

قسم الكيمياء
كيمياء الكم والاطياف (2+1)
المرحلة الرابعة
الكورس 2+1

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Chapter One: General Introduction and Classical Mechanics I**One-Dimensional Potential Energy Curve (Morse Curve)**

The minimum in the curve indicates a stable A-B molecule with an equilibrium distance R_e and a dissociation energy D_e . D_e is the amount of energy necessary to dissociate the molecule into its component atoms A + B. Note that the dissociation energy is equal to binding or formation energy for a specific bond.

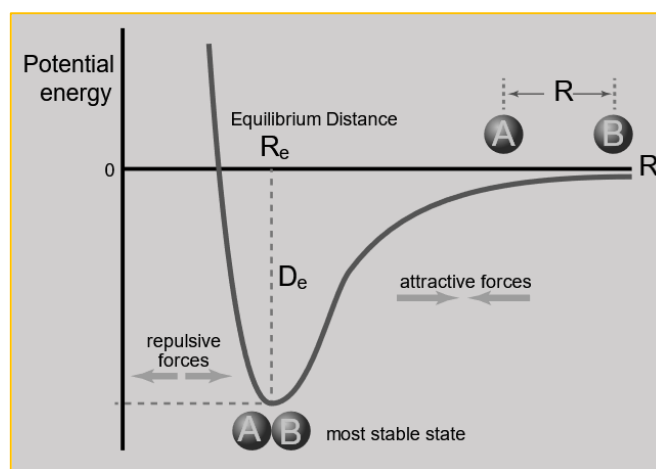


Figure: Energy of diatomic molecule AB plotted against the internuclear distance. R_e is the equilibrium distance between the nuclei and D_e is the dissociation energy.

Two-Dimensional Contours and Three-Dimensional Hypersurfaces of Molecular Energy

The example below shows an illustration for energy variation when a molecule (or more than one molecule) change their geometrical parameters (bond distances R , angles θ , dihedral angles ξ). Energy is then a function of these parameters. Note that the location of any particle (atom, nucleus, electron...etc) can be described via its x , y , and z coordinate.

$$E=f(R, \theta, \xi)$$

$R=f(r_1, r_2, r_3, \dots, r_{(3N)})$, where: N: the total number of atoms
 r_i : the distance between atom i and a geometrical index in the space.

In addition to the energy, the derivation of energy is not less important than the energy itself. The derivation of energy leads to very important physical properties, as in the following examples (The examples are for your knowledge, i.e. not compulsory but optional):

- First order derivative of energy (∂E) can give:
Forces on nuclei; spin density; dipole moment.
- Second order derivative of energy ($\partial^2 E$) can give:
polarizability; vibrational frequencies; infrared intensities, indirect spin-spin coupling constant, rotational spectra in magnetic field; nuclear spin-rotation tensor; electronic g-tensor; magnetizability; nuclear magnetic shielding tensor; nuclear spin-rotation tensor.
- Third order derivative of energy ($\partial^3 E$) can give:
Cubic force constants; first hyperpolarizability; polarizability derivative.
- Fourth order derivative of energy ($\partial^4 E$) can give:
quartic force constants

Also, knowing the equilibrium structure of a molecule, in addition to dealing with its excited states, can be achieved via geometry optimisation, a process performed under quantum chemical software packages.

Historically, many critical points of development can be found when reviewing the way that how a system was treated and how its physical properties (including energy calculation) was obtained. Maybe the main highlighted ones can be mentioned here as:

Classical mechanics

Quantum theory

Quantum mechanics

Quantum mechanics became important during the twentieth century. Before that time, laws of classical mechanics, which introduced in the seventeenth century by Isaac Newton, were used. These laws of classical mechanics were very successful at explaining the motion of huge objects like planets or even objects such as pendulums and projectiles. However, classical mechanics failed when it was applied to very small particles, such as individual atoms, nuclei, and electrons, and very small energy transfer.

Classical mechanics

Classical mechanics describes the behaviour of particles in terms of two equations:

A: One explains that total energy is constant in the absence of external forces.

B: The other explains how particles response when forces acting on them.

in the following, fundamentals of classical mechanics become more understandable via some treatments.

(a) The trajectory in terms of the energy

The velocity, v , of a particle is the rate of change of its position:

$$v = \frac{dr}{dt} \quad \text{_____}(1.1)$$

The velocity is a vector, with both direction and magnitude. The magnitude of the velocity is the speed. The linear momentum, p , of a particle of mass m is related to its velocity, v , by

$$p = mv \quad \text{_____}(1.2)$$

Like the velocity vector, the linear momentum vector points in the direction of travel of the particle (figure 1.3).

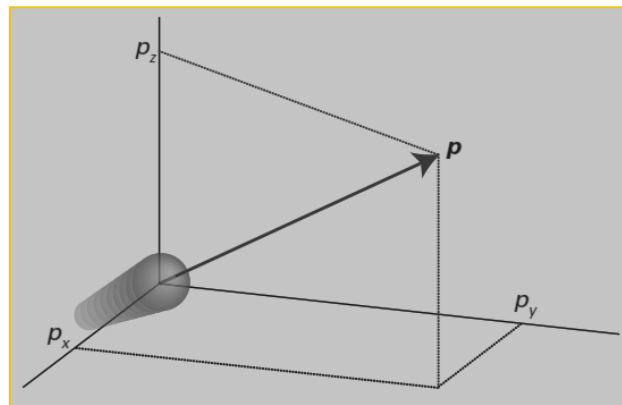


Figure : The linear momentum of a particle is a vector property and points in the direction of motion.

