

Quantum Mechanics

- No real understanding of the chemical bond is possible in terms of classical mechanics because very small particles such as ***electrons do not obey the laws of classical mechanics.***
- Their behavior is determined by quantum mechanics, which was developed in the second half of the 1920s culminating in a mathematical formalism that we still use today.
- Quantum mechanics is used by chemists as ***a tool to obtain the wave function and corresponding energy and geometry of a molecule*** by solving the fundamental equation of quantum mechanics, called the Schrödinger equation.
- The Schrödinger equation can only be completely solved for the hydrogen atom, or isoelectronic ions, with just one electron. ***Approximation methods must be used for multi-electron atoms and polyatomic molecules.***
- The most characteristic feature of quantum mechanics which differentiates it from classical mechanics is its probabilistic character.

Classical → statistical

Quantum → probabilistic

Dual Wave-Particle Nature of Light

- Light is not just emitted or absorbed in light quanta but that it travels through space as small bundles of energy called photons.
- Although photons are regarded as mass-less particles, their energy is remarkably expressed in terms of the frequency of a wave.
- Although light has no mass it has momentum, which depends on the wavelength of the light.

$$E = h \cdot \nu$$

$$\nu = c/\lambda$$

$$E = h \cdot c/\lambda$$

$$\lambda = h/p$$

$$E = p \cdot c$$

de Broglie wavelength

$$(E = m \cdot c^2)$$

$$E_{\text{photon}} \propto \nu_{\text{photon}} \propto 1/\lambda_{\text{photon}} \propto p_{\text{photon}}$$

- In summary, the energy of light is transmitted in the form of particle-like photons, which have an **energy that depends of the frequency and momentum of the photon.**

Wave vs. Particle Nature of Light

- In the famous Young's slit experiment it was proven that wave theory describes the *statistical* result of observing a large number of photons.
- The ***behavior of an individual photon cannot be predicted, but we can predict the probability*** of detecting a single photon at a particular point.
- This probability is proportional to the intensity of the light, that is, to the square of the amplitude of the wave, at that point.
- This is a very important conclusion because it will prove to be valid for non-zero-mass particles as well, such as electrons.

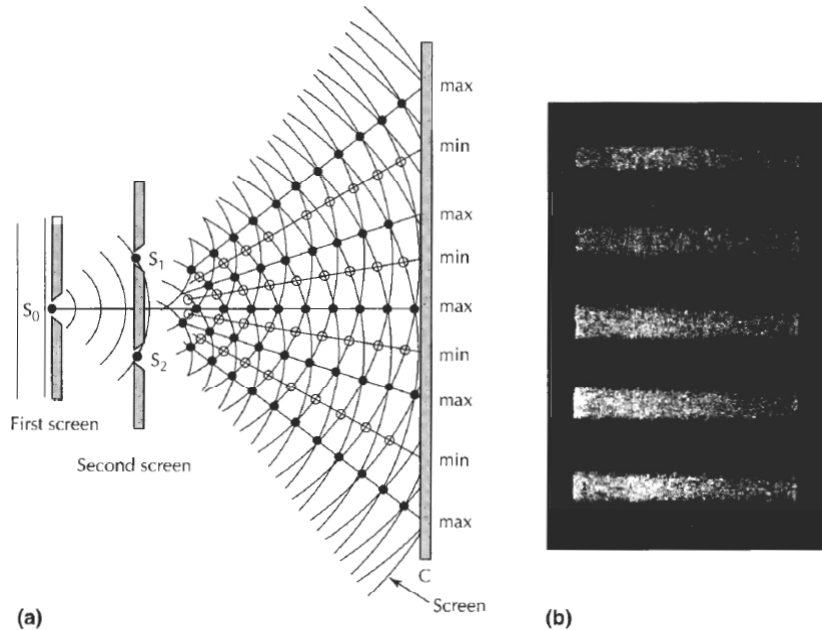


Figure 3.1 (a) Schematic diagram (not to scale) of Young's double-slit experiment. The narrow slits acts as wave sources. Slits S_1 and S_2 behave as coherent sources that produce an interference pattern on screen C. (b) The fringe pattern formed on screen C could look like this. (Reproduced with permission from R. A. Serway *Physics for Scientists and Engineers with Modern Physics*, 3rd ed, 1990, Saunders, Figure 37.1.)

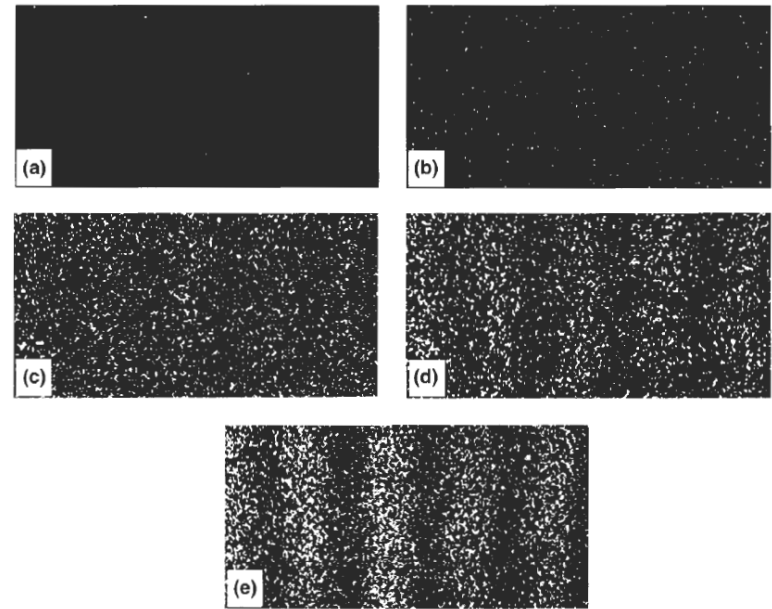
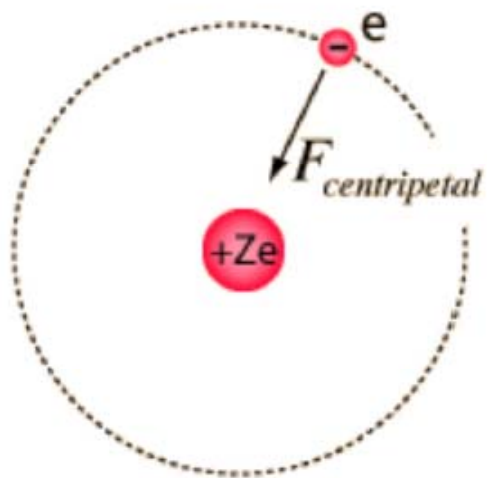


Figure 3.2 The cumulative pattern generated by photons sent one by one through a two-slit interferometer. Number of photons: (a) 10, (b) 100, (c) 3000, (d) 20,000, and (e) 70,000. (Reproduced with permission from Tonomura et al, *Amer. J. Phys.* 57, 117, 1987.)

Classical Model of the Atom

- In 1913 Bohr proposed a model of the hydrogen atom to account for its *line spectrum*, which showed that ***the energy of the electron in the hydrogen atom is quantized***.
- Bohr's hypothesis was a combination of Rutherford's atomic model, Planck's quantum theory, Einstein's photon theory of light, which proposed that the single electron revolves around the nucleus in a circular orbit. The energy being defined by the singly charged electron and nucleus (proton) and the distance between them according to Coulombs law.
i.e., the larger the orbital radius the higher the energy of the electron.
- Bohr's model was reasonable from a quantitative perspective, however, there were problems:
 - Bohr could not qualitatively explain why the energies were quantized.
 - According to classical electromagnetic theory, an electron rotating around a positive nucleus should emit electromagnetic radiation, continuously losing energy and spiraling into the nucleus.
 - Attempts to apply Bohr's theory to multi-electron atoms failed



The orbit energy is negative because this is a bound state.

Newton's Second Law

$$= \frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

so

Kinetic Energy T

$$T = \frac{mv^2}{2} = \frac{Ze^2}{8\pi\epsilon_0 r}$$

Potential Energy

$$U = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

Total Energy

$$T + U = \frac{-Ze^2}{8\pi\epsilon_0 r}$$

This is the energy of a single electron in orbit around a bare nucleus.

Shortcomings of the Bohr Model

- While the Bohr model was a major step toward understanding the quantum theory of the atom, it is not in fact a correct description of the nature of electron orbits. Some of the shortcomings of the model are:
 1. It fails to provide any understanding of why certain spectral lines are brighter than others. There is ***no mechanism for the calculation of transition probabilities***.
 2. The Bohr model treats the electron as if it were a miniature planet, with definite radius and momentum. This is ***in direct violation of the uncertainty principle*** which dictates that position and momentum cannot be simultaneously determined.
- The Bohr model gives us ***a basic conceptual model of electrons orbits and energies***. The precise details of spectra and charge distribution must be left to quantum mechanical calculations, as with the Schrödinger equation.
- Bohr's theory specified the precise path of the electron, however, as we now know ***the concept of a well-defined orbit for an electron is not consistent with quantum mechanics***.

The Uncertainty Principle

- In 1923 de Broglie made the bold suggestion that matter, like light, has a **dual wave-particle nature** such that non-zero-rest particles with a momentum p should have a corresponding wavelength according to:

$$\lambda = h/p$$

de Broglie wavelength

$$\lambda = h.c/p.c$$

$$(p = m.c)$$

$$\lambda = h.c/m.c^2$$

$$(E = m.c^2)$$

$$\lambda = h.c/E$$

$$E = h.c/\lambda$$

$$E_{\text{particle}} \propto v_{\text{particle}} \propto 1/\lambda_{\text{particle}} \propto p_{\text{particle}}$$

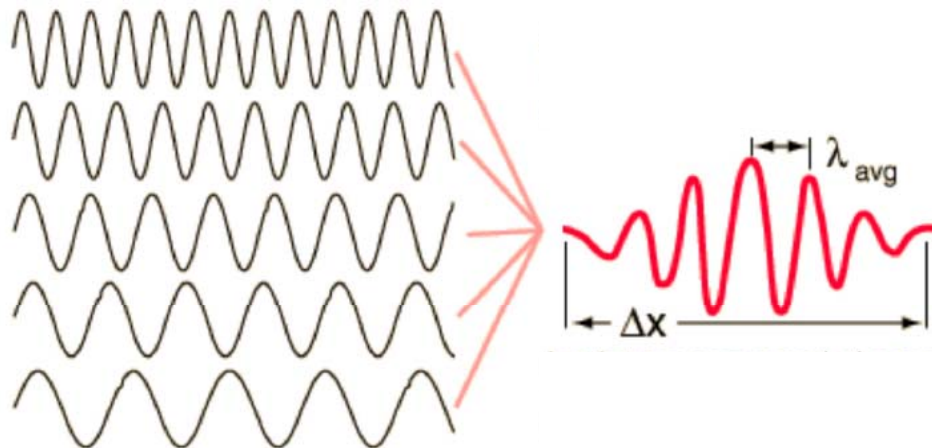
- This was later proven experimentally when electrons were observed to produce a diffraction pattern similar to those of X-rays when passed through a thin gold foil (*Thompson 1927*).
- As you proceed downward in size to atomic dimensions, it is no longer valid to consider a particle like a hard sphere, because the smaller the dimension, the more wave-like it becomes.
- It no longer makes sense to say that you have precisely determined both the position and momentum of such a particle.
- The wave nature of the electron is defined by the quantum mechanical wavefunction Ψ which is related to the probability of finding the electron at any point in space.***

- A perfect sine wave for the electron wave spreads that probability throughout all of space, and the position of the electron is completely uncertain.
- A sine wave of wavelength λ implies that the **momentum p is precisely known but the probability of finding the particle is spread out over all space.**



$$p = h/\lambda$$

- Adding several waves of different wavelengths produces an interference pattern which begins to localize the wave.
- This process, however, increases the uncertainty in momentum.



