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 $c = 3 \times 10^8\ ms^{-1}$.

$$\lambda\nu = c$$

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

Black Body

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

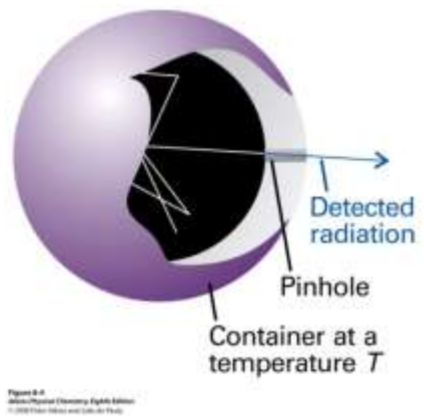

Figure 1.1: Representation of a blackbody

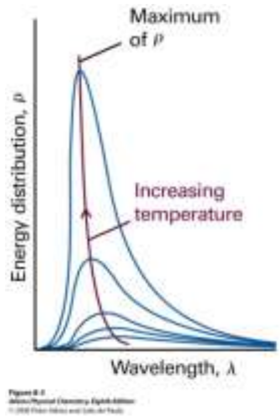

Figure 1.2: Change in the emission maxima from the blackbody as a function of temperature

Rayleigh-Jeans Law

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

Equipartition principle – average energy of each oscillator = kT

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

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

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

Short wavelengths: $hc/\lambda kT \gg 1 \therefore e^{hc/\lambda kT} \to \infty$ faster than $\lambda^5 \to \infty$. 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 $= 25\ \mathrm{J\ K^{-1}\ mol^{-1}}$

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

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

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 $C_{V,m} = 3Rf \quad f = \left(\frac{\theta_E}{T}\right)^2 \left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T - 1}}\right)^2$

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

At high temperatures ($\theta_E \ll T$) , expand $f = \left(\frac{\theta_E}{T}\right)^2 \left\{\frac{1 + \theta_E/2T + \ldots}{(1+\theta_E/T + \cdots) - 1}\right\}^2 \approx 1$ 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.

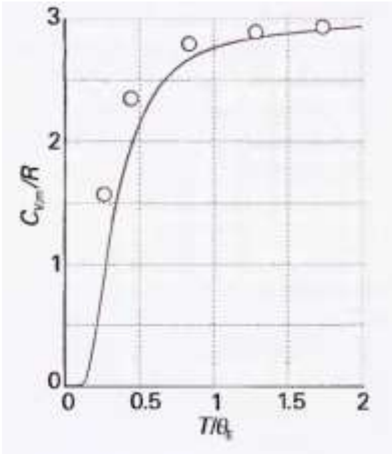

Figure 1.3: Temperature dependence of heat capacities

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

Atomic and Molecular Spectra

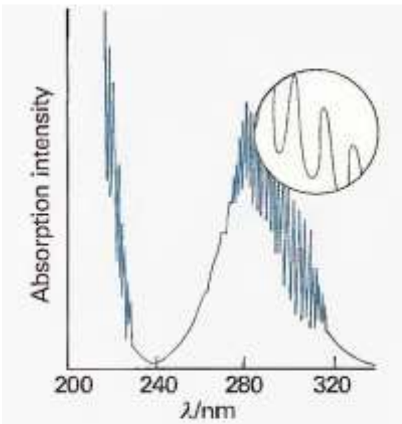

Figure 1.4: Molecular spectrum of SO_2.

