The Quantum Theory of Atoms and Molecules

The breakdown of classical physics:

Quantisation of Energy

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Classical mechanics

Classical Mechanics Laws – Determinism

1. Can predict a precise *trajectory* for particles, with precisely specified locations and momenta at each instant;

Example: If a particle of mass m, initially at rest at position x_0 , is subject to a time varying force of the form $F = \alpha t$, derive an expression for the particle's position at some later time t.

2. Classical Mechanics allows the translation, rotation and vibrational modes of motion to be excited to **_any_** energy simply by controlling the forces applied.
i.e. Energy is *continuous.*

Okay for planets, cars, bullets, etc. but **_fails_** when applied to transfers of very small quantities of energy and to objects of very small masses (atomic/molecular level, light interaction).

Quantum theory

Energy is **not** continuous

e.g. atomic line spectra

Example: On the left is the image is a helium spectral tube excited by means of a 5kV transformer. At the right are the spectral lines through a 600 line/mm diffraction grating. Helium wavelengths (nm): (s = strong, m = med, w = weak)

UV	438.793 w
↑	443.755 w
	447.148 s
	471.314 m
Blue	492.193 m
Yellow	501.567 s
Yellow	504.774 w
Red	587.562 s
Dark red	667.815 m
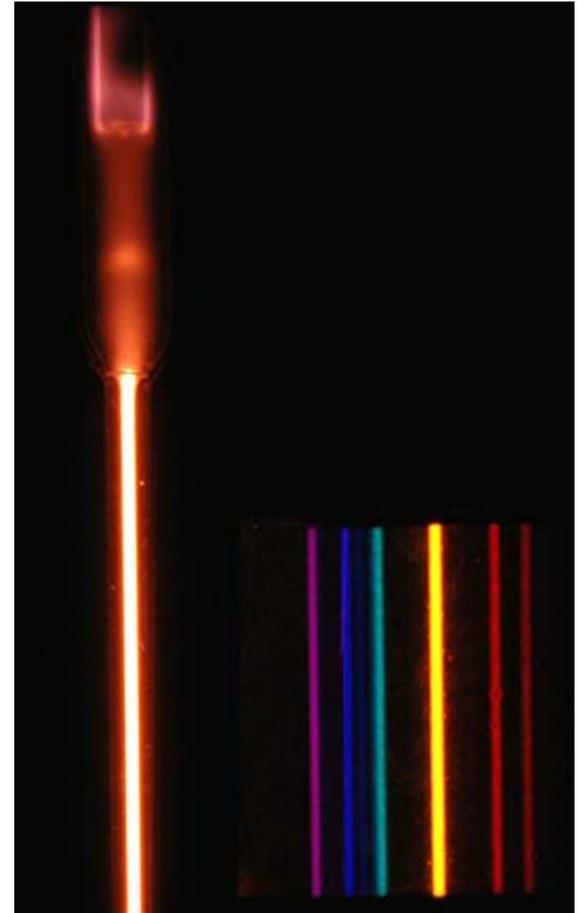
The classical atom

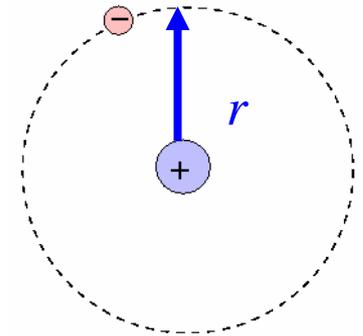**H atom:** An electron with mass m_e moving in a circular orbit of radius r around a single proton.

Electrostatic attraction provides the centripetal force required to keep the electron in orbit:

$$F = \frac{m_e\, v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

The kinetic energy, *KE*, is

$$KE = \frac{1}{2} m_e v^2 = \frac{e^2}{8\pi\varepsilon_0 r}$$

$$E_{tot} = KE + PE = -\frac{e^2}{8\pi\varepsilon_0 r}$$

In agreement with the observation that atoms are stable – $E_{tot} < 0$.

But *disagrees* with electromagnetic theory which predicts that accelerated electric charges radiate energy in the form of electromagnetic waves.

An electron on a curved path is accelerated and therefore should continuously lose energy, spiralling into the nucleus!

The Bohr condition

Bohr postulate: Electron is only permitted to be in orbits that possess an angular momentum, L, that is an integer multiple of $h/2\pi$:

$$L = m_e vr = n\hbar$$

NB. **L is quantised!**

(see atomic orbitals later in course!)