In terms of the linear momentum, the total energy—the sum of the kinetic and potential energy of a particle is:

$$E = E_k + V(x) = \frac{p^2}{2m} + V(x) \quad \text{_____}(1.3)$$

This equation can be used to show that a particle will have a definite trajectory, or definite position and momentum at each instant.

For example, consider a particle free to move in one direction (along the x-axis) in a region where $V = 0$ (so the energy is independent of position). From the definition of the kinetic energy,

$$E_k = \frac{1}{2}mv^2 \quad \text{_____}(1.4)$$

and $v = dx/dt$

From equations (1.2) and (1.3):

$$\frac{dx}{dt} = \left(\frac{2E_k}{m} \right)^{1/2} \quad \text{_____}(1.5)$$

A solution of this differential equation is:

$$x(t) = x(0) + \left(\frac{2E_k}{m}\right)^{1/2} t \quad \text{_____}(1.6)$$

The linear momentum is a constant:

$$p(t) = mv(t) = m \frac{dx}{dt} = (2mE_k)^{1/2} \quad \text{_____}(1.7)$$

Hence, if we know the initial position and momentum, we can predict all later positions and momenta exactly.

The force, F , experienced by a particle free to move in one dimension is related to its potential energy, V , by:

$$F = \frac{dV}{dx} \quad \text{_____}(1.8)$$

This relation implies that the direction of the force is towards decreasing potential energy (figure 1.4). In three dimensions:

$$F = -\nabla V \quad \text{_____}(1.9)$$

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \quad \text{_____}(1.10)$$

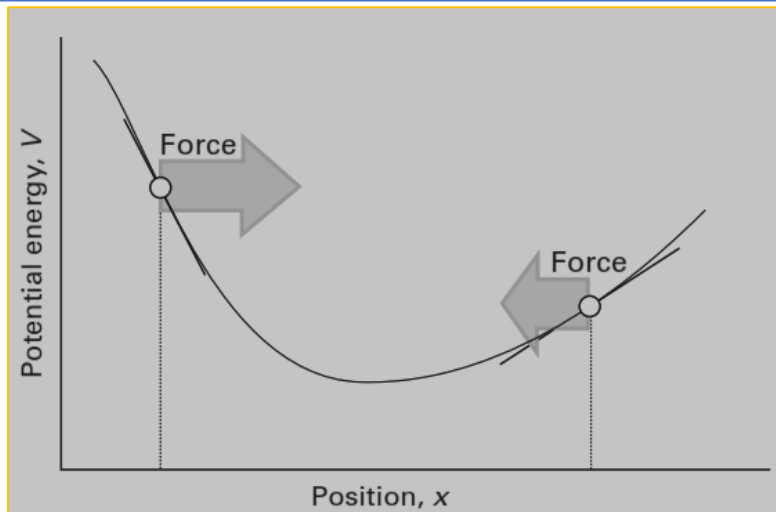


Figure: The force acting on a particle is determined by the slope of the potential energy at each point.

Newton's second law of motion states that the rate of change of momentum is equal to the force acting on the particle. In one dimension:

$$F = \frac{dp}{dt} \quad \text{_____ (1.11)}$$

Because $p = m(dx/dt)$ (equation 1.7) in one dimension, it is sometimes more convenient to write this equation as:

$$F = m \frac{d^2x}{dt^2} \quad \text{_____ (1.12)}$$

If a particle of mass m is initially stationary and is subjected to a constant force F for a time τ , then its kinetic energy increases from zero to:

$$E_k = \frac{F^2 \tau^2}{2m} \quad \text{_____ (1.13)}$$

Rotational motion

The rotational motion of a particle about a central point is described by its angular momentum, J . The angular momentum is a vector its magnitude gives the rate at which a particle circulates and its direction indicates the axis of rotation (figure. 1.5).

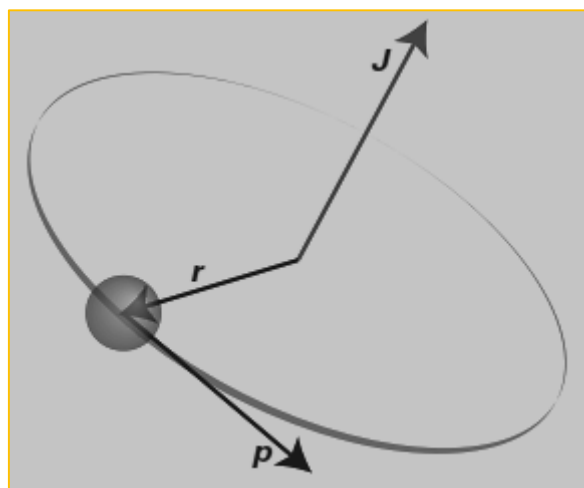


Figure: The angular momentum of a particle is represented by a vector along the axis of rotation and perpendicular to the plane of rotation. The length of the vector denotes the magnitude of the angular momentum.

