

Particle- Wave Duality

- In 1923, Louis de Broglie, a French physicist, proposed a hypothesis that revolutionized the treatment of the atomic structure.
- If light can exhibit properties of both a **wave** and **particle**, then all matter, usually thought of as particles, should exhibit **wave-like behaviour**.
- **Wavelength of a substance can be obtained from**
 $\lambda_{\text{DeBroglie}} = h/mv = h/p$

Calculation of de Broglie wavelength of an electron

$$\text{Mass} = 9.11 \times 10^{-31} \text{ kg}$$

$$\text{Speed} = 10^6 \text{ m / sec}$$

$$\lambda = \frac{6.63 \times 10^{-34} \text{ Joules} \cdot \text{sec}}{(9.11 \times 10^{-31} \text{ kg})(10^6 \text{ m/sec})} = 7.28 \times 10^{-10} \text{ m}$$

This wavelength is in the region of X-rays

de Broglie wavelength of a ball

- Mass = 1 kg
Speed = 1 m / sec

$$\lambda = \frac{6.63 \times 10^{-34} \text{ Joules} \cdot \text{sec}}{(1 \text{ kg})(1 \text{ m/sec})} = 6.63 \times 10^{-34} \text{ m}$$

$$\lambda_{\text{DeBroglie}} \propto 1/m$$

- De Broglie concluded that most particles are too heavy to observe their wave properties.
- Wave properties can be detected for only small particles.
- De Broglie predicted that the mass of an electron was small enough to exhibit both particle and wave like properties.

- In 1927, Clinton J. Davisson and Lester H. Germer shot electron onto a nickel crystal and observed diffraction of the electron similar to diffraction of waves against crystals (X-rays).
- In the same year, an English Physicist, George P. Thomson obtained same results as Davisson and Germer when he fired electrons towards thin metal foil.

Heisenberg Uncertainty Principle

Heisenberg concluded that the dual nature of matter places a fundamental limitation on how precisely we can know both the location and the momentum of any object

This principle states that both the position (Δx) and the momentum (Δmv) of an electron cannot be known beyond a certain level of precision

$$(\Delta x) (\Delta mv) \geq \frac{h}{4\pi}$$

Both the position and the momentum of an electron cannot be known with a high degree of certainty

If the momentum is known with a high degree of certainty

- i. Δmv is small
- ii. Δx (position of the electron) is large

If the exact position of the electron is known

- i. Δmv is large
- ii. Δx (position of the electron) is small

- Based on the **Heisenberg Uncertainty Principle** rather than trying to define the exact position and momentum of an electron, the probability of finding the electron in a given volume of space should be determined.

The probability of finding an electron at a given point in space is determined from the function Ψ^2

- where Ψ is a mathematical function which describes the behaviour of an electron-wave

Schrödinger wave equation

- Edwin Schrödinger proposed that all moving particles with wave nature can be described by an equation he derived called the **Schrödinger wave equation**.
- The equation provides information about the wave function and helps to determine the probability of finding an electron at any point around the nucleus.
- The equation can be solved exactly only for a hydrogen-like system (H, He^+).

Time independent equation

$$\partial^2\Psi/\partial x^2 + \partial^2\Psi/\partial y^2 + \partial^2\Psi/\partial z^2 + 8\pi^2m/h^2(E-V)\Psi = 0$$

OR

$$\nabla^2\Psi + (8\pi^2m/h^2) (E-V) \Psi = 0$$

x, y, and z are the 3 space co-ordinates

m = mass of electron, h = Planck's constant,

E = Total energy, V = potential energy of electron,

Ψ = wave function (amplitude of wave)

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

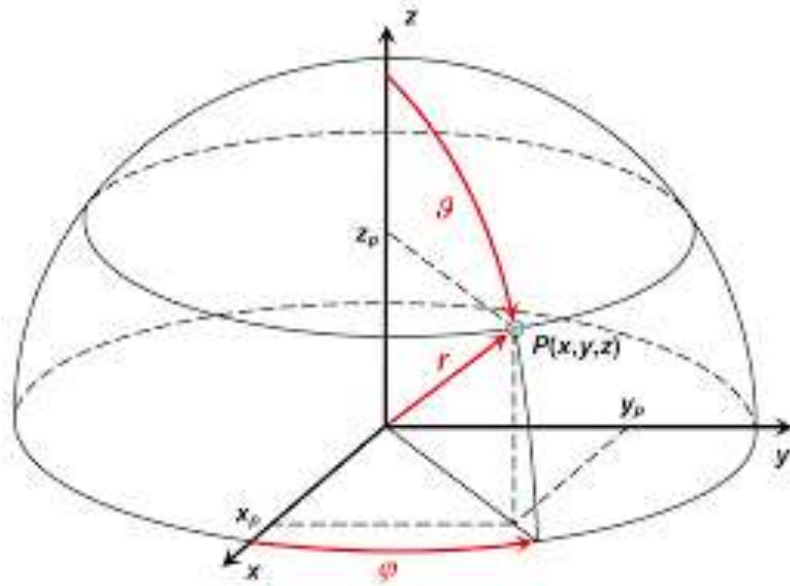
- The wave function Ψ represents the amplitude of the electron wave and is therefore a function of space co-ordinates x, y, z .
- The probability of finding an electron in a volume of space is proportional to the square of the wave function (Ψ^2).
- If Ψ^2 is maximum then the probability of finding electron is maximum.