- Heisenberg showed that Δx , the uncertainty in the measurement of the position of x , and Δp , the uncertainty in the measurement of the momentum p , can never be smaller than $h/4\pi$.

$$\Delta x \Delta p \geq \hbar/2$$

$$\Delta x \Delta p \geq h/4\pi$$

(note: $\hbar = h/2\pi$)

- ***In summary, there is no way of accurately measuring simultaneously both the position and velocity of an electron.***
- This is not a statement about the inaccuracy of measurement instruments, nor a reflection on the quality of experimental methods; it arises from the wave properties inherent in the quantum mechanical description of nature.
- Even with perfect instruments and technique, the uncertainty is inherent in the nature of things.

- Consider an electron orbiting the hydrogen atom

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

$$\text{If } v = 2.19 \times 10^6 \text{ m s}^{-1} \pm 2.19 \times 10^4 \text{ m s}^{-1} \quad (e^- \text{ velocity with } \pm 1 \% \text{ error})$$

$$\begin{aligned} \Delta p &= m \cdot \Delta v = (9.11 \times 10^{-31} \text{ kg})(4.38 \times 10^4 \text{ m s}^{-1}) \\ &= 4.00 \times 10^{-26} \text{ kg m s}^{-1} \end{aligned}$$

$$\Delta x \geq h / (4\pi \cdot \Delta p)$$

$$\Delta x \geq (6.63 \times 10^{-34} \text{ J s}) / (4)(3.14)(4.00 \times 10^{-26} \text{ kg m s}^{-1})$$

$$\geq (6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}) / (5.02 \times 10^{-25} \text{ kg m s}^{-1})$$

$$\geq 3.32 \times 10^{-9} \text{ m}$$

This is an enormous uncertainty in position considering the diameter of an electron is $< 10^{-18} \text{ m}$

The Wave Function

- The Schrödinger equation (1926) plays the role of Newton's laws and conservation of energy in classical mechanics
 - i.e., it predicts the future behavior of a dynamic system. It is a wave equation in terms of the wavefunction which ***predicts analytically and precisely the probability of events or outcome.***
- The detailed outcome is not strictly determined, but given a large number of events, the Schrodinger equation will predict the distribution of results.
- ***The kinetic and potential energies are transformed into the Hamiltonian which acts upon the wavefunction to generate the evolution of the wavefunction in time and space.*** The Schrodinger equation gives the quantized energies of the system and gives the form of the wavefunction so that other properties may be calculated.
- From the Schrödinger equation we can obtain the wave function of any small particle, and thus the corresponding energy E for any atomic or molecular system.
- ***Schrödinger's equation is a fundamental postulate of quantum mechanics*** which cannot be derived but is justified given its agreement with experiment.

- The Schrödinger equation in its simplest form can be written as:

$$H\Psi = E\Psi$$

where Ψ is the wavefunction, E is the energy and H is the **Hamiltonian operator**. The form of the H depending upon the system under consideration

(typically H takes the form of a first or second derivative, d/dx or d^2/dx^2)

- For an atom, **H contains a kinetic energy term and a potential energy term** that results from the Coulomb attraction between electrons and the nucleus and interelectron repulsion.
- This type of equation, where an operator (H) operates on a function (Ψ) to give the function times a constant (E), has many solutions.
- Each solution is called a state, and the lowest energy state is called the ground state.
- ***Only certain solutions of E are possible using the time-independent Schrödinger equation, namely those for which Ψ is a continuous single-valued function.***
- Hence, in contrast to classical mechanics, Schrödinger's equation can qualitatively explain the quantization of atomic/polyatomic energies.

- Thus, in principle, we can **obtain the wave function and the energy for any atomic or molecular system**, but insuperable mathematical difficulties prevent us from obtaining exact solutions to all but the very simplest ***one-electron systems***.
- **Let us consider a free single particle** moving in one dimension with zero potential energy ($V = 0$) where h is Planck's constant, and m is the mass of the particle. For this system H is expressed as

$$H = \left(-\frac{h^2}{8\pi^2m} \cdot \frac{d^2}{dx^2} \right)$$

$$\left(-\frac{h^2}{8\pi^2m} \cdot \frac{d^2}{dx^2} \right) \psi(x) = E\psi(x)$$

$$\left(-\frac{h^2}{8\pi^2mE} \cdot \frac{d^2}{dx^2} \right) \psi(x) = \psi(x)$$

• Let $k^2 = \frac{8\pi^2mE}{h^2}$

$$\left(-\frac{1}{k^2} \cdot \frac{d^2}{dx^2} \right) \psi(x) = \psi(x)$$

• Multiply both sides by k^2

$$\left(-\frac{d^2}{dx^2} \right) \psi(x) = k^2\psi(x)$$

$$\frac{d^2}{dx^2} \psi(x) + k^2\psi(x) = 0$$

$$\frac{d^2}{dx^2} \psi(x) + k^2 \psi(x) = 0$$

- A convenient form of the general solution of this equation is

$$\psi = A \cos(kx) + B \sin(kx)$$

where A and B are proportionality constants.

- Since there are no constraints or restrictions on the value of k the value of E may have any positive value, i.e. **the free particle energy is not quantized.**
- No let us consider a particle which is no longer free but confined to a limited region of space. We do this by assuming $V = 0$ for the region $x = 0$ to $x = a$ but everywhere outside this region $V = \infty$.

i.e., a particle in a box

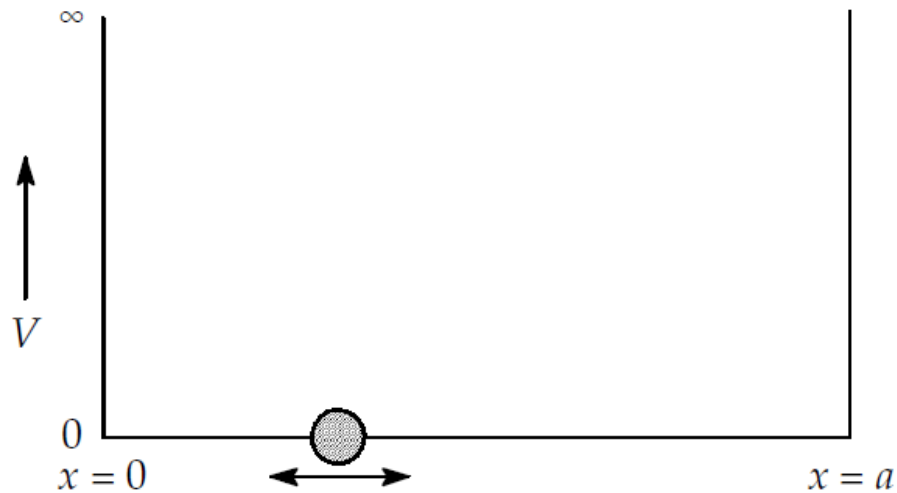
- Although this situation is physically unrealizable, it provides an illustration of some important quantum mechanical concepts without obscuring its principles.
- The operator is now expressed as

$$H = \left(-\frac{h^2}{8\pi^2m} \cdot \frac{d^2}{dx^2} + V \right)$$

- The time-independent Schrödinger equation now takes the form:

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

- When $V = \infty$ the only solution to this equation is $\Psi = 0$. Therefore, **if Ψ is to be single valued and continuous it must be 0 at $x = 0$ and $x = a$** .
- Thus, the potential energy walls imposed are **boundary conditions** on the form of Ψ .
- By applying *boundary conditions* to Ψ in essence we restrict the allowed values of E .
i.e., quantization.



Proof

Substituting the allowed values of x into Ψ gives the following relationship: $\psi = A \sin \left(\frac{n\pi x}{a} \right)$

Now we substitute this term into the eqn. $\left(-\frac{h^2}{8\pi^2 m} \cdot \frac{d^2}{dx^2} \right) \psi(x) = E\psi(x)$

Resulting in $-\frac{h^2}{8\pi^2 m} \left(-\frac{n^2 \pi^2}{a^2} \right) A \sin \left(\frac{n\pi x}{a} \right) = EA \sin \left(\frac{n\pi x}{a} \right)$

simplify $\left(\frac{h^2 n^2}{8ma^2} \right) A \sin \left(\frac{n\pi x}{a} \right) = EA \sin \left(\frac{n\pi x}{a} \right)$

Thus, the allowed energies are given by the expression $E = \frac{h^2 n^2}{8ma^2}$

Energy level diagram for a particle in a box

In summary:

- Solutions that meet the *boundary conditions* must have the form:

$$\psi = A \sin\left(\frac{n\pi x}{a}\right)$$

Note that when $x = 0$ and when $x = a$

$$\sin(n\pi x/a) = 0$$

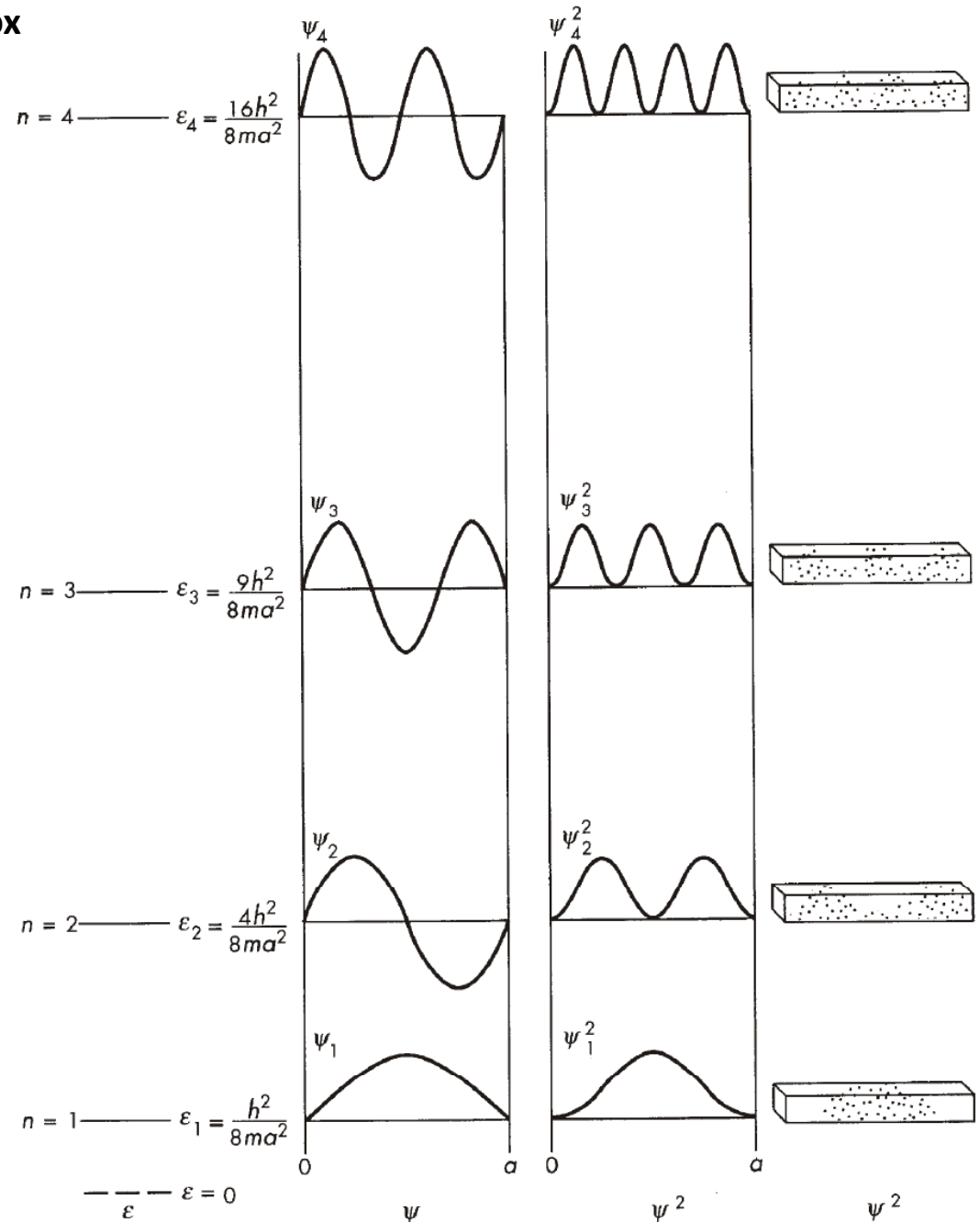
- Solving Schrödinger's eqn. thus gives

$$E = \frac{h^2 n^2}{8ma^2}$$

where $n = 0, 1, 2, 3, \dots$ etc.