The magnitude of the angular momentum, J , is given by the expression:

$$J = I\omega \quad \text{_____} (1.14)$$

Where: ω is the angular velocity of the body, its rate of change of angular position (in radians per second), and I is the moment of inertia.

Translational case	Rotational case
m	I
v	ω
p	J

For a point particle of mass m moving in a circle of radius r , the moment of inertia about the axis of rotation is given by the expression:

$$I = mr^2 \quad \text{_____}(1.15)$$

To accelerate a rotation, it is necessary to apply a torque, T , a twisting force. Newton's equation is then:

$$T = \frac{dJ}{dt} \quad \text{_____}(1.16)$$

If a constant torque is applied for a time τ , the rotational energy of an initially stationary body is increased to:

$$E_k = \frac{T^2\tau^2}{2I} \quad \text{_____}(1.17)$$

The implication of this equation is that an appropriate torque and period for which it is applied can excite the rotation to an arbitrary energy.

The harmonic oscillator

A harmonic oscillator consists of a particle that experiences a restoring force proportional to its displacement from its equilibrium position:

$$F = -kx \quad \text{_____}(1.18)$$

An example is a particle joined to a rigid support by a spring. The constant of proportionality k is called the force constant, and the stiffer the spring the greater the force constant. The negative sign in F signifies that the direction of the force is opposite to that of the displacement x (figure 1.6).

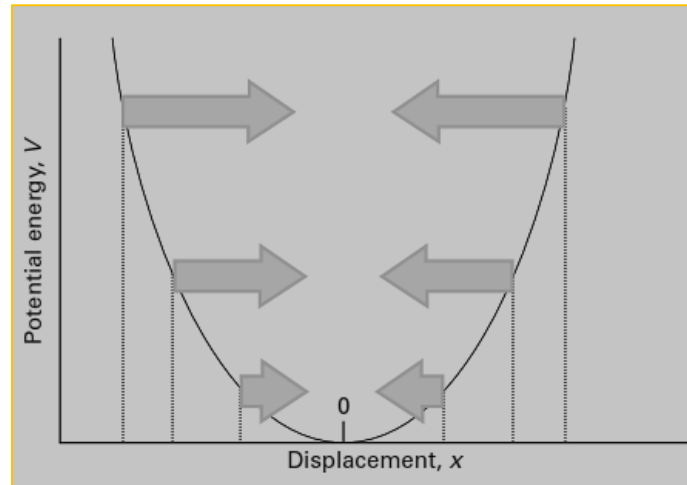


Figure: The force acting on a particle that undergoes harmonic motion. The force is directed toward zero displacement and is proportional to the displacement. The corresponding potential energy is parabolic (proportional to x^2)

The motion of a particle that undergoes harmonic motion is found by substituting the expression for the force, equation 1.18, into Newton's equation, equation 1.12. The resulting equation is:

$$-kx = m \frac{d^2x}{dt^2} \quad \text{_____ (1.19)}$$

A solution is:

$$x(t) = A \sin \alpha t$$

$$p(t) = m\alpha A \cos \alpha t$$

$$\alpha = \left(\frac{k}{m}\right)^{\frac{1}{2}}$$

These solutions show that the position of the particle varies harmonically (that is, as $\sin \alpha t$) with a frequency $\nu = \alpha / 2\pi$. They also show that the particle is stationary ($p = 0$) when the displacement, x , has its maximum value, A .

$$E_k = \frac{p^2}{2m} = \frac{(m\alpha A \cos \alpha t)^2}{2m} = \frac{1}{2} m\alpha^2 A^2 \cos^2 \alpha t \quad \text{_____} (1.21)$$

Then, because $\alpha = (k/m)^{1/2}$, this expression may be written:

$$E_k = \frac{1}{2} kA^2 \cos^2 \alpha t \quad \text{_____} (1.22)$$

The force on the oscillator is $F = -kx$, so it follows from the relation $F = -dV/dx$ that the potential energy of a harmonic oscillator is:

$$V = \frac{1}{2} kx^2 = \frac{1}{2} kA^2 \sin^2 \alpha t \quad \text{_____} (1.23)$$

The total energy is therefore:

$$E_{\text{total}} = \frac{1}{2} kA^2 \cos^2 \alpha t + \frac{1}{2} kA^2 \sin^2 \alpha t = \frac{1}{2} kA^2 \quad \text{_____} (1.24)$$

Note that $\cos^2 \alpha t + \sin^2 \alpha t = 1$

Quantum Theory

The basic principles of classical mechanics are reviewed in the previous examples which showed that classical physics:

- (i) Predicts a trajectory for particles, with precisely specified locations and momenta at each instant.

- (ii) Allows the translational, rotational, and vibrational modes of motion to be excited to any energy simply by controlling the forces that are applied.