- The volume of space where probability of finding electron is maximum is called **electron density, electron cloud** or **an atomic orbital**.
- The electron cloud is a smeared out distribution whose density varies from place to place according to the magnitude of ψ^2

Acceptable solutions to the wave equation should have the following properties:

- Ψ must be single valued at all time in space.
- Ψ must be finite (must not go to infinity)
- Ψ must be continuous
- the summation of $\Psi^2 dv = 1$ (Probability of finding electrons over all space from + and – infinity must be equal to one)

The solution of the wave equation for the electrons of an atom can be simplified using the spherical polar coordinates (r, θ, ϕ) which defines the position relative to the nuclei



$$\begin{aligned}x &= r \sin\theta \cos\phi \\y &= r \sin\theta \sin\phi \\z &= r \cos\theta\end{aligned}$$

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) = R \Theta \Phi$$

$$\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

$$\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi)$$

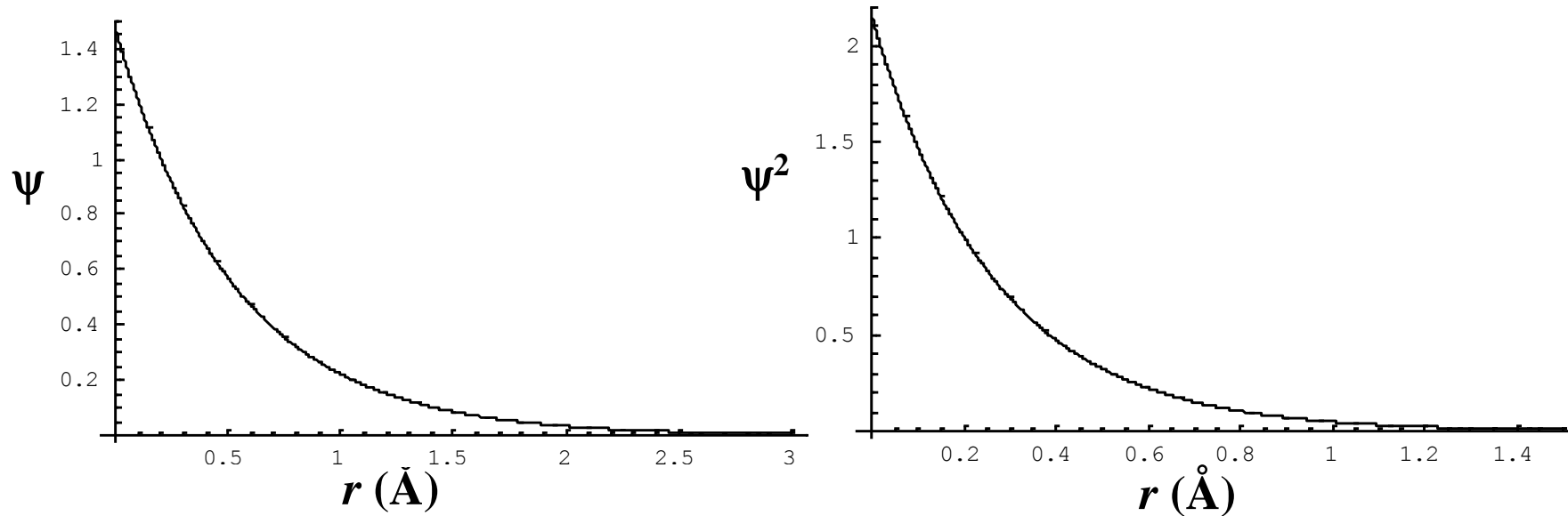
$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned}$$

$$\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi)$$

$$\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

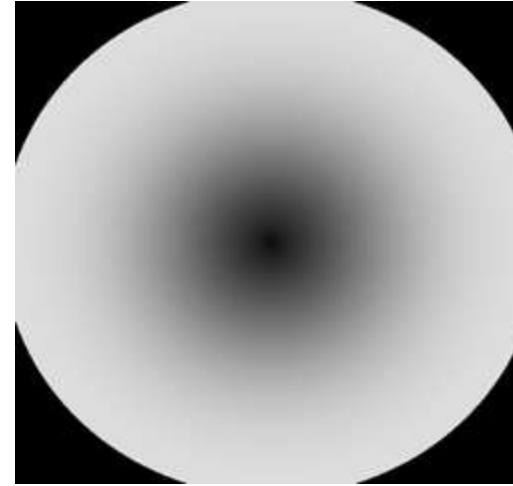
$$\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi)$$

The variation of the wave function with distance, r ($r = [x^2 + y^2 + z^2]^{1/2}$), from the nucleus is called the Radial wave function (R) for the ground state H-atom.



The probability of finding the electron increases the closer the nucleus is approached

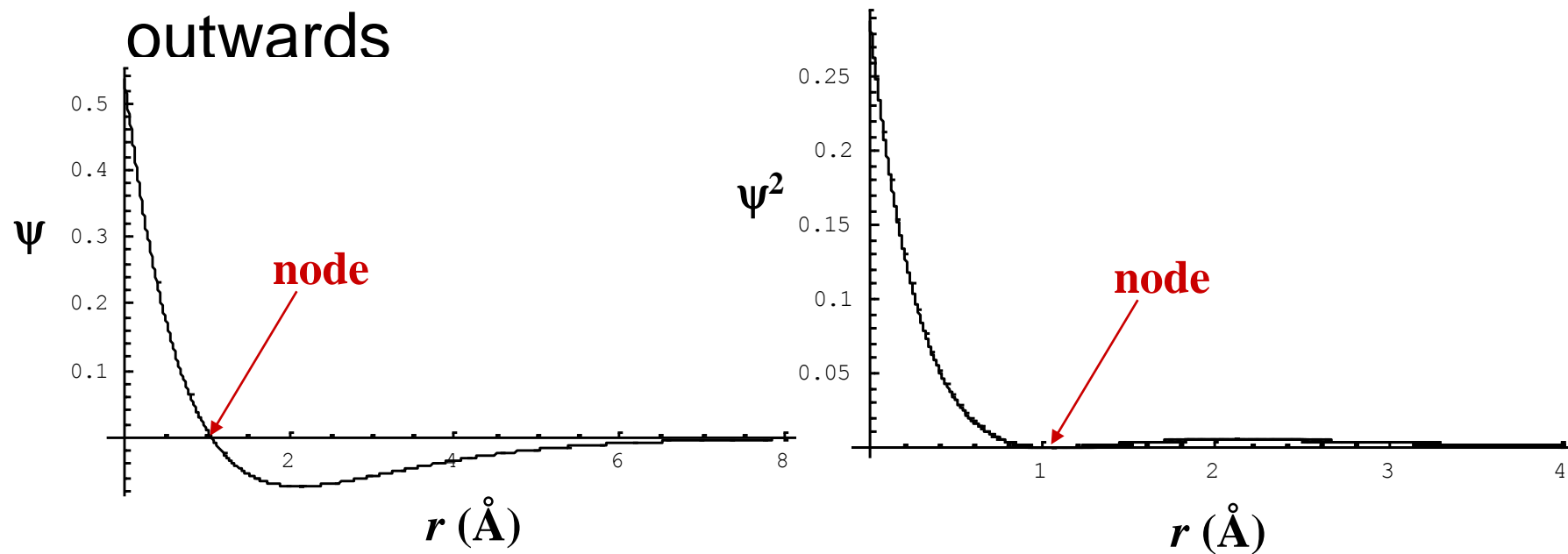
The angular wave functions θ and ϕ expresses the angular shape of the wave function. $Y(\theta, \phi)$



$$\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

The H-electron can be excited by the absorption of radiation energy, to higher energy states. Each higher energy state has its own characteristic wave function.

