

Classical Physics

- 1) precise trajectories for particles – simultaneous specification of position and momentum
- 2) any amount of energy can be exchanged – implies the various modes of motion (translational, vibrational, rotational) can have continuous energies

Light

electromagnetic field

frequency ν , wavelength λ , speed in vacuum $c = 3 \times 10^8 \text{ ms}^{-1}$.

$$\lambda\nu = c$$

wavenumber, $\bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$

Black Body

An object capable of emitting/absorbing all frequencies of radiation uniformly

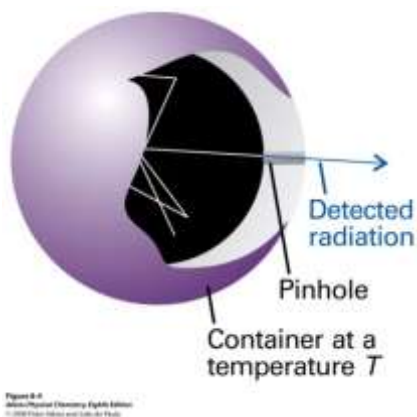


Figure 1.1: Representation of a blackbody

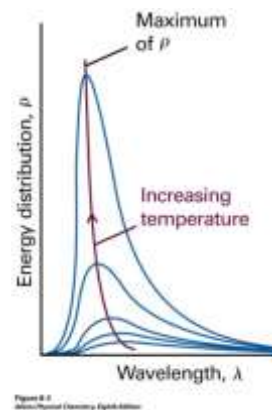


Figure 1.2: Change in the emission maxima from the blackbody as a function of temperature

Rayleigh-Jeans Law

Classical viewpoint – electromagnetic field is a collection of oscillators of all frequencies

Equipartition principle – average energy of each oscillator = kT

$$dE = \rho d\lambda \quad \rho = 8\pi kT/\lambda^4$$

Ultraviolet catastrophe

As wavelength decreases, the energy density increases to infinity

Planck's hypothesis

All possible frequencies are not allowed – energy of each oscillator is restricted to discrete values

Quantization, $E = nh\nu$ $n = 0, 1, 2 \dots$ where h is the Planck constant ($= 6.626 \times 10^{-34}$ J.s)

$$dE = \rho d\lambda \quad \rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

Short wavelengths: $hc/\lambda kT \gg 1 \therefore e^{hc/\lambda kT} \rightarrow \infty$ faster than $\lambda^5 \rightarrow \infty$. So no UV catastrophe! The hypothesis fits well with the observed data. (Actually the value of h was determined by fitting)

Why this works?

Classical – heat black body – all oscillators with all frequencies excited – the excitation of high frequencies leads to UV catastrophe

Planck – oscillators can be excited only if energy $h\nu$ is available. Higher frequencies implies higher energies which is too large to supply by heating the walls of the blackbody

Heat Capacities

Dulong and Petit Law: Measured value for solids = $25 \text{ J K}^{-1} \text{ mol}^{-1}$

Mean energy of an atom as it oscillates about its mean position = kT for each direction (equipartition principle). This gives a total of $3kT$ for the three directions. For a mole, $U_m = 3RT$

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = 3R = 24.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

At lower temperatures, molar heat capacities are lower than $3R$.

Einstein's explanation (1905): Each atom oscillates about its equilibrium position with frequency ν . Used Planck's hypothesis – energy of oscillation equals $nh\nu$. This gives,

$$U_m = \frac{3N_A h\nu}{e^{h\nu/kT} - 1}$$

Differentiate w.r.t. T to get $C_{V,m} = 3Rf$ $f = \left(\frac{\theta_E}{T} \right)^2 \left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T} - 1} \right)^2$

Einstein temperature $\theta_E = h\nu/k$ corresponds to the frequency of oscillation.

At high temperatures ($\theta_E \ll T$), expand $f = \left(\frac{\theta_E}{T} \right)^2 \left\{ \frac{1 + \theta_E/2T + \dots}{(1 + \theta_E/T + \dots) - 1} \right\}^2 \approx 1$ ignoring the higher terms which gives the high temperature result $C_{V,m} = 3R$

At low temperatures ($\theta_E \gg T$), $f \approx \left(\frac{\theta_E}{T} \right)^2 \left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}} \right)^2 = \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T}$ Exponential decays faster to zero than $1/T$ goes to infinity.