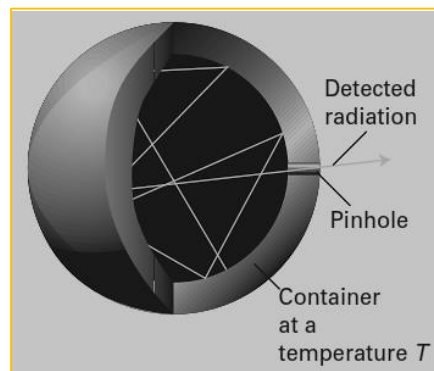
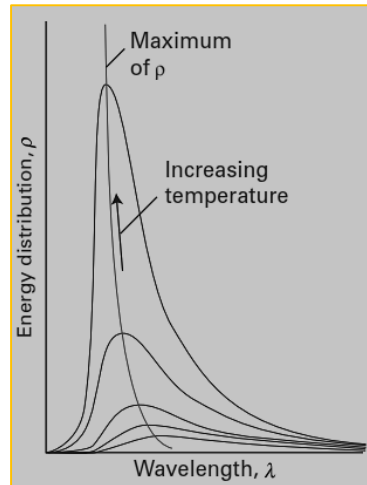
These conclusions agree with everyday experience, however, they do not extend to individual atoms and molecules. In the following, careful experiments will show that classical mechanics fails when applied to the transfers of very small energies and to objects of very small mass.

Black-body radiation

A hot object emits electromagnetic radiation. At high temperatures, the proportion of the radiation is in the visible region of the spectrum. When the temperature is raised, a higher proportion of short-wavelength blue light is generated. This behaviour is seen when a heated metal bar glowing red hot becomes white hot when heated further.

A good approximation to a black body (which is an object capable of emitting and absorbing all wavelengths of radiation uniformly) is a pinhole in an empty container maintained at a constant temperature, because any radiation leaking out of the hole has been absorbed and re-emitted inside so many times as it reflected around inside the container that it has come to thermal equilibrium with the walls

The approach adopted by nineteenth-century scientists to explain black-body radiation was to calculate the energy density, $d\vec{E}$, the total energy in a region of the electromagnetic field divided by the volume of the region ($J.m^{-3}$), due to all the oscillators corresponding to wavelengths between λ and $\lambda+d\lambda$.



This energy density is proportional to the width, $d\lambda$, of this range, and is written:

$$d\ddot{E}(\lambda, T) = \rho(\lambda, T)d\lambda \quad \text{_____} \quad (2.1)$$

where ρ , the constant of proportionality between $d\ddot{E}$ and $d\lambda$, is called the density of states ($\text{J}\cdot\text{m}^{-4}$). The total energy density in a region is the integral over all wavelengths:

$$\ddot{E}(T) = \int_0^{\infty} \rho(\lambda, T)d\lambda \quad \text{_____} \quad (2.2)$$

increasing temperature increases the energy density. The total energy within a region of volume V is this energy density multiplied by the volume:

$$E(T) = V\ddot{E}(T) \quad \text{_____} \quad (2.3)$$

Lord Rayleigh thought that the electromagnetic field as a collection of oscillators of all possible frequencies. He regarded the presence of radiation of frequency ν (and therefore of wavelength $\lambda = c/\nu$) as signifying that the electromagnetic oscillator of that frequency had been excited (figure 2-2 (a)).

The average energy of each oscillator, regardless of its frequency, is kT . On that basis, he and James Jeans arrived at the Rayleigh–Jeans law for the density of states:

$$\rho(\lambda, T) = \frac{8\pi kT}{\lambda^4} \text{ (2.4)}$$

Although the Rayleigh–Jeans law is quite successful at long wavelengths (low frequencies), it fails badly at short wavelengths (high frequencies).

The equation therefore predicts that oscillators of very short wavelength are strongly excited even at room temperature.

Heat Capacities

In 1819, Dulong and Petit were able to propose their law that ‘the atoms of all simple bodies have exactly the same heat capacity’ of about $25 \text{ J.K}^{-1} \text{ mol}^{-1}$. Dulong and Petit’s observations were done at room temperature, and it was unfortunate for them and for classical physics when measurements were extended to lower temperatures and to a wider range of materials.

Dulong and Petit’s law was easy to explain in terms of classical physics by assuming that each atom acts as a classical oscillator in three dimensions. The calculation predicted that the molar heat capacity, $C_{V,m}$, of a monatomic solid should be equal to $3R = 24.94 \text{ J.K}^{-1} \text{ mol}^{-1}$, where R is the gas constant ($R=N_A k$, N_A is Avogadro’s constant). That the heat capacities were smaller than predicted.

Einstein recognized the similarity between this problem and black-body radiation, for if each atomic oscillator required a certain minimum energy before it would actively oscillate and hence contribute to the heat capacity, then at low temperatures some would be inactive and the heat capacity would be smaller than expected. He applied Planck's suggestion for electromagnetic oscillators to the material, atomic oscillators of the solid, and deduced the following expression:

$$C_{v,m}(T) = 3Rf_E(T) \quad , \quad f_E(T) = \left\{ \frac{\theta_E}{T} \cdot \frac{e^{\theta_E/2T}}{1 - e^{\theta_E/T}} \right\}^2 \quad \text{—————(2.7)}$$

where the Einstein temperature, θ_E , is related to the frequency of atomic oscillators by $\theta_E = h\nu/k$.