Hence

$$KE = \frac{1}{2} m_e v^2 = \frac{n^2 h^2}{8\pi^2 m_e r^2}$$

Comparing our two expressions for the kinetic energy yields:

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi\, m_e e^2}$$

The above result predicts that the orbital radius should increase as n increases where n is known as the *principal quantum number*. Hence the total energy, $E_{tot}(n)$, is

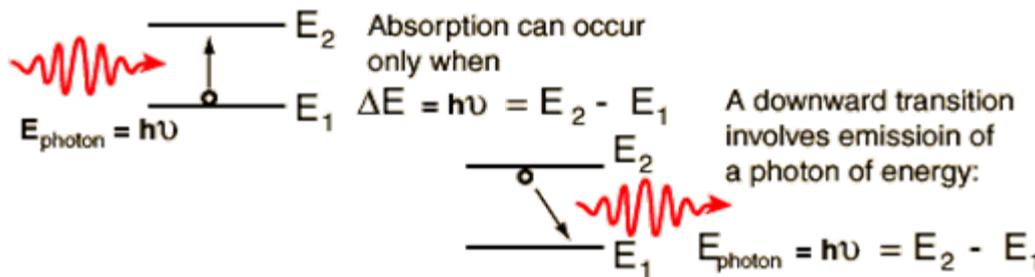$$E_{tot}(n) = -\frac{m_e e^4}{8\,\varepsilon_0^2\, h^2 n^2} = -\frac{\mathfrak{R}}{n^2}$$

where $\mathfrak{R}$ is known as the *Rydberg constant.*

* To be strictly accurate we should not use m_e but the reduced mass of the electron-proton system, μ. $\mu = \dfrac{m_e m_p}{(m_e + m_p)} \approx m_e$

Bohr model

Quantisation of L limits the electron's motion to discrete energy levels (**quantum states**) with energy $E(n)$.

Radiation is only absorbed/emitted when a quantum jump takes place:
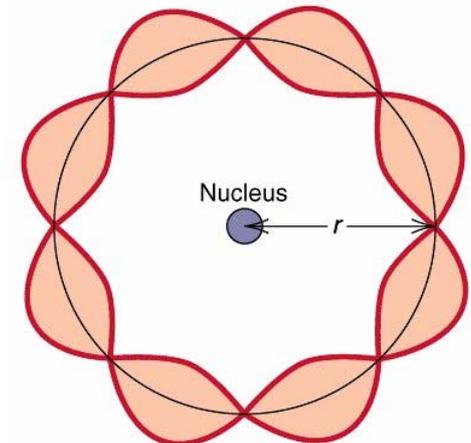

Transition energies are:

$$\Delta E = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Same as the Rydberg formula $\Rightarrow$ Bohr's theory is in agreement with experimentally observed spectra.

Combining de Broglie's relation (see later) with Bohr condition shows that the circumference of the orbit must be an integer number of wavelengths, λ.

$$mvr = pr = \frac{nh}{2\pi}$$

$$2\pi\, r = \frac{nh}{p} = n\lambda$$

An example – from Prelims (2009)

9. (a) (i) Explain how the de Broglie expression relating momentum to wavelength and the quantization condition on circular orbits leads to the quantization of angular momentum, L, as $L = n\hbar$, where n is an integer. [4]

(ii) In the Bohr theory of the hydrogen atom the energy, E, of the electron orbiting the nucleus is the sum of the kinetic and potential energies. Assuming an infinitely heavy nucleus, write down the expression for the electron energy, expressing the kinetic energy as a function of the angular momentum. [2]

(iii) Assuming the quantization condition for the angular momentum, minimise the total energy as a function of the electron radius, r. Hence (or otherwise) show that the stationary radius and energy are

$$r_n = \left(\frac{n^2 \hbar^2}{m_e} \right) \left(\frac{4\pi\varepsilon_0}{e^2} \right)$$

and

$$E_n = -\frac{1}{2} \left(\frac{e^2}{4\pi\varepsilon_0 r_n} \right)$$

respectively. Here, m_e and e are the mass and charge of the electron, respectively, and n is the principal quantum number. [6]

Failures of the Bohr model

Bohr's postulate encapsulates wave-particle duality: *Electron's orbit must contain an integral number of de Broglie wavelengths*: $n\lambda = 2\pi r_n$ $(n = 1, 2, 3,\ldots)$

Bohr theory can predict the size of orbits:

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi m_e e^2}$$

For $n = 1$, $r = 52.9$ pm $= a_0$ **Bohr radius H-atom.**

Problems

1. It fails to provide any understanding of why certain spectral lines are brighter than others. There is no mechanism for the calculation of transition probabilities.

2. The Bohr model treats the electron as if it were a miniature planet, with definite radius and momentum. This is in direct violation of the uncertainty principle which dictates that position and momentum cannot be simultaneously determined – see later.