The first available excited state of the hydrogen atom, has a wave function of spherical symmetry and changes sign once in going from the nucleus outwards



Solutions to wave equation

- Complete solution to wave equation for hydrogen requires three quantum numbers.
- Each set of quantum numbers (n, l, m_l) identifies the wave function of a particular quantum state.
- n is obtained from the radial part (r) of the wave function. (distance/radius)
- l and m_l are obtained from the angular part (θ and ϕ) of the wave function. (shape)

Principal Quantum Number (n)

Determines

- the energy of orbital.
- Distance of orbital from nucleus
- Size of orbital

The smaller the value of n , the lower the energy, the closer the orbital to the nucleus and the smaller the orbital.

- The principal quantum number can have any positive value: 1, 2, 3, . . .

Orbitals with the same value for n are said to be in the same shell.

Angular Momentum Quantum Number (l)

- Gives shape of orbital
- Gives number of angular nodes present in an orbital
- In multi-electron atoms determines energy together with n
- It can have values from 0, 1, 2, 3, . . . to a maximum of $(n - 1)$.
- For a given n , there will be n different values of l ,
- $n=1$ $l=0$
- $n=2$ $l=0, 1$
- $n=3$ $l=0, 1, 2$
- $n=4$ $l=0, 1, 2, 3$

- Each l value has a corresponding letter label
- $l = 0$ s orbital
- $l = 1$ p orbital
- $l = 2$ d orbital
- $l = 3$ f orbital
- $l = 4$ g orbital

Magnetic Quantum Number (m)

This quantum number specifies the different orientations possible for a given orbital.

Each different value of l represents a different orbital.

- The magnetic quantum number depends on the value of l and can have any integer value from $-l$ to 0 to $+l$.
- For a given l value there will be $(2l + 1)$ values of m_l and therefore $(2l + 1)$ orbitals.

l	no of orbitals	m_l values	orbital labels
0	$[2(0) + 1] = 1$	0	
1	$[2(1) + 1] = 3$	-1, 0, +1	x, y, z
2	$[2(2) + 1] = 5$	-2, -1, 0, +1, +2	xy, xz, yz, $x^2 - y^2$, z^2

- An orbital is defined by 3 quantum numbers

If $n=1; l=0, m=0$	1s orbital
• If $n=2; l=0, m=0$	2s
• If $n=2; l=1, m=-1$	$2p_x$
• If $n=2; l=1, m=0$	$2p_y$
• If $n=2; l=1, m=+1$	$2p_z$

Q: What are possible values of l and m_l for H in the ground state and its excited state ($n=1$ and $n=2$)?

$$n=1 \quad l=0, \quad m_l=0$$

$$n=2 \quad l=0, 1$$

$$l=0 \quad m_l=0$$

$$l=1 \quad m_l=-1, 0, +1$$

The orbitals will have possible n, l, m combinations as

$$2, 0, 0 \text{ (2s);}$$

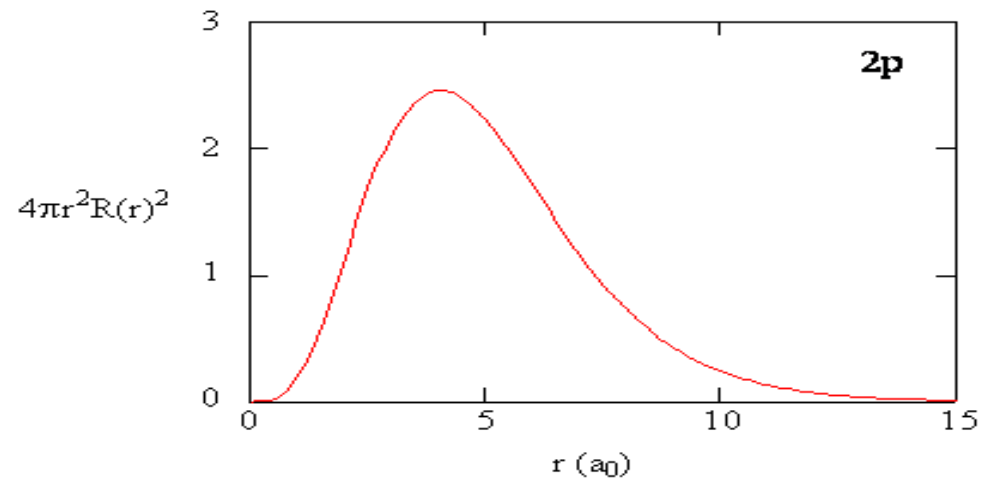
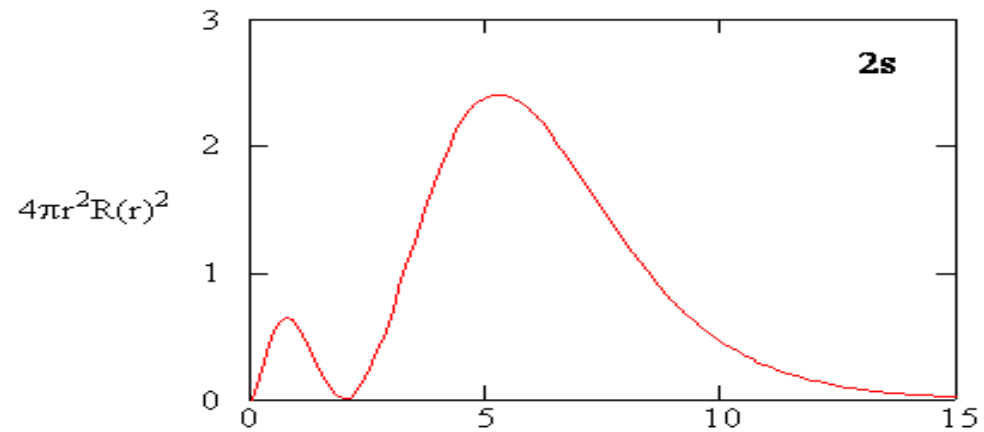
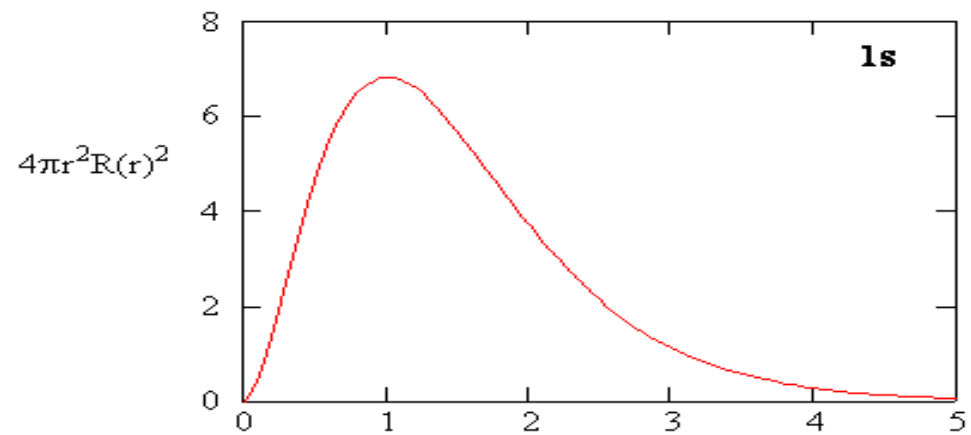
$$2, 1, -1 \text{ (2p}_x\text{); } 2, 1, 0 \text{ (2p}_z\text{); } 2, 1, +1 \text{ (2p}_y\text{)}$$