In fact, the fit between plotted and experimental curves of $C_{v,m}(T)/R$ is not particularly good at very low temperatures (figure 2.3), but that can be traced to Einstein's assumption that all the atoms oscillated with the same frequency. When this restriction was removed by Debye, he obtained:

$$C_{v,m}(T) = 3Rf_D(T) \quad , \quad f_D(T) = 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad \text{—————(2.8)}$$

where the Debye temperature, θ_D , is related to the maximum frequency of the oscillations that can be supported by the solid. This expression gives a very good fit with observation.

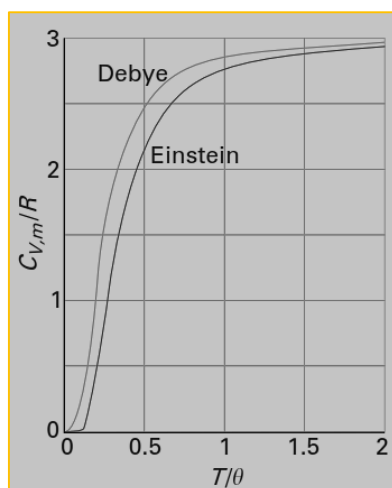


Figure: The Einstein and Debye molar heat capacities. The symbol θ denotes the Einstein and Debye temperatures, respectively.

The importance of Einstein's contribution is that it complemented Planck's. Planck had shown that the energy of radiation is quantized; Einstein showed that matter is quantized too. Quantization appears to be universal.

Atomic and molecular spectra

The most compelling and direct evidence for the quantization of energy comes from spectroscopy, the detection and analysis of the electromagnetic radiation absorbed, emitted, or scattered by a substance. The record of light intensity transmitted or scattered by a molecule as a function of frequency (ν), wavelength (λ), or wavenumber ($\tilde{\nu} = \nu/c$) is called its spectrum.

A typical atomic spectrum and a typical molecular spectrum both is that radiation is emitted or absorbed at a series of discrete frequencies. This observation can be understood if the energy of the atoms or molecules is also confined to discrete values, for then, energy can be discarded or absorbed only in discrete amounts. Then, if the energy of an atom decreases by ΔE , the energy is carried away as radiation of frequency ν , and an emission 'line', a sharply defined peak, appears in the spectrum. We say that a molecule undergoes a spectroscopic transition, a change of state, when the Bohr frequency condition.

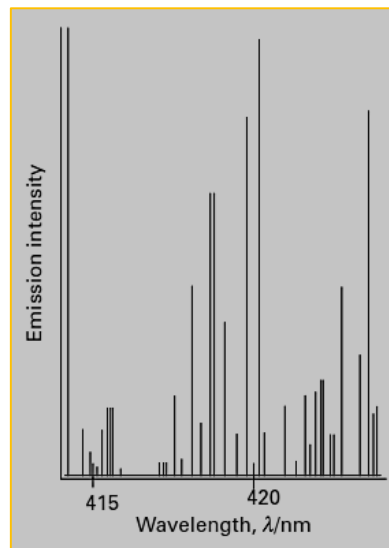


Figure: A region of the spectrum of radiation emitted by excited iron atoms consists of radiation at a series of discrete wavelengths (or frequencies).

Wave-Particle Duality

As established that the energies of the electromagnetic field and of oscillating atoms are quantized. In the following, two experimental evidence that led to the revision of two basic concepts concerning natural phenomena will be given.

One experiment shows that electromagnetic radiation, (which classical physics treats as wave-like), also displays the characteristics of particles. Another experiment shows that electrons (which classical physics treats as particles), also display the characteristics of waves. So, particles taking on the characteristics of waves, and waves the characteristics of particles.

The particle character of electromagnetic radiation

The observation that electromagnetic radiation of frequency ν can possess only the energies $0, h\nu, 2h\nu, \dots$ suggests that it can be thought of as consisting of $0, 1, 2, \dots$ particles, each particle having an energy $h\nu$. Then, if one of these particles is present, the energy is $h\nu$, if two are present the energy is $2h\nu$, and so on.

These particles of electromagnetic radiation are now called photons. The observation of discrete spectra from atoms and molecules can be pictured as the atom or molecule generating a photon of energy $h\nu$ when it discards an energy of magnitude ΔE , with $\Delta E = h\nu$.

So far, the existence of photons is only a suggestion. Experimental evidence for their existence comes from the measurement of the energies of electrons produced in the photoelectric effect. As in the following:

The photo electric effect is the ejection of electrons from metals when they are exposed to ultraviolet radiation. The experimental characteristics of the photoelectric effect are as follows.

- No electrons are ejected, regardless of the intensity of the radiation, unless its frequency exceeds a threshold value characteristic of the metal.
- The kinetic energy of the ejected electrons increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
- At low light intensities, electrons are ejected immediately if the frequency is above the threshold.