Reason: At low temperatures fewer atoms have the energy to oscillate.

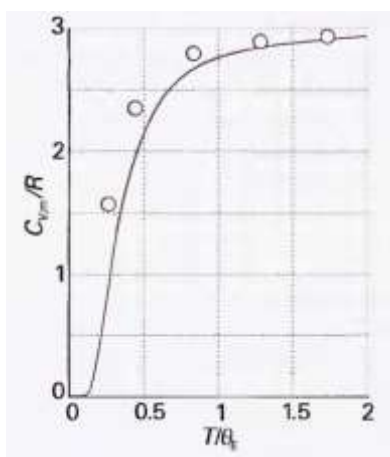


Figure 1.3: Temperature dependence of heat capacities

Further: All atoms do not oscillate with the same frequency. There is a distribution of frequencies ranging between 0 to ν_D . Read Debye's formula for the heat capacities.

Atomic and Molecular Spectra

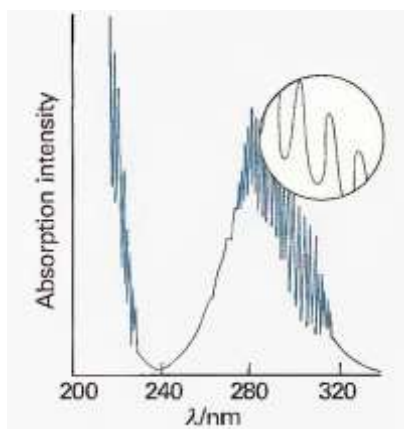


Figure 1.4: Molecular spectrum of SO_2 .

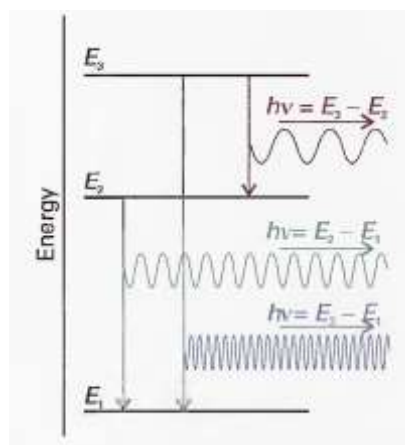


Figure 1.5: Energy levels in a molecule

Radiation is absorbed/emitted in discrete steps and not continuously. This suggests the energy levels in an atom/molecule are quantized. The frequency of radiation absorbed/emitted is given by the Bohr frequency condition

$$\Delta E = h\nu$$

Wave-particle duality

Atomic and molecular spectra show that EM radiation of frequency ν can possess only the energies $0, h\nu, 2h\nu \dots$ suggesting the radiation is composed to $0, 1, 2 \dots$ number of particles called photons.

Photoelectric effect

Ejection of electrons from a metal surface upon irradiation with light

- 1) No electrons are ejected unless the frequency of radiation is higher than a threshold value (work function). The intensity of radiation does not matter
- 2) The K.E. of ejected electron varies linearly with the frequency of the light used. It is independent of the intensity
- 3) All that the intensity does is to change the number of electrons ejected, i.e. the current

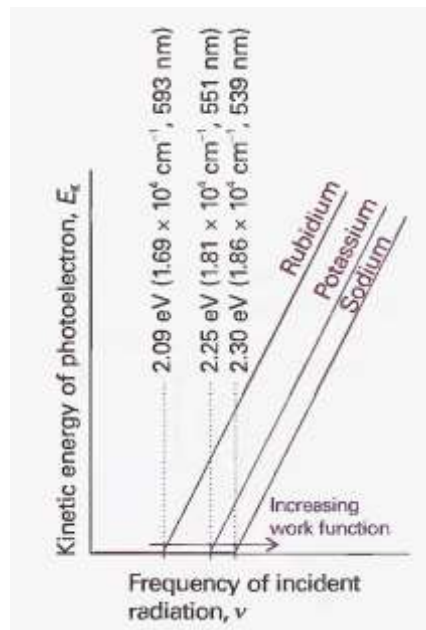


Figure 1.7: The photoelectric effect

Electron collides with a particle carrying sufficient energy required to eject it.

$$KE = \frac{1}{2}mv_e^2 = h\nu - \phi$$

Wave character of particles:

Davisson and Germer (1927) – diffraction of electrons by a crystal. The basis of TEM and SEM. Diffraction requires constructive and destructive interference of waves. Hence, particles must possess wavelike character.

de Broglie relationship (1924): $\lambda = h/p$. A very fundamental statement.

