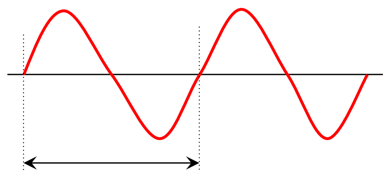
Chapter 7

Energy

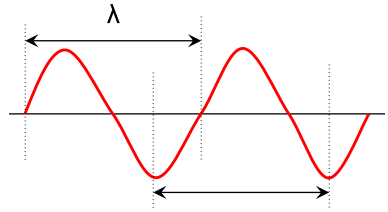
What is the frequency (in s^{-1}) of the electromagnetic radiation from radio waves (λ = 325 cm)?

Wave Nature of Light/Electromagnetic Radiation

Frequency (ν) – the number of cycles the wave undergoes per second expressed as 1/second or s^{-1} or Hertz, Hz



Wavelength (λ) – the distance between any point on a wave to the corresponding point on the next wave expressed in meters

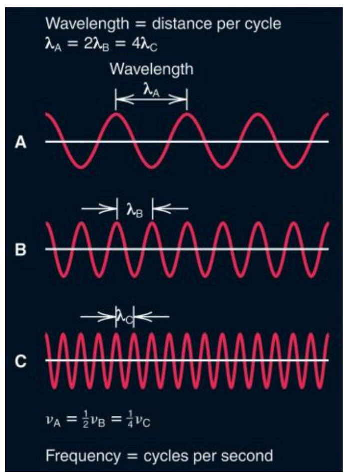


Relationship between λ and ν

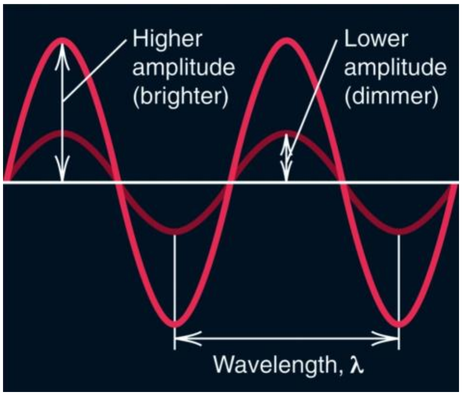
$$\nu \times \lambda = c$$

$$\frac{\cancel{\text{cycles}}}{\text{s}} \times \frac{\text{m}}{\cancel{\text{cycle}}} = \frac{\text{m}}{\text{s}}$$

$c = 3.00 \times 10^8$ m/s in a vacuum for all λ
(actual 2.99792458×10^8 m/s)

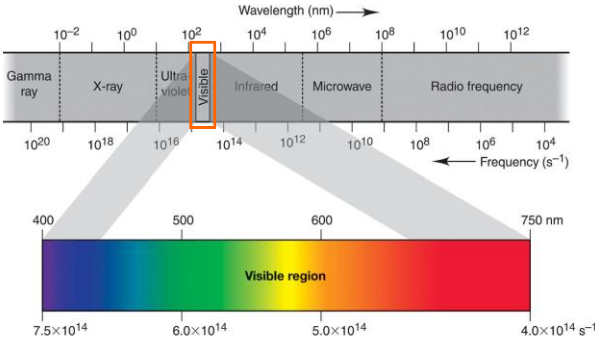


Amplitude – the height of the crest (or the depth of the trough)



The Electromagnetic Spectrum

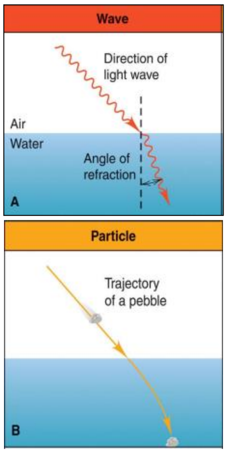
Visible light represents only a small portion of the ***electromagnetic spectrum*** (**Figure 7.3**). *All waves in the spectrum travel at the same speed through a vacuum but differ in frequency and, therefore, wavelength.*