These observations strongly suggest that the photoelectric effect depends on the ejection of an electron when it is involved in a collision with a particle-like projectile that carries enough energy to eject the electron from the metal.

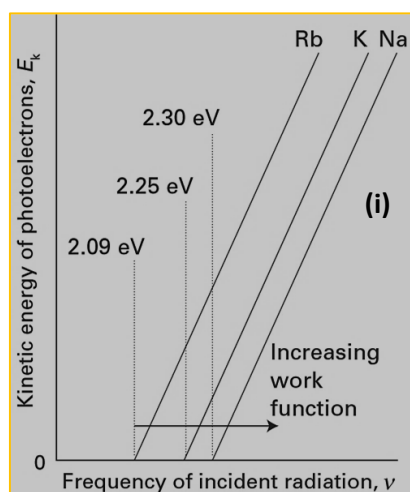


Figure: The relation between the frequency and the kinetic energy of the ejected electrons in photoelectric effect experiment.

If we suppose that the projectile is a photon of energy $h\nu$, where ν is the frequency of the radiation, then the conservation of energy requires that the kinetic energy of the ejected electron ($\frac{1}{2} m_e v^2$) should obey

$$\frac{1}{2} m_e v^2 = h\nu - \Phi \quad \text{_____} (2.9)$$

In this expression Φ is a characteristic of the metal called its work function, the energy required to remove an electron from the metal to infinity, the analogue of the ionization energy of an individual atom or molecule.

A practical application of equation (2.9) is that it provides a technique for the determination of Planck's constant, for the slopes of the are all equal to h .

The wave character of particles

Although contrary to the wave theory of light that the light consists of particles, no significant efforts, however, had taken the view that matter is wave-like. The possibility that the matter is wave-like has been established since 1925 when crucial experiment was performed by Clinton Davisson and Lester Germer, who observed the diffraction of electrons by a crystal. Diffraction is the interference caused by an object in the path of waves. Depending on whether the interference is constructive or destructive, the result is a region of enhanced or diminished intensity of the wave. The polycrystalline sample works as a diffraction grating via the ordered planes of atoms.

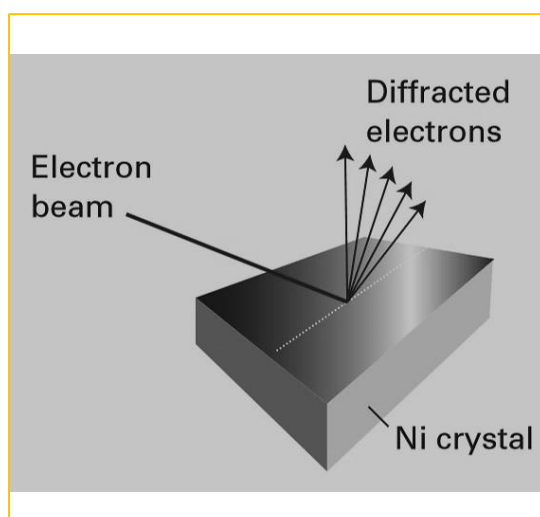


Figure: Davisson-Germer experiment which performed on a nickel crystal. The electrons of the scattered electron beam show a diffraction which follow a similar behaviour of waves.

At almost the same time, G.P. Thomson, showed that a beam of electrons was diffracted when passed through a thin gold foil.

The Davisson–Germer experiment shows clearly that particles have wave-like properties, and the diffraction of neutrons is a well-established technique for investigating the structures and dynamics of condensed phases.

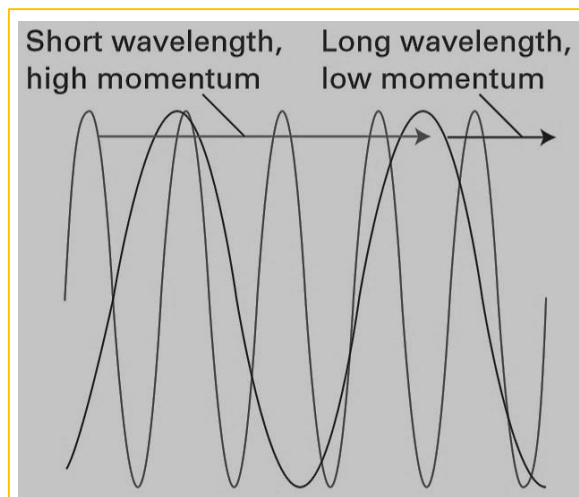


Figure: An illustration of the de Broglie relation between momentum and wavelength. A particle with high momentum has a wavefunction with a short wavelength, and vice versa.

Selected Topics in Quantum Theory

Bohr Model of the Atom

Before the discovery of quantum mechanics, Bohr applied the concept of quantization to the problem of the structure of the hydrogen atom. He accepted the Rutherford model of the nuclear atom and asserted that:

- An electron remains in a stationary state, an orbit around the central nucleus, until it undergoes a transition.
- A transition between stationary states differing in energy by ΔE is accompanied by the emission or absorption of radiation with a frequency ν determined by the condition $\Delta E = h\nu$. The latter assertion is the Bohr frequency condition.
- The permitted stationary states may be found by balancing the Coulombic attractive force between the electron and nucleus against the centrifugal effect of the angular momentum of the electron in its orbit.