Hydrogen Spectra

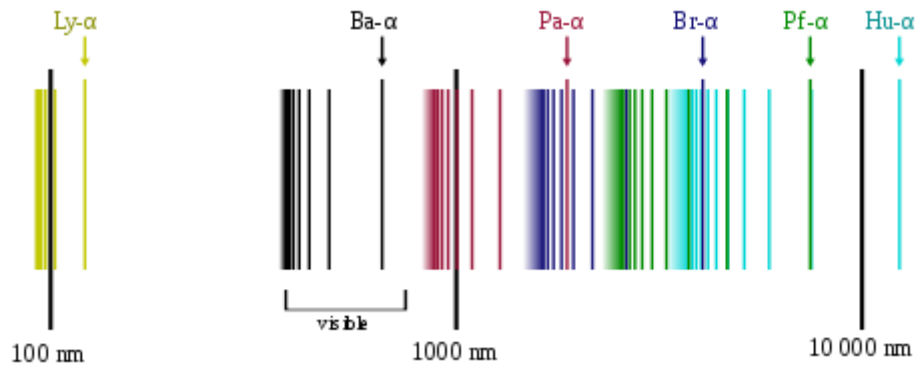


Figure 1.6: Emission spectrum of hydrogen atom on a log scale

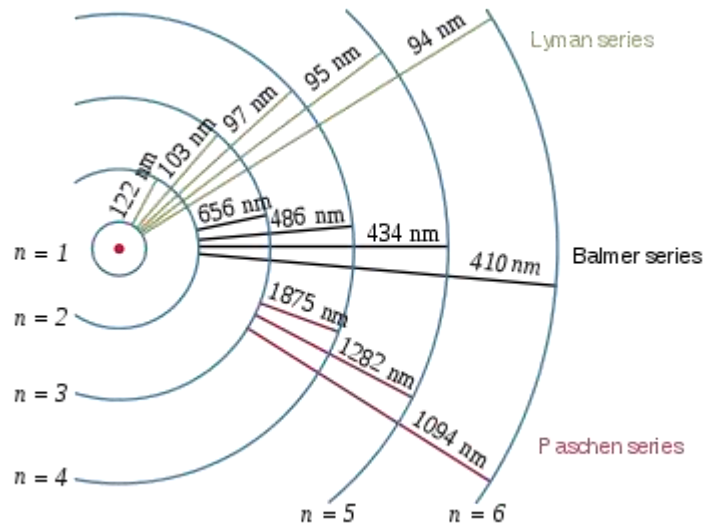


Figure 1.7: Atomic interpretation of the hydrogen spectrum

Rydberg Formula:

$$\bar{\nu} = \frac{1}{\lambda} = 109680 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \quad (n_2 > n_1)$$

Bohr Theory for H-atom: Electron revolving around the nucleus

Coulomb's Law $f = e^2/4\pi\epsilon_0 r^2$ $\epsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$

Centrifugal force $f = m_e v^2/r$

Bohr's assumption – integral wavelengths fit the circular orbit for constructive interference

$$2\pi r = n\lambda$$

which, on using the de Broglie equation gives

$$m_e v r = \frac{n h}{2\pi} = n \hbar$$

Equate the two forces and substitute the above expression for the first Bohr radius, a_0

$$a_0 = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2} = \frac{4\pi\epsilon_0 \hbar^2 n^2}{m_e e^2} = \frac{4\pi(8.85419 \times 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^2)(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(9.109 \times 10^{-31} \text{ kg})(1.6022 \times 10^{-19} \text{ C})^2} = 52.92 \text{ pm}$$

$$\text{Total energy of the electron} = \text{KE} + \text{PE} = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\text{Using the above equations, } E = -\frac{e^2}{8\pi\epsilon_0 r}$$

$$\text{And substituting for } r, E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2}$$

And transitions between two states n_1 and n_2 will be given by

$$\Delta E = \frac{m_e e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = h\nu$$

or

$$\bar{\nu} = \frac{m_e e^4}{8\epsilon_0^2 ch^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

and the Rydberg constant R_∞ is given by $\frac{m_e e^4}{8\epsilon_0^2 ch^3}$