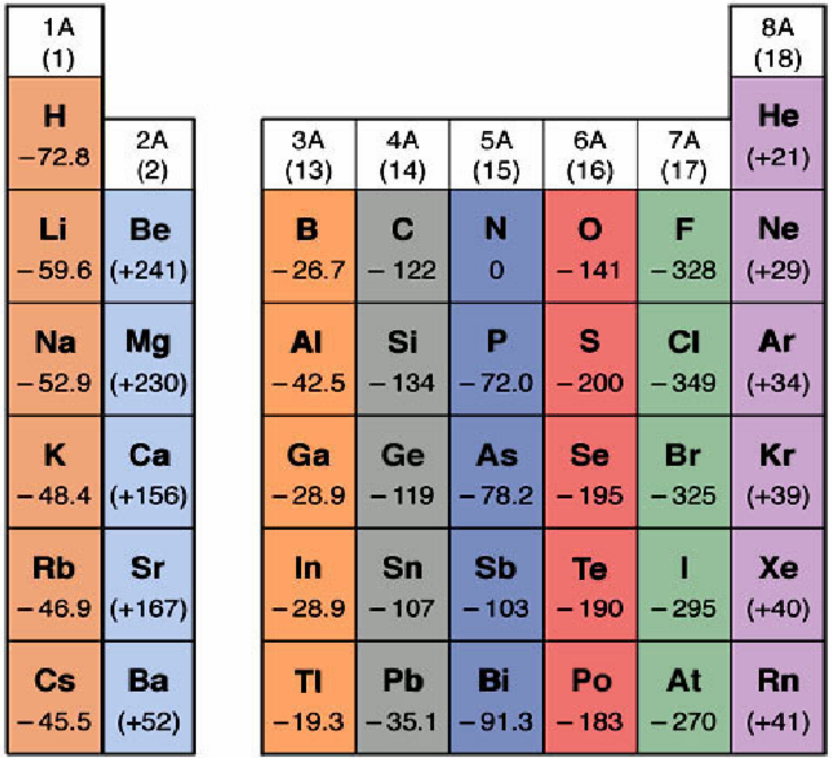
3. Electron Affinity (EA)

The electron affinity is like ionization energy. It is the energy required to *add* an electron to a neutral atom in the gas phase.

The general trends in EA are hard to discern

We expect EA to decrease *in magnitude* (less negative) down a group as we move further from the nucleus. Only observed for Groups 1 and 8, or elements after Ne.

We expect EA to increase (more negative) across a row as the nuclear charge increases and size decreases. There are plenty of exceptions to this.



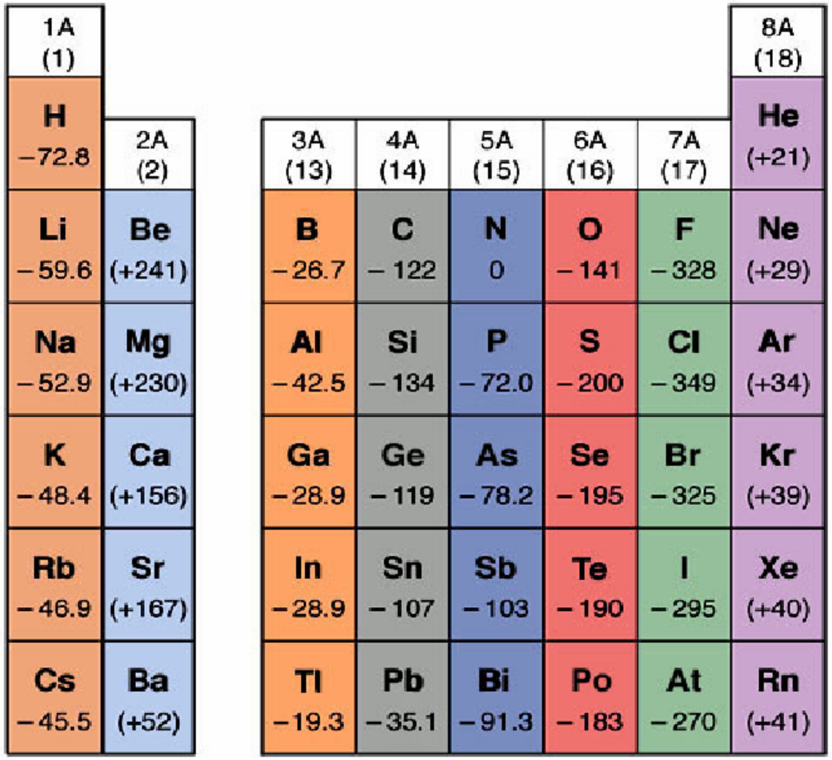
1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
H −72.8							**He** (+21)
Li −59.6	**Be** (+241)	**B** −26.7	**C** −122	**N** 0	**O** −141	**F** −328	**Ne** (+29)
Na −52.9	**Mg** (+230)	**Al** −42.5	**Si** −134	**P** −72.0	**S** −200	**Cl** −349	**Ar** (+34)
K −48.4	**Ca** (+156)	**Ga** −28.9	**Ge** −119	**As** −78.2	**Se** −195	**Br** −325	**Kr** (+39)
Rb −46.9	**Sr** (+167)	**In** −28.9	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** (+40)
Cs −45.5	**Ba** (+52)	**Tl** −19.3	**Pb** −35.1	**Bi** −91.3	**Po** −183	**At** −270	**Rn** (+41)

Periodic Atomic Properties and Quantum Theory

3. Electron Affinity (EA)

Adding an electron is more sensitive to detailed electron configurations than ionization energy or atomic radius. This is evident in the behaviour within some groups.

- Group 8 elements have closed shell configurations and *positive* EA's, so they do not form anions.
- Groups 6 and 7 have large, negative EA's, and readily form anions.
- Groups 1 & 2 have small EA's and do not form anions easily. A second electron can be added to Group 1 (ns^1) more easily than Group 2 (ns^2), which has a positive EA.
- Subtle effects in groups 3-5 arise from electron-electron and spin pairing interactions.



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Summary I

You should now be able to

- Name the key experimental observations that led to the development of quantum mechanics.
- Convert between wavelength, frequency and energy of light.
- Calculate the allowed energy of a hydrogen-like atom of atomic number Z and quantum number n, and the wavelength of a transition between energy levels.
- Identify the key features of waves in 1-3 dimensions -- displacement, amplitude, nodes
- Understand the representations of waves as cross-sectional graphs, contour plots and lobe representations
- Explain the meaning of the orbital quantum numbers, n, l, m_l, and the designation of orbitals as e.g. 1s, 3d, 4p, 4f...

Summary II

- Recognise the shapes of atomic orbitals in these representations
- Understand how the wavefunction relates to electron charge density
- Draw out the electron configuration for atoms in the s- and p-blocks of the periodic table, including unpaired electrons.
- Explain why the orbitals with the same principal quantum number but different azimuthal quantum numbers have different energies in multi-electron atoms.
- Explain the periodic trends in atomic radius and ionization energy in terms of quantum theory
- Define Electron Affinity and explain some features of its periodic trends in terms of electronic configurations derived from quantum theory.