

Quantum Mechanics and Atomic Structure

In Chem 5 and the first two weeks of Chem 6, we explored the equilibrium and kinetic properties of molecular reactions. Now, we will investigate some more fundamental aspects of molecules and chemical reactions:

- Why do only certain combinations of atoms form stable molecules?
- What are the molecular structures of molecules?
- How are the characteristics of molecules related to the macroscopic properties, such as chemical reactivity and physical properties (state of aggregation, solvent properties, etc.)? Can we develop the ability to predict these properties? What gives rise to the periodicities of elemental properties embodied in the periodic table?

To answer these questions - we clearly need to get a better picture of what atoms are and how they are bound together both within a molecule (i.e., what is a “chemical bond”?) and among molecules (what holds the molecules in liquids and solids together?)

ATOMS:

How would you “define” an atom? Probably by talking about

composition and internal structure

extremely tightly localized *nucleus* comprised of

protons (positively charged)

neutrons (electrically neutral, almost identical mass)

electrons (negatively charged, much lower mass) far outside the nucleus

... or something like that. You might talk about electrostatic attractions between the positively charged nucleus and negatively charged electrons that hold it together.

In short - you would discuss the atoms as **particles**, consisting of **subatomic particles**. That's what people tried to do at the beginning of the 20th century. We will describe how it was discovered that treating atomic constituents as exhibiting solely “particle-like behavior” inevitably lead to problems: inconsistencies and incorrect predictions. In fact, in order to begin to understand the glue that holds together a covalent bond, we will need to revise our picture completely.

First lets briefly discuss the situation at the end of the 19th century:

PARTICLES AND WAVES

By the late 19th century, physicists thought they had most physical phenomena pretty well understood. All things pretty much fell into two distinct categories: waves and particles. “Particles” were defined by the way they interacted with each other, and similarly for waves.

So a “particle” is something that exhibits “particle-like behavior”. First, we’ll discuss a bit about particles, and particularly electrostatic forces between them. Then we’ll talk about early experiments to determine the properties of atoms. Then, we’ll return to a discussion of wave-like behavior, and show how the only way to describe

Particle-type properties

- countable: can’t have 37% of a particle.
- has a mass m (measured by a force in a gravitational field).
- subject to Newton’s Laws of motion (late 17th century):

\mathbf{r} = position (vector)

$$\mathbf{r} = x\hat{x} + y\hat{y} + z\hat{z}$$

\mathbf{v} = velocity (vector): $\mathbf{v} = d\mathbf{r}/dt$

$$\mathbf{v} = v_x\hat{x} + v_y\hat{y} + v_z\hat{z}$$

$$\text{speed} = \text{magnitude of velocity} = v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$$

\mathbf{p} = momentum (vector) $\mathbf{p} = m\mathbf{v}$

$$\mathbf{p} = p_x\hat{x} + p_y\hat{y} + p_z\hat{z}$$

If a force (vector) \mathbf{F} is exerted on the particle, it will alter the momentum according to

$$\mathbf{F} = d\mathbf{p}/dt = m d\mathbf{v}/dt = m \mathbf{a}$$

“equation of motion”

The particle has a **trajectory**: $\mathbf{r}(t)$ the position as a function of time

If $\mathbf{F} = 0$, then the velocity doesn’t change, i.e., neither the speed nor the direction of the motion of the particle. If $\mathbf{F} \neq 0$, then the velocity does change, in a way that can be predicted by integrating the equation of motion.

If you know the initial position and velocity, and you know the force acting on the particle as a function of the position of the particle, you can, in principle, predict exactly the position and velocity of the particle at any later time.

This can be used to predict the orbits of astronomical objects, trajectories of projectiles, etc., to excellent precision.

Conservation Laws of physics: in collisions between particles:

$$\text{Conservation of momentum } \mathbf{p}_1(\text{in}) + \mathbf{p}_2(\text{in}) = \mathbf{p}_1(\text{out}) + \mathbf{p}_2(\text{out})$$

$$\text{Conservation of energy } E_1(\text{in}) + E_2(\text{in}) = E_1(\text{out}) + E_2(\text{out})$$

Energy is a scalar (not a vector): $E = E_{\text{kinetic}} + E_{\text{potential}}$

$E_{\text{kinetic}} = mv^2/2 = p^2/2m$ has a well-defined “absolute” value; not relative to an arbitrary zero.

$E_{\text{potential}}$ defined by spacial position, relative to its value at some arbitrary location at which the energy is defined to be zero. For example - the gravitational potential energy: relative to an arbitrary height.

Forces: for chemistry, only electrostatic forces contribute significantly (gravitational forces are only significant for much greater masses, and weak/strong forces for much smaller distances - involved in holding neutrons and protons together in the nucleus).

Suppose you have two particles, carrying electrical charges Q_1 and Q_2 , separated by a distance r . (Charges are given in units of Coulombs "C"; we'll discuss the units later.) Then Coulomb's law (1775) says that the force between them is inversely proportional to the square of the distance, and has direction along the line joining them:

$$F_{\text{Coul}} = Q_1 Q_2 / \alpha r^2$$

where α is a fundamental constant:

$$\alpha = 1.11265 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

Forces have dimensions of energy/distance (units of J m^{-1}), so the units of α make sense. A negative force (Q_1 and Q_2 of opposite sign) means they are attracted; a positive force (Q_1 and Q_2 of the same sign) means they repel each other.

Remember - a positive velocity $\mathbf{v} = d\mathbf{r}/dt$ means \mathbf{r} is increasing, i.e., they are moving apart, a negative velocity means they are coming together. So, if \mathbf{F} is negative, the Q_1 and Q_2 can have signs as well as magnitudes. Since $\mathbf{F} = m d\mathbf{v}/dt$, if the charges are of opposite sign, then $d\mathbf{v}/dt$ is negative, and the velocity decreases.

One other way of thinking about electrostatic interactions: Electric Field (\mathcal{E})

If a test particle with charge Q_1 is placed in an electric field (\mathcal{E}) then $F = Q_1 \mathcal{E}$

If the field arises from a charged particle Q_2 at a distance \mathbf{r} from the test particle, then

$$F = Q_1 Q_2 / \alpha r^2$$

So, the electric field due to a particle of charge Q_2 , at a distance r from that particle, is given by

$$\mathcal{E} = Q_2 / \alpha r^2$$

How are forces related to potential energies? (see pp. 31-33 in Oxtoby)

In general: $dE_{\text{pot}}/d\mathbf{r} = -\mathbf{F}$

So, if I can know the potential energy surface (i.e., the value of E_{pot} at each position \mathbf{r}), I can predict the force at a given position by taking a derivative, and if I know the force at each position in space, I can determine the E_{pot} by integrating. In one dimension (x): $dE_{\text{pot}}/dx = -F$, so

$$dE_{\text{pot}} = -F dx$$

$$\text{Integrate: } E_{\text{pot}}(x_2) - E_{\text{pot}}(x_1) = -\int F dx$$

Note - you can never say what the value of E_{pot} is at a point \mathbf{r} ; only what it is relative to some standard position.