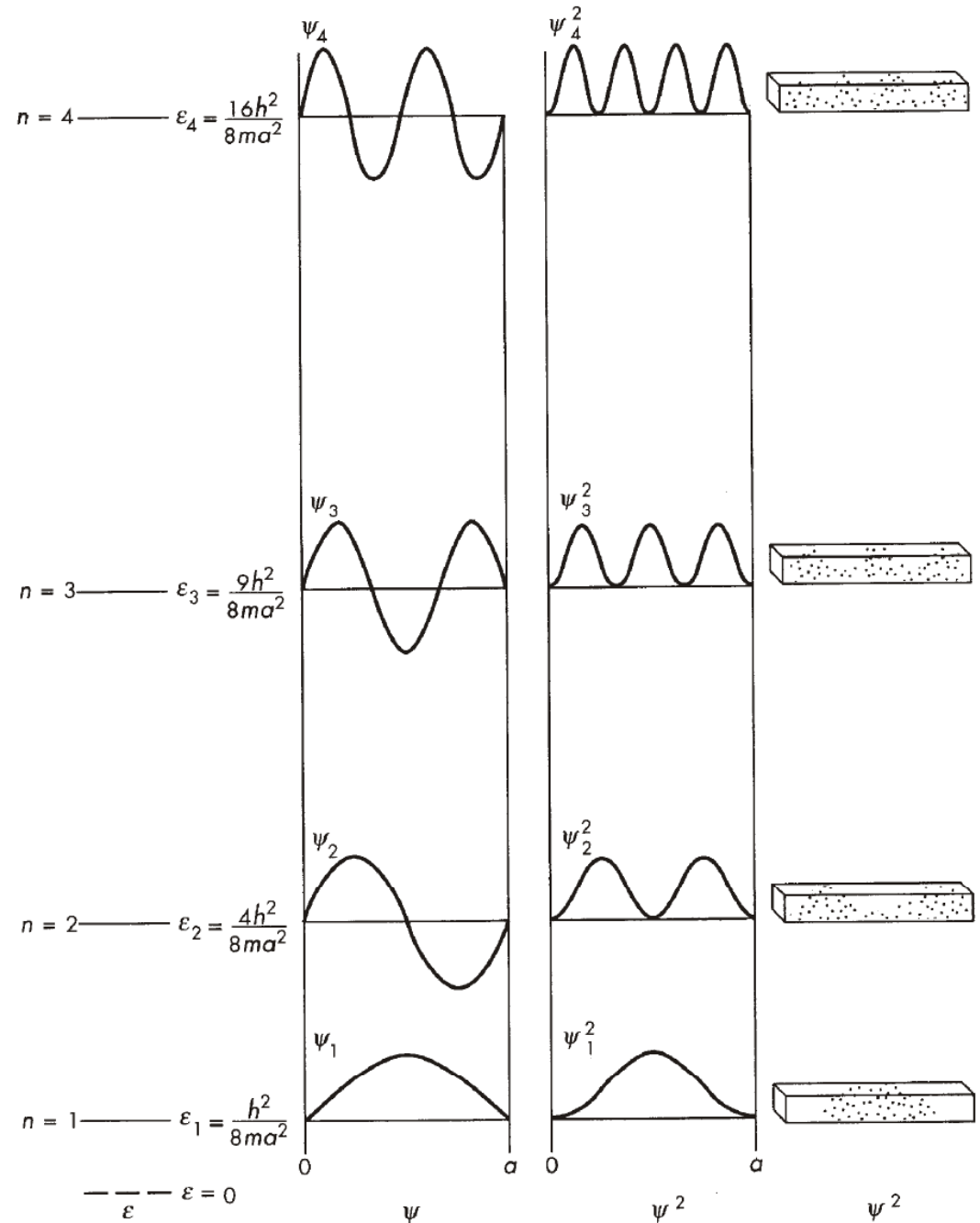
- Allowed energies for Ψ are quantized into discrete states such that

$$E \propto n^2$$



$$E = \frac{h^2 n^2}{8ma^2}$$

- Solutions exist for the time-independent Schrodinger equation only for certain values of energy.
- These values are called **eigenvalues** of energy
- The energy of the particle in its lowest energy state is called its **zero-point energy**.
- Each solution has certain points where $\Psi = 0$.
- These points are called **nodes**.



Probability and Electron Density (Ψ^2)

- Earlier we compared **wave (photon)** and **particle (electron)** nature using a **statistical** and **probabilistic** interpretation, respectively.
- The probability of detecting a photon of light at a given point is dependent upon the intensity of light at that point, which is proportional to the square of the amplitude of the light wave.¹

$$I \propto A^2$$

- Thus, the probability of finding a particle at a given point must be proportional to the square of the amplitude of the matter wave, i.e., Ψ^2 .

$$P \propto \Psi^2$$

- This is the "Copenhagen Interpretation" of Ψ , devised by Max Born and co-workers.
- In the Copenhagen interpretation there is **no way of exactly predicting where the electron will be** at a given instant, i.e., its behavior is intrinsically probabilistic.
- The electron is best represented as a "cloud" with the area of greatest density indicating where there is the greatest probability of finding the electron.
- In order to use Ψ to determine the value of any physical observable, it must be normalized so that the probability, Ψ^2 , integrated over all space is equal to one.

¹Strictly, a point has no volume, therefore $\Psi = 0$ and $\Psi^2 = 0$. The term "point" here means "a vanishingly small volume element".

Restrictions on Ψ

- Ψ has a value for every point in space.

Otherwise the probability would be undefined somewhere.

- Ψ can have only one value at any point.

Otherwise the probability would be ambiguous at some points.

- Ψ cannot be infinite at any point in space.

Otherwise its position would be fixed, in violation of the Heisenberg Uncertainty Principle.

- Ψ can be zero at some points in space (node).

This means the electron is not there.

- Probability of the electron at a point (zero volume) is vanishingly small.

Therefore, we calculate Ψ^2 for small volume segment $dx dy dz$.

$$P(x, y, z) dx dy dz = P d\tau$$

- The sum of Ψ^2 over all space is unity.

The electron must be somewhere.

$$\int \Psi^2 dx dy dz = \int \Psi^2 d\tau = \int P d\tau = 1$$

Atomic orbitals

- The three dimensional time-independent Schrödinger wave eqn. describes one electron systems, e.g. H, He⁺, Li²⁺, where E represents total electronic energy of the wavefunction or orbital Ψ

$$\left[-\frac{h^2}{8\pi^2m} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) - \frac{e^2}{r} \right] \psi = E\psi$$

- Orbitals ***assumed*** to be unchanged for multi-electron atoms
- Schrödinger and Born suggested that ψ^2 can be used to map atomic orbitals about the nucleus, i.e. ψ^2 is a **measure of electron density**
- E is governed by four quantum numbers
 1. ***principal (n)***: dictates orbital energy
 2. ***secondary or azimuthal (l)***: dictates shape and orientation
 3. ***magnetic (m_l)***: dictates shape and orientation with l
 4. ***spin (m_s)***: dictates spin state of the electron

- n can be any whole number from one to infinity; 1, 2, 3,.... ∞ .
- l is limited to 0, 1, 2...($n-1$).
- m_l is governed by l (hence the subscript) has the values 0, ± 1 , ± 2 ,.... $\pm l$.
- m_s is limited to $+\frac{1}{2}$ or $-\frac{1}{2}$.
- Principal quantum number n written as prefix to l
- l is often used as shorthand for labeling orbitals.

- ***l* is often used as shorthand for labeling orbitals:**

***l* = 0 → s orbital (*sharp*)**

***l* = 1 → p orbital (*principal*)**

***l* = 2 → d orbital (*diffuse*)**

***l* = 3 → f orbital (*fundamental*)**

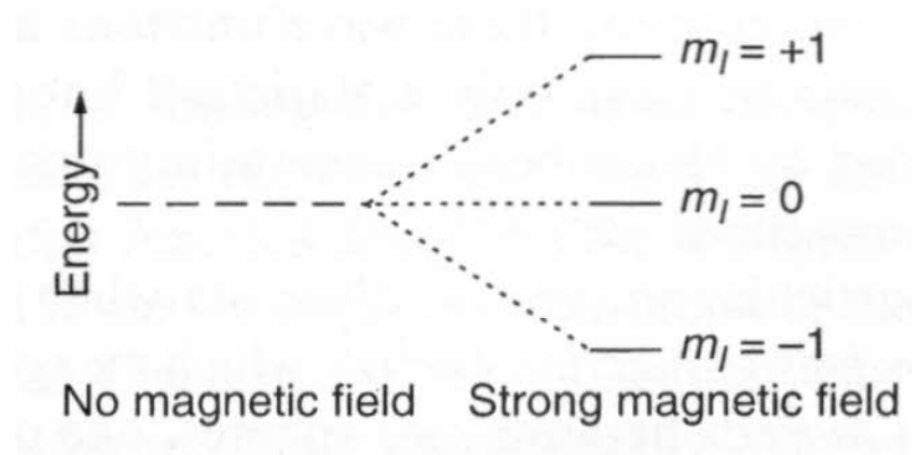
***l* = 4 → g orbital**

***l* = 5 → h orbital**

***l* = 6 → i orbital**

***l* = 7 → k orbital ...l, m, n etc...alphabetically (no j)**

The magnetic quantum number denotes the energy levels available within a subshell



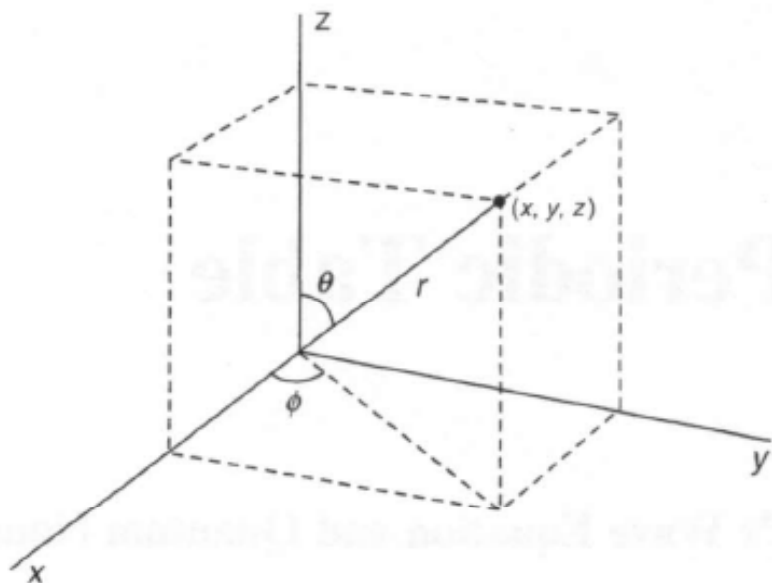
$$l = 0 \rightarrow m_l = 0$$

$$l = 1 \rightarrow m_l = +1, 0, -1 \text{ (3 p orbitals)}$$

$$l = 2 \rightarrow m_l = +2, +1, 0, -1, -2 \text{ (5 d orbitals)...etc.}$$

s orbitals

1. Spherical in shape and dependent on radial parameters, i.e. ψ^2 independent of angular coordinates at fixed r value.
2. The distribution of ψ^2 is not homogeneous for $n > 1$ and has $n - 1$ nodes.
3. Electrons still *penetrate* close to the nucleus for $n > 1$ s orbitals.

