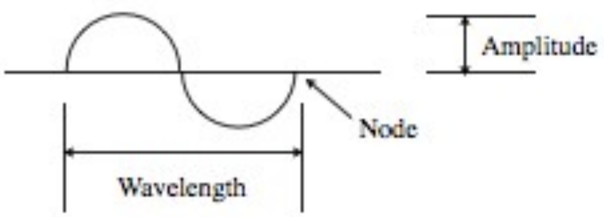
Electromagnetic radiation

Matter has wave-like and particle-like properties.
Wave properties become important for subatomic particles.

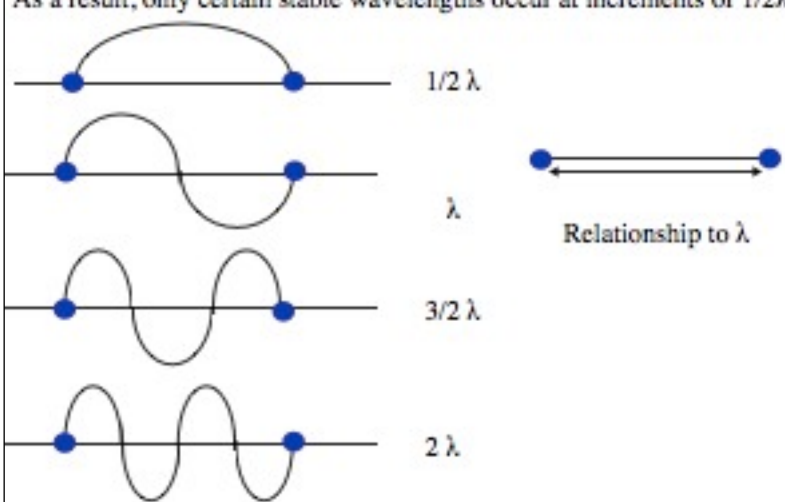
Syllabus Learning Outcomes : 12

Electromagnetic radiation travels as waves
Waves have amplitude and wavelength



Electrons in atoms are like waves traveling on a string of fixed length.

As a result, only certain stable wavelengths occur at increments of 1/2λ



Electromagnetic radiation / waves

- Waves have a frequency (ν, the Greek letter nu) with units of cycles per second (or hertz, Hz)
- Electromagnetic radiation obeys $c = \lambda \cdot \nu$
- c is the speed of light in a vacuum, 3.00×10^8 m/s
- Radiation travels at the speed of light

- Long wavelengths have low frequencies
- Short wavelengths have high frequencies

Example $c = \lambda \cdot \nu$ for electromagnetic radiation

- What is the frequency of red light that has a wavelength of 650nm and blue light that has a frequency of 475nm?

- Solution: convert wavelength to m, solve for frequency.
- $\nu = 3.00 \times 10^8 \text{m/s} / 6.50 \times 10^{-7} \text{m} = 4.62 \times 10^{14} \text{s}^{-1}$
- (long wavelengths have low frequencies)
- $\nu = 3.00 \times 10^8 \text{m/s} / 4.75 \times 10^{-7} \text{m} = 6.32 \times 10^{14} \text{s}^{-1}$
- (short wavelengths have high frequencies)

Wavelength and color of visible light

$\lambda < 400$nm is ultraviolet, then x-ray and gamma ray

$\lambda = 440$nm

$\lambda = 475$nm

$\lambda = 510$nm

$\lambda = 575$nm

$\lambda = 590$nm

$\lambda = 650$nm

Short wavelength, high frequency, high energy

Long wavelength, low frequency, low energy

$\lambda > 800$nm is infrared, then microwaves and radio waves

Because matter behaves like a wave, energy is quantized. 7

The energy of one photon is proportional to frequency or inversely proportional to wavelength as given by:

$E_{photon} = h\nu = hc/\lambda$

h = Planck's constant = 6.634×10^{-34} Js

Equation tells us:
Long wavelengths ↔ low frequencies ↔ low energies
Short wavelengths ↔ high frequencies ↔ high energies

Photoelectric Effect 8

Classical theory said that E of ejected electrons should increase with increase in light intensity, but this was not seen.

What happens is that no electrons are ejected until light has a minimum energy.

After that, the number of electrons ejected depends on intensity

One explanation is for light to be discrete particles called photons.

