1.1 Waves and particles according to Classical Physics

Conventional properties of waves: Constructive and destructive interference of waves; diffraction of waves from crystal surfaces. Wavelength (λ) is the major property in explaining such properties.

Some conventional properties of a particle:

(i) Mass, m

(ii) A well-defined position in space; i.e. the location of a particle can be exactly measured.

(iii) Linear Momentum, $\vec{p}$, defined as $\vec{p}=m\vec{v}$ where $\vec{v}$ is the velocity (vector) of the particle. When two particles with initial momenta $\vec{p}_1$ and $\vec{p}_2$ collide, some momentum is transferred between the particles such that the total momentum does not change: i.e. $\vec{p}_1 + \vec{p}_2 = \vec{p}'_1 + \vec{p}'_2$, where $\vec{p}'_1$ and $\vec{p}'_2$ are the momenta of the particles after the collision. The particles may be identical ($m_1=m_2$) or different ($m_1 \neq m_2$).

(iv) In a collection of particles, we can count how many particles there are in the collection.

According to the laws of classical mechanics and optics, waves have none of such "particle" properties; likewise, particles do not have a characteristic such as wavelength.

Light

Light is a form of energy that exhibits wave-like behavior as it travels through empty space. Light is classified according to the wavelength λ of its wave. Lights with λ between approximately 400 nm and 700 nm are visible to the human eye. When a light beam with a wavelength within this range reaches the eye, it is conceived by the eye as a color between violet and red. E.g., when a source emits light with λ near 700 nm, our eyes sense it as red color. In vacuum, lights with all wavelengths travel with the same speed, c. Speed of light in vacuum is:

$c = 2.997\,924\,58\times10^{8}$ m/s (exact value)

Wavelength (λ) and frequency (ν) of a given light are not independent:

$$\lambda\nu = c \qquad \text{eq 1.1}$$

Therefore, a given type of light can be characterized by specifying its frequency instead of wavelength. In most of this course we will use the frequency (ν) of the light for this purpose.

SI unit for λ is the meter (m), and that of ν is 1/second (s^{-1}). The latter unit is also called herz (Hz).

1.2 Contemporary views about properties of light and particles

Experiments during the first quarter of the 20.th century unequivocally proved that in addition to its wave properties, light has some of the particle properties listed above. Likewise, microscopic particles (electrons, atoms, molecules) can exhibit wave property (this implies a wavelength associated with the particle). Whether wave or particle properties will be displayed depends on the circumstances; i.e. the type of experiment done.

Particle properties of light: Experiments designed to study the transfer of energy from a monochromatic (i.e. single-frequency) light beam to a collection of particles indicate that energy in the light beam could only be transferred in "packets" of energy, called photons. Each photon in the beam moves in the direction of the beam with the speed of light, and carries an energy proportional to the frequency ν of the light wave:

$E_{photon} = h\nu$ Energy of a photon eq 1.2

where the proportionality factor, h, is called Planck's constant. Its value is experimentally determined to be:

$h = 6.626\,075\times10^{-34}$ J s Planck's constant

Another common name for a photon is "light quantum" (plural: quanta).

Intensity, I, of a light wave is the amount of energy that flows per second across unit area perpendicular to the direction of travel. SI unit of I is J m^{-2} s^{-1} or W m^{-2}. Intensity and frequency are independent characteristics of a wave. Let E_{light} be the energy that has crossed in 1 second an area of 1 m^2. Numerical value of E_{light} is the same as that of I. It must be true that E_{light} contains an integer number N of photons such that

$E_{light} = N\, E_{photon} = Nh\nu$ eq 1.3

This result indicates that photons in a light beam can be counted, conventionally a particle property. Note that N is directly proportional to intensity I of light.

Exercise 1.1 Calculate the number of photons emitted in 1 sec by a 35 W sodium lamp that produces nearly monochromatic light with λ=589.3 nm (yellow light). *Ans*. 1.038×10^{20} photons/s.

Experiments show that a photon has no mass (i.e. zero mass), and no electric charge. However, a photon does have a momentum (a particle property). The direction of the photon momentum is that of the light wave, and its magnitude is related to the wavelength of the photon.

$p_{photon} = h/\lambda$ Momentum of a photon eq 1.4

Wave properties of particles: Beams of particles such as electrons, neutrons, or atoms exhibit wave properties when diffracted from surfaces of crystals. The wavelength associated with a particle of mass *m* and speed v is

$\lambda_{particle} = h/\, mv = h/p$ de Broglie wavelength of a particle eq 1.5

Electron diffraction is used in modern day electron microscopes (there are two types: scanning electron microscope or SEM, and transmission electron microscope or TEM).

The fact that particles display wave properties shatters the traditional notion that the position of a particle can be exactly measured.