Example:

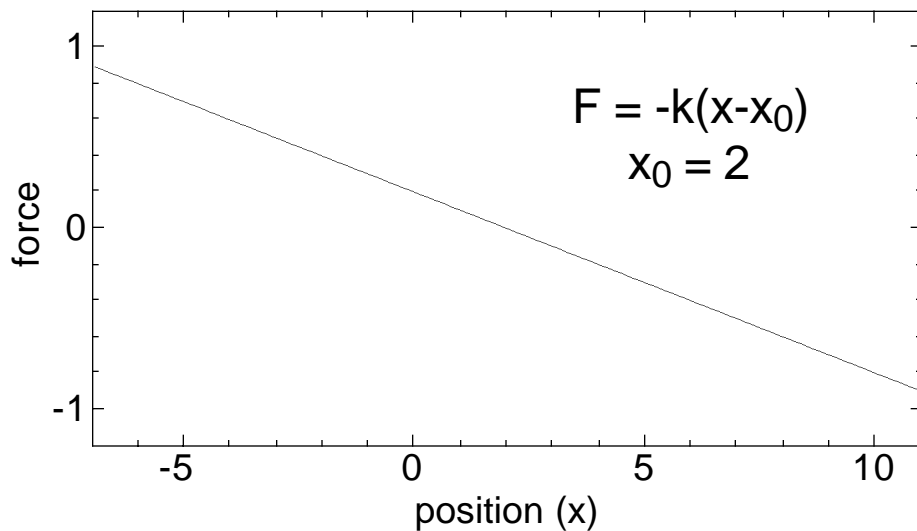
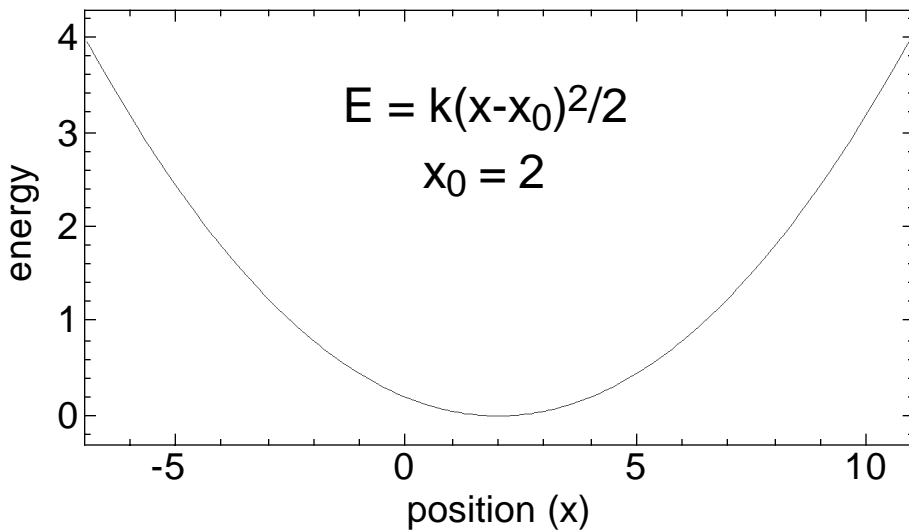
- A slope on a mountain - the gravitational potential is mgh , where h is the height, or altitude. If the ground is not flat, i.e., if the altitude h varies with position x , then $E(x) = mg h(x)$, and the force is $F = -mg (dh/dx)$. When the slope is positive (altitude increases as you go in a particular direction) the force is in the opposite direction.

- Hooke's law spring: restoring force is proportional to the distance from equilibrium spring length (x_0):

$$F(x) = -dE/dx = -kx$$

Corresponds to the bottom of a parabolic potential energy "well":

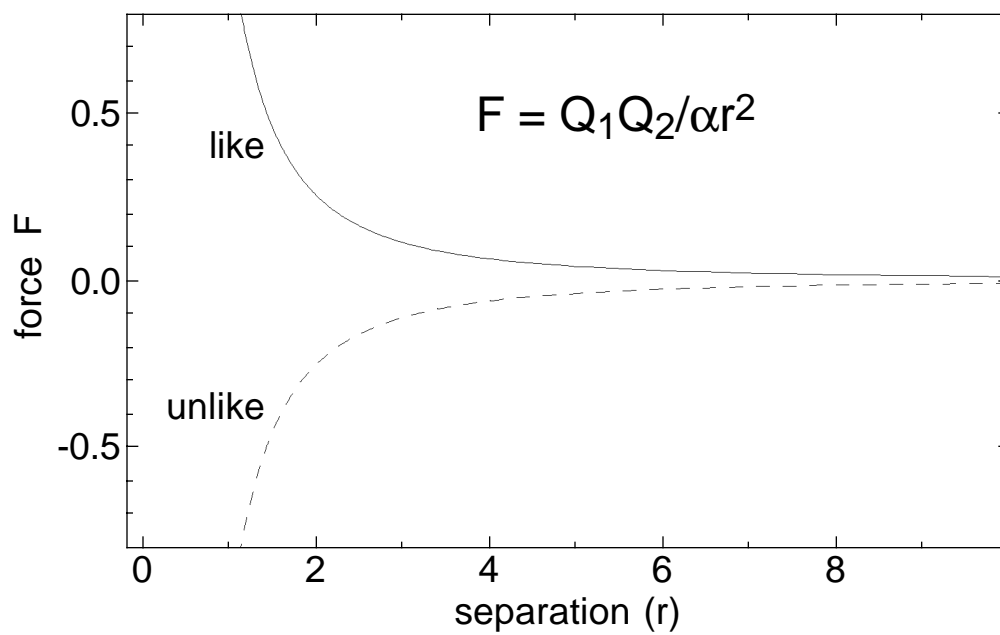
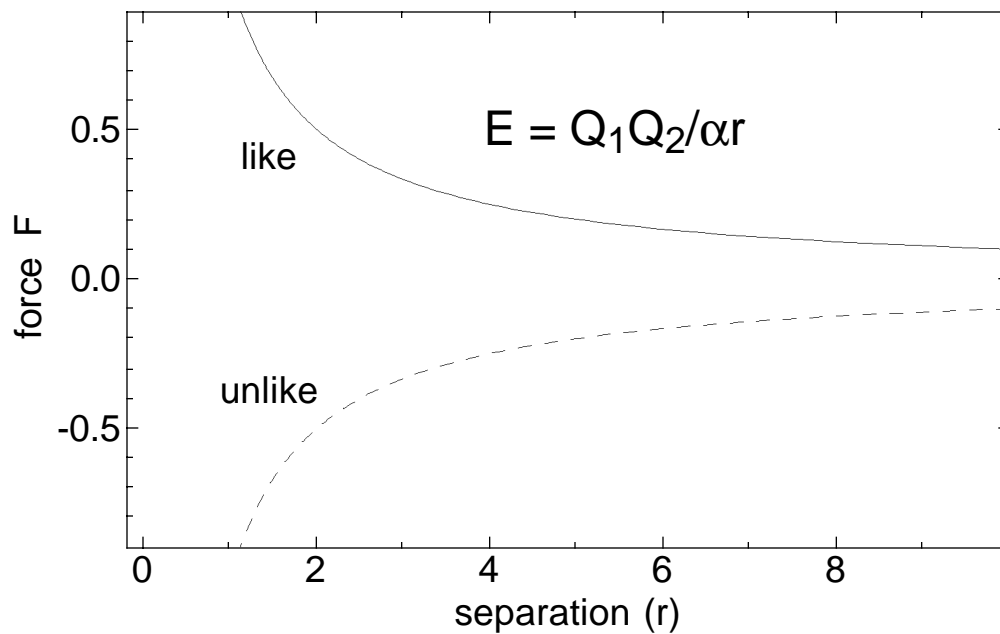
$$E_{\text{pot}}(x) = E(0) + k(x-x_0)^2/2$$



For Coulomb force between particles separated by a distance r , let $r_1 = \infty$, and $r_2 = r$

$$E_{\text{Coul}}(r) = -\int (Q_1 Q_2 / \alpha r^2) dr = Q_1 Q_2 / \alpha r$$

The zero of energy is defined at infinite separation: $E_{\text{Coul}}(r = \infty) = 0$.



Early experiments to determine atomic structure

(1) 1897: J. J. Thomson does extremely clever experiment. “Cathode rays” (turns out later to be electrons) observed in a Cathode Ray Tube (CRT).

How?

---- OXTOBY OVERHEAD ----

---- DEMO WITH MAGNETS ----

Here's the idea: Apply a high voltage between metal electrodes in a nearly evacuated tube.

Negatively charged particles are emitted from the negative electrode (cathode). These “cathode rays” are accelerated toward and through the positive electrode (anode) and smash against the far end of the tube. They leave tracks by the light emitted by the residual gas along their path.

The electrons can be deflected in one direction by an electric field, and in the opposite direction by a magnetic field. The former depends only on the strength of the electric field, the latter by both the strength of the magnetic field and the velocity of the particle. By determining the deflection when only the electric field is present, and then applying a compensating magnetic field, i.e., of strength adjusted such that there is no net deflection of the electrons, it is straight forward to show that $e/m_e \approx 1.76 \times 10^{11} \text{ C kg}^{-1} \approx 1.76 \times 10^8 \text{ C g}^{-1}$. (Details of the derivation are given in pp. 15-17 in Oxtoby.)