This means that we can "count" light like we would count marbles.

Let's try the model to see if it works.

Example: Photoelectric Effect 9

What is the energy of 1.00mol of red photons (λ=650nm)?

Solution: convert λ to meters and use $E_{photon} = hc/\lambda$

$E_{photon} = (6.634 \times 10^{-34} Js)(3.00 \times 10^{8} m/s) / 6.50 \times 10^{-7} m = 3.06 \times 10^{-19} J$

This is the energy of 1 photon; we need 1 mol of photons.

$(3.06 \times 10^{-19} J / 1 \text{ photon}) (6.02 \times 10^{23} \text{ photon / mol}) = 184000 J = 184 kJ$

E_{mol}= 184kJ. It turns out that red light can break chemical bonds! The model agrees with experiment.

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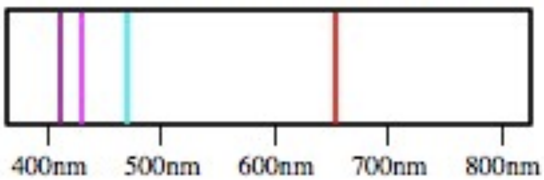
Building on this, Niels Bohr explained sharp line emission spectra for atoms that contained one electron.

White light is composed of all colors of light.

Excited atoms emit only certain wavelengths of light, where the wavelengths depended on the particular element.

Bohr's model was able to predict this emission spectrum for hydrogen.



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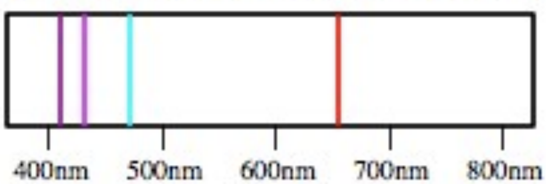
Bohr said that the energy of a quantized state is a constant divided by an integer, n

$E_{photon} = C/n^2$

C is the constant. n is the orbit of the electron in an atom. The spectrum below was predicted by calculating the difference in energy between two orbits, such as between n=1 and n=2 in hydrogen. Energy differences between certain pairs of orbits gave rise to the colors shown below, which predicted the emission spectrum of hydrogen.



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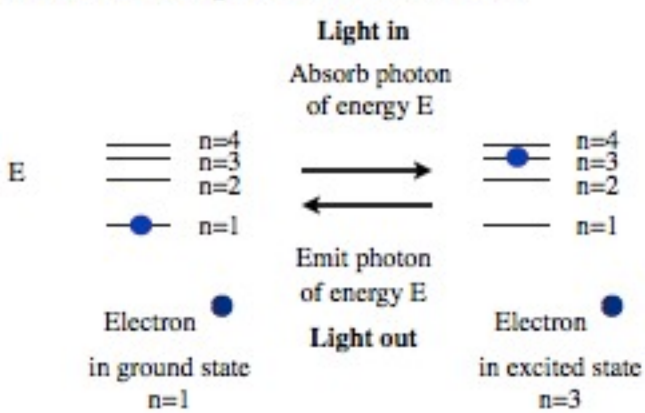
Photon absorption and emission



A photon of the correct energy could be absorbed by an electron in hydrogen, and than emitted to produce light of that energy

de Broglie: moving matter is a wave

Bohr's model worked only for 1 electron atoms, so a better model was needed.

de Broglie proposed that all moving objects behave like waves:
$E = mc^2 = h\nu = hc/\lambda$

Solving for wavelength, he found $\lambda = h/mc$. For objects not moving at the speed of light, replace speed of light, c, by velocity, v: $\lambda = h/mv$.

For electrons (and low mass particles), wave properties could be measured.

Using $v = 1.5 \times 10^6$ m/s and $m = 9.1 \times 10^{-31}$ kg, $\lambda = 0.49$ nm.

Moving electrons behaved as if they had a wavelength. Objects with large mass had negligible wavelengths. The model was accepted.

Quantum Mechanics and Schrodinger

Schrodinger said that electrons held in atoms behave like waves.

He developed the wave equation: $H\Psi = E\Psi$ (beyond the scope of this course) which gave rise to the concept of electrons existing in orbitals that had an energy E and a shape described by Ψ^2.

Each solution, Ψ, of his equation described an **orbital**, which is allowed energy state for an electron in an atom.