Example 1.1 (from Atkins' Physical Chemistry, 8th edition, exercise 8.6b) A photon powered spacecraft of mass 10.0 kg emits radiation of wavelength 225 nm with a power of 1.50 kW entirely in the backward direction. To what speed will it have accelarated after 10.0 year if released into free space?

Solution 1.1

Given:

Mass of the spacecraft: $m_s = 10.0kg$

Wavelength of the photon: $\lambda_p = 225nm$

Power of the spacecraft: $P_s = 1.50kW$

Time of flight: $t = (10.0 \cdot 365 \cdot 24 \cdot 60 \cdot 60)s$

Known:

Momentum of photon wavelength, λ_p: $p = \frac{h}{\lambda_p}$

Total energy emitted by the spacecraft: $E_T = P_s \cdot t$

Energy of single photon wavelength, λ_p: $E_p = \frac{h \cdot c}{\lambda_p}$

Solution:

Number of photons emitted in 10.0 years: $N_p = \frac{E_T}{E_p} = 5.36 \cdot 10^{29}$

Total momentum of photons: $p_T = N_p \cdot p = 1.58 \cdot 10^3 kg \frac{m}{s}$

Speed of the spacecraft: Due to conservation of momentum, momentum of spacecraft, p_s, after 10 years should have the same magnitude in the opposite direction of the total angular momentum of the photons, p_T, hence:

$p_s = p_T$, $\quad v_s = \frac{p_s}{m_s} = 158 \frac{m}{s}$

1.3 Energy exchange between light and particles

a. **Energy from light to a substance**. A beam of light of a given frequency ν and intensity I impingent on a sample of a substance is viewed as a system of N independent, identical particles (i.e. the photons in the light beam), all moving in parallel and in the direction of the beam. Remember that N is proportional to the intensity I of light. N must be large enough to be measurable (N is usually of the order of Avogadro's number, N_A). Each photon in the aggregate has the same energy hν. Similarly, the sample of the material system is composed of M identical "real" particles (e.g. electrons, or atoms, or molecules). Unless N is extremely large as in lasers, only one photon from the light system interacts with just one particle from the material system. Thus it is an interaction between two particles of different types (a photon and a material particle). Of course, there must be a large number of such two-particle interactions (involving particles from the two systems) concurrently occurring in order to be observable in the laboratory. A particularly important interaction between a photon and a particle A of the material system is one in which the energy of the photon is completely transferred to A. In this process, a photon from the light beam disappears (i.e. N decreases by one), and the energy of the A particle increases by an amount hν. The process is called absorption of light by the substance. It is conveniently represented by the chemical equation:

hν + A $\rightarrow$ A* Absorption of light of frequency ν eq 1.6

where A* is the energized A particle. In chemical equations involving light, a photon is symbolized by $h\nu$. Let the initial energy of A be E_i, and its final energy be E_f. Conservation of energy requires that $E_i + E_{photon} = E_f$, or

$$\mathbf{h}\nu = \Delta E \quad \text{eq 1.7a}$$

where

$$\Delta E = E_f - E_i. \quad \text{eq 1.7b}$$

b. **Energy levels of a material particle.** Numerous experiments have shown that an arbitrary particle A has some stability only when A possesses certain special values of its energy. Energies of this type are referred to as the "allowed energy levels" of particle A (Figure 1.1)

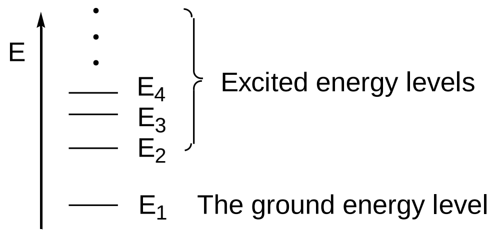

Figure 1.1 Energy level diagram illustrating the allowed energies of a particle A.

The material particle has an infinite number of allowed energies.[1] There is a lowest value, E_1; i.e. the particle can not possess energies below this value. E_1 is called the ground energy level of particle A; and when the particle has this energy, it is said to be in its ground state. All other higher energies E_2, E_3, ... are called excited energy levels of the particle. Energy values, e.g. between E_1 and E_2 or between E_2 and E_3, etc. are forbidden. Thus the allowed energies are discrete, and we say that the particle has quantized energy levels. There is no upper limit for the particle's energy. Each different particle (e.g. a H atom, a C atom, a H_2O molecule, etc.) has a different set of allowed energies, characteristic of the particle under study. Indeed, a major objective of Quantum Chemistry is to predict (i.e. to calculate) these special energy values for a given particle using only theoretical methods.

