Atomic Structure

De Broglie Waves

Not only the light but every materialistic particle such as electron, proton or even the heavier object exhibits wave-particle dual nature.

De-Broglie proposed that a moving particle, whatever its nature, has waves associated with it. These waves are called “**matter waves**”.

Energy of a photon is

$$E = h\nu$$

For a particle, say photon of mass, m

$$E = mc^2$$

$$mc^2 = h\nu$$

$$mc^2 = \frac{hc}{\lambda}$$

$$\lambda = \frac{h}{mc}$$

Suppose a particle of mass, m is moving with velocity, v then the wavelength associated with it can be given by

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p}$$

(i) If $v = 0 \Rightarrow \lambda = \infty$ means that waves are associated with **moving** material particles only.

(ii) De-Broglie wave does not depend on whether the moving particle is charged or uncharged. It means matter waves are not electromagnetic in nature.

Heisenberg Uncertainty Principle

It states that only one of the "position" or "momentum" can be measured accurately at a single moment within the instrumental limit.

or

It is impossible to measure both the position and momentum simultaneously with unlimited accuracy.

$\Delta x \rightarrow$ uncertainty in position

$\Delta p_x \rightarrow$ uncertainty in momentum

then $$\Delta x \Delta p_x \geq \frac{\hbar}{2} \qquad \therefore \hbar = \frac{h}{2\pi}$$

The product of Δx & Δp_x of an object is greater than or equal to $\frac{\hbar}{2}$

If Δx is measured accurately i.e. $\Delta x \to 0 \quad \Rightarrow \Delta p_x \to \infty$

The principle applies to all canonically conjugate pairs of quantities in which measurement of one quantity affects the capacity to measure the other.

Like, energy E and time t.

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

and angular momentum L and angular position θ

$$\Delta L \Delta \theta \geq \frac{\hbar}{2}$$

Quantization of Energy

Max Planck (1858-1947)
Solved the "ultraviolet catastrophe"

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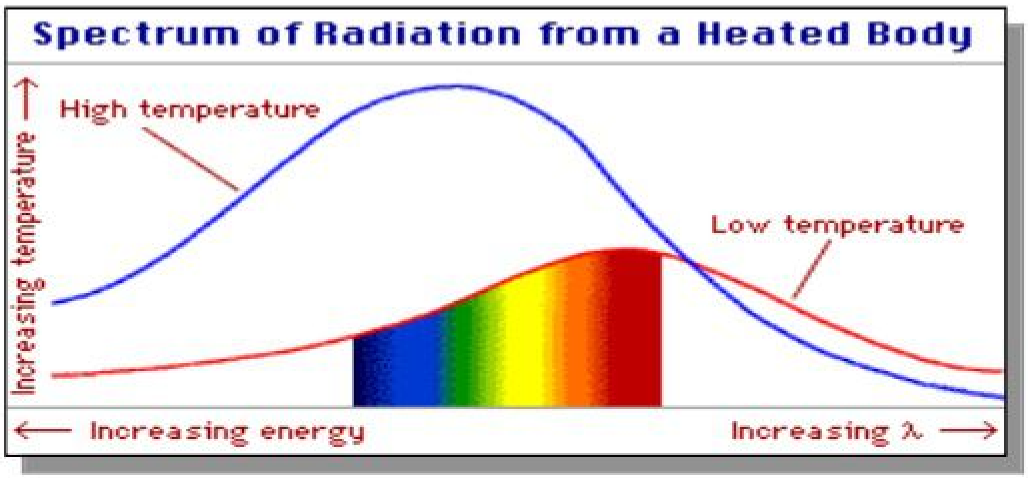
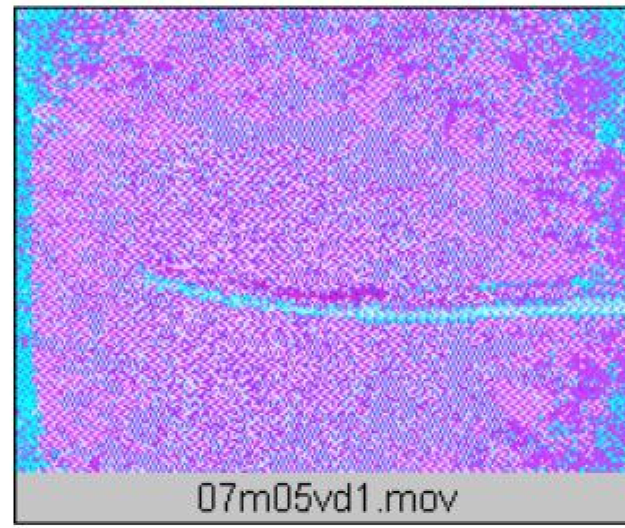




- **Planck's hypothesis:** ***An object can only gain or lose energy by absorbing or emitting radiant energy in QUANTA.***

Quantization of Energy (2)

Energy of radiation is proportional to frequency.

$$E = h \cdot \nu$$

where h = Planck's constant = 6.6262×10^{-34} J•s

Light with large λ (small ν) has a small E.