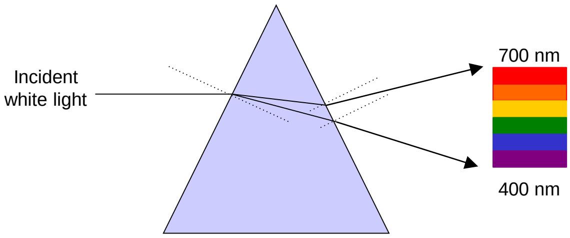


What is the frequency (in s^{-1}) of the electromagnetic radiation from radio waves (λ = 325 cm)?

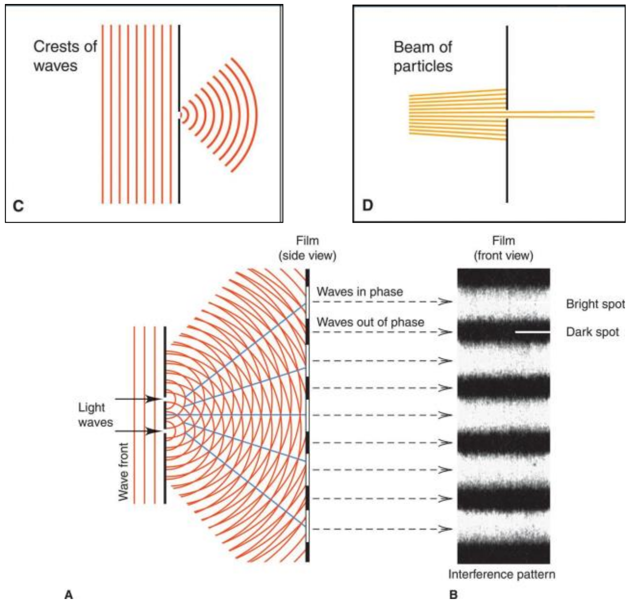
The Classical Distinction between Energy and Matter

Refraction – light of a given wavelength travels at different speeds through different transparent media – vacuum, air, quartz, water, etc. When a wave strikes a boundary (say between air and water) at any angle other than 90°, the change in speed results a change in direction that we observe as the ***angle of refraction*** **(Figure 7.4A)**.





Diffraction – a wave striking the edge of an object will bend around it.



https://www.youtube.com/watch?v=Iuv6hY6zsd0&t=391s

A cook uses a microwave oven to heat a meal. The wavelength of the radiation is 1.20 cm. What is the energy of one photon of this microwave radiation?

The Particle Nature of Light

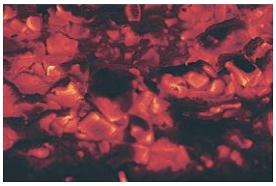
At the turn of the 20th century, three phenomena involving matter and light confounded physicists:

- ***Blackbody radiation***
- ***The Photoelectric Effect***
- ***Atomic Spectra***

Blackbody Radiation and the Quantum Theory of Energy

A ***black body*** (term coined in 1860) - an object that absorbs all electromagnetic radiation that falls on it.
Predicted that a black body will produce a continuous spectrum of visible light if it is heated to very high temperatures (>1000K).

Observation: When a solid object is heated above 700K, it begins to emit visible light. HOWEVER, the spectrum of light has a maximum wavelength that shifts to smaller wavelengths as the temperature of the object increases!



smoldering coal (1000K)

electric heating element (1500K)

light bulb filament (>3000K)

All attempts to explain this observation using classical physics failed.

In 1900, the German physicist Max Planck (1858 – 1947) proposed that a hot, glowing object could emit (or absorb) only certain quantities of energy – in other words, he proposed that **energy must be quantized**.

Max Planck received Nobel Prize in Physics in 1918.

$E = nh\nu$ $\quad$ $h = 6.626 \times 10^{-34}$ Js (4 significant digits)

E = the energy of the radiation
ν = frequency
n = a positive integer (1, 2, 3 and so on) called a ***quantum number***
h = a proportionality constant known as ***Planck's constant***

By Planck's equation – matter changes its energy only by absorbing (or emitting) small defined quantities, or ***quanta***, of energy = hν.