Now we return to $\Delta E = E_f - E_i$ in eqs 1.7a,b. The quantities E_f and E_i are not arbitrary; rather, they must correspond to two of the allowed energies of the particular particle A under study. The design of light absorption experiments is such that the experimenter knows the initial state of A. This state is usually the ground state so that $E_i = E_1$.[2, 3] The final energy E_f can be any one of E_2, E_3, … so that many

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[1] In contrast, a light particle, i.e. a photon, has only one state with an energy given by eq 1.2.

[2] The experimenter knows only that A is in the lowest-energy state possible; he does not know the numerical value of E_1. Absolute energies can not be measured; only relative energies such as E_n-E_1 where n=2, 3, … are observable.

[3] Experiments are always performed using a macroscopic sample containing M identical A particles where M is a very large integer. The conditions of the experiments are adjusted to minimize the interactions between the particles. The experimental results are then interpreted assuming that the particles do not interact with each other (independent particles) so that numerical results for a single A particle can be extended to those of M particles by a proportionality constant.

possibilities exist for ΔE. Only when the photon energy is exactly equal to one of these allowed ΔE values of A, the energy of the photon may be accepted by A (Figure 1.2).

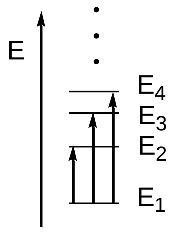

Figure 1.2 Only those photons with frequencies ν_n such that $h\nu_n = E_n - E_1$ where n=2,3,4, … may be absorbed. Light with other frequencies than these will not be absorbed by particle A.

In absorption experiments, frequency of the incident light is monitored and those frequencies of light absorbed by the A particles are measured. The latter provides direct information about ΔE values, i.e. the (relative) allowed energies of particle A.

c. **Photoelectric effect**. When a sheet of metal is illuminated with light of short wavelength (e.g. visible or UV light), electrons are ejected from the metal (Figure 1.3). The emitted electrons are called photoelectrons. In the experiment, kinetic energy of the photoelectrons and their number are measured as a function of the frequency ν of the illuminating light. It is found that electrons are ejected from the metal only for light frequencies larger than a threshold frequency, ν_{min} , which is characteristic of the metal under investigation.

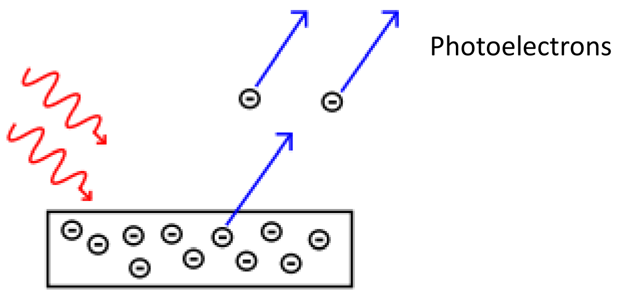

Figure 1.3 Electrons are ejected when a sheet of metal is exposed to light having a frequency ν larger than a threshold frequency, ν_{min}. (Picture from Wikipedia)

The photoelectric effect can be explained by a consideration of the energy levels of an electron in a metal (Figure 1.4). The full set of allowed energies is qualitatively split into two types: A quantized (i.e. discrete) subset of values at lower energies, and a continuous subset at high energies. The gap between neighboring levels in the quantized part decreases as E increases, and becomes vanishingly small when E reaches E_{Cont}.[4] Energy levels change continuously afterwards. Energies belonging to the quantized part correspond to states of the electron in which it is held inside or near the surface of the metal, by attractive forces due to the positively charged nuclei. As the energy approaches E_{Cont}, the average distance of the electron from the surface of the metal becomes larger. Attractive forces always decrease with increasing distance. At E= E_{Cont}, the electron is sufficiently far away from the surface such that both the kinetic energy of the electron and the attractive forces are zero. At larger

[4] Note that E_{Cont} is the highest energy value in the quantized part; i.e. $E_{Cont}=E_{\infty}$. It also forms the start of the continuous part.

distances there are no attractive forces, and the electron gains kinetic energy (i.e. speeds up). When a particle moves

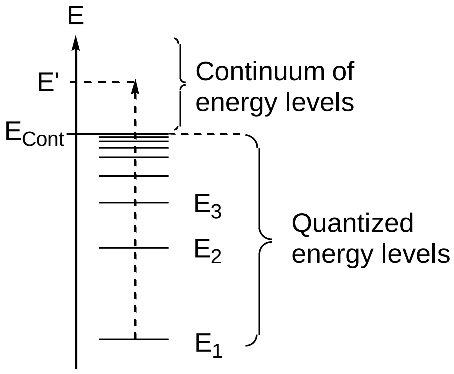

Figure 1.4 Allowed energy values of an electron. When the electron has an energy belonging to the discrete set, the electron is bound to the metal. At energies larger than E_{Cont} the electron is "free"; i.e. it is far away from the surface of the metal. The dotted arrow shows the excitation of an electron after absorbing a photon, from the ground energy level to the level with energy E' in the continuum.

in the absence of forces, it is called a free particle. The absolute energy of a free particle is the sum of its kinetic energy, $mv^2/2$, plus an arbitrary constant which has the same value regardless of whether the particle is free or bound. Since only the differences in energy values are measurable, this arbitrary constant cancels out, and therefore plays no role.