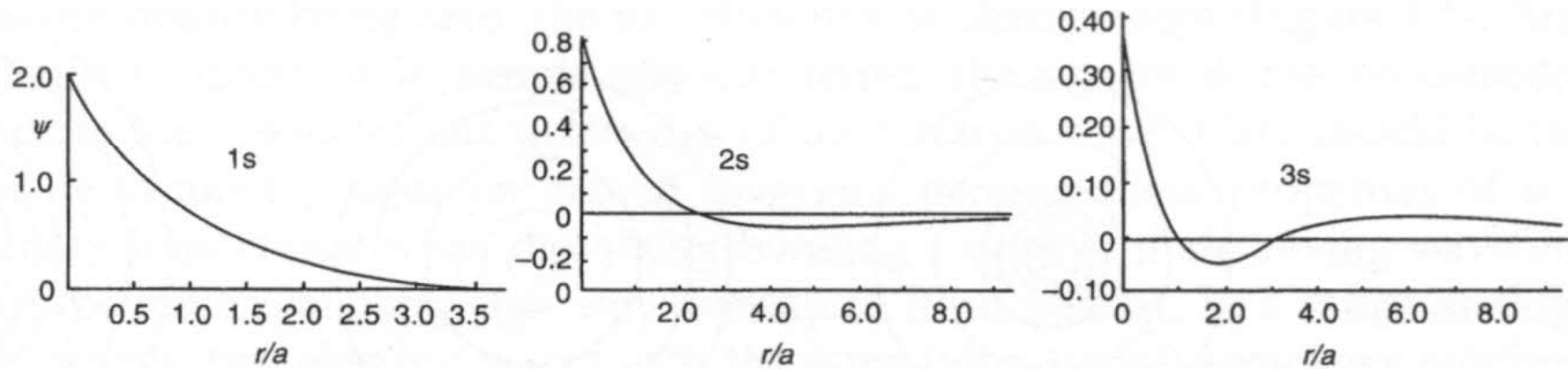


$$\psi_{1s} = \left(\frac{1}{\pi a^3} \right)^{1/2} \exp\left(-\frac{r}{a}\right)$$

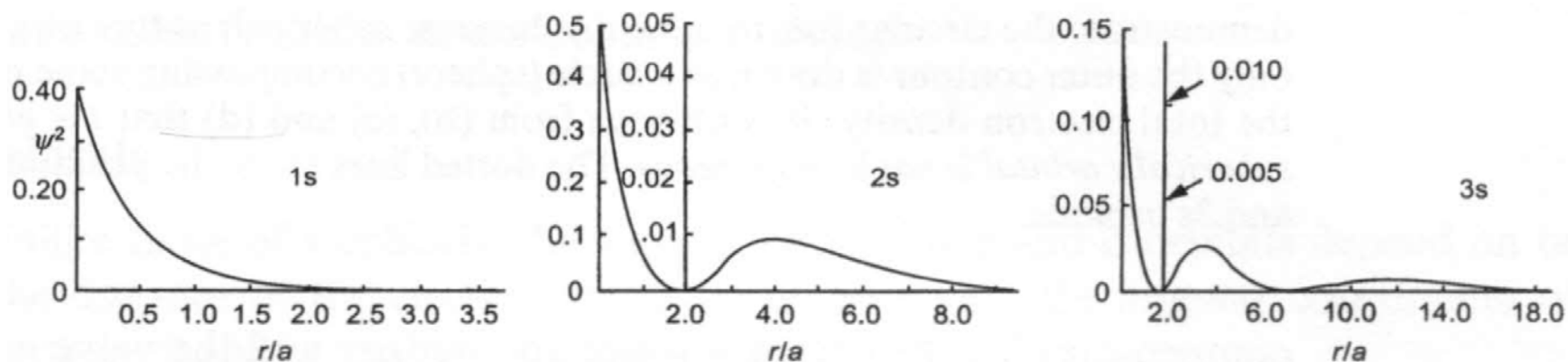
$$\psi_{2s} = \frac{1}{4} \left(\frac{1}{\pi a^3} \right)^{1/2} \left(2 - \frac{r}{a} \right) \exp\left(-\frac{r}{2a}\right)$$

Representations of Orbitals

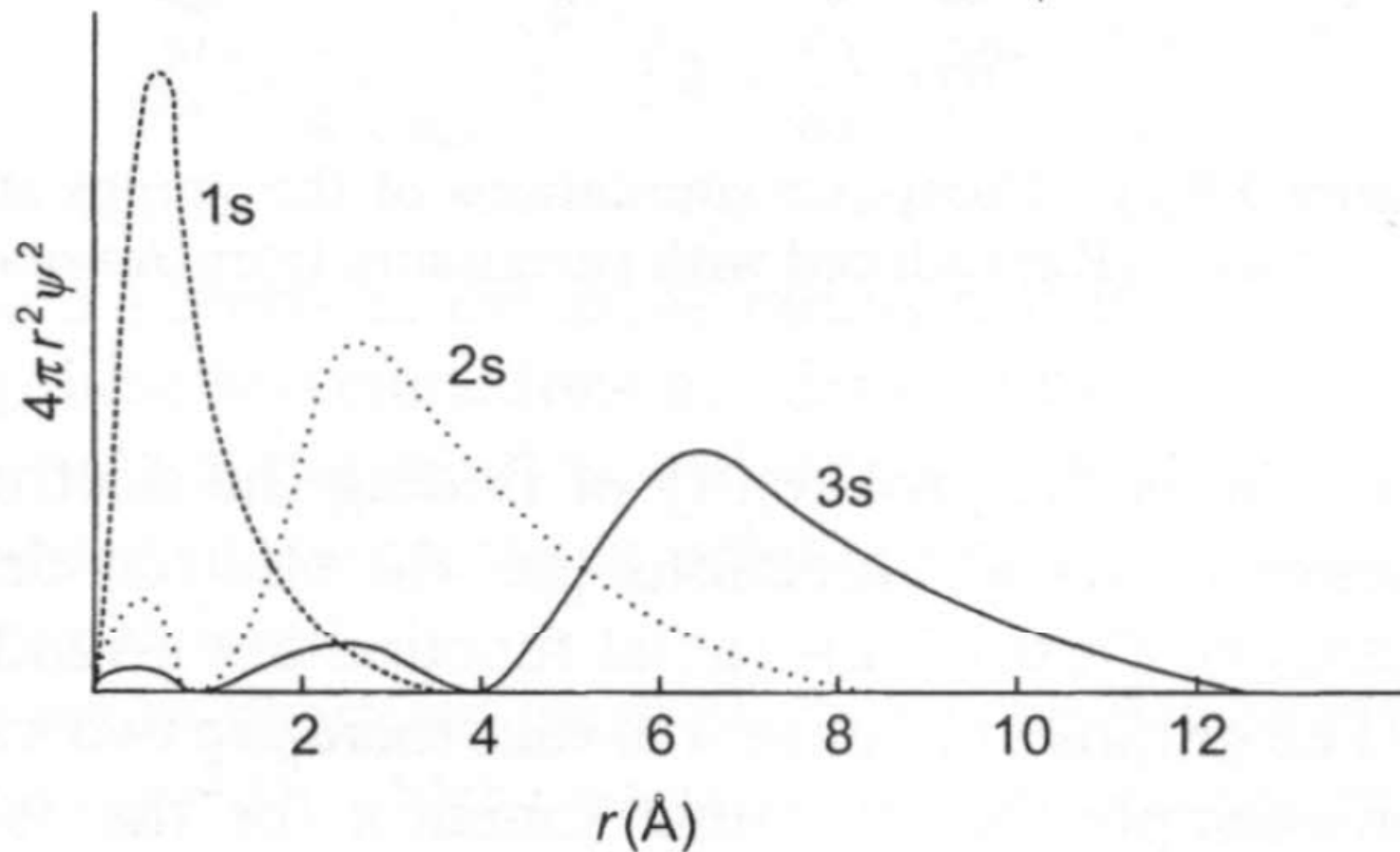
- **Radial Plot:** *(R = radial function)*
2-D plot of R vs. r or R^2 vs. r without trying to show the 3-D aspects of the distribution. Sometimes a particular direction in space is chosen (x, y, z).
- **Radial Distribution Function:**
2-D plot of $4\pi r^2 R^2$ vs. r . Probability of finding the electron within a vanishingly thin spherical shell with a radius of r from the nucleus. Going out from the nucleus, this shows the variation in probability on the surface of increasingly larger spherical shells.
- **Electron Charge Cloud (Electron Density) Diagram**
3-D picture of Ψ^2 in which higher probability is rendered by darker shading. Most of such diagrams are meant to show approximately 90-99% of the total probability.
- **Contour Diagram**
2-D cross section through the probability distribution, Ψ^2 . Lines on the drawing connect regions of equal probability.
- **Boundary Surface Diagram**
3-D solid model representing a surface that encloses approximately 90-99% of Ψ^2 . 2-D cross sections are routinely used to represent the various orbitals.



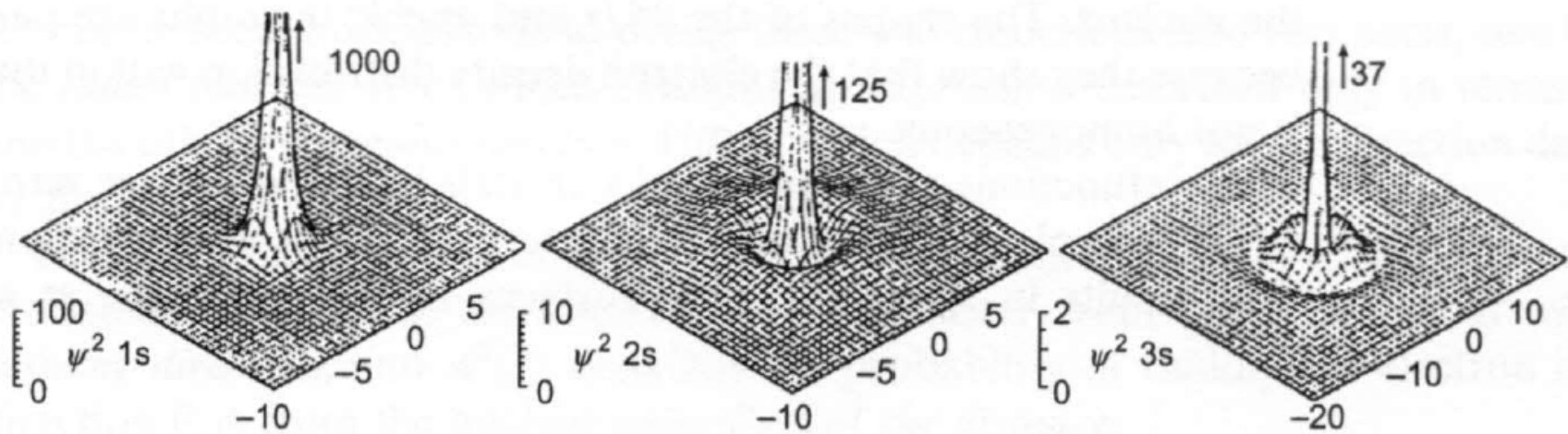
- Plots of ψ vs. 'distance from the nucleus' (r) in units of Bohr radius (a) for 1s, 2s and 3s orbitals.
- The phase of ψ changes sign where it crosses over $\psi = 0$ (**node**)



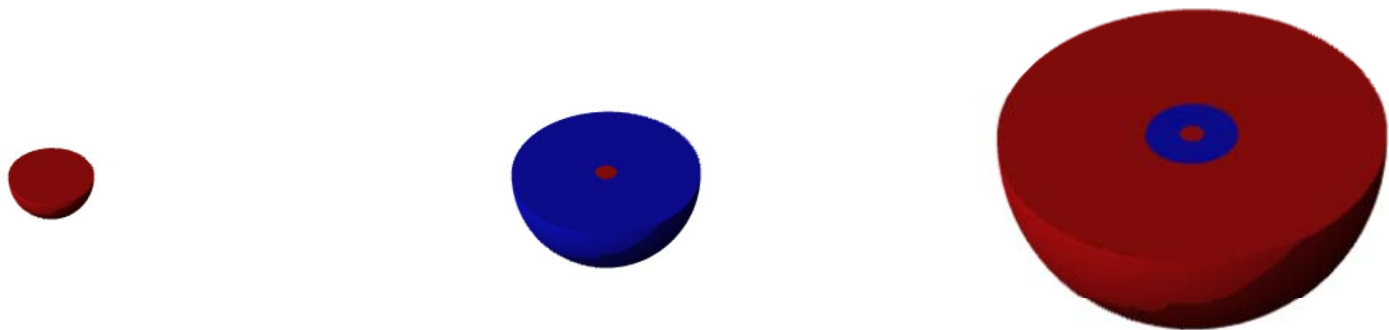
- Plot of ψ^2 vs r for the 1s, 2s and 3s orbitals.
- ψ^2 represents the electron density, i.e. the probability of finding an electron at a particular point in an orbital.
- There is a high electron density at, and close to, the nucleus for all s orbitals. This sharply decreases as r increases (hence second y-axis in plots of 2s and 3s).
- In contrast ψ^2 is zero at the nucleus for both p, d and f orbitals.