Schrodinger's model worked better than previous models to explain the interaction between light and atoms (matter).

The position of an electron could not be predicted, only the region in space where the electron was likely to be found.

Wave Functions, Ψ

Each wave function describes an orbital, which is a region in space where an electron is likely to be found.

Each Ψ depends on the value of 3 quantum numbers: n, ℓ, and m_ℓ.

n is the (major) principal quantum number of the shell, and it corresponds to the row of the periodic table where that shell begins. n is related to the energy and size of the orbitals in that shell.

ℓ is the angular momentum quantum number. It corresponds to the subshell or shape of the orbital. Like n, ℓ also affects the energy of an orbital.

m_ℓ is the magnetic quantum number that describes the orientation of an orbital in space. It corresponds to the number of orbitals that can exist in each subshell (ℓ).

Orbitals

One orbital holds a maximum of 2 electrons.

Ground state orbitals can belong to the s, p, d or f subshells as described by values of ℓ= 0, 1, 2, and 3 respectively.

The filling of orbitals by electrons partially follows the order of elements on the periodic table.

Quantum number rules

Only certain quantum numbers (and thus orbitals) are permitted. The steps below describe the allowed quantum numbers.

n can be any integer value: 1, 2, 3, 4, 5, 6, 7, ...
(n corresponds to the row on the periodic table where the shell begins, so n values greater than 7 refer to excited state atoms currently.)

ℓ can be any value from 0 up to n-1.
(For example, when n=1, ℓ can only be 0. When n=2, ℓ can be 0 or 1.)

m_ℓ can be any value from -ℓ to ℓ.
(For example, when ℓ=0, m_ℓ can only be 0. When ℓ=1, m_ℓ can be -1, 0, or 1.)

More about the ℓ quantum number

When ℓ=0, we have an s subshell, or s orbital. The 3D shape of an s orbital per Schrodinger's wave equation is a ball or sphere:

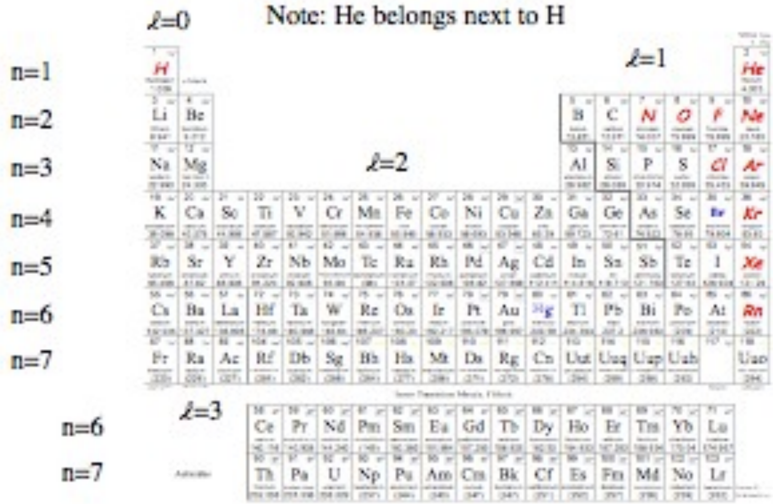
When ℓ=1, we have a p subshell, or p orbital. The 3D shape of a p orbital is similar to two elongated balloons tied together at the stems: (We will call this shape dumbbell.)

When ℓ=2, we have a d subshell, or d orbital. The 3D shape of four of the d orbitals is similar to a cloverleaf formed by four elongated balloons tied together by the stems:

One d orbital looks similar to a p orbital with a doughnut around its waist:

The ℓ quantum number is more commonly referred to using s, p, d or f.

Periodic table labeled with n and ℓ



Periodic table and ℓ quantum number

Elements with the last electrons filling ℓ=0 are noted as s-block elements.

Elements with the last electrons filling ℓ=1 are noted as p-block elements.

Elements with the last electrons filling ℓ=2 are noted as d-block elements (or transition elements).

Elements with the last electrons filling ℓ=3 are noted as f-block elements (or inner-transition elements).