(2) Robert Millikan and Fletcher (1906): Determined e , and thus using Thomson's result for e/m , determined the mass of the electron m_e . Here's how they did it:

They sprayed (using an “atomizer”; bad name!) extremely small drops of oil into a box. There was an ionizing source inside the box that gave off electrons which were either absorbed by the drops directly, or by gas molecules in the box which then gave up the negative charge in collisions with the drops. The net effect was to place a negative charge equal to the charge on an electron on some of the drops. A drop of mass M drifts down slowly under the influence of gravity $F = M_{\text{drop}}g$ (balanced by frictional forces that give it a well-defined terminal drift velocity); by watching with a microscope they could measure the drift speed which allowed them to determine M_{drop} . Then, an electric field was applied (metal plates with positive charge at the top and negative charge at the bottom of the box. The charge on the plates resulted in an electric field opposite to the gravitational field that results in a force $Q_{\text{drop}}\mathbf{E}$ on the drop. The field \mathbf{E} could be adjusted until there was no net force on the drop (no acceleration - determined through by direct observation). At that point: $Q_{\text{drop}}\mathbf{E} = M_{\text{drop}}g$, so the charge on the drop could be determined: $Q_{\text{drop}} = M_{\text{drop}}g/\mathbf{E}$. They found that Q_{drop} was always an integer multiple of a fundamental charge, which they correctly assumed was the charge on an electron: $e \approx 1.60 \times 10^{-19} \text{ C}$. Using the e/m value determined by Thomson a decade before ($e/m_e = 1.76 \times 10^{11} \text{ C kg}^{-1}$), they were able to determine

the electron mass $m_e \approx 9.11 \times 10^{-31}$ kg.

Now Faraday, back in 1833, had used electrochemical cells to figure out that it took a charge of about 96,485 C to plate out exactly one mole (108 g) of Ag $[\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag}(\text{s})]$

This number gives Avogadro's number; using modern values:

$$N_o = (96,485 \text{ C} / \text{mol}) / (1.60218 \times 10^{-19} \text{ C}) = 6.022 \times 10^{23} \text{ mol}^{-1}$$

Anyway, clearly $m_e \ll m_{\text{H atom}} = (1.00783 \text{ g mol}^{-1}) / N_o = 1.66 \times 10^{-27}$ kg

In fact, $m_{\text{proton}} \approx m_{\text{neutron}} \approx 1836 m_e$.

Thus, virtually all of the mass of an atom is in the positively charged part!

“Thomson” atom: he proposes that the positive charge of the atom is spread out in space like a “jelly”, with very low mass electrons (enough to give an atom that is electrically neutral overall) interspersed throughout.

(3) Rutherford, Geiger, Marsden (1911). Radium has just been discovered by Marie Skłodowska-Curie and Pierre Curie. It gives off α -particles [Helium nucleus He^{2+} , mass = 4 g / mol, with positive charge (+2)] with high kinetic energies. Rutherford makes a very thin sheet of gold foil (5×10^{-5} cm thick) and directs a beam of these massive, high-velocity (and thus high-momentum) α -particles at the foil. The α -particles would be repelled by the positive charges in the gold; the electrons are irrelevant because, since they are so low in masses, they would have little effect on the trajectories of the α -particles.) Based on Thomson's “jelly-like” model in which the positive charge in the gold foil is diffusely dispersed throughout, the α -particles shouldn't feel much, and ought to go straight through the sheet with little deflection of their linear trajectories.

Experimental results: they put a “scintillation screen” around the gold foil - made of ZnS which gives off light when bombarded with an α -particle. As expected, there is a bright spot along the line of the α -particle beam on the other side of the gold foil; those α -particles were undeflected. However, to their great surprise, they occasionally see very large deflections in all directions, in some cases even scattered backwards off the gold foil! “It was almost as incredible as if you fired a 15” shell at a piece of tissue paper and it came back and hit you.”

They realize that only if the positive charge is concentrated in a very small region of space could they account for such strong scattering. In fact, they calculate what would be predicted if the positive charge is localized in tiny spheres of much smaller radius than the atomic radius, and an excellent fit to the experimental data is found if the radius of the localized positive charge is roughly a factor of 10^{-4} times smaller (or less) than the radius of the atom: $r_{\text{nucleus}} \sim 10^{-4} r_{\text{atom}}$. They call this localized positive charge the “nucleus” of the atom.

How do you determine r_{atom} ? For example, for Li metal: Atomic mass = 6.94 g/mol; density = 0.534 g/cm³.

The molar volume of a mole of close-packed spheres = $(6.94 \text{ g/mol}) / (0.534 \text{ g/cm}^3) = 13.00 \text{ cm}^3/\text{mol}$. But close packed spheres occupy only 74% of space, so the actual volume occupied by 1 mol of spherical Li atoms is

$V(\text{per mole of spheres, not including interstitial space}) = 0.74(13.00 \text{ cm}^3/\text{mol}) \approx 9.6 \text{ cm}^3/\text{mol}$ and thus

$$V_{\text{atom}} = (V/\text{mol}) / N_{\text{O}} = 9.6 \text{ cm}^3/\text{mol} / 6.022 \times 10^{23} \text{ atoms/mol} \approx 1.60 \times 10^{-23} \text{ cm}^3$$

But $V_{\text{atom}} = (4\pi/3)r_{\text{atom}}^3$, so

$$r_{\text{atom}} = [(3/4\pi)V_{\text{atom}}]^{1/3} \approx 1.56 \times 10^{-8} \text{ cm} = 1.56 \text{ \AA} = 0.156 \text{ nm}.$$

(1 nm = $10^{-9}\text{m} = 10^{-7}\text{cm} = 10 \text{ \AA}$; 1 \AA = $10^{-10}\text{m} = 10^{-8}\text{cm}$)

Since $V = (4/3) \pi r^3$, $V_{\text{nucleus}} \sim 10^{-12}$ to $10^{-14} V_{\text{atom}}$!

Since virtually all of the mass of the atom is in the nucleus, this means that

$$\text{density}_{\text{nucleus}} = m_{\text{nucleus}}/V_{\text{nucleus}} = m_{\text{atom}}/V_{\text{nucleus}} \sim 10^{13} m_{\text{atom}}/V_{\text{atom}} = 10^{13} \text{ density}_{\text{atom}} \\ \sim 10^{13} \text{ g/cm}^3 \text{ (} 10^8 \text{ tons per cubic centimeter) That's pretty dense!}$$

So: Rutherford proposed a model with electrons, of charge e^- moving in planetary orbits around a tiny but massive nucleus of charge Ze^- .

But ... there's a problem. Even in circular orbits, in which the speed remains constant, the velocity is constantly changing, because the direction of the motion is not linear. (There is a force, so by Newton's law, there must be an acceleration.) The electrons in such a model would thus be accelerating, and the laws of electromagnetism (Maxwell), well known in the second half of the 19th century, said that a charged particle that accelerates must radiate energy. But, as we will show in a few lectures, as the energy drops, the radius must drop. In fact, such a model would predict that the negatively charge particle would rapidly spiral in to the nucleus: the atom would cease to exist in a tiny fraction of a second!! **WHAT'S WRONG??** *Maybe electrons don't act as "particles"!!*

WAVES:

Let's examine the other kind of physical entity besides particles: waves. In particular - what does it mean for something to behave in a "wave-like" manner?