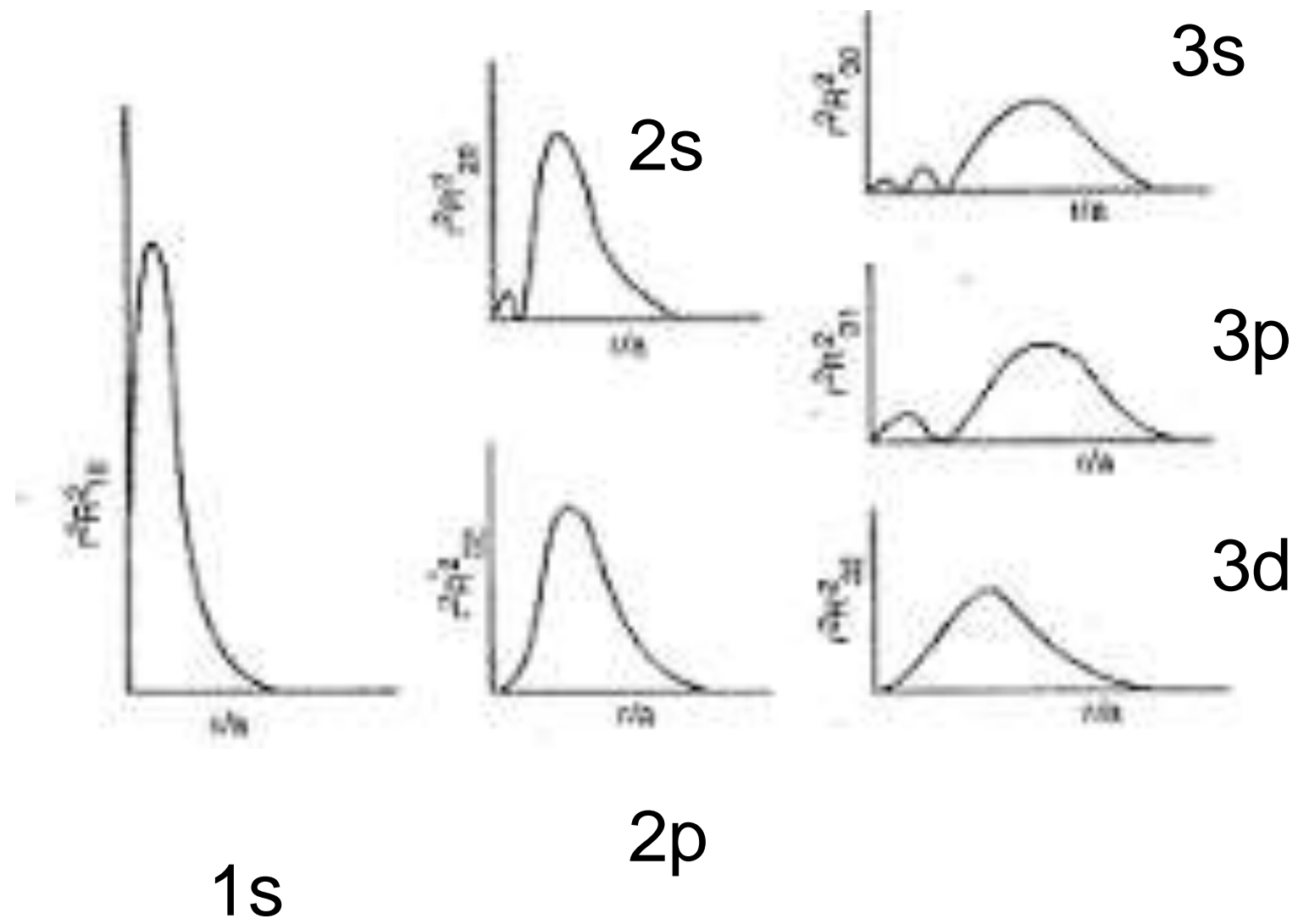
Representation of Orbitals in 3-D space

- The volume of space with a high probability of finding the electron can be obtained by determination of values of Ψ^2 at various points around the nucleus.
- This gives a 3-dimensional representation of an atomic orbital will have both radial and angular components. (sphere with different radii)