Light with a short λ (large ν) has a large E.

Pauli's exclusion principle

- In 1925, Wolfgang Pauli discover the principle that governs the arrangements of electrons in many electron atoms
- The Pauli exclusion principle states that ***no two electrons in an atom can have the same set of four quantum numbers n, l, m, s.***
- For a given orbital, thus e value of n, l,m are fixed
- Thus if we want to put more than one e in an orbital and satisfy the Pauli exclusion principle, our only option is to assign different values of **s** to those two e
- We know that their can be only two s value possible for e
- We conclude that, ***an orbital can hold a max. of two e, and they must have opposite spin.***

Example of Pauli's Exclusion Principal:

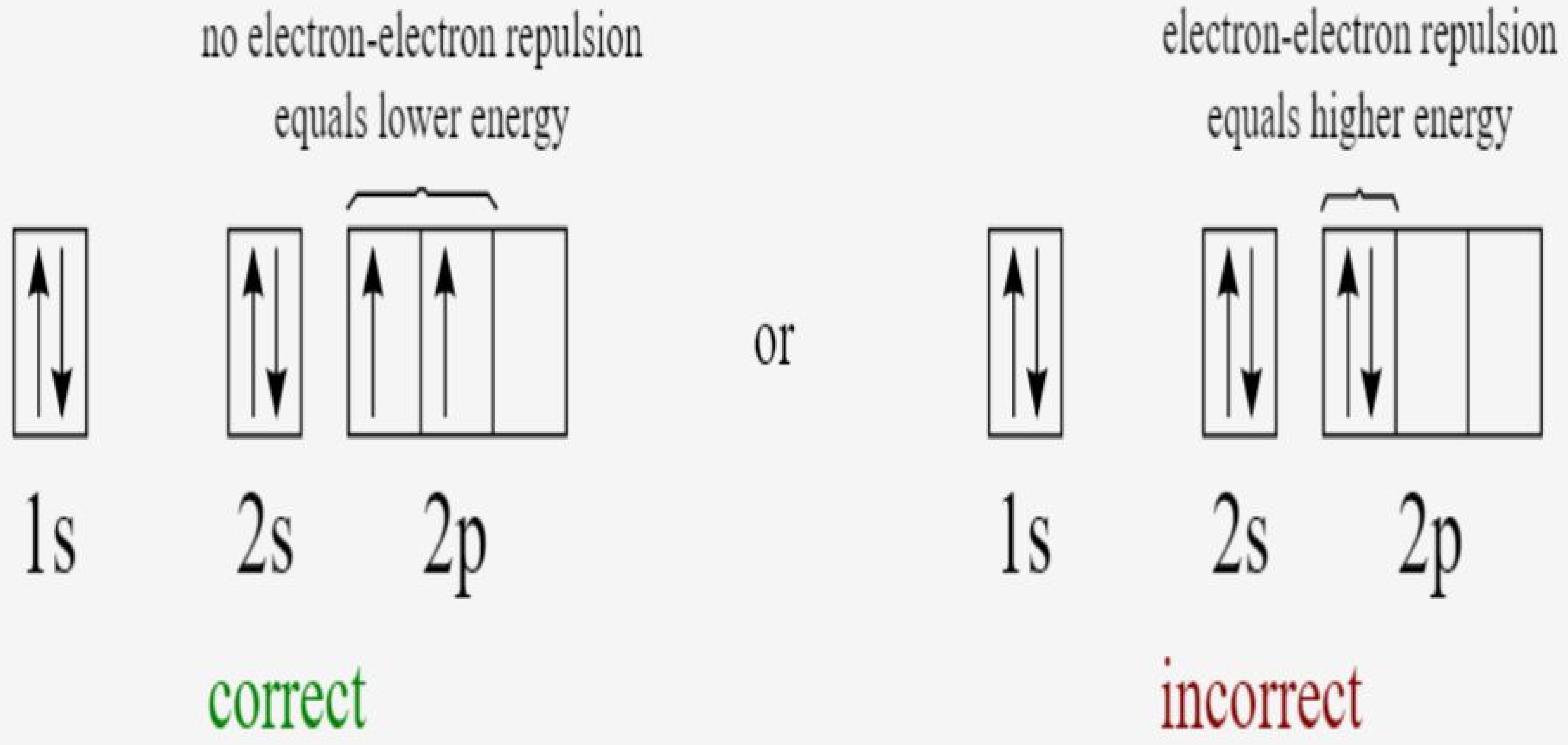
- Consider the second shell (n=2)
- There are 4 orbitals, one s orbital (l=0) and three p orbitals (l=1)

n	l	m	s	
2	0	0	+1/2	2 e are in 2s orbital
2	0	0	-1/2	
2	1	+1	+1/2	2 e are in $2p_x$ orbital
2	1	+1	-1/2	
2	1	-1	+1/2	2 e are in $2p_y$ orbital
2	1	-1	-1/2	
2	1	0	+1/2	2 e are in $2p_z$ orbital
2	1	0	-1/2	

HUND'S RULE

- States that "**when electrons occupy orbitals of equal energy, one electron enters each orbital until all the orbitals contain one electron with parallel spins. Second electrons then add to each orbital pairing the spins of the first electron.**"

HUND'S RULE



Example of Hund's rule: Orbital diagram for carbon, showing the correct application of Hund's Rule.