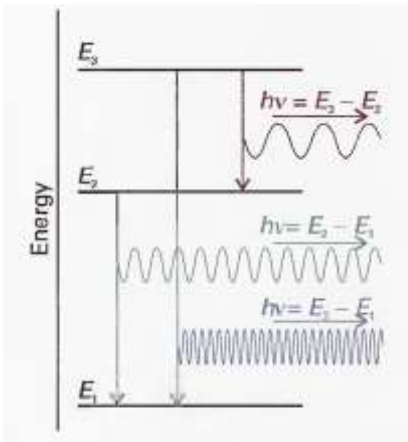

Figure 1.5: Energy levels in a molecule

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 $0, h\nu, 2h\nu$ ... suggesting the radiation is composed to 0, 1, 2 ... 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

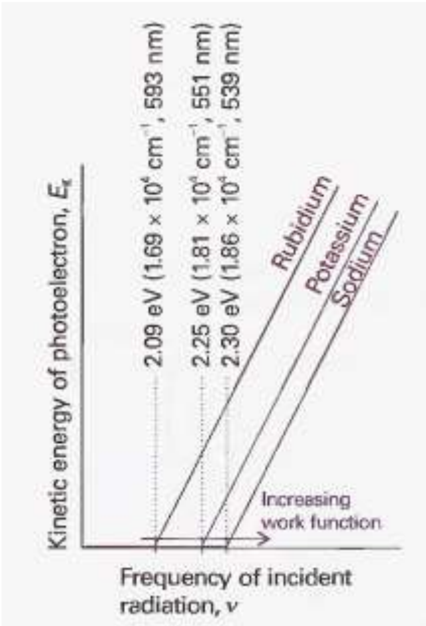

Figure 1.7: The photoelectric effect

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 (1952) – 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

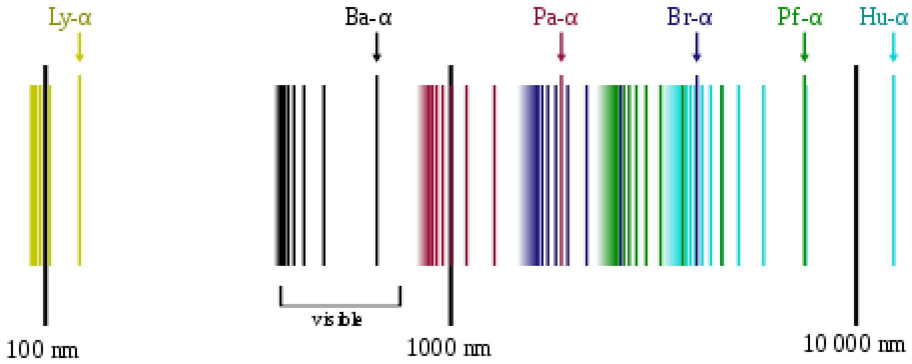

Figure 1.6: Emission spectrum of hydrogen atom on a log scale

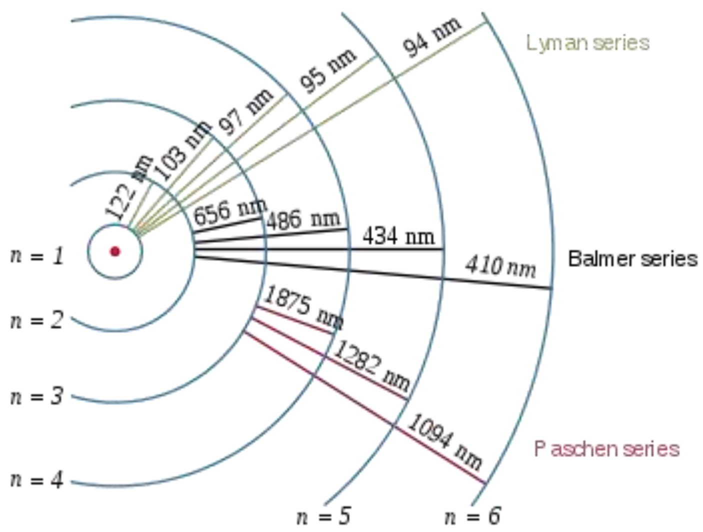

Figure 1.7: Atomic interpretation of the hydrogen spectrum

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 $f = e^2/4\pi\epsilon_0 r^2$ $\qquad$ $\epsilon_0 = 8.85419 \times 10^{-12}\ \text{C}^2.\text{N}^{-1}.\text{m}^{-2}$

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

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

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

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

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

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

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

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

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