Radial distribution function $(4\pi r^2 R(r)^2)$

The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the nucleus

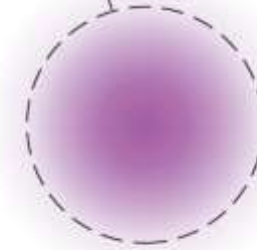




Angular probability function

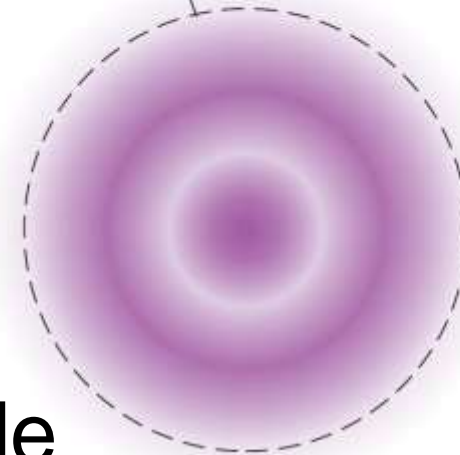
This gives the shape of the orbital.

99% contour



1s orbital

99% contour



1 radial node

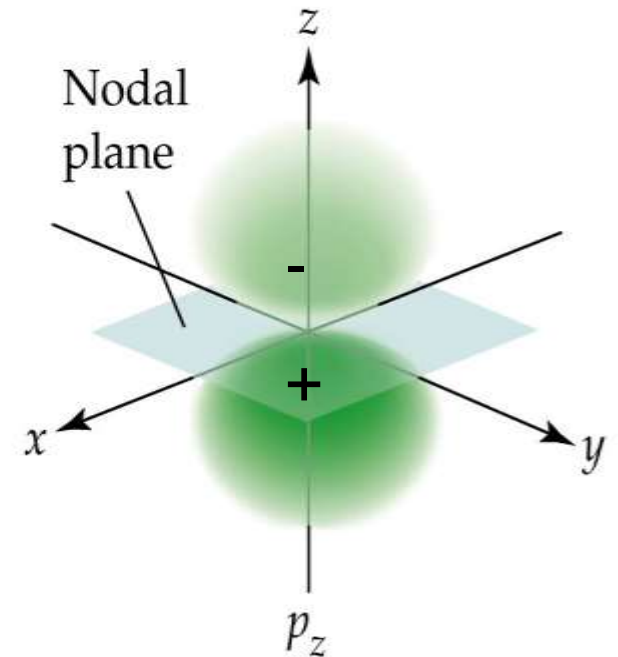
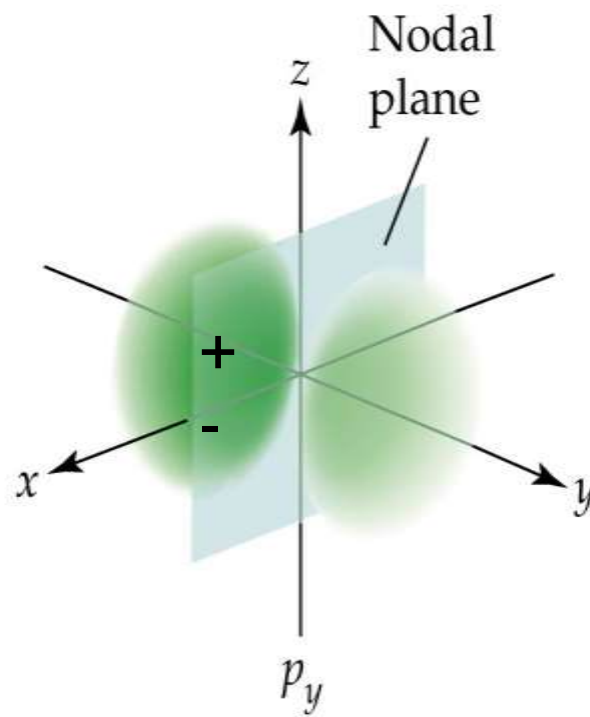
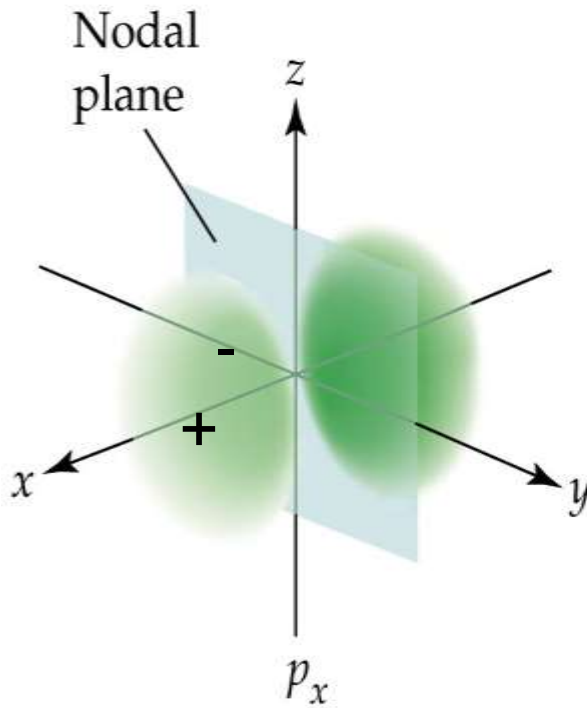
2s orbital