Standard example: light (= electromagnetic radiation)

PROPERTIES:

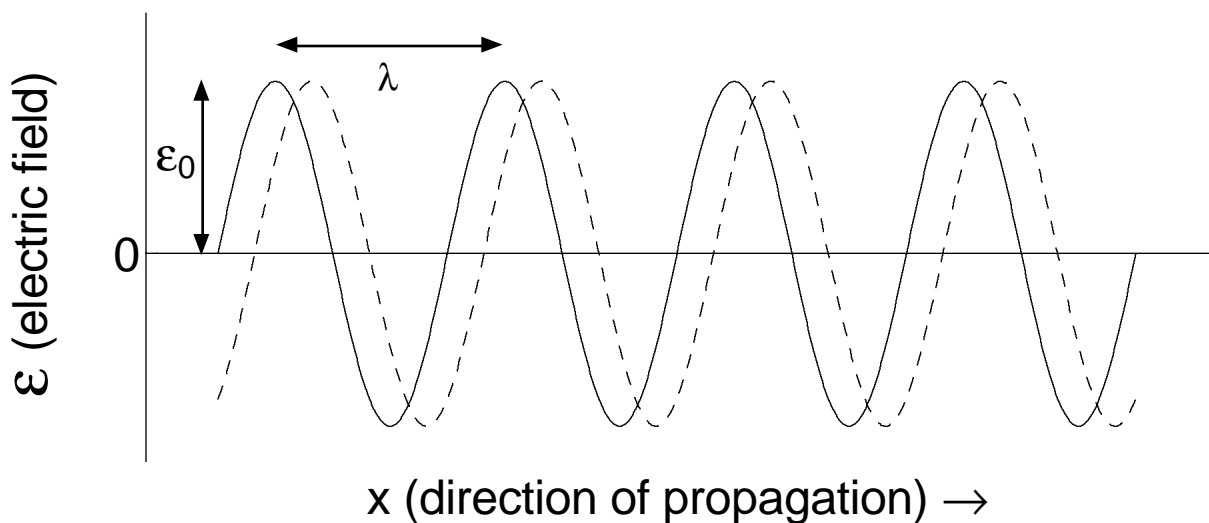
- *Not* localized (unlike particles)
- Superposable (unlike particles)
- Characterized by

amplitude (\mathcal{E} , for light) wavelength λ frequency ν
speed (c , for light) phase ϕ

J. C. Maxwell - light "propagates" like a wave (and doesn't require a medium, unlike sound)

An oscillating charge radiates: emits light (E-M fields that travel through space) of frequency equal to the oscillation frequency of the charge that emits it.

SO: light is extended in space, extending along a line in the direction of propagation (x). At a particular moment, the electric (\mathcal{E}) and magnetic (H) fields have values at each point along the line. (I'll ignore the magnetic component (H) for now.) In particular, if I plot the value of \mathcal{E} on the line as a function of position (x) along the line, you get a sinusoidal curve; a "wave function":



The periodicity of the oscillation determines the wavelength λ . Suppose the solid line represents $\mathcal{E}(x)$ at time $t=0$. Now suppose I wait a short time Δt ; the field travels along the line a little bit, as shown by the dashed line. After waiting a time τ , called the period of the wave, it has traveled one wavelength, and thus is identical to the way it was at time $t=0$.

The frequency ν of the wave is the number of periods in one second, i.e., $\nu = 1/\tau$. In other

words, if I look at one place in space (x), the frequency is the number of waves that pass by in one second. Frequency has dimensions of $(\text{time})^{-1}$; typical units are s^{-1} . Since this is so common it has its own name: $1 \text{ s}^{-1} = 1 \text{ Hz}$ (Hertz). So $1 \text{ MHz} = 10^6 \text{ Hz} = 10^6 \text{ s}^{-1}$; $1 \text{ KHz} = 10^3 \text{ Hz}$.

How fast does light travel? In vacuum, it is found that the speed of light (the speed at which the crest of a wave propagates) is independent of the wavelength - it is a universal constant

$$c \approx 2.998 \times 10^8 \text{ m/s}$$

that relates the wavelength and the frequency: $v = c/\lambda$, or

$$c = \lambda v = \lambda/\tau$$

So, the mathematical expression for a sinusoidal wave of amplitude \mathbf{E}_0 , wavelength λ , speed c , and phase ϕ (a shift to the right or left by an angle ϕ) is:

$$\mathbf{E} = \mathbf{E}_0 \sin[2\pi(x - ct)/\lambda + \phi]$$

Last thing about waves: what is the energy of a wave?

The intensity of light (and thus the energy of a wave) is proportional to the sum of the squares of the amplitudes of the electric and magnetic fields:

$$E \propto I \propto \mathbf{E}_0^2 + H_0^2$$

ELECTROMAGNETIC SPECTRUM

name	wavelength range λ	frequency range $\nu = c/\lambda$
γ -rays	$\sim 10^{-12} \text{ m}$	$\sim 10^{20} \text{ Hz}$
x-rays	$\sim 10^{-9} \text{ m}$ (nm)	$\sim 10^{17} \text{ Hz}$
visible	$\sim 4 \times 10^{-7} \text{ to } 7 \times 10^{-7} \text{ m}$ $= 4000 \text{ to } 7000 \text{ \AA} = 400 \text{ to } 700 \text{ nm}$	$\sim 10^{15} \text{ Hz}$
infrared	$10^{-6} \text{ to } 10^{-3} \text{ m}$ (micron to millimeter)	$10^{14} \text{ to } 10^{11} \text{ Hz}$
microwave	$10^{-3} \text{ to } 1$ (millimeter to meter)	$10^{11} \text{ to } 10^8 \text{ Hz}$
radio	$1 \text{ to } 10^3$ (meter to kilometer)	$10^8 \text{ to } 10^5$
FM	3 meter	$10^8 \text{ Hz} = 100 \text{ MHz}$
AM	300 meter	$10^6 \text{ Hz} = 1 \text{ MHz} = 1000 \text{ KHz}$
a/c current	$5 \times 10^6 \text{ m} = 5000 \text{ km}$	60 Hz

How do we know something is a wave?

Answer: examine how waves interact with each other (the analogy to “collisions” for particles)

DIFFRACTION: classical ideas about interactions among waves

Waves exhibit superposition in the following sense:

If two waves cross at a point in space, the electric field at the crossing point is the sum of the electric field of the two incident waves: $\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2$

The intensity at the crossing point is thus proportional to

$$I_{\text{total}} \propto (\mathcal{E}_1 + \mathcal{E}_2)^2 = \mathcal{E}_1^2 + \mathcal{E}_2^2 + 2\mathcal{E}_1\mathcal{E}_2 = I_1 + I_2 + 2\mathcal{E}_1\mathcal{E}_2$$

Remember, waves oscillate around zero; the field is negative half the time and positive half the time.

Constructive interference: Suppose the two waves have the same λ and amplitude \mathcal{E}_0 and are “in phase”, i.e., they hit their maximal values (crest) simultaneously, and their minimum values simultaneously. Then $\mathcal{E}_1 = \mathcal{E}_2$ at all times, so

$$I_{\text{total}} \propto (\mathcal{E}_1 + \mathcal{E}_2)^2 = (2\mathcal{E}_1)^2 = 4\mathcal{E}_1^2 = 2(\mathcal{E}_1^2 + \mathcal{E}_2^2) = 2(I_1 + I_2)$$

In other words: the intensity of the light at the point of superposition is greater (in this case by a factor of two) than the sum of the intensities of the incident light!

Even more impressive: **Destructive interference.** Suppose, as before, that the two waves have the same λ and amplitude \mathcal{E}_0 , but they are 180° “out of phase”, i.e., when one hits its maximal value, the other is hitting its minimum (most negative) value. Then $\mathcal{E}_1 = -\mathcal{E}_2$ at all times, so

$$I_{\text{total}} \propto (\mathcal{E}_1 + \mathcal{E}_2)^2 = 0$$

In other words: two light waves that are “out of phase” but otherwise identical annihilate each other!

LESSON: light intensity is not conserved at the point where light waves intersect!

How do we know that this happens? DIFFRACTION PATTERNS

First, let imagine that monochromatic light (only one wavelength) impinges on a diffraction grating. The grating consists of a set of very thin slits, equally spaced at a separation d . The light is blocked except at the slits. The slits are sufficiently narrow so that at each slit the light acts as if it were absorbed and re-emitted (in all directions), always starting out with zero amplitude at the slit (in other words, a sine wave with $\phi = 0$.)

---- draw diffraction diagrams ----

A screen, perpendicular to the line of the incident light, is placed far from the grating. Pick a point on the screen which is at an angle $\theta \neq 0$ from the beam line. The path lengths from different slits

in the grating to the point on the screen will not be the same; the length increases by an amount

$$s = d \sin(\theta)$$

from one slit to the next. So, from a large number of slits, the path lengths differ by s , $2s$, $3s$, $4s$, ... As a result, in general, all the waves (one from each slit) that intersect at the point on the screen have all different phases; some positive, some negative. At any given moment, the result is essentially complete cancellation, i.e., destructive interference:

$$\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2 + \mathcal{E}_3 + \dots \approx 0$$

so the intensity is zero at that point on the screen ...