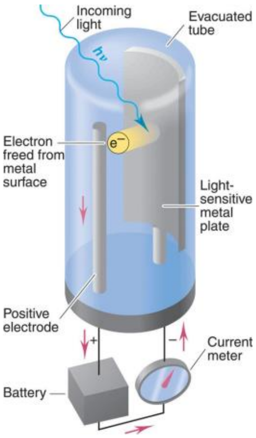
$E_{\text{absorbed (or emitted) radiation}} = E_{\text{final}} - E_{\text{initial}} = \Delta E_{\text{atom}} = \Delta nh\nu$

$\Delta n = 1$ $\quad$ $\Delta E_{\text{atom}} = h\nu$

Photoelectric effect – the flow of electric current when monochromatic light falls on a metal plate

1. ***Presence of a threshold frequency*** – light shining on the metal plate must have a minimum frequency or no current flows **AND** different metals have different minimum frequencies.

2. ***Absence of time lag*** – current flows the moment the minimum frequency light shines on the metal plate regardless of light intensity. (Wave theory associated light energy with wave amplitude, so dim light should take longer to transfer enough energy to free electrons.)



Einstein's theory to explain photoelectric effect

$\Delta E_{atom} = E_{photon} = h\nu$

Albert Einstein received Nobel Prize in Physics in 1921.

1. ***Why is there a threshold frequency?*** Light consists of an enormous number of photons. The brightness is related to the number of photons not to the energy of each photon. A photon must have the minimum energy(frequency) to free electrons.

2. ***Why no time lag?*** Electrons are freed the moment a photon possessing enough energy is absorbed; electrons do not 'save up' energy from several photons.

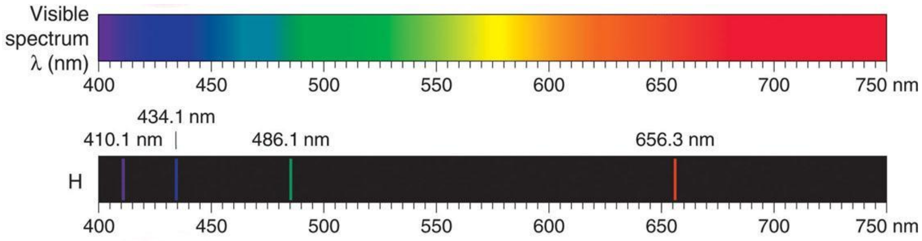
A cook uses a microwave oven to heat a meal. The wavelength of the radiation is 1.20 cm. What is the energy of one photon of this microwave radiation? (Planck's constant = 6.626 x 10^{-34} Js)

$$E_{photon} = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{Js}) \times (3.00 \times 10^{8}\ \text{m/s})}{1.20\ \text{cm} \times (10^{-2}\ \text{m/1 cm})} = 1.6\underline{5}65 \times 10^{-23}\text{J}$$

$$= 1.66 \times 10^{-23}\ \text{J}$$

Atomic Spectra

The wavelengths of these lines are characteristic of the element producing them.



The Bohr Model of the Hydrogen Atom

Niels Bohr received the Nobel Prize in Physics in 1922.

Postulates of the Model

1. *The hydrogen atom has only certain energy levels aka* ***stationary states.***

2. *The atom does not radiate energy while in one of its stationary states.*

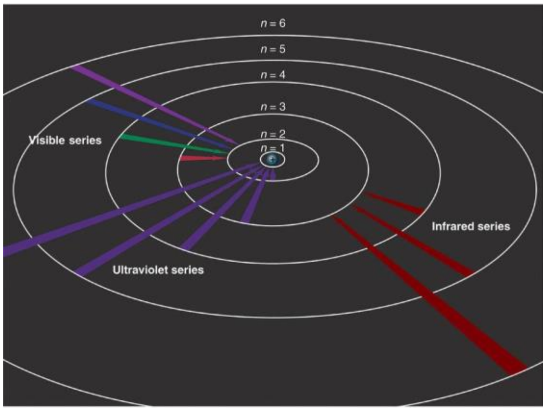
3. *The atom changes to another stationary state only by absorbing or emitting a photon whose energy equals the difference in energy between the two states:*