- Plot of radial electron density functions for the 1s, 2s and 3s orbitals of the H atom.
- Maximum radial electron density for 1s occurs at the Bohr radius, $r = 0.53 \text{ \AA}$.



3-D representations of the radial electron density functions of the 1s, 2s and 3s orbitals for the H atom.

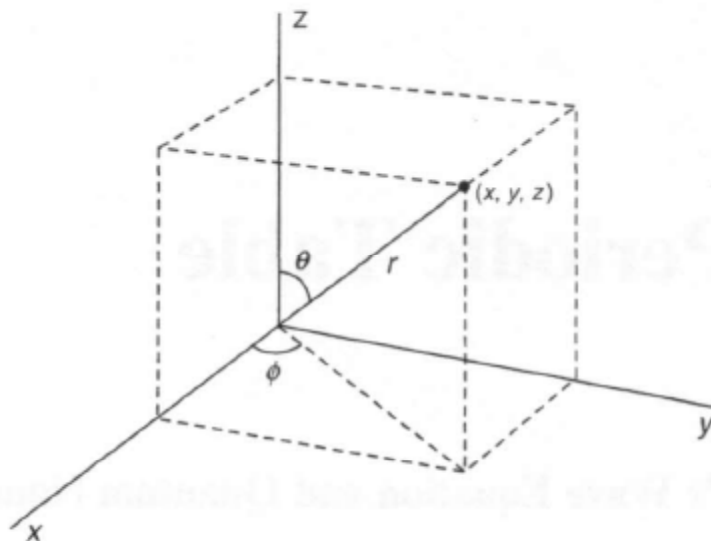


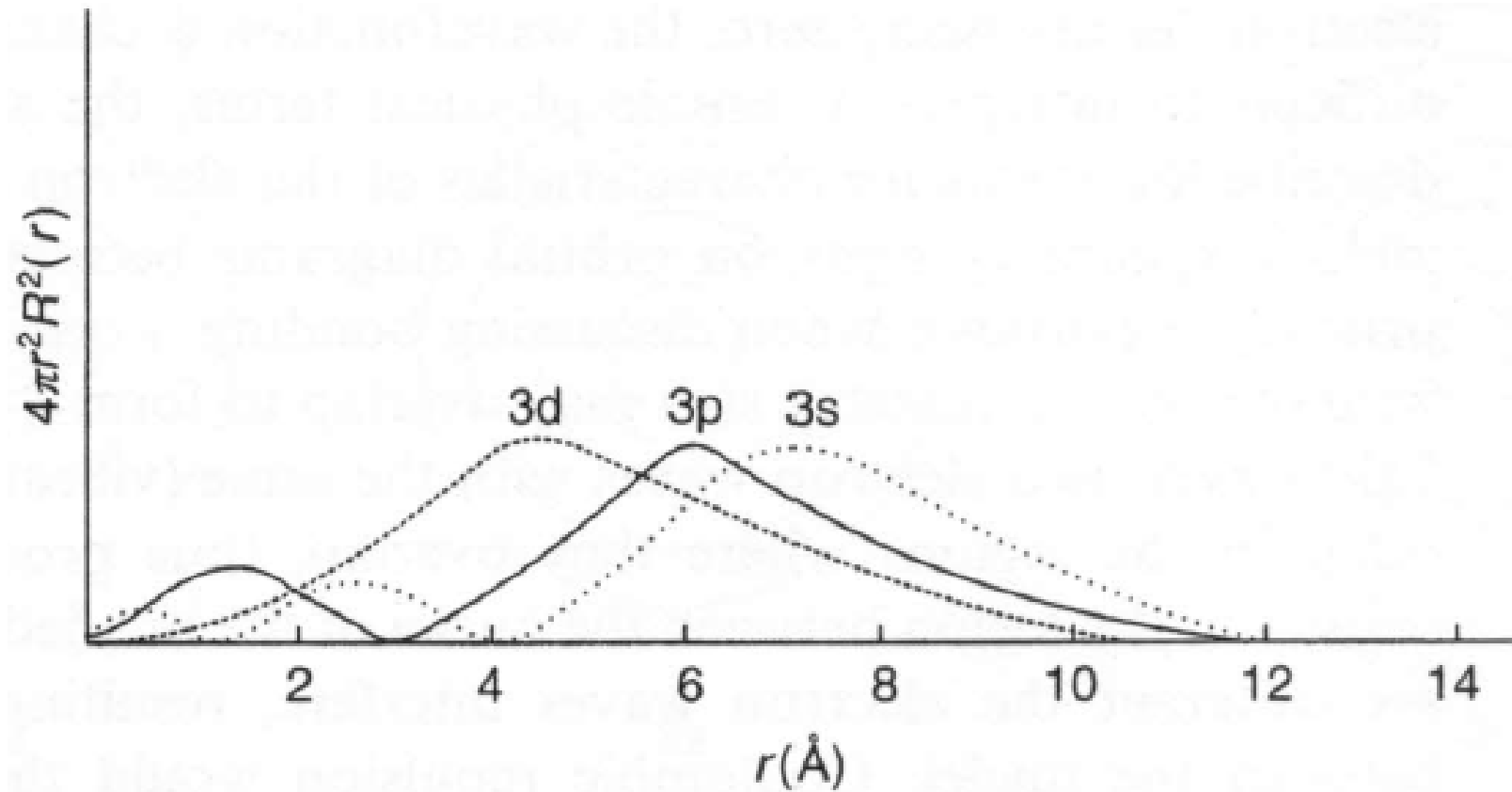
p and d orbitals

- **p and d orbitals are more diffuse than s orbitals**, therefore less penetrating.
- **Penetration effect** for orbitals of the same n value:

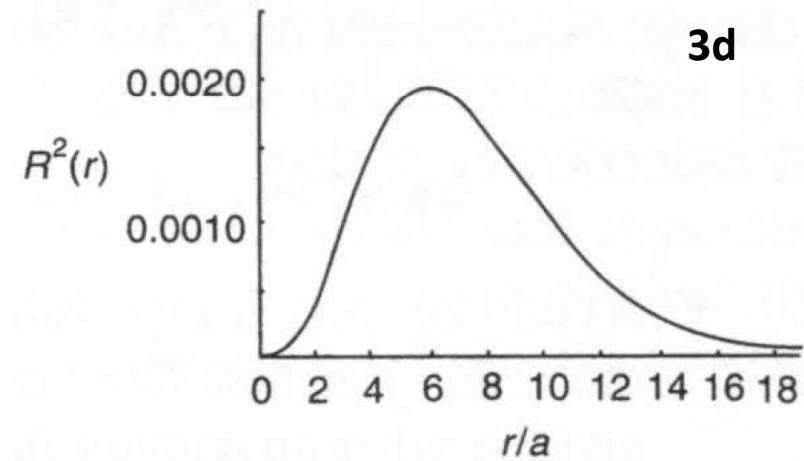
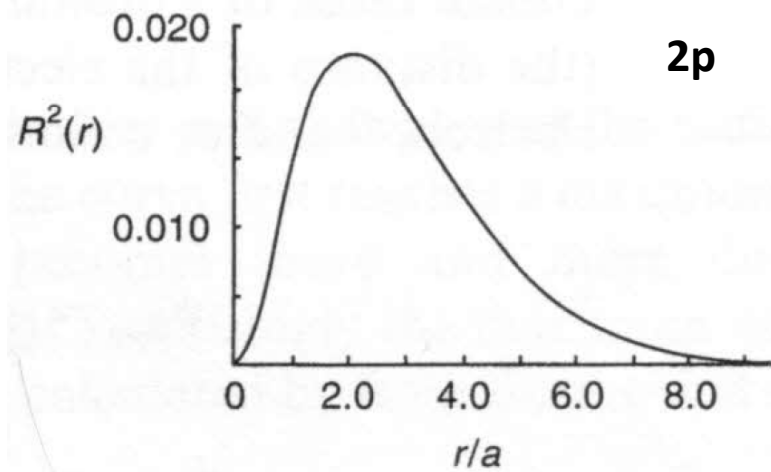
$$s > p > d > f$$

- Unlike s orbitals, ψ for orbitals with $l > 0$ (p, d, f etc.) depends on both distance (r) and **angular coordinates (θ, ϕ) of the electron**.

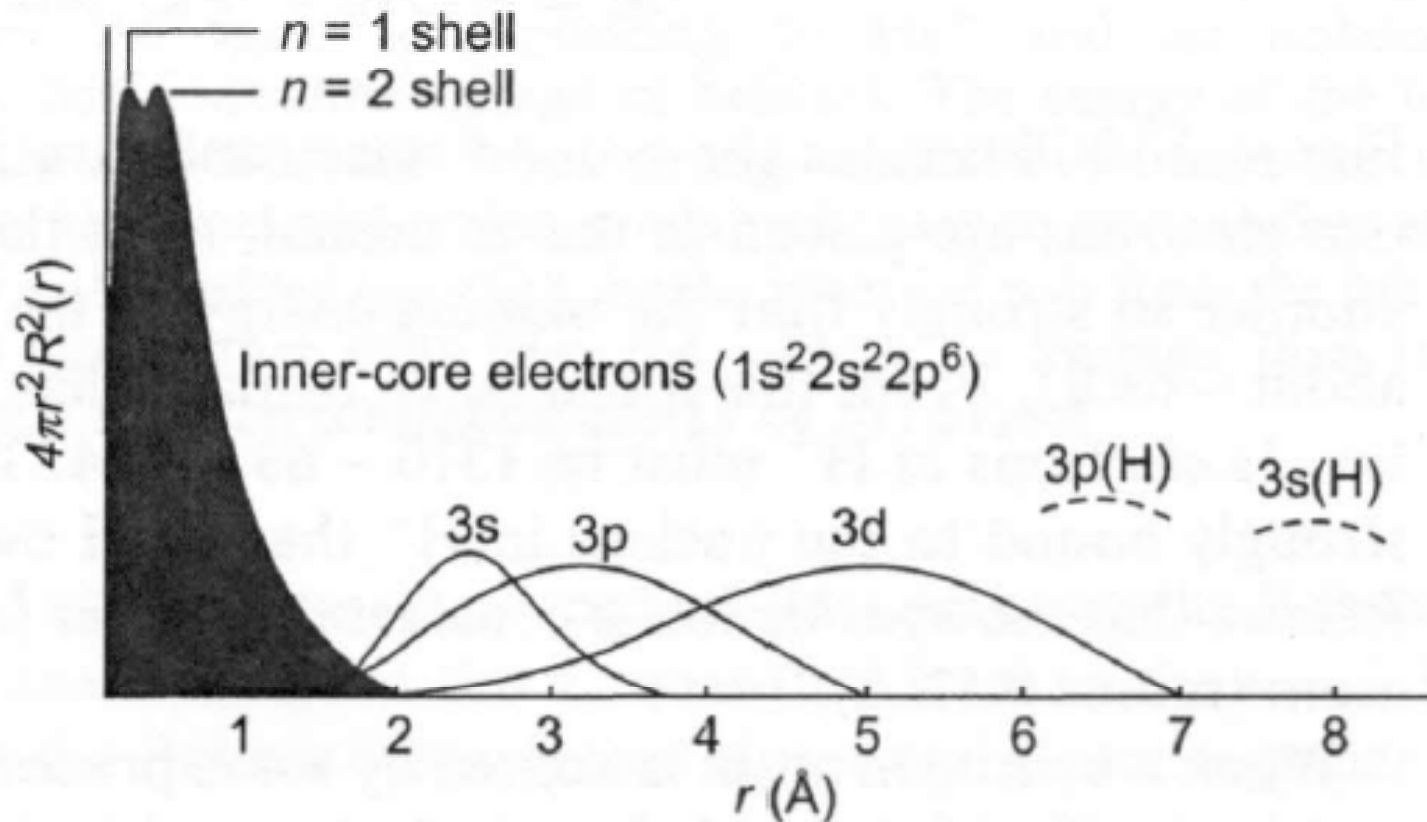




- Plot of **radial electron distribution function vs. distance (r)** for 3s, 3p and 3d orbitals of the H atom (*normalized*).