P orbitals

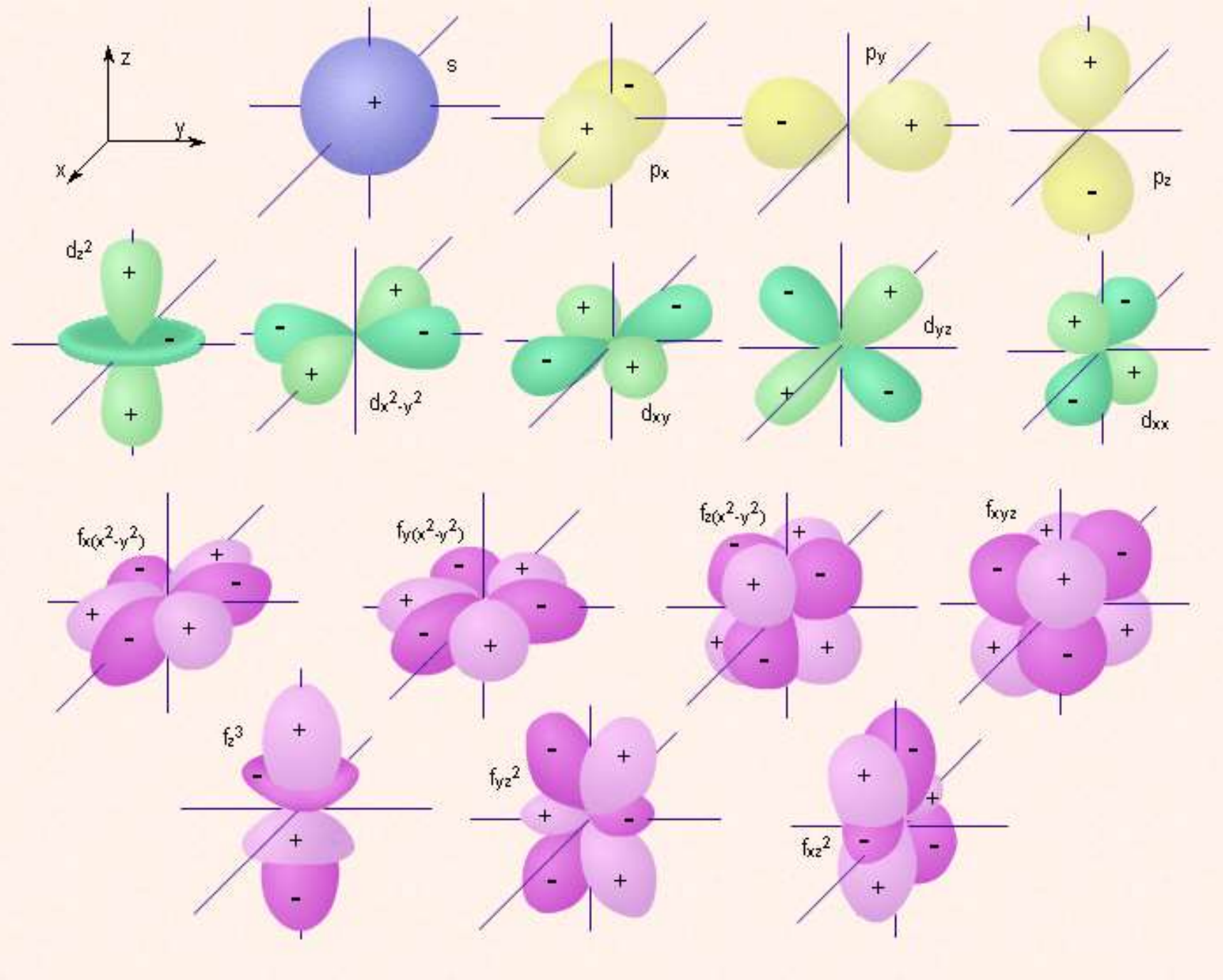
$$n = 2, l = 1, m = -1$$

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

$$n = 2, l = 1, m = 1$$



$$\Psi_{2p}$$



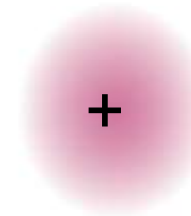
Nodes present in orbitals

A node is a region with the wave function = 0

Total nodes (distance related)

- For a given n value we have $n-1$ nodes
- Made up of radial and angular nodes
- Radial nodes = $n-(l+1)$
- Angular nodes = l

- For $n=1$ $l=0$
- Total node = $n-1 = 1-1 = 0$
- $n=2$ $l=0$ or 1
- Total node = $2-1 = 1$
- Radial nodes = $2-(0+1) = 1$
- Angular node = 0
- For $l=1$ Radial node = $2-(1+1) = 0$
- Angular node = 1



Orbital energies in a hydrogen-like species

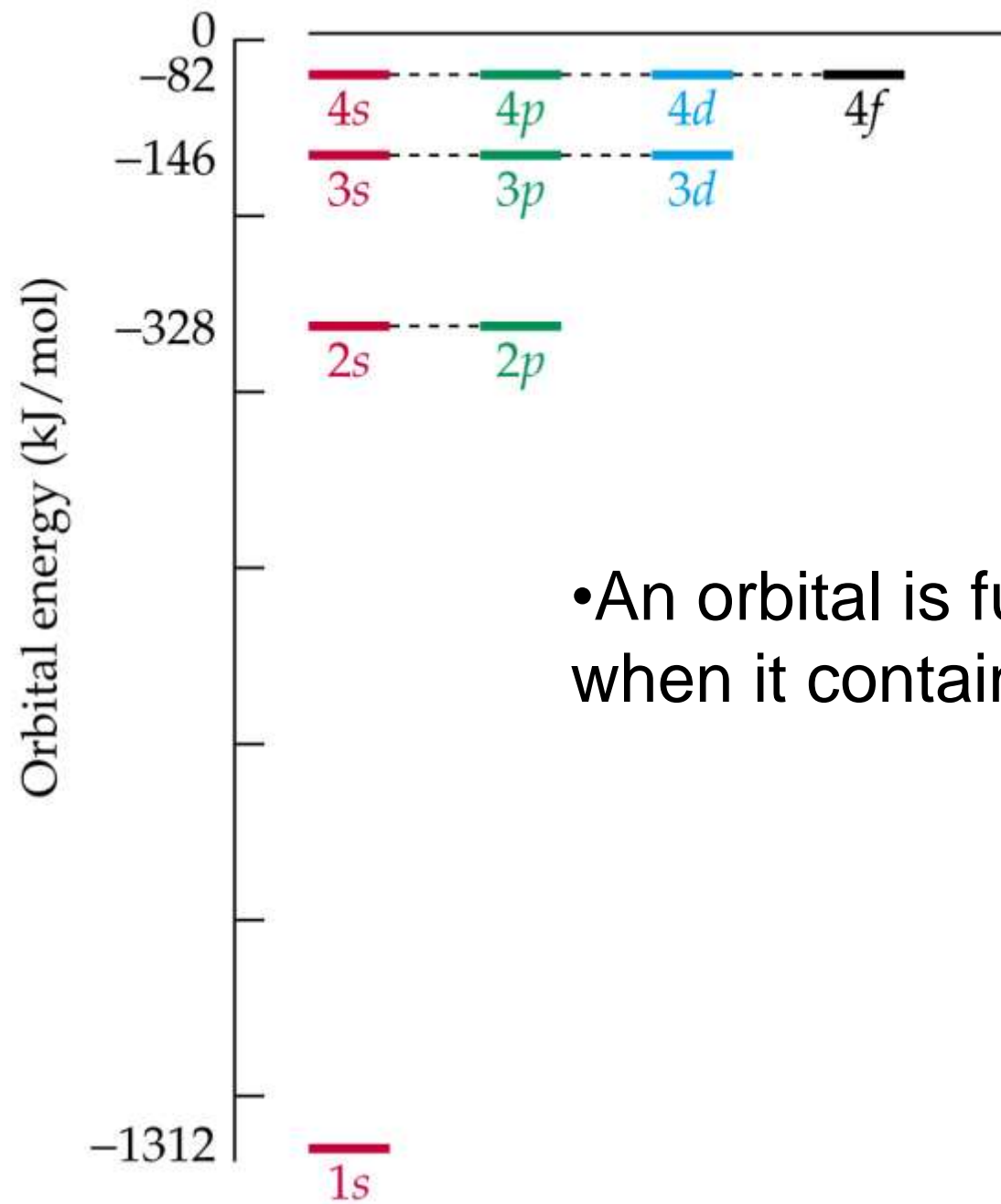
Solutions of the Schrodinger equation give orbital energies, E (energy levels),