... EXCEPT if the extra path length of the wave from one slit to the next is an integer multiple of λ , the wavelength of the light. Then:

All the waves are perfectly "in phase", they exhibit complete constructive interference:

$$\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2 + \mathcal{E}_3 + \dots \approx n\mathcal{E}_1$$

And the intensity is $I \approx n^2\mathcal{E}_1^2 = n(\mathcal{E}_1^2 + \mathcal{E}_2^2 + \mathcal{E}_3^2 + \dots) \approx n(I_1 + I_2 + I_3 + \dots)$

which is thus n times greater than the sum of the intensities of all the incident light waves.

So - a bright spot is observed for

$$d \sin(\theta) = 0, \lambda, 2\lambda, 3\lambda, \dots$$

or more generally

$$d \sin(\theta) = m\lambda,$$

where $m = 0, 1, 2, 3, \dots$ is called the order of the diffraction

Diffraction spots occur at angles such that $\sin(\theta) = m\lambda/d$, or

$$\theta = \sin^{-1}(m\lambda/d)$$

Note: θ increases with *increasing* λ

θ increases with *decreasing* d .

---- DIFFRACTION DEMO ----

use 250 line/in, 13,400 line/in with monochromatic $\lambda = 632.8 \text{ nm} = 6.328 \times 10^{-5} \text{ cm}$ (He/Ne laser)

For diffraction grating with 13,400 lines/inch:

$$d = (13,400 \text{ lines/inch})^{-1} (2.54 \text{ cm/inch}) = 1.90 \times 10^{-4} \text{ cm}$$

If $\lambda = 632.8 \text{ nm} = 6.328 \times 10^{-5} \text{ cm}$, then

$$\lambda/d = 6.328 \times 10^{-5} \text{ cm} / 1.90 \times 10^{-4} \text{ cm} = 0.334$$

So: spots appear at

m	θ
0	0
1	$\sin^{-1}(0.334) = 19.5^\circ$

$$2 \quad \sin^{-1}(2 \times 0.334) = \sin^{-1}(0.668) = 41.9^\circ$$

DEMO: 250 lines/inch:

$$d = (250 \text{ lines/inch})^{-1} (2.54 \text{ cm/inch}) = 0.0102 \text{ cm}$$

If $\lambda = 632.8 \text{ nm} = 6.328 \times 10^{-5} \text{ cm}$, then

$$\lambda/d = 6.328 \times 10^{-5} \text{ cm} / 0.0102 \text{ cm} = 0.00623$$

$$m \quad \theta$$

$$0 \quad 0$$

$$1 \quad \sin^{-1}(0.0062) = 0.357^\circ$$

$$2 \quad \sin^{-1}(0.124) = 0.714^\circ, \text{ etc.}$$

Suppose you have light that is not monochromatic: what you would observe?

Each wavelength will generate spots of orders $m = 1, 2, \dots$, the positions of which depend on the wavelength. So a diffraction grating can be used to separate light of different wavelengths.

Try using the “student” gratings to look at

- a white incandescent lamp (continuous - all frequencies observed)
- a fluorescent bulb

SUMMARY: What, classically, is the “signature” of a wave (or of wave-like behavior)?

When two waves interact - the observable property (for light, the intensity) at the intersection point is not, in general, the sum of the values of that observable property (intensity) of the separate incident waves. Rather, they can exhibit interference, either constructive or destructive. This can be understood quantitatively if waves superpose in the sense that the total wave function (the electric field, for light) is the sum of the wave functions of the incident waves, and if the observable (intensity) is the square of the wave function.

PROBLEMS with this “classical” treatment of light as a wave:

The problems occur when light interacts with matter. Various experiments around the turn of the 20th century were inconsistent with light behaving purely as a wave, when it interacted with matter.

Two examples:

1. Blackbody Radiation. Hard to understand (complicated physics) - but the first example to be understood using a “quantum” hypothesis: (Planck, 1897)
2. Photoelectric Effect. Much easier to understand, and more relevant to chem: (Einstein, 1905).

Blackbody radiation:

Suppose you make a hollow box (cavity). Inside the cavity light exists at all frequencies (e-m

radiation). If we wish the light to come to equilibrium, then we need some mechanism for light at one frequency to be converted to light at other frequencies; kind of “light reactions”. To do this, you imagine putting a small “black-body” (so called because it can absorb light at all frequencies) in the box, i.e., an object that can absorb light at some frequency and re-emit it at different frequencies. (Actually, the walls of the cavity may serve this function). So, suppose the light in the cavity reaches a dynamic equilibrium, i.e., the amount of light at any frequency is not changing with time. There is light of a wide range of frequencies in the box - but what are the relative amounts of each? How does this distribution depend on temperature?

You have some intuition about the answer to this question. First of all, you know that as the temperature of an object rises, it “glows” brighter and brighter - it emits more and more radiation. You also know that the distribution shifts to shorter and shorter wavelengths - red stars are at lower temperature than yellow or white stars, and blue stars are the hottest. So, two things happen with rising T : the intensity at all frequencies goes up, but more so at shorter than at longer wavelengths, so the center of the distribution shifts to lower λ , (higher frequencies).

First, a quick comment about probability densities, as opposed to probabilities. If I ask

“What is the intensity of light at some exact value of λ ?”,

the answer is zero; the probability of having any exact value is zero. It is like asking

“In the US population, what is the probability of finding someone who weigh exactly 150.00000... pounds?”

But I can ask about the fraction of people with weights in some range, say, between 150 and 151 pounds. Clearly, the fraction between 150 and 151 pounds is different from the fraction between 250 and 251, although in both cases I considered a range of 1 pound. Also, the fraction between 150 and 151 is about twice as big as the fraction between 150 and 150.5 lbs.; clearly as the range gets smaller, the fraction drops in proportion (as long as the ranges are fairly small).

So - back to light. Consider the intensity of light in some narrow range of wavelengths, say, between λ and $\lambda + \Delta\lambda$. Again, if you make the range $\Delta\lambda$ smaller and smaller, the intensity of light in the range decreases in proportion (for small enough $\Delta\lambda$). So, one usually asks the question about the probability distribution as follows:

“If we let $I(\lambda) d\lambda$ be the intensity of the radiation at wavelengths between λ and $\lambda + d\lambda$, then how does $I(\lambda)$ depend on λ ?”

Anyway, classical physics of the late 19th century says that the blackbody can absorb and re-emit arbitrary amounts of light, regardless of frequency. From the wave perspective - the energy

of light is proportional to the square of the amplitude of the electric field, which, according to classical physics, can vary continuously. Thus exchange of energy of any magnitude would be permitted. With this “continuum” idea and using techniques of “statistical mechanics” (not very accessible to modern freshman chemistry students!!) it is possible to predict how the intensity $I(\lambda)$ depends on λ (and on temperature) for such a cavity, and the following relationship is obtained: $I(\lambda) = 2\pi ck_B T/\lambda^4$, where k_B (Boltzmann’s constant) is $k_B = R/N_o$. The temperature and wavelength dependence is thus

$$I(\lambda) \propto T/\lambda^4 \propto T \nu^4$$

At long wavelengths (low frequencies), the experimental results are consistent with these predictions: $I(\lambda)$ drops off rapidly with increasing λ . But as you go to shorter wavelengths (higher frequencies), negative deviations from the predictions are observed. The prediction says that the intensity should rise rapidly and without limit as the wavelengths get shorter, while experimentally, it goes through a maximum and drops off as λ is decreased. The totally incorrect prediction at high frequencies is called the “ultra-violet catastrophe” (it is catastrophic in the sense that it predicts the intensity to increase without limit.) **What’s wrong?**