It can be inferred from Figure 1.4 that if the energy of the incident photon is less than (E_{Cont}–E_1), the electron will not be ejected from the metal. The minimum photon energy to "free" the electron (i.e. the "binding energy" of the electron) is

$h\nu_{min} = E_{Cont} - E_1 \equiv W$ Work function eq 1.8

For historical reasons, the energy W is called the "work function" of the metal. It is a characteristic property of the metal under study. Using the experimentally determined threshold frequency ν_{min} of light for a given metal, W for that metal can be calculated from eq 1.8. If the incoming photon energy is higher than W so that the electron makes a transition from the ground level to a continuum level with energy E' in Figure 1.4, the electron will be ejected. An amount, W, of the photon energy will be used up in freeing the electron, and the remainder appears as kinetic energy of the emitted electron.

$h\nu = E' - E_1 = (E_{Cont} - E_1) + (E' - E_{Cont}) = W + \frac{1}{2}m_e v^2$ eq 1.9

where m_e= 9.109×10^{-31} kg is the electron mass.

These ideas can also be applied to gaseous samples of atomic or molecular substances. In this case photons are absorbed by individual atoms or molecules in the sample. If the photon energy is sufficiently large, an electron is ejected from the atom (or the molecule) that absorbed the photon. The quantity W in eqs 1.8 and 1.9 should then be interpreted as the ionization energy (IE) of the atom (or molecule) in question. The experimental technique utilizing these principles is known as photoelectron spectroscopy (PES).

Exercise 1.2 The quantized part of the allowed energies of the electron in the hydrogen atom is given by the formula

$$E_n = -\frac{R}{n^2}, \quad n = 1,2,3,\ldots$$

where R=13.5986 eV. Find in eV units: a) IE of H atom. b) Kinetic energy of the ejected electron after absorbing an X-ray photon of λ=8.2 nm.

d. **Emission of light by a material particle**. A particle in an excited energy level has little stability compared with the same particle in the ground level. Such a particle has a spontaneous tendency to lose its excess energy by emitting a photon. Emission of light by the particle can be represented by the chemical equation

$A^* \rightarrow A + \mathbf{h}\nu$ Emission of light of frequency ν

Let the initial and final energies of the particle be E_i and E_f, respectively. We know that $E_f < E_i$. Energy conservation gives

$\mathbf{h}\nu = E_i - E_f$,

This relation determines the frequencies of photons that may be emitted by the energized particle. An example is shown in Figure 1.5. The initial energy of the particle is $E_i = E_3$. There are only two possibilities for E_f : E_1 and E_2. If a transition to the level E_2 occurs, the frequency ν_1 of the emitted light is determined from

$\mathbf{h}\nu_1 = E_3 - E_2$

If, on the other hand, a transition occurs to the ground level, light with a larger frequency ν_3 will be emitted

$\mathbf{h}\nu_3 = E_3 - E_1$

In a macroscopic sample of A particles, there will be many A particles with the initial energy E_3. Some of them will make a transition to the level E_2, and others to E_1. Since the particles having energy E_2 are also unstable they will emit light with the frequency ν_2 satisfying

$\mathbf{h}\nu_2 = E_2 - E_1$

In summary, an aggregate of A particles, all of which are assumed to have the same initial energy E_3, are expected to emit light with three different frequencies ν_1, ν_2, and ν_3, arranged in increasing order. Note that thus far we did not say anything about which of these three possibilities is most likely. This is a difficult question, and depends on additional factors such as "selection rules" for the transitions between energy levels. Known selection rules for some common transitions will be stated later.

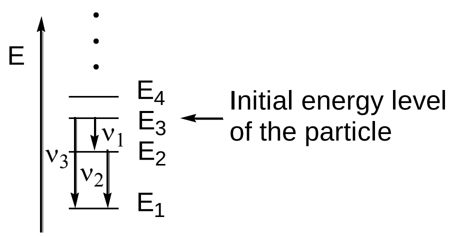

Figure 1.5 Emission of light by an excited particle initially at energy level E_3.

Additional Exercises for this part:

From **LKJ**: Exercises in page 572

From **A**: Exercies: 8.2b, 8.4b, 8.6a, 8.6b, 8.8a, 8.10a, 8.10b

From **M**: Problems: 1.2, 1.19, 1.22, 1.28, 1.29