$$E = k/n$$

- $k = \text{a constant} = 1.312 \times 10^3 \text{ kJ mol}^{-1}$

For each value of n there is only one energy solution

In hydrogen-like species, all atomic orbitals with the same principal quantum number (e.g. 3s, 3p and 3d) have same energy and are therefore degenerate.



- An orbital is fully occupied when it contains 2 electrons

Spin Quantum Number, m_s

- In order to explain the observation of two closely spaced spectral lines (Zeeman effect). A fourth quantum number called the spin quantum number (**s**) was introduced.
- The electrons are assumed to spin about their axis and this quantum number refers to the two possible orientations of the spin axis of an electron.
- It may have a value of either $+1/2$ or $-1/2$.

- An electron in an atomic orbital is defined by a unique set of four quantum numbers: n , l , m_l and m_s .
- $n=1, l=0, m_l = 0 ; m_s = -1/2$
- $n=1, l=0, m_l = 0 ; m_s = +1/2$
- $n=2, l=1, m_l = 0 ; m_s = -1/2$
- $n=2, l=1, m_l = 0 ; m_s = -1/2$

NOTE

- An atomic orbital is defined by a unique set of three quantum numbers.
- An electron in an atomic orbital is defined by a unique set of four quantum numbers: n , l , m_l and m_s .

THE NEUTRON

- James Chadwick in 1932
Discovered that the nucleus is heavier than could be account for with just protons.
The extra mass called the neutron and had NO charge.
Has same mass as the proton.

Multi-electron systems

- Electrons occupy orbitals like those of a Hydrogen atom but energies of orbitals are not the same as those for the hydrogen atom.
- Nuclear attraction for electrons increases as atomic number increases, this lower the energy of the electrons'

- Within the atom, there is electron-electron repulsion which opposes electron-nuclear attraction.
- The repulsion “shields” the electron from the full attraction of the nucleus making the electrons experience an “effective” nuclear charge which is less than the full nuclear charge.

Factors Affecting Orbital Energies

- The energies of orbitals in multi –electron atoms are affected by
 - nuclear charge (Z)
 - shielding by other electrons.
 - Orbital Shape
- A **high nuclear charge** increases nucleus-electron interactions and lowers orbital energy.

Shielding and Orbital Energy

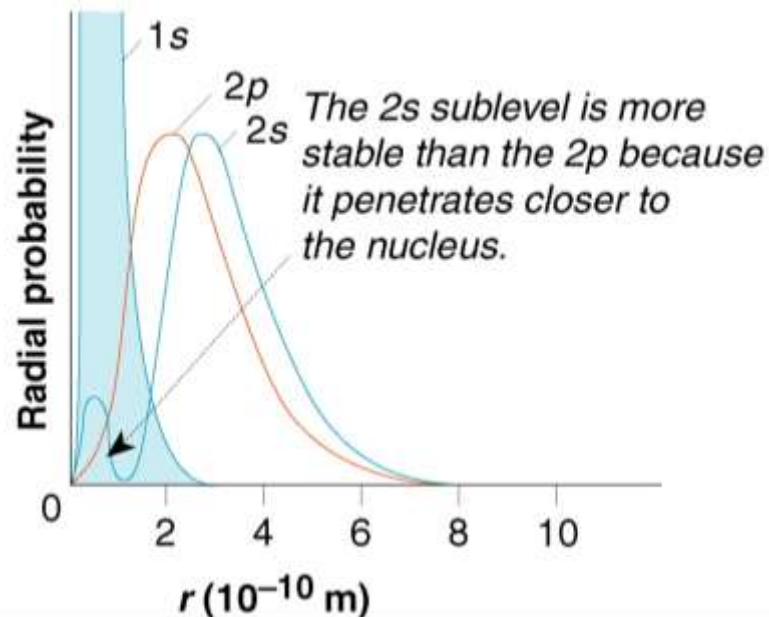
- **Shielding** by other electrons reduces the full nuclear charge to an ***effective nuclear charge*** (Z_{eff}).
- Electrons in the ***same*** energy level shield each other to some extent.
- Electrons in ***inner*** energy levels shield the outer electrons very effectively.
- The further from the nucleus an electron is, the lower the Z_{eff} for that particular electron.

Orbital Shape and energy.

Orbital shape causes electrons in some orbitals to “penetrate” close to the nucleus.