Finally, Bohr brought in Planck's constant (specifically, as $\hbar = h/2\pi$ and introduced a quantization postulate:

- The only orbital angular momenta permitted are integral multiples of \hbar .

When Bohr carried through the calculation on the basis of this model, he deduced that the energies of the electron in its permitted orbits (figure 3.1(a)) are:

$$E = -\frac{hcR}{n^2}, \quad n = 1, 2, 3, \dots \quad (3.1)$$

Where

$$R = \text{Rydberg Constant} = 109737 \text{ cm}^{-1}$$

This expression is in excellent agreement with experiment (and in exact agreement with the solutions of the Schrödinger equation, which came later). In particular, It reproduces the positions of all the series in the spectrum of atomic hydrogen.

The refinement of Bohr's initially promising model proceeded in two steps. The first took into account the fact that the orbital motion occurred about the centre of mass of the system rather than about the nucleus itself. This refinement merely involved replacing the mass of the electron in the Bohr formula by the reduced mass (μ) of the proton and the electron.

The second improvement was introduced Arnold Sommerfeld in 1915. In the generalization of the Bohr theory, known as the Bohr-Sommerfeld atom, the orbits are allowed to be elliptical (figure 3-1(b)). The eccentricity (the degree of ellipticity) of the elliptical orbits is determined by a quantum number k , the azimuthal quantum number. The energy of an orbit is independent of its eccentricity.

Note that the Bohr radius a_0 , is the radius of the lowest energy orbit in the now outdated Bohr model of the hydrogen atom. It is defined as:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad , \quad a_0 = 0.529177249 \text{ \AA} \quad \text{_____} (3.2)$$

According to the quantum-mechanical picture of the atom, the most probable radius at which an electron will be found in the ground state (the 1s orbital) of the hydrogen atom is equal to a_0 . The Bohr radius is a convenient unit of distance when discussing the structures of atoms and molecules.

Based on Plank's postulations of quantization, Sommerfeld put some steps to treat some physical systems. These rules can be list as follows:

1. Describing classical equations of the motion of the system under investigation.

2. Defining the action integral (\oint) as a step towards obtaining quantization properties of the system.

$$\oint P_k dq_k = n_k h \quad , \quad n_k = \text{a quantum number} \quad \text{_____} \quad (3.3)$$

3. Solving the action integral of the system for complete and repetitive motions only by the aid of geometrical coordinates information of the system.

Using the above steps, Sommerfeld was able to solve the energetic and kinetic problems of some systems as in the following:

Particle in a Box

System description:

- The system consists of a particle (m) moving in a region of space. The potential energy of the particle is zero ($E_{\text{pot}}(\text{or } V) = 0$) in any direction of x , y and z coordinate, but equals to infinite at the edges (walls) of the region.
- The box may be one-dimensional, in which the particle is free to move between 0 and a along the x axis.
- a , b and c are the points located at the ends of x , y and z coordinate of the box, respectively.
- During the motion of the particle in the box, it is impossible to proceed (or pass) the walls of the box but rather the particle reflects its movement (using opposite direction and opposite momentum (takes negative sign)).
- The motion, the collision and the reflection of the particle for this system, is called elastic collision.

Mathematical Solution:

$$\oint p_x dx = \int_0^a p_x dx + \left[- \int_a^0 p_x dx \right] = n_x h \quad \text{_____} (3.4)$$

$$= 2ap_x = n_x h \quad \text{_____} (3.8)$$

$$\therefore p_x = \frac{n_x h}{2a},$$

$$E_{\text{total}} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \quad \text{_____} (3.11)$$

From equations 3.9 and 3.11 we can obtain:

$$E_{\text{total}} = \frac{n_x^2 h^2}{8 m a^2} + \frac{n_y^2 h^2}{8 m b^2} + \frac{n_z^2 h^2}{8 m c^2} \quad \text{_____} (3.13)$$

When $a = b = c$:

$$E_{\text{total}} = \frac{n^2 h^2}{8 m a^2} \quad \text{_____} (3.14)$$

An example for this kind of systems is an electron moves in a conjugated system.

This allows us to calculate energy difference of electron excitation, i.e, the energy difference (ΔE) between two electronic quantum numbers.

Rigid Rotator

System description:

- The simplest rigid rotator consists of two point-masses (a and b) which are held apart at a fixed distance perfectly rigid and weightless bond. This ideal is approached quite closely by a diatomic molecule in its ground vibrational state.
- The system is mathematically equivalent to a particle of mass μ moving on a surface. If the rotator is not acted on by any external forces, we can take the potential energy (V) to be equal to zero on the surface.