ELECTRONIC CONFIGURATION OF SELECTED ELEMENTS

ELEMENT	TOTAL ELECTRONS	ORBITAL DIAGRAM 1s	2s	2p	ORBITAL NOTATION
H	1	↑			$1s^1$
Li	3	↑↓	↑		$1s^2$, $2s^1$
N	7	↑↓	↑↓	↑ ↑ ↑	$1s^2$, $2s^2$, $2p^3$
O	8	↑↓	↑↓	↑↓ ↑ ↑	$1s^2$, $2s^2$, $2p^4$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓	$1s^2$, $2s^2$, $2p^6$

Schrodinger Wave equation

In 1926 Erwin Schrodinger gave a mathematical concept of

"wave - particle dualism"

He thought that elevons have standing wave just like the waves of stretched string.

This was a new idea at that time and gave the development of wave mechanics. The wave like behaviour of a microscopic particle lies beyound the reach of our senses. But credit goes to Schrodinger that he developed an equation called Schrodinger wave equation.

Derivation of Schrodinger wave equation

Standing wave have an equation

$$\psi = A \sin\left(\frac{2\pi x}{\lambda}\right)$$

ψ is the wave function which represents the amplitude of the wave.

A = constant which give maximum value to ψ.

By taking differentitation

$$\frac{d\psi}{dx} = A \sin\left(\frac{2\pi x}{\lambda}\right)$$

Rules

$$\frac{d}{dx} \sin = \cos$$

$$\frac{d}{dx} x = 1$$

$$\frac{d}{dx} (c) = 0$$

$$\frac{d\psi}{dx} = A \sin\left(\frac{2\pi x}{\lambda}\right)$$

$$\frac{d\psi}{dx} = A \cos\left(\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$\frac{d\psi}{dx} = \frac{A 2\pi}{\lambda} \cos\left(\frac{2\pi x}{\lambda}\right)$$

Differentiate this equation again

$$\frac{d^2\psi}{dx^2} = \frac{A 2\pi}{\lambda} \cos\left(\frac{2\pi x}{\lambda}\right)$$

$$\frac{d^2\psi}{dx^2} = \frac{A 2\pi}{\lambda} \left(-\sin\left(\frac{2\pi x}{\lambda}\right)\right)\left(\frac{2\pi}{\lambda}\right)$$

$$\frac{d}{dx} \cos = -\sin$$

$$\frac{d^2\psi}{dx^2} = \frac{A 4\pi^2}{\lambda^2} \left(-\sin \frac{2\pi x}{\lambda}\right)$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\left(A\sin\frac{2\pi x}{\lambda}\right)$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi$$

as we know that

$$\psi = A\sin\frac{2\pi x}{\lambda}$$

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi^2}{\lambda^2}\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \qquad \text{—— i}$$

From de-Broglie wave equation

$$\lambda = \frac{h}{mv}, \quad \lambda^2 = \frac{h^2}{m^2v^2} \qquad \text{—— ii}$$

$$K.E = \frac{1}{2}mv^2 \qquad K.E = E$$

$$E = \frac{1}{2}mv^2$$

$$v^2 = \frac{2\varepsilon}{m} \quad \text{—— iii}$$

Putting the value of eq-iii in eq-ii

$$\lambda^2 = h^2 / m^2 \frac{2\varepsilon}{m}$$

$$\lambda^2 = h^2 / 2\varepsilon m \quad \text{—— iv}$$

putting the value of eq-iv in eq-i

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2/2\varepsilon m}\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 \varepsilon m}{h^2}\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}\varepsilon\psi = 0 \quad \text{—— v}$$

$$E = K.E + P.E$$

$$E = \varepsilon + P$$

$$\varepsilon = E - P \quad \text{—— vi}$$

putting the value of eq-vi in eq-v

$$\frac{d\psi^2}{dx^2} + \frac{8\pi^2 m}{h^2}(E-P)\psi = 0$$

This is a schrodinger wave equation when particle move in one dimension.

If particle move in three dimension then equation is

$$\frac{d^2\psi}{dx^2} + \frac{\partial^2\psi}{dy^2} + \frac{\partial^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E-P)\psi = 0$$

above equation shows that amplitude 'ψ' changes with respect to x, y, z axis.

⇒ Above equation also known as celebrated wave equation.