Planck (1897) I’ll give a more modern description than Planck’s approach (which is described in the book.) Suppose if, for some bizarre reason, when the light wave of frequency ν interacts with the blackbody, it can only give up or receive energy in discrete amounts ϵ , i.e., sort of a “particle of light”. (Why? Planck suggests that the “oscillating” vibrations of charges in the black body material are, for some unknown reason, only permitted to have energies $\epsilon = nh\nu$, where n is a positive integer, and thus can only give up energy as light in multiples of $h\nu$.) *This is contrary to our usual ideas about light, i.e., exhibiting classical wave-like “behavior”. In fact, it is more like what we would call classical “particle” behavior!* And, he says, suppose further that this energy ϵ in these energy “packets” (called “photons”) is determined by the frequency of the light:

$$\epsilon = h\nu$$

where h is some constant of proportionality. He pluts this seemingly crazy idea into the statistical mechanical (physics) machinery to predict the dependence of intensity on λ (or on $\nu = c/\lambda$) and predicts the much more complicated expression:

$$I = (2\pi hc^2/\lambda^5) (e^{h\nu/k_B T} - 1)^{-1}$$

where k_B is “Boltzmann’s constant”; $k_B = R/N_o$. He finds that with appropriate choice of the constant h , he can fit the experimental data perfectly with this equation, including both the wavelength and temperature dependence! The value of this constant, now called “Planck’s constant” is **$h = 6.626 \times 10^{-34} \text{ J s}$**

Note that this complicated formula reduces to the simple form at low frequencies (long

wavelengths), when the argument of the exponential is much less than one.

First, remember from math that

$$e^x = 1 + x + x^2/2 + x^3/6 + \dots$$

is the Taylor series expansion for e^x . For small x , we can truncate the series to very good approximation as $e^x \approx 1 + x$. So, if $x = h\nu/k_B T \ll 1$, or equivalently, $\lambda \gg hc/k_B T$, then

$$e^{h\nu/k_B T} \approx 1 + h\nu/k_B T, \quad \text{and thus} \quad e^{h\nu/k_B T} - 1 \approx h\nu/k_B T$$

$$I \approx (2\pi hc^2/\lambda^5) (h\nu/k_B T)^{-1} = 2\pi ckT / \lambda^4$$

which is the correct expression for long wavelengths. Note that in this limit, Planck's constant has disappeared!

This is THE FIRST "QUANTIZATION" HYPOTHESIS: the first time that making the (non-classical) assumption that something is discrete (i.e., not continuous) resolves an apparent contradiction between theoretical predictions and experiment. So, light can exhibit "particle-like" behavior.

Second example: PHOTOELECTRIC EFFECT

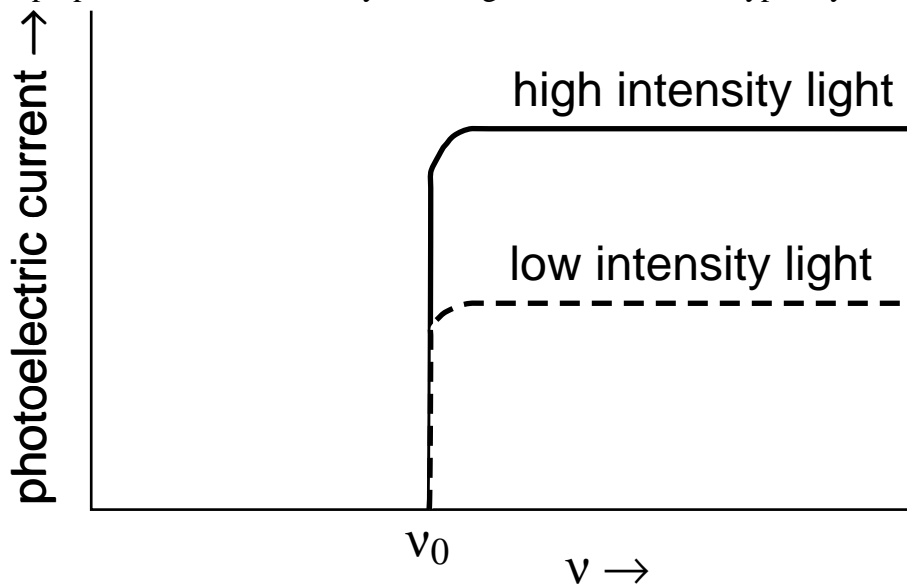
Cannot be explained treating light as having only wave-like properties

Set up: Two pure elemental metal plates separated by a small distance (say, made of cesium metal.) Attach them in an electrical circuit, place voltage across the plates; one has – and one has + charge. No current flows because of the gap between the plates.

Suppose you wanted to pop an electron out of the metal, an electron that is bound by a “binding energy” Φ . One way of supplying that energy is by shining light on the metal, where it can be absorbed by a metal atom on the surface. An electron will be emitted from the atom if the atom absorbs an amount of energy from the light that is greater than Φ ; the excess energy will be retained by the electron as kinetic energy ($E_{\text{kin}} = m_e v^2/2$). (Sometimes it also loses energy colliding with other atoms near the surface, so it may not keep it all as kinetic energy.)

So, shine a beam of monochromatic (single-frequency) light on the negative plate. If the light frequency ν is less than a certain value ($\nu < \nu_0$), or equivalently, if $\lambda > \lambda_0 = c/\nu_0$, nothing happens, regardless of the intensity of the beam. Strange! Based on classical wave ideas of light, if the intensity is large (large amplitude of wave), it should be able to give up plenty of energy to an atom! But apparently not...

However, if you shine a monochromatic beam of frequency above the “threshold” frequency, i.e., $\nu > \nu_0$, electrons are ejected from the metal surface. How many electrons, and with what E_{kin} ? They are accelerated towards the positively charged plate, and thus a current flows: this “photoelectric current” is easily measured. The value of the threshold frequency depends only on the identity of the metal; among the elemental metals it is smallest for cesium. The photoelectric current, which is proportional to the number of electrons emitted by the metal per second, is found to be proportional to the intensity of the light beam. The data typically look like this:



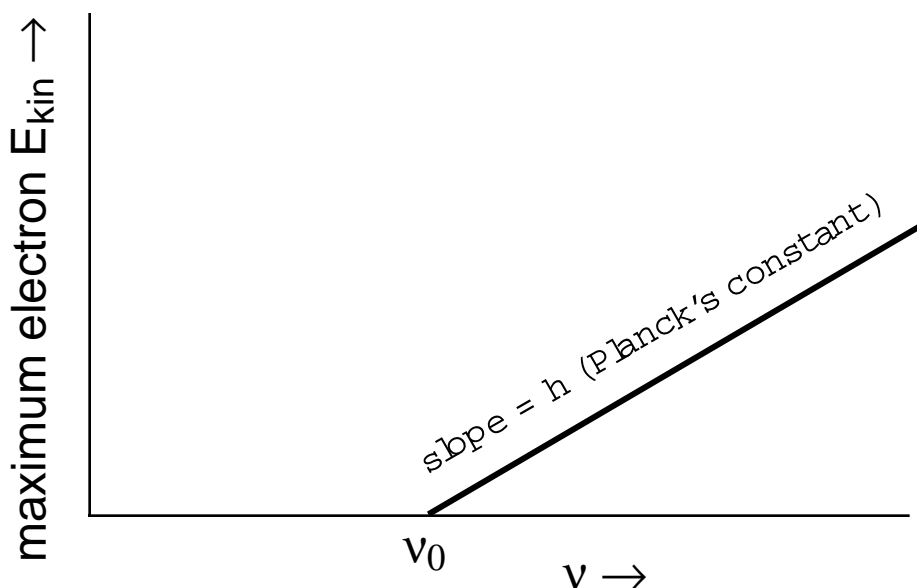
You can measure something else: the kinetic energy of the emitted electrons E_{kin} . For a given light frequency ν , you discover that the electrons have a range of energies, but their maximum kinetic energy depends only on ν . Presumably, the maximum E_{kin} corresponds to the case where all the energy in excess of Φ goes to the electron's E_{kin} (none lost in interactions with other atoms on the way out of the metal.) In fact, a plot of the maximum E_{kin} of the electrons as a function of ν is a straight line, with x-intercept ν_0 . And now some really bizarre results:

1. For all metals, the values of ν_0 and Φ are related by a constant of proportionality of $6.626 \times 10^{-34} \text{ J s}$, the same value (h) as the constant of proportionality between energy and frequency $\epsilon = h\nu$ that Planck used to get the correct formula for black-body radiation!!

$$\Phi = h\nu_0$$

2. The slope of this line is, again, $h = 6.626 \times 10^{-34} \text{ J s}$

The data look like this:



The equation for the observed straight line that relates the light frequency and the emitted electron's maximum kinetic energy is:

$$E_{\text{kin}} = h(\nu - \nu_0) = h\nu - \Phi$$

EINSTEIN in 1905 (he got the Nobel Prize for this):

This can be understood if one assumes that light is quantized in the following sense: when light interacts with matter, it can give up or accept energy only in discrete packets or “quanta” (G. N. Lewis named them “photons”); the energy of the created or destroyed photon being proportional to the light frequency, with Planck’s constant as the constant of proportionality:

$$\varepsilon = h\nu = hc/\lambda$$

Each atom in the metal can absorb at most one photon at a time. From this perspective, changing the intensity of the light just alters the *number* of photons that impinge on an area of the metal surface per second, and thus on the number of surface atoms at any moment that are in the vicinity of a photon that they can absorb. But the energy of each photon is determined only by the light frequency.