Periodic table and m_ℓ quantum number

m_ℓ gives the number of orbitals in each subshell (s, p, d, and f)
Because 2 electrons fit in each orbital, there are 2 elements for each orbital.
When n=1 (first row of periodic table), ℓ=0, and m_ℓ=0 by the quantum number rules. One orbital exists (as given by the one value of m_ℓ), called the 1s orbital. One orbital holds up to 2 electrons. With 1 proton and 1 electron, we have hydrogen. With 2 protons and 2 electrons (ignoring neutrons), we have helium. No other elements are allowed in the first row because there are no more allowed orbitals to fill.

For any value of n, whenever ℓ=0, we are in the s block and 2 elements will exist as shown by the example above.

Periodic table and quantum numbers

Let's try n=2 (second row of periodic table), where ℓ=0 or 1.

When ℓ=0, m_ℓ=0 by the quantum number rules. One orbital exists, called the 2s orbital. With 3 protons and 3 electrons (ignoring neutrons), we have lithium. With 4 protons and 4 electrons (ignoring neutrons), we have beryllium. No other elements are allowed in the 2s orbital. As before, only 2 elements are allowed in an s orbital.

When ℓ=1, m_ℓ=-1, 0, and 1 by the quantum number rules. Three orbitals (3 m_ℓ values) exist, called the 2p orbitals. They all have a dumbbell shape, but differ in their orientation in space (along the x, y, and z coordinate axes). Three orbitals gives 6 electrons ($2e^-$/orbital), and 6 elements. These elements are B, C, N, O, F, and Ne.

For any value of n, whenever ℓ=1, we are in the p block and 6 elements will exist as shown by the example above.

Periodic table and quantum numbers

There are 8 total elements (four orbitals, where one orbital is s and three are p) in the n=2 shell. You can count the eight elements in the second row of the periodic table.

You can count the eight elements in the second row of the periodic table, so four orbitals must be filled. One s orbital (2 elements) is filled in the s block and 3 orbitals (6 elements) get filled in the p block.

Periodic table and quantum numbers

Let's try n=3 (third row of periodic table), where ℓ=0, 1, or 2.

When ℓ=0, m_ℓ=0 by the quantum number rules. One orbital exists, called the 3s orbital. This corresponds the elements Na and Mg.

When ℓ=1, m_ℓ=-1, 0, and 1 by the quantum number rules. Three orbitals exist, called the 3p orbitals. This corresponds to the elements Al, Si, P, S, Cl, and Ar.

When ℓ=2, m_ℓ=-2, -1, 0, 1, and 2 by the quantum number rules. Five orbitals (5 m_ℓ values) exist, called the 3d orbitals. This corresponds to the ten transition elements (electrons) Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn.

For any value of n, whenever ℓ=2, we are in the d block which holds $10e^-$, corresponding to 10 elements as shown by the example above.

Periodic table and quantum numbers

On the periodic table, note that the 4s orbital fills before the 3d. We will deal with this using the Aufbau filling order in the next discussion.

The n=3 shell holds 18 elements/electrons (2 in the s, 6 in the p, 10 in the d)

The difference between a 1s, 2s, 3s, and 4s orbital is size and energy. All are spherically/ball shaped. The 2s orbital is larger and higher in energy (higher frequency, shorter wavelength) than the 1s. The 2s orbital (and larger s orbitals) have nodes, which you can ignore for now.

A similar difference holds between 2p, 3p, and 4p, as well as 3d, 4d, and 5d. Larger n values mean electrons have higher energy (higher frequency, shorter wavelength), and they have more nodes. You can ignore the nodes for now.

Periodic table and quantum numbers

Let's try n=4 (fourth row of periodic table), where ℓ=0, 1, 2, or 3.

When ℓ=0, m_ℓ=0 by the quantum number rules. One orbital exists, called the 4s orbital. This corresponds the elements K and Ca.

When ℓ=1, m_ℓ=-1, 0, and 1 by the quantum number rules. Three orbitals exist, called the 4p orbitals, that hold 6e^-.

When ℓ=2, m_ℓ=-2, -1, 0, 1, and 2 by the quantum number rules. Five orbitals exist, called the 4d orbitals, that hold 10e^-.

When ℓ=3, m_ℓ=-3, -2, -1, 0, 1, 2, and 3. Seven orbitals exist (corresponding to 7 m_ℓ values), called the 4f orbitals. The f shell holds 14 electrons/elements.

The n=4 shell holds 32 electrons/elements (2+6+10+14) in the s, p, d, and f subshells, respectively.