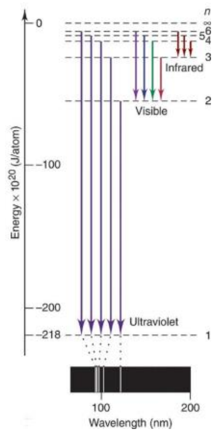
$\Delta E_{atom} = E_{state\ A} - E_{state\ B} = E_{photon} = h\nu$

where energy of state A is higher than energy of state B.

In Bohr's model, the quantum number *n* (1, 2, 3 and so on) is associated with the radius of an electron orbit and is directly related to the electron's energy **(Figure 7.10).** . .

Example: Lower *n* ≡ smaller orbit radius ≡ lower (more negative) energy
n = 1, lowest energy level called the ***ground state.***
n = 2 or higher called ***excited states***.





<u>Limitations of the Bohr Model</u>

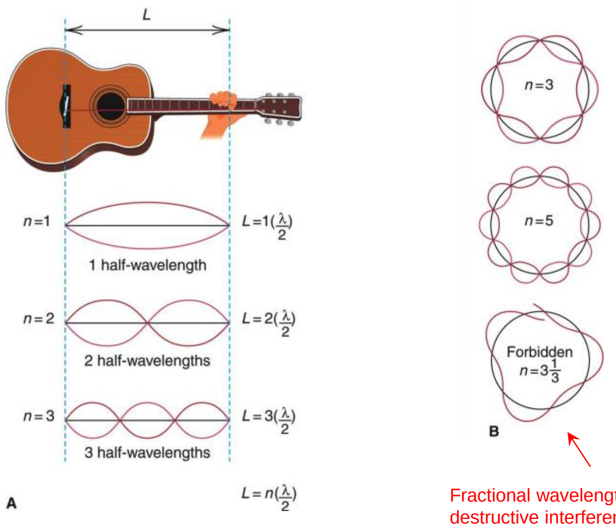
Despite its great success in predicting the spectral lines of H, the Bohr model failed to predict the spectrum of any other atom.

Specifically, it works only on one-electron systems but fails when two or more electrons are involved. <u>It cannot account for additional nucleus-electron and electron – electron interactions</u>.

Bohr's model of the hydrogen atom *assumed* that an atom only had certain allowable energies in order the *fit/explain* the hydrogen atom line spectra. But Bohr's assumptions had no basis in physical theory.

Find the de Broglie wavelength of an electron with a speed of 1.00 x 10^6 m/s.

The Wave-Particle Duality of Matter and Energy



Louis de Broglie was awarded Nobel Prize in Physics in 1929.

Fractional wavelengths would result in destructive interference of wave crests and troughs causing the wave to rapidly die out.

Combining Einstein's famous mass – energy equation, $E = mc^2$ and the photon energy equation, $E = h\nu = hc/\lambda$, de Broglie derived an equation for the wavelength of any particle of mass, m, moving at speed, u . . .

$$\frac{hc}{\lambda} = mc^2 \Rightarrow hc = mc^2\lambda \Rightarrow \frac{h\cancel{c}}{m\cancel{c^2}} = \lambda$$

$\lambda = \frac{h}{mc}$ and substitute u (speed of a particle) for c (speed of light) → $\lambda = \frac{h}{mu}$

This equation states that an object's wavelength is ***inversely*** proportional to its mass! (**Table 7.1**)

Substance	Mass (g)	Speed (m/s)	λ (m)
slow electron	9×10^{-28}	1.0	7×10^{-4}
fast electron	9×10^{-28}	5.9×10^{6}	1×10^{-10}
alpha particle	6.6×10^{-24}	1.5×10^{7}	7×10^{-15}
one-gram mass	1.0	0.01	7×10^{-29}
baseball	142	25.0	2×10^{-34}
Earth	6.0×10^{27}	3.0×10^{4}	4×10^{-63}

Find the de Broglie wavelength of an electron with a speed of 1.00×10^6 m/s (electron mass = 9.11×10^{-31}kg; $h = 6.626 \times 10^{-34}$Js).