A penetrating orbital is an orbital with a non-zero probability of being found in an inner shell.

Penetration increases nuclear attraction and decreases shielding.



- s orbitals have a non-zero probability density close to the nucleus, penetrate through inner shells
- s electrons feel stronger nuclear attraction; are tightly bound and hence lower in energy
- p orbitals have zero probability density at the nucleus; less penetrating than s and hence p electrons are higher in energy.
- d orbitals less penetrating than p and hence d electrons are higher in energy than p
- Penetrating ability: $s > p > d > f$
- Energy: $s < p < d < f$

Observed filling of orbitals

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

Effective Nuclear Charge

- Effective Nuclear Charge is the actual charge felt by the outer electrons after taking into account shielding of the electrons. It is denoted by the symbol **Z^* or Z_{eff}**
- ***J.C. Slater in 1930*** proposed a formula for calculation of Effective Nuclear Charge

$$Z_{\text{eff}} = Z - S$$

where S = Slater's screening constant ,

Z = atomic number or nuclear charge

Slater's Rules:

1) Write the electron configuration for the atom using the following design;

(1s)(2s,2p)(3s,3p) (3d) (4s,4p) (4d) (4f) (5s,5p) (5d)
(5f) (6s,6p)..... etc.

2) Any electrons to the right of the electron of interest contributes nothing towards shielding.

3) All other electrons in the same group as the electron of interest shield to an extent of 0.35 nuclear charge units irrespective of the orbital the electrons are in.

4) In case of 1s electron shielding another 1s electron the screening constant value is taken to be 0.30.

5) If the electron of interest is an s or p electron:

- All electrons with one less value i.e. $(n - 1)$ value of the principal quantum number shield to an extent of 0.85 units of nuclear charge.
- All electrons with two or more less values i.e. $(n - 2, n - 3, n - 4 \text{ etc.})$ values of the principal quantum number shield to an extent of 1.00 units.

6) If the electron of interest is a *d* or *f* electron: All electrons to the left shield to an extent of 1.00 units of nuclear charge.

7) Add up the shielding amounts from steps 2 through 5 and subtract from the atomic number value to obtain the effective nuclear charge value.

Calculate Z^* for a valence electron in fluorine ($Z = 9$).

- Electronic configuration of fluorine is $1s^2, 2s^2, 2p^5$
- Grouping of orbitals : $(1s^2)(2s^2, 2p^5)$
- One electron out of the 7 valence electrons becomes the electron of interest. The other remaining 6 valence electrons will contribute 0.35 each towards shielding.
- The electrons in $(n - 1)$ orbitals i.e. $1s$ orbital will contribute 0.85 each towards shielding.

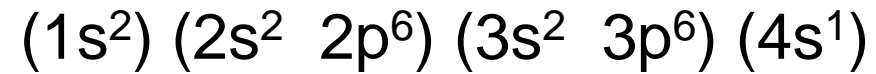
S = 0.35 x (No. of electrons in the same shell i.e. n orbital) + 0.85 x (No. of electrons in the (n – 1) shell)

$$\mathbf{S} = 0.35 \times 6 + 0.85 \times 2 = 3.8$$

Z_{eff} = **Z – S** = 9 – 3.8 = 5.2 for a valence electron.

- Slater's rules provides a quantitative justification for the sequence of orbitals in the energy level diagram.
- It helps to explain the filling of ns - orbital (4s, 5s, 6s etc. – orbitals) prior to the filling of (n - 1)d orbital (3d, 4d, 5d...etc.).
- Consider the case of **Potassium (Z = 19), in which the last electron is added to 4s orbital**

❖ The configuration of **Potassium** according to Slater is



$$\begin{aligned} \mathbf{S} &= 0 \times 0.35 + 8 \times 0.85 + 10 \times 1.00 \\ &= 16.80 \end{aligned}$$

Therefore, Effective Nuclear Charge

$$\mathbf{Z^* = Z - S = 19 - 16.80 = 2.20}$$

Suppose the last electron enters the 3d orbital rather than 4s orbital,

Then the configuration electron configuration is



So,

$$\mathbf{S} = 0 \times 0.35 + 18 \times 1.00 = 18.00$$

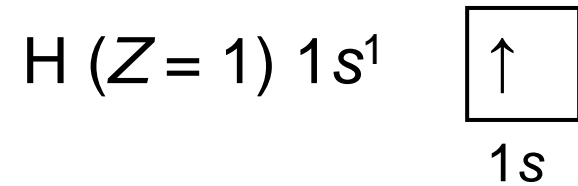
Therefore Effective Nuclear Charge

$$\mathbf{Z^* = Z - S = 19.00 - 18.00 = 1.00}$$

- The 4s electron experiences greater Effective Nuclear charge ($Z_{\text{eff}} = 2.20$) compared to 3d electron ($Z_{\text{eff}} = 1.00$) in Potassium atom.

Rules for assigning electrons into orbitals

The **aufbau principle** is applied – electrons are always placed in the lowest energy orbitals available.

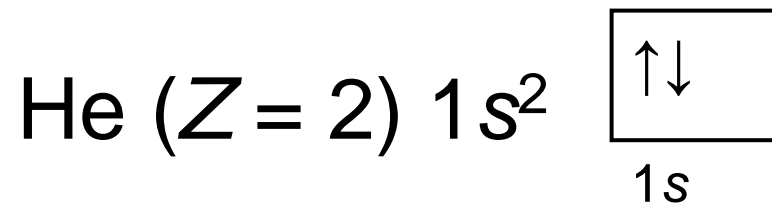


1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s,
5d, 4f, 6p, 7s, 6d, 5f, 7p

Rules for assigning electrons into orbitals

The **Pauli's exclusion principle** states 'no two electrons in an atom can have same set of four quantum numbers'.

Each orbital contain a maximum of 2 electrons, which must have opposite spins.



H $n=1$ $l=0, m=0$ $s=1/2$

He $n=1$ $l=0, m=0$ $s=-1/2$

Building Orbital Diagrams

Hund's rule specifies that when orbitals of equal energy (degenerate) are available, the lowest energy electron configuration has the maximum number of unpaired electrons with parallel spins.