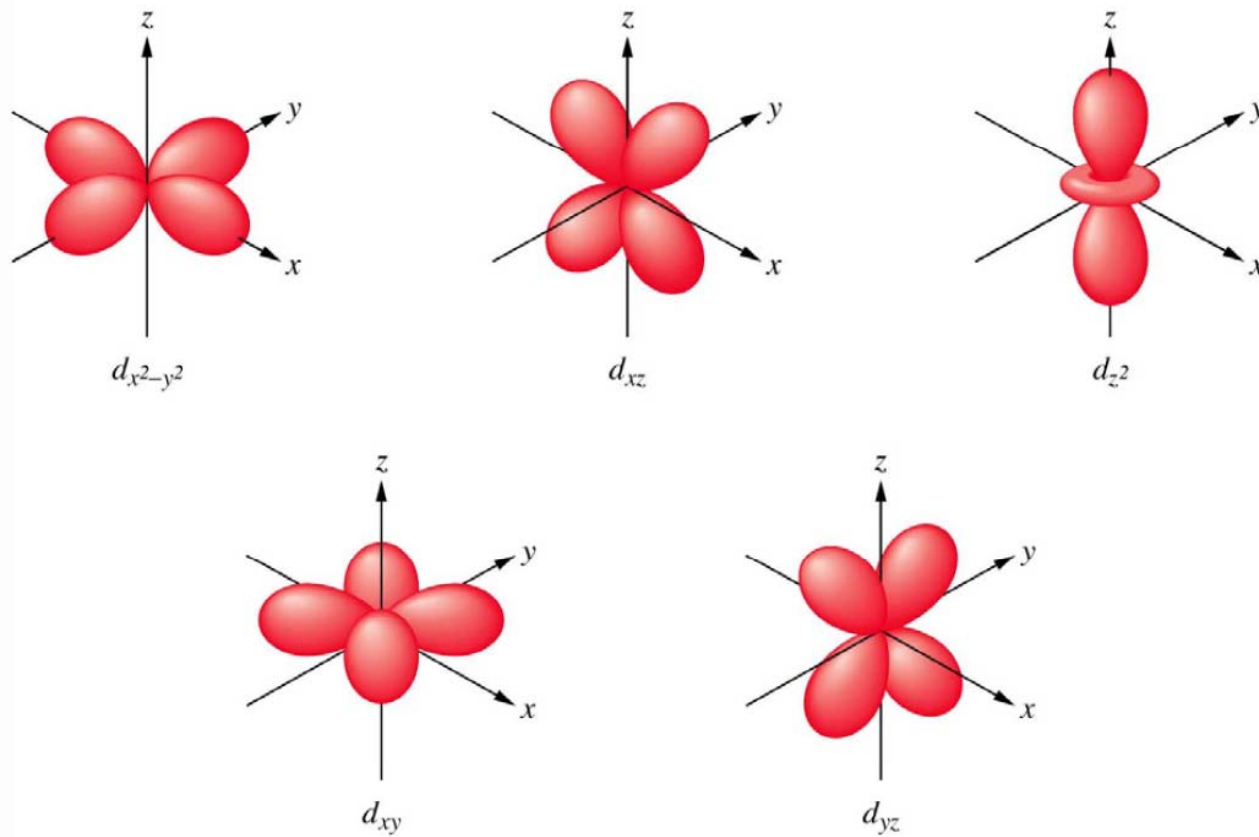
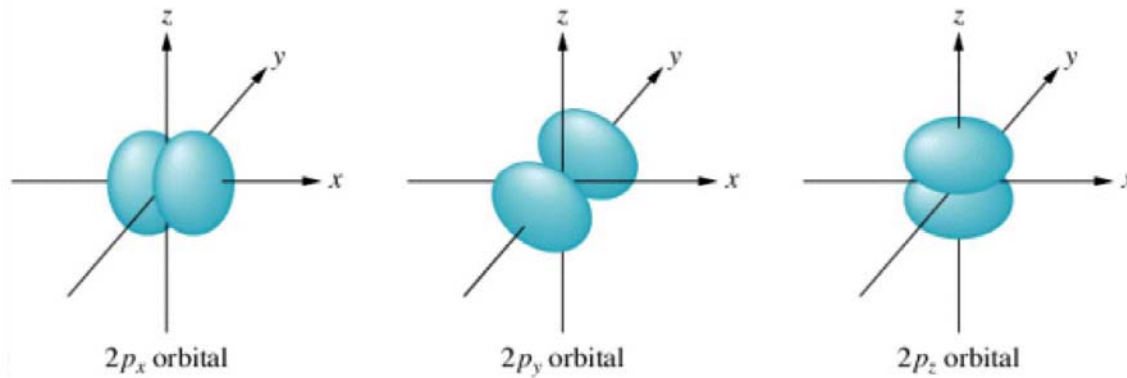
- Plot of $R^2(r)$ vs. r in units of Bohr radius (a) for 2p and 3d orbitals.
- $R(r)$ is defined as the radial function of ψ , dependent on r and independent of θ and ϕ .



- A plot of radial electron density functions for the Na atom.
- Note the difference in penetration effect for the 3s, 3p and 3d orbitals.
- Included for comparison is the maxima for the H atom 3p and 3s orbitals.

| | $s (l=0)$ | $p (l=1)$ | | | $d (l=2)$ | | | | | $f (l=3)$ | | | | | | |
|-------|-----------|-----------|-----------|-------|-----------|-----------|----------|-----------|---------------|-----------|------------|------------|-----------|------------------|-------------------|-------------------|
| | $m=0$ | $m=0$ | $m=\pm 1$ | | $m=0$ | $m=\pm 1$ | | $m=\pm 2$ | | $m=0$ | $m=\pm 1$ | | $m=\pm 2$ | | $m=\pm 3$ | |
| | s | p_z | p_x | p_y | d_z^2 | d_{xz} | d_{yz} | d_{xy} | $d_{x^2-y^2}$ | f_z^3 | f_{xz}^2 | f_{yz}^2 | f_{xyz} | $f_{z(x^2-y^2)}$ | $f_{x(x^2-3y^2)}$ | $f_{y(3x^2-y^2)}$ |
| $n=1$ | | | | | | | | | | | | | | | | |
| $n=2$ | | | | | | | | | | | | | | | | |
| $n=3$ | | | | | | | | | | | | | | | | |
| $n=4$ | | | | | | | | | | | | | | | | |
| $n=5$ | | | | | | | | | | ... | ... | ... | ... | ... | ... | ... |
| $n=6$ | | | | | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $n=7$ | | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

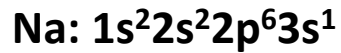
http://en.wikipedia.org/wiki/Atomic_orbital



ψ angular component of the 2p and 3d atomic orbitals for the H atom

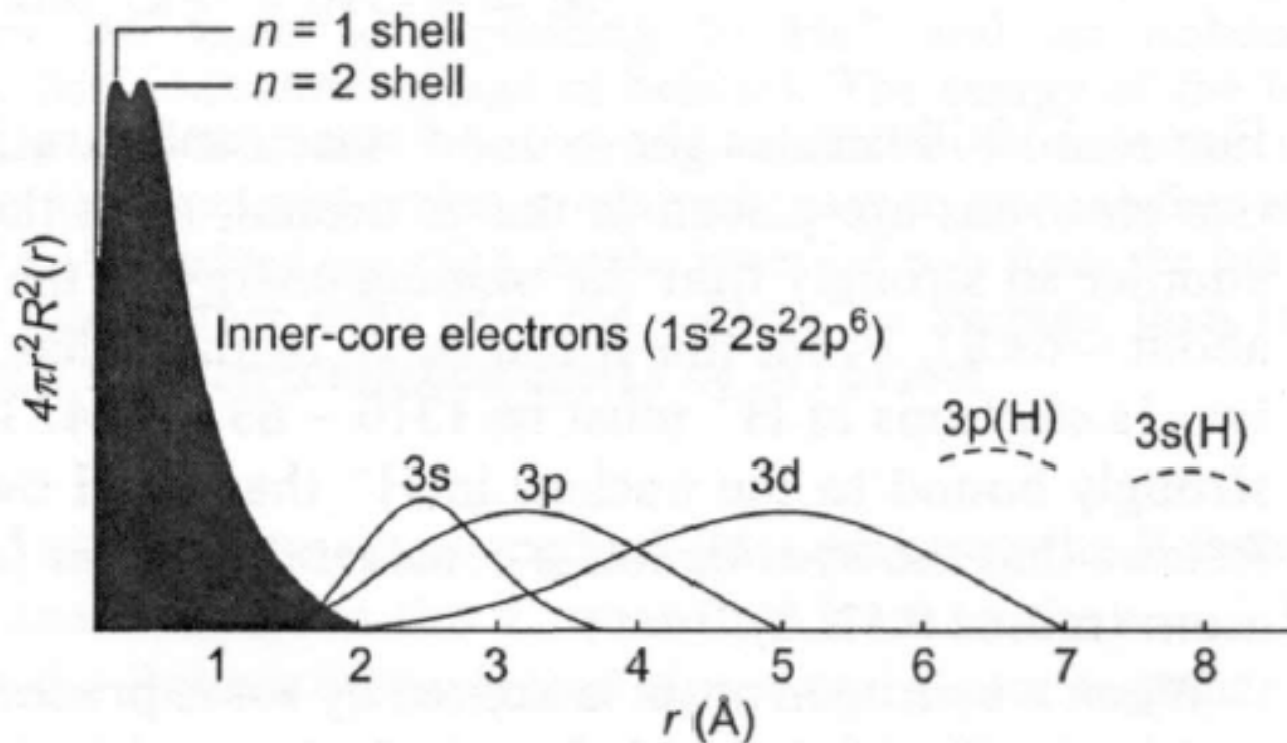
Shielding and penetration effect: *effective nuclear charge*