So: conservation of energy says that if a photon of energy $\varepsilon = h\nu$ is absorbed by the atom, and if $\varepsilon > \Phi$, then the electron escapes, carrying with it the excess energy as kinetic energy:

$$\varepsilon \text{ (lost by light)} = \Phi + E_{\text{kin}}$$

$$\text{or } E_{\text{kin}} = \varepsilon - \Phi = h\nu - \Phi = h(\nu - \nu_0)$$

as observed experimentally.

So: both the Black-body radiation distribution and Photoelectric effects can only be understood if light exhibits particle-like behavior, in which energy is exchanged to/from the light in discrete particle-like “photons”, with photon energy and light frequency related by a single (fundamental) constant of proportionality h .

DIVERSION ABOUT UNITS

For energies, the Joule is convenient for *macroscopic* amounts. But for individual atoms or molecules, it isn't very convenient. Use a more *microscopic* unit: electron volt “eV”:

1 eV is the energy acquired when an electron is accelerated through an electrical potential difference of 1V (V = volt): $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

This looks familiar: the charge on an electron is $e = 1.602 \times 10^{-19} \text{ Coulombs}$!

Not surprising: that's how these units are related: $1 \text{ J} = 1 \text{ V}\cdot\text{C}$, i.e., it takes 1 J of energy to take 1 Coulomb of charge across an electrical potential of 1 V; a “volt” is a joule/Coulomb.

Other common units: “wavenumber”: $\tilde{\nu} = 1/\lambda = \nu/c$; so $\varepsilon = h\nu = hc/\lambda = hc\tilde{\nu}$;

- unfortunately $\tilde{\nu}$ is almost always given in units of cm^{-1}

- for the photoelectric effect: $E_{\text{kin}} = hc\tilde{\nu} - \Phi = hc(\tilde{\nu} - \tilde{\nu}_0)$

To give you a sense for numerical values: a photon of energy of $\varepsilon = 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ (in the infrared region of the spectrum) has

$$\nu = \varepsilon/h = 1.602 \times 10^{-19} \text{ J} / (6.626 \times 10^{-34} \text{ J s}) = 2.42 \times 10^{14} \text{ s}^{-1}$$

$$\lambda = hc/\varepsilon = c/\nu = 1.24 \times 10^{-6} \text{ m} = 1240 \text{ nm}$$

$$\tilde{\nu} = 1/\lambda = (1.24 \times 10^{-6} \text{ m})^{-1} = 8,064 \text{ cm}^{-1}$$

Photoelectric effect calculations: using

$m_e v^2/2 = E_{\text{kin}} = \varepsilon - \Phi = h\nu - \Phi = hc/\lambda - \Phi = h(\nu - \nu_0) = hc(\tilde{\nu} - \tilde{\nu}_0)$
relates the electron's kinetic energy to its binding energy in the metal, the difference between the light frequency and the threshold frequency, etc.

Example: Cesium (lowest value of Φ among all pure elemental metals)

$$\Phi = 3.43 \times 10^{-19} \text{ J} = (3.43 \times 10^{-19} \text{ J}) (1 \text{ eV} / 1.602 \times 10^{-19} \text{ J}) = 2.14 \text{ eV}$$

$$\nu_0 = \Phi/h = (3.43 \times 10^{-19} \text{ J}) / (6.626 \times 10^{-34} \text{ J s}) = 5.18 \times 10^{14} \text{ s}^{-1} = 5.18 \times 10^{14} \text{ Hz}$$

$$\tilde{\nu}_0 = \nu_0/c = (5.18 \times 10^{14} \text{ s}^{-1}) / (2.998 \times 10^8 \text{ m s}^{-1}) = 1.73 \times 10^6 \text{ m}^{-1} \approx 17,300 \text{ cm}^{-1}$$

$$\lambda_0 = c/\nu_0 = (2.998 \times 10^8 \text{ m s}^{-1}) / (5.18 \times 10^{14} \text{ s}^{-1}) = 5.79 \times 10^{-7} \text{ m} = 579 \text{ nm}$$

SO: get photoelectric current if

$$\nu > 5.18 \times 10^{14} \text{ s}^{-1}; \quad \tilde{\nu} > 17,300 \text{ cm}^{-1}$$

$$\lambda < 579 \text{ nm} \quad \varepsilon > 2.14 \text{ eV}$$

Note the signs: ε *increases* with increasing ν , $\tilde{\nu}$, ε , but *decreases* with increasing λ .

(high photon energies correspond to short wavelengths and high frequencies)

Exercise: What is the E_{kin} of an electron ejected when light of wavelength $\lambda = 420 \text{ nm}$ hits a piece of cesium metal? *Answer:* $E_{\text{kin}}(\text{max}) = 0.81 \text{ eV} = 1.30 \times 10^{-19} \text{ J}$

SPECTROSCOPY:

There are many examples besides the photoelectric effect in which light is either absorbed or emitted by atoms or molecules. In analogy with the photoelectric effect, a gas-phase atom (rather than one on the surface of a metal) can absorb light; if the frequency of the light is high enough, an electron can be emitted. Or, if the frequency is too low, it may be able to absorb the light, allowing one electron in the atom to rise to a higher energy. Or, for molecules, the energy absorbed from light could go toward rotating the molecule faster, or making vibrating bonds vibrate with greater amplitude, etc. If it is high enough in frequency, the light can be absorbed and the energy used to break a covalent bond, such as in the Cl_2 molecule in the chain reaction demo. In all these cases, **the energy of the photon is equal to the change in the energy of the molecule or atom.** If we say that the atom or molecule has initial energy E_i and final energy $E_f > E_i$ then

$$\varepsilon = E_f - E_i$$

is just a statement of the conservation of energy.

Exercise: Consider the Cl_2 reaction, $\text{Cl}_2(\text{g}) \rightarrow 2 \text{Cl}(\text{g})$ in which the light splits the dimer apart. For this rxn, $\Delta H_{\text{rxn}} = 2\Delta H_f^\circ[\text{Cl}(\text{g})] \approx 2(121) = 242 \text{ kJ/mol}$. So $\Delta E = \Delta H - \Delta PV = \Delta H - RT = 242 - 2.5 \approx 240 \text{ kJ/mol}$. On a per molecule basis, $\Delta E = 240 \text{ kJ/mol} / 6.02 \times 10^{23} \text{ mol}^{-1} \approx 4.0 \times 10^{-19} \text{ J}$. This corresponds to light of wavelength $\lambda = c/\nu = hc/h\nu = hc/\varepsilon \approx 500 \text{ nm}$. So,

light with $\lambda < 500$ nm (blue) will break apart the Cl_2 bond, but yellow, green or red light will not.