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

$$= \frac{6.626 \times 10^{-34}\ \text{Js}}{(9.11 \times 10^{-31}\ \text{kg}) \times (1.00 \times 10^6\ \text{m/s})}$$

1 J = 1 Nm $= \left[1\ \text{kg}\ \frac{\text{m}}{\text{s}^2}\right]\text{m} = 1\ \text{kg}\ \frac{\text{m}^2}{\text{s}^2}$

1N = 1 kg$\frac{\text{m}}{\text{s}^2}$

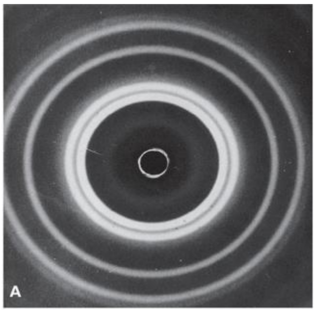
$$= \frac{6.626 \times 10^{-34}\ \cancel{\text{kg}}\ \frac{\text{m}^{\cancel{2}}}{\cancel{\text{s}}}}{(9.11 \times 10^{-31}\ \cancel{\text{kg}}) \times (1.00 \times 10^6\ \cancel{\text{m}}/\cancel{\text{s}})}$$

$= 7.2\underline{7}33 \times 10^{-10}$ m

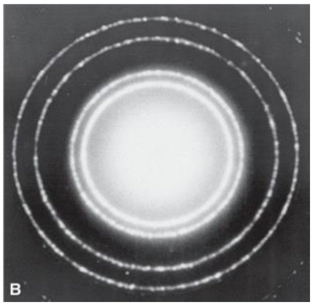
$\equiv 7.27 \times 10^{-10}$ m

If particles behave as waves, electrons should exhibit the wave properties of diffraction and interference. ***What experimental evidence supports the assertion that electrons behave like waves?***

In 1927, Clinton Davisson (1881-1958; Nobel Prize in Physics in 1937) and Lester Germer (1896-1971) aimed a beam of electrons at a nickel crystal and obtained a diffraction pattern! (**Figure 7.13**).



x-ray diffraction of aluminum foil

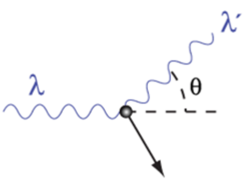


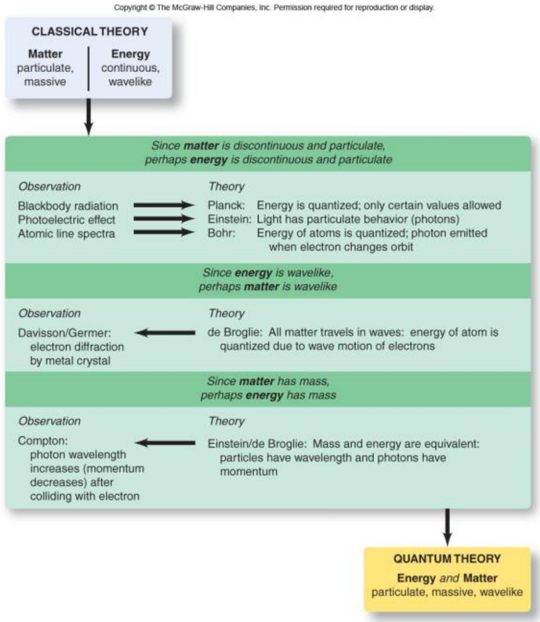
electron diffraction of aluminum foil

The Particle Nature of Photons

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

What experimental evidence supports the assertion that photons behave like particles? Experimental evidence for the particle nature of light was obtained in 1923 when Arthur Compton directed x-ray photons at a sample of graphite and observed that the wavelength of the reflected photons increased! (The x-ray photons transferred part of their momentum to electrons in the graphite.) This observation earned Compton the Nobel Prize in Physics in 1927.