- Consider



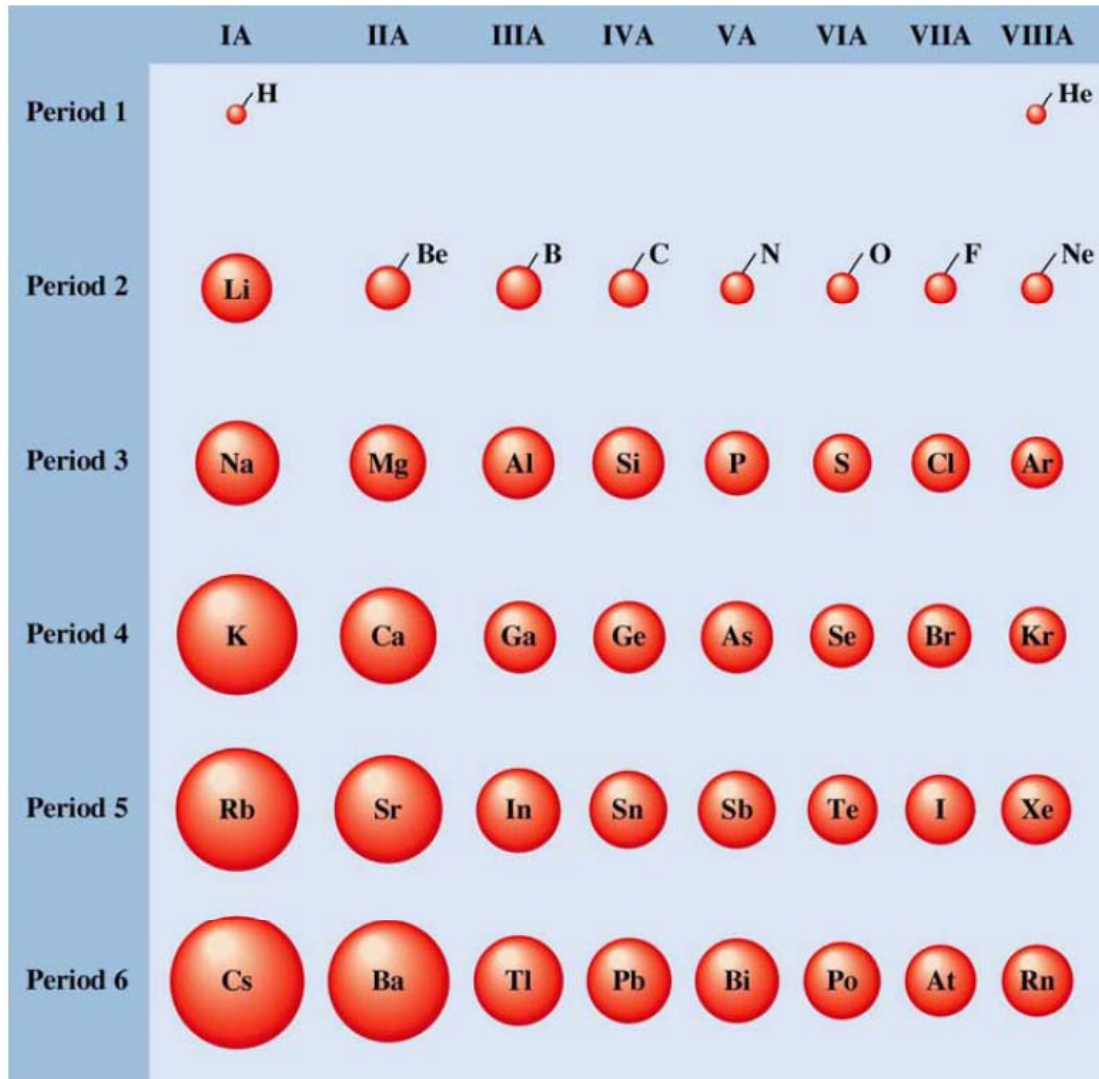
- **Inner shell electrons experience greater positive charge (greater attraction) and are held closer to the nucleus**
- In absence of this ***penetration effect*** the outermost $3s^1$ electron would experience an attraction from the +11 nuclear charge moderated by the ten inner-shell electrons in the $n = 1$ and $n = 2$ shells.
- The ten $1s^2 2s^2 2p^6$ electrons serve to repel the outermost $3s^1$ electron shielding it from the +11 charge such that it experiences an ***effective nuclear charge*** of ca. +1

(Slater's rules)



A plot of radial electron density functions for the Na atom.

- The smallest orbitals are the most strongly bound to the nucleus
- Hence atomic radii decrease moving across the periodic table within the same period



An illustration of the periodic trend in main group atomic radii

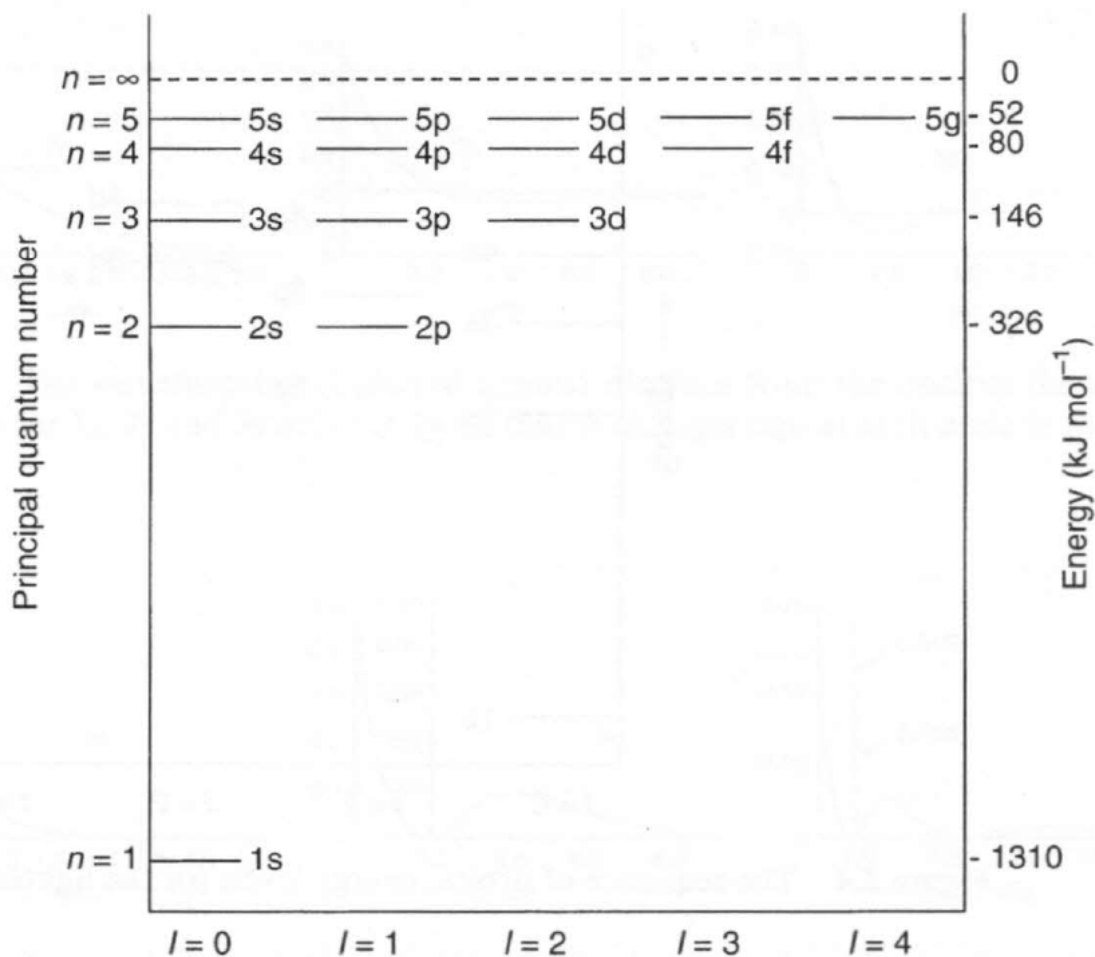
The Hydrogen Atom

- The energy of a bound electron relative to a free electron is given by the expression:

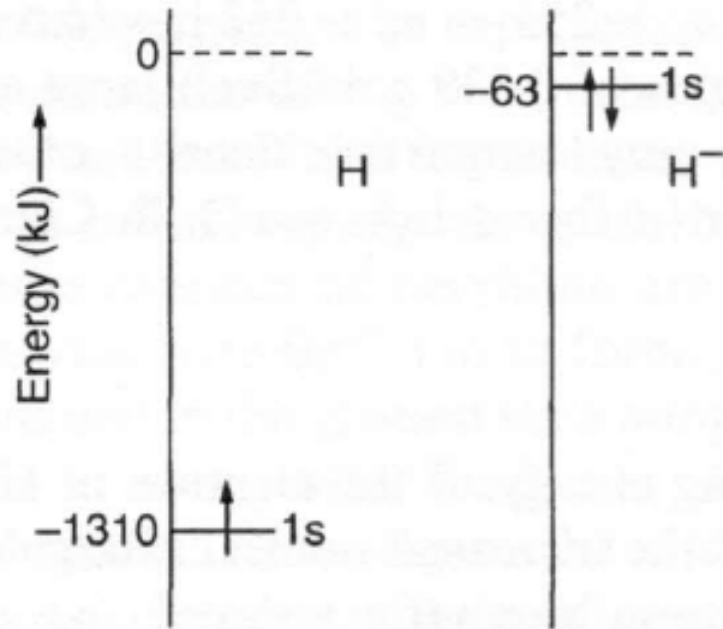
$$E = -\frac{2\pi^2me^2Z^2}{h^2} \times \frac{1}{n^2}$$

- For the H atom

$$E = -1310 \times \frac{1}{n^2} \text{ kJ mol}^{-1}$$



- Orbital energies for a one-electron systems are thus defined only by the principal quantum number n .**
- As n increases the orbitals become larger and the electrons are further from the nucleus resulting in a lower electron binding energy (Coulomb's law).



Ground state electronic structures of the H atom and the hydride ion H⁻

- When 2e are placed in the H atom, as in H⁻, they repel each other so strongly that the binding energy of the electrons falls from -1310 kJ to -63 kJ.
- Thus the repulsion energy of the 2e amounts to $1310 - 63 = 1247$ kJ.
- This repulsion effect increases the size of the atom from 0.53 Å for H to 1.5 Å for H⁻.

Summary

Orbitals in One-electron Atoms (H, He⁺, Li²⁺, ...)

1. All orbitals with the same value of the principal quantum number n have the same energy;

e.g., $4s = 4p = 4d = 4f$. (This is not true for multielectron atoms.)

2. The number of equivalent (degenerate) orbitals in each subshell is equal to $2l + 1$.

3. For orbitals with the same l value, size and energy increase with n ;

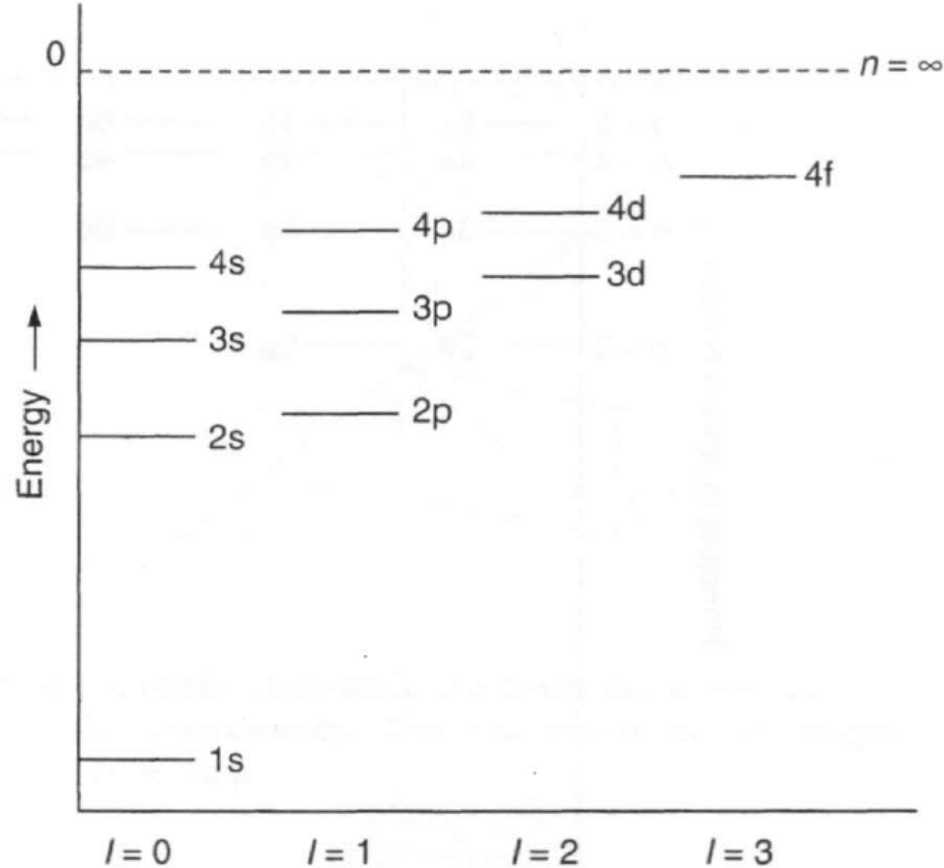
e.g., $1s < 2s < 3s$.