We can also get photon emission, which is the opposite of absorption. If the molecule or atom loses energy, i.e., if $E_{\text{final}} < E_{\text{initial}}$, its lost energy $\Delta E = E_{\text{initial}} - E_{\text{final}}$ results in the creation of a photon that carries that much energy: $\epsilon = \Delta E$. Again: the energy of the photon is equal in magnitude to the change in energy of the atom or molecule:

Absorption:	$E_{\text{final}} > E_{\text{initial}}$	$\Delta E > 0$	$\epsilon = \Delta E = E_f - E_i$
Emission:	$E_{\text{final}} < E_{\text{initial}}$	$\Delta E < 0$	$\epsilon = -\Delta E = E_i - E_f$

Suppose you have a substance that is allowed to have *any* energy (not the case for atoms and molecules): i.e., suppose a *continuum* of energies were allowed. Let's say that it starts out with some energy E_i , and along comes light of frequency ν . From this light, a photon of energy $\epsilon = h\nu$ could be absorbed, since the molecule would end up with energy $E_f = E_i + h\nu$ that it is permitted to have.

However, suppose the substance is a molecule or atom, which is permitted (for reasons we have not yet discussed) to have only certain *discrete* values of the energy. We'll use the following language: the atom or molecule can be in one of a set of "states", labelled 0, 1, 2, 3, ..., associated with which is a well-defined energy $E_0, E_1, E_2, E_3, E_4, \dots$ in order of increasing energy. The state of lowest energy, E_0 , is called the "ground" state, and the others are "excited" states.

A few notes in passing:

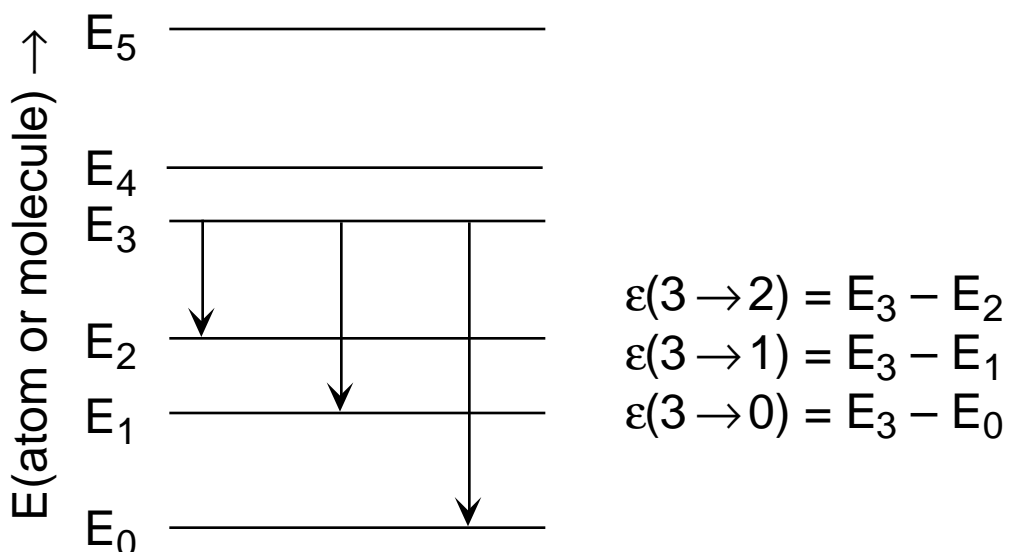
- Sometimes the ground state is called "1", rather than "0".
- In atoms and molecules, there is often a simple pattern that relates all these energies.
- The allowed energies are often "discrete" up to a point, beyond which a continuum of energies is allowed; such is the case for an electron in an atom (more of that soon), for which the states are discrete when the electron is bound, but continuous when it escapes from the atom (having a continuum of possible kinetic energies beyond the energy needed to leave the atom.)

Suppose I have an atom or molecule initially in a "state" with energy E_3 , for example. What frequencies of light can it absorb? What can it emit?

Emission: Consider emission first. If the atom or molecule emits light, it loses energy. But its final state must be an "allowed" state, which must be of lower energy, i.e., E_0, E_1 , or E_2 . So the only three possible losses of energy of the molecule are:

$$\Delta E = E_3 - E_2, E_3 - E_1, E_3 - E_0$$

If I prepare a collection of molecules all in this state #3 with energy E_3 , I should see only three colors of light of frequencies $\nu = \epsilon/h = \Delta E$. For example:

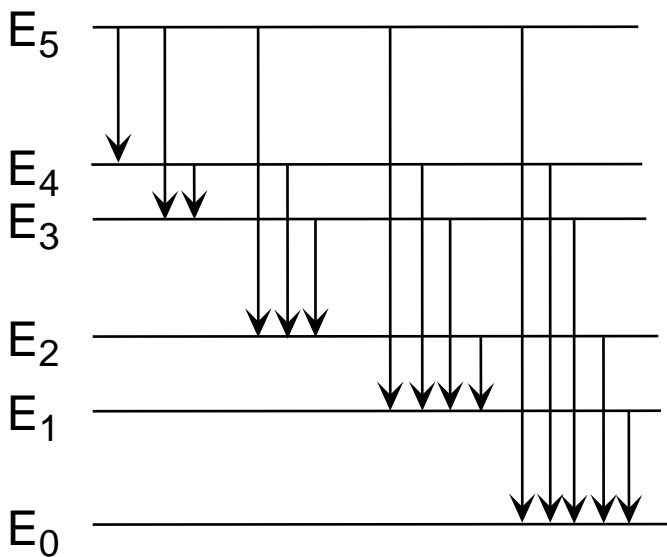


The emission spectrum is a listing of the frequencies of light that are observed to be emitted, or more precisely, a plot of the intensity of the emission as a function of frequency (or wavelength.)

---- draw schematic emission spectrum ----

Since the emission occurs only at discrete frequencies, each emission frequency is called a spectral "line". In this case, the spectrum (Intensity vs. frequency) would comprise three sharp lines.

Now suppose I have a collection of the same molecules, but which are not all initially in state 3, but rather are distributed in some way among all the states. Then, light of energy corresponding to all possible *differences* in molecule energy should be observed. For the case shown above, in which only 6 different energies are permitted, this would result in:



5 emission lines from molecules that end up in the ground state

with frequencies $\nu = (E_5 - E_0)/h, (E_4 - E_0)/h, \dots, (E_1 - E_0)/h$

4 lines from molecules that end up in the first excited state, and so on:

a total of $5 + 4 + 3 + 2 + 1 = 15$ lines at frequencies $(E_n - E_m)/h$, for $5 \geq n > m \geq 0$.

If the energy levels of the molecule are not related in some simple way, the resulting emission “spectrum” will be quite complex! From the plot above, I’d guess that the lowest frequency (largest wavelength) spectral line would result from the photon emitted when a molecule in state #4 ends up in state #3; the highest frequency would correspond to a molecular transition from the highest energy state (#5) to the ground state.

Clearly, if you know the values of the energies of all the allowed states (6 in this case), you can predict the position of all the emission lines (15 in this case). But it generally works in reverse experimentally: you measure the emission spectrum, from which, with a bit of work, you can deduce the allowed energies, the differences in all possible pairs of which give rise to the emission spectrum. Note that, in general, if n is the number of states, there will be at most $n(n-1)/2$ emission lines. The number of lines is reduced if different pairs of energy levels differ in energy by the same amount.

Example: suppose the energy levels are equally spaced. Then

$$E_n - E_{n-1} = E_1 - E_0$$

$$E_n - E_{n-2} = 2(E_1 - E_0)$$

$$E_n - E_m = (n-m)(E_1 - E_0)$$

and the emission spectrum would be a series of equally spaced lines. The lowest frequency would correspond to a transition from an energy level to the level immediately lower, and so on.

---- gas discharge tube demos: H, Ne, etc. ---- not quantitative, but point out the colors of the visible lines for the H atom (red, blue, violet, ...)

Absorption:

---- show OXTOPY transparency ----

An absorption spectrum is obtained as follows. White light (containing all frequencies) shines on a substance (a collection of molecules, for example). The molecules are initially distributed (although far from equally) in all of their allowed states. For a molecule initially in state “ m ” with energy E_m , the only light that can be absorbed is light with frequency ν , such that $h\nu = E_n - E_m$, where $n > m$. The light that passes through the sample is dispersed (spread out with respect to frequency using, for example, a prism). The spectrum is the opposite of an emission spectrum: light of all frequencies is observed except at the frequencies at which light was absorbed by the molecules.