<u>The Heisenberg Uncertainty Principle</u>

What is the exact location of an electron in an atom?

<u>The uncertainty principle states that it is impossible to know the exact position and momentum (speed) of the electron simultaneously.</u>

For a particle of mass *m*,

$$\Delta x \cdot \underbrace{m\Delta u}_{\text{Uncertainty in momentum}} \geq h/4\pi$$

where Δx is the uncertainty in position and Δ*u* is the uncertainty in speed.

Werner Heisenberg awarded Nobel Prize in Physics in 1932 for a research published in 1927 ‘creating the field of quantum mechanics’.

An electron moving near an atomic nucleus has a speed of 6×10^6 m/s +/- 1%. What is the uncertainty in its position (Δx)?

$\Delta x \cdot m\Delta u \geq h/4\pi$

$\Delta u = (6 \times 10^6 \text{ m/s}) \times 0.01 = 6 \times 10^4$ m/s

Mass of electron, $m = 9.11 \times 10^{-31}$ kg

$$\Delta x \geq \frac{h/4\pi}{\Delta u \cdot m}$$

$$\geq \frac{(6.626 \times 10^{-34} \text{ kg m}^2/\text{s})/4\pi}{(6 \times 10^4 \text{ m/s}) \cdot (9.11 \times 10^{-31} \text{ kg})}$$

$$\geq 9.646 \times 10^{-10} \text{ m}$$

$$\geq 1 \times 10^{-9} \text{ m}$$

Average radius of atom is 0.3-3.0 Å – $0.3\text{-}3.0 \times 10^{-10}$ m

The Quantum-Mechanical Model of the Atom

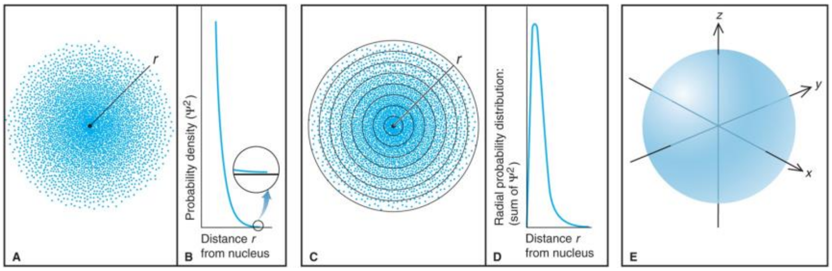
In 1926, Erwin Schrödinger derived an equation that is the basis for the quantum-mechanical description of the hydrogen atom:

$$\underbrace{\left[-\frac{h^2}{8\pi^2 m_e}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) + V(x, y, z)\right]}_{\mathcal{H}} \Psi(x, y, z) = E\,\Psi(x, y, z)$$

- Ψ (Greek letter psi) is called the ***wave function***, a mathematical description of the three – dimensional space where an electron is most likely to be found; also called an ***atomic orbital***.

- $\mathcal{H}$ is a Hamiltonian operator (a set of mathematical operations) that yield the allowed energy value of the electron.

While we cannot know *exactly* where an electron is at any moment, Ψ^2 gives the ***probability density***, a measure of the probability that the electron can be found within a particular volume.



Quantum Numbers of an Atomic Orbital

1. ***Principle quantum number*** (n) is a *positive integer* (1, 2, 3 and so on) that specifies the energy level (i.e., this is related to the orbital size and the electron's relative distance from the nucleus).

2. ***Angular momentum quantum number*** (l) is an *integer from 0 to n - 1* and is related to the *shape* of the orbital.