Mathematical Solution:

a) Some simplifications

$$J = I \omega \quad \text{_____} (1.14)$$

$$\omega = \frac{J}{I} ; \quad \omega^2 = \frac{J^2}{I^2} \quad \text{_____} (1.14)$$

$$E_k = \frac{1}{2} I \omega^2 \quad \rightarrow \quad E_k = \frac{J^2}{2 I} \quad \text{_____} (1.17)$$

- Here J is the angular momentum, I is the moment of inertia, ω the angular velocity, and μ the reduced mass of the system, r_i the distance between a and b (bond length), r_a and r_b are the distance from the centre of mass to particle a and b, respectively.

b) Sommerfield's treatment:

$$\oint_0^{2\pi} J_\varphi d\varphi = k h \quad \text{_____} (3.4)$$

k is the rotational quantum number, $k = 0, 1, 2, 3, \dots$

$$\oint_0^{2\pi} J_\varphi d\varphi = J_\varphi \varphi \Big|_0^{2\pi} = k h \quad \text{_____} (3.5)$$

$$J_\varphi = \frac{k h}{2\pi} = k \hbar \quad \text{_____} (3.6)$$

$\therefore J_\varphi$ quantised since it depends on a quantum number k .

$$E_{\text{total}} = E_{\text{kinetic}} = E_{\text{rotation}} \quad \text{_____} (3.10)$$

$$E_{\text{total}} = \frac{J_\varphi^2}{2I} \quad \text{_____} (3.11)$$

$$E_{\text{total}} = \frac{\left(\frac{k h}{2\pi}\right)^2}{2I} \rightarrow E_{\text{total}} = \frac{k^2 h^2}{4\pi^2} \times \frac{1}{2I} \quad \text{_____} (3.11)$$

$$E_{\text{total}} = \frac{k^2 \hbar^2}{2I} \quad \text{_____} (3.11)$$

$$\therefore E_{\text{total}} \sim \frac{1}{I}, \quad \rightarrow \quad E_{\text{total}} \sim k^2$$

One-Dimensional Harmonic Oscillator

Mathematical Solution:

a) Some simplifications

$$x(t) = A \sin \alpha t$$

$$p(t) = m\alpha A \cos \alpha t$$

$$\alpha = \left(\frac{k}{m}\right)^{\frac{1}{2}}$$

$$v = \frac{1}{2\pi} \times \sqrt{\frac{k}{m}}$$

$$k = 4\pi^2 v^2 m$$

$$\alpha = \sqrt{\frac{4\pi^2 v^2 m}{m}} \rightarrow \alpha = 2\pi v$$

Note that, since:

$$p(t) = mv(t)$$

Therefore;

$$v(t) = (2\pi v)A \cos(2\pi v)t$$

b) Sommerfield's treatment:

$$\oint_{t=0}^{t=1/v} p_x dx = n h \rightarrow \oint_{t=0}^{t=1/v} mv dx = n h \text{_____} (3.4)$$

n is the vibrational quantum number of harmonic oscillator, $n = 0, 1, 2, 3, \dots, \infty$

$$dx = \frac{dx}{dt} dt \rightarrow dx = v dt \text{_____} (3.4)$$

$$\oint_{t=0}^{t=1/v} mv^2 dt = n h \text{_____} (3.4)$$

$$\oint_{t=0}^{t=\frac{1}{v}} m((2\pi\nu)A \cos(2\pi\nu)t)^2 dt = n h$$

$$\cos^2(X) = \frac{1}{2}(1 + \cos(2X)); X = \alpha t = 2\pi\nu t$$

$$2m\pi^2\nu^2 A^2 \left(\frac{1}{v} - 0\right) + 2m\pi^2\nu^2 A^2 \left(\sin\left(2\pi\nu \times \frac{1}{v}\right) - \sin(2\pi\nu \times 0)\right) = n h$$

$$2m\pi^2\nu^2 A^2 \frac{1}{v} - 0 + 2m\pi^2\nu^2 A^2 (\sin(2\pi) - \sin(0)) = n h$$

$$2m\pi^2\nu A^2 + 2m\pi^2\nu^2 A^2 (0 - 0) = n h$$

$$2m\pi^2\nu A^2 = n h \rightarrow A = \sqrt{\frac{n h}{2m\pi^2\nu}}$$

$$E_{\text{total}} = E_{\text{kinetic(total)}} + E_{\text{potential(total)}}$$

$$E_{\text{total}} = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

$$E_{\text{total}} = \frac{(m(2\pi\nu)A \cos(2\pi\nu)t)^2}{2m} + \frac{1}{2}(4\pi^2\nu^2 m) \times (A \sin(2\pi\nu)t)^2$$

$$E_{\text{total}} = \frac{(m (4\pi^2 v^2) A^2 \cos^2(2\pi v)t)}{2} + \frac{1}{2} (4\pi^2 v^2 m) \times (A^2 \sin^2(2\pi v)t)$$

$$E_{\text{total}} = 2m\pi^2 v^2 A^2 (\cos^2(2\pi vt) + \sin^2(2\pi vt))$$

$$E_{\text{total}} = 2m\pi^2 v^2 A^2 \rightarrow E_{\text{total}} = 2m\pi^2 v^2 \left(\sqrt{\frac{n h}{2m\pi^2 v}} \right)^2$$

$$E_{\text{total}} = 2m\pi^2 v^2 A^2 \rightarrow E_{\text{total}} = 2m\pi^2 v^2 \frac{n h}{2m\pi^2 v} \rightarrow E_{\text{total}} = n h v$$