4. For orbitals of the same l value, the number of nodes increases with n .

(i.e., l only defines degeneracy for one-electron systems)

Multi-electron atoms

- *The energy of an electron in an atomic orbital of a multi-electronic system is defined by both the principal quantum number n and the secondary quantum number l .*
- Sequence of orbital energy levels for the lighter elements other than the H atom:



Helium Atom

- Binding energy four times that found for H atom due to increased nuclear charge

(Z = 2; E = 5240 kJmol⁻¹)

$$E = -\frac{2\pi^2 me^4 Z^2}{h^2} \times \frac{1}{n^2}$$

- He is a much smaller atom than H due to the increased nuclear charge.
- First ionization energy = 2373 kJmol⁻¹
 - repulsion energy = (5240 – 2373) kJmol⁻¹ = 2867 kJmol⁻¹
 - reduced orbital size increases repulsion energy relative to Hydride ion.

Aufbau (building-up) principle

- The hypothetical ground state electronic configuration of He: $1s^1 2s^1$ has a calculated total binding energy of 6550 kJmol^{-1} .
- This compares with 7613 kJmol^{-1} for the He: $1s^2$ configuration.
- Thus it is more favorable to pair electrons in the 1s orbital than to individually occupy 1s and 2s orbital
- This is a perfect illustration of what is known as the '**aufbau principle**'.

The orbitals of lower energy are filled in first with the electrons and only then the orbitals of high energy are filled.

The orbitals of lower energy are filled in first with the electrons and only then the orbitals of high energy are filled.

- Each added electron is subject to the electric field created by the positive charge of atomic nucleus *and* the negative charge of other electrons that are bound to the nucleus.
- Although in hydrogen there is no energy difference between orbitals with the same principal quantum number n , this is not true for the outer electrons of other atoms.
- In the classical model orbitals with the highest angular momentum are further from the nucleus.
- In reality, orbitals with a low angular momentum (l) have a greater penetration effect, are closer to the nucleus and feel on average a stronger nuclear charge.
- This explains why 4s orbitals are filled before even 3d orbitals.

- The *aufbau principle* is governed by **Madelung's rule**:

When considering consecutive neutral atoms the electron shells fill up on the order of the quantum number sum ' $n + l$ '

For electrons in states of equal ' $n + l$ ' the order of filling goes with increasing n .

- The rule is based on the total number of nodes in the atomic orbital ' $n + l$ ' which is related to the energy.
- This rule is obeyed remarkably well over the whole periodic table.

$$4s \text{ '}n + l\text{'} = 4 \qquad \text{vs.} \qquad 3d \text{ '}n + l\text{'} = 5$$

- 4s orbitals are filled before 3d orbitals.

Pauli exclusion principle

No two electrons can have the same four quantum numbers, that is, if n , l , and m_l are the same, m_s must be different such that the electrons have opposite spins.

- The Pauli exclusion principle is part of one of our most basic observations of nature.
- In a multi-electron atom, one could imagine a dense electron cloud where collisions take place all of the time, resulting in redirection and perhaps loss of energy for the electrons.
- The Pauli principle effectively blocks the loss of energy because only one nuclear particle can occupy a given energy state.
- In this dense collection of matter, all the low energy states will fill up. This means that the particles cannot take part in interactions which would lower their energy, because there are no lower energy states they can go to.

Hund's rules

1. **Maximum multiplicity:** For a given electron configuration, the term with maximum multiplicity ($2S + 1$) has the lowest energy.
 - A greater total spin state ($2s + 1$) forces the unpaired electrons to reside in different spatial orbitals manifested in a lower energy state,
 - The different occupied spatial orbitals decrease the screening of electron-nuclear attractions.
 - As a result of Hund's rule, constraints are placed on the way atomic orbitals are filled using the *aufbau principle*. Before any two electrons occupy an orbital in a subshell, other orbitals in the same subshell must first each contain one electron. Also, the electrons filling a subshell will have parallel spin before the shell starts filling up with the opposite spin electrons (after the first orbital gains a second electron).
 - As a result, when filling up atomic orbitals, the **maximum number of unpaired electrons (and hence maximum total spin state)** is assured.

Hund's rules

2. Total orbital angular momentum: For a given multiplicity, the term with the largest *orbital angular momentum* (L) has the lowest energy.

- This rule deals again with reducing the repulsion between electrons. If all electrons are orbiting in the same direction (higher orbital angular momentum) they meet less often than when orbiting in opposite directions.
- When orbiting the nucleus in opposite directions the repulsive force increases, which separates electrons. This adds potential energy to them, so their energy level is higher.

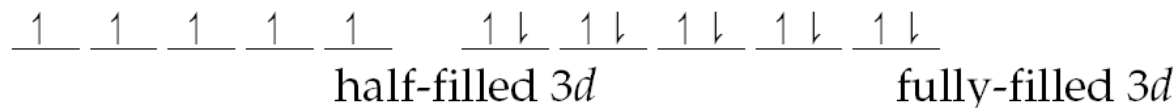
3. Total angular momentum: For atoms with less than half-filled shells, the level with the lowest value of *total angular momentum* (J) lies lowest in energy.

$$J = s + l$$

- This rule considers the energy shifts due to spin-orbit (S-L) coupling.

Exchange Energy

- Configurations in which a subshell is half- or fully-filled have extra stability.

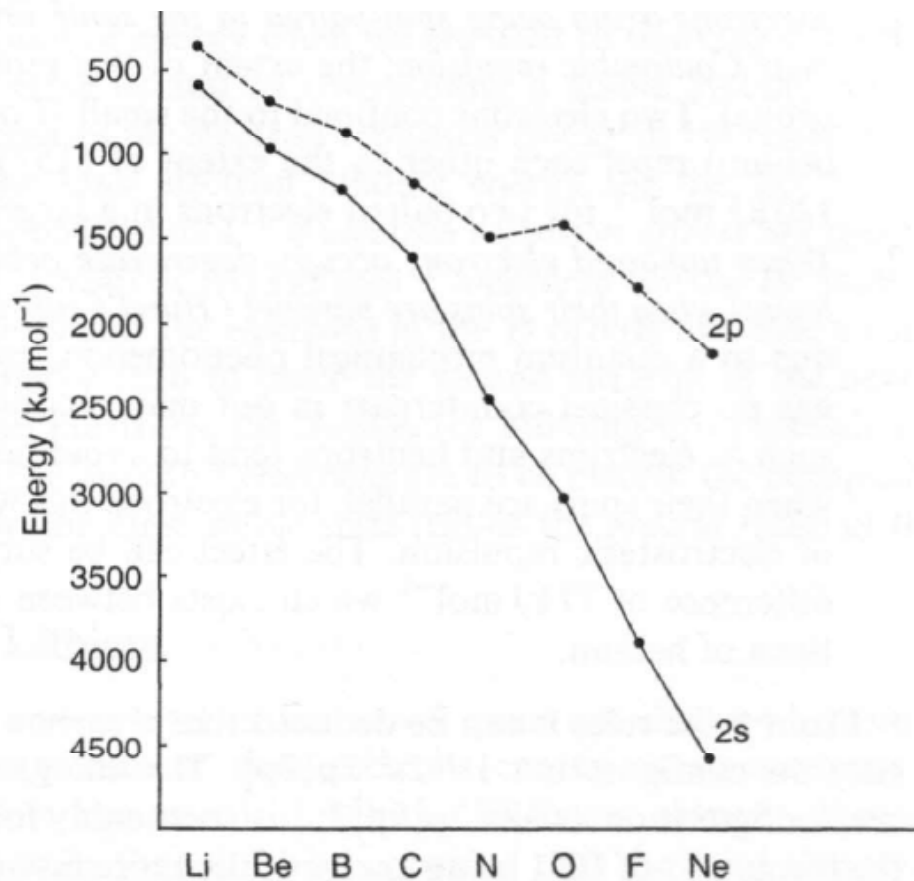


- These configurations result in a symmetrical distribution of electronic charge, which minimizes repulsions.
- The slight energy advantage of these configurations is called **exchange energy**.
- Exchange energy becomes more significant with greater orbital multiplicity (i.e., more orbitals per subshell)

$$s < p < d < f$$

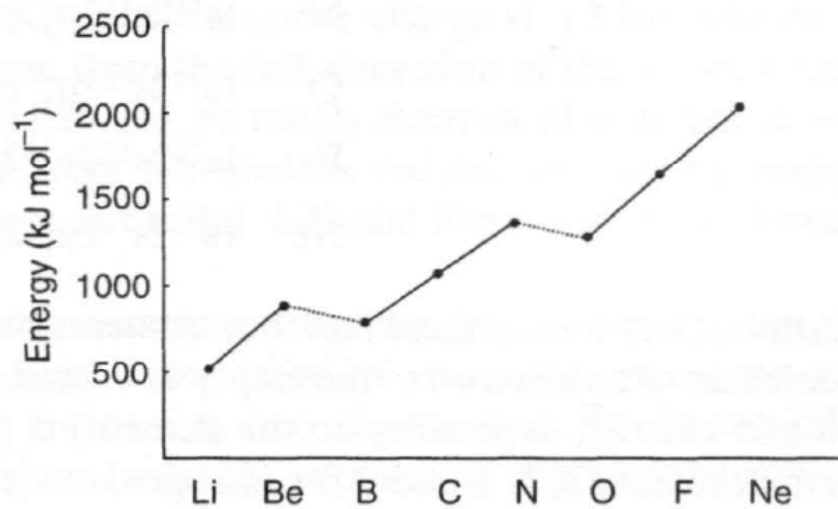
- Exchange energy sometimes results in ground-state configurations that deviate from the aufbau predictions.

e.g., ${}_{24}\text{Cr}$ is $3d^5 4s^1$ (not $3d^4 4s^2$) and ${}_{29}\text{Cu}$ is $3d^{10} 4s^1$ (not $3d^9 4s^2$)

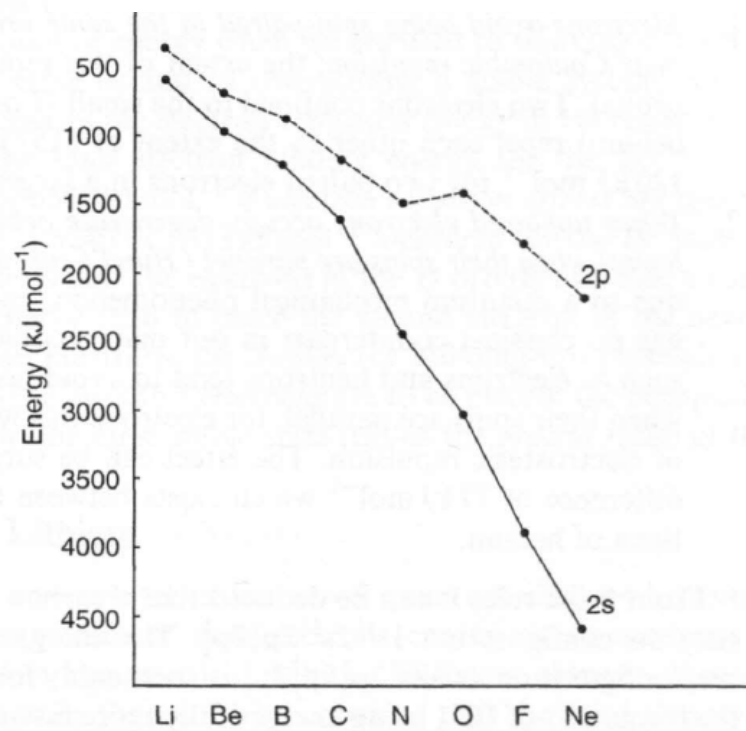


A plot of energy trends of the 2s and 2p orbitals across the first period

- The energy difference between the 2s and 2p orbitals for a given atom gives the magnitude of the 2s ***penetration effect***.
- The 2s orbital becomes more tightly bound to the nucleus as we move from Li to Ne, decreasing in size and shielding the 2p orbitals from the nuclear charge.



The variation in first ionization energies across the first period



A plot of energy trends of the 2s and 2p orbitals across the first period