Example: For n = 2, l has two possible values l = 0 and l = 1.

3. ***Magnetic quantum number*** (m_l) is *an integer from –l through 0 to +l* describes the orientation of the atomic orbital in space. Note: The number of m_l values indicated the number of orbitals.

Example: For l = 2, m_l has five possible values m_l = -2, -1 , 0, +1 and +2.

Table 7.2 The Hierarchy of Quantum Numbers for Atomic Orbitals

Name, Symbol (Property)	Allowed Values	Quantum Numbers
Principal, n (size, energy)	Positive integer (1, 2, 3, . . .)	1 2 3
Angular momentum, l (shape)	Integers from 0 to $n - 1$	0 0 1 0 1 2
Magnetic, m_l (orientation)	Integers from $-l$ to 0 to $+l$	0 0 −1 0 +1 0 −1 0 +1 −2 −1 0 +1 +2

We specify an atomic orbital by naming its three quantum number values.

n	***l***	**Orbital Name**	m_l	**# Orbitals**
1	0	1s	0	1
2	0	2s	0	1
	1	2p	-1, 0, +1	3
3	0	3s	0	1
	1	3p	-1,0,+1	3
	2	3d	-2,-1,0,+1,+2	5
4	0	4s	0	1
	1	4p	-1,0,+1	3
	2	4d	-2,-1,0,+1,+2	5
	3	4f	-3,-2,-1,0,+1,+2,+3	7

Give the name, magnetic quantum numbers and the number of orbitals for each sublevel with the given quantum numbers:

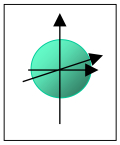
(a) $n = 2$, $l = 0$

(b) $n = 3$, $l = 2$

What is the shape and orientation of the p_x orbital?

Shapes of Atomic Orbitals

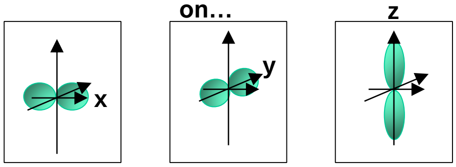
1. The s orbital (l = 0)



The 2s orbital is larger than the 1s orbital, the 3s orbital is larger than the 2s orbital and so on…

Shape: sphere

2. The p orbital (l = 1)

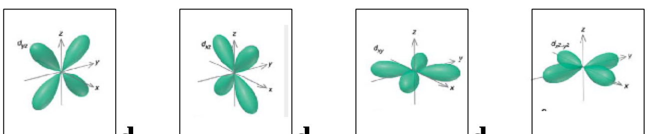


p_x p_y p_z

Shape: dumb bell lying along the x-axis (p_x), the y-axis (p_y) or the z-axis (p_z)

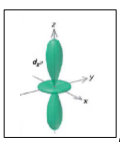
3. The d orbital (l = 2)

Shape: Four lobed clover



d_{yz} d_{xz} d_{xy} d_{x2-y2}

d_{yz}	d_{xz}	d_{xy}	d_{x2-y2}
Lobes lie in yz-plane and bisect y-, z- axes	Lobes lie in xz-plane and bisect x-, z-axes	Lobes lie in xy-plane and bisect x-, y-axes	Lobes lie in xy-plane along the x-, y- axes



d_{z2}

Shape: Dumb bell with doughnut around middle

Equations from Chapter 6 and 7

$\Delta E = q + w$ — What are q and w and their units? What is ΔE?

ΔH — What does ΔH stand for? What units are used for it?

$c = \dfrac{q}{m \times \Delta T}$ — What do the variables in this equation stand for? What are their units? What is specific heat capacity?

$c = v \times \lambda$ — What are the variables and their units?

What is Hess' s Law and what equation is derived from it?

$\Delta H_{rxn} = \Sigma m \Delta H_{f(products)} - \Sigma n \Delta H_{f(reactants)}$

$E = nhv$
$\Delta E = hv$
$E_{photon} = hv$

$\lambda = \dfrac{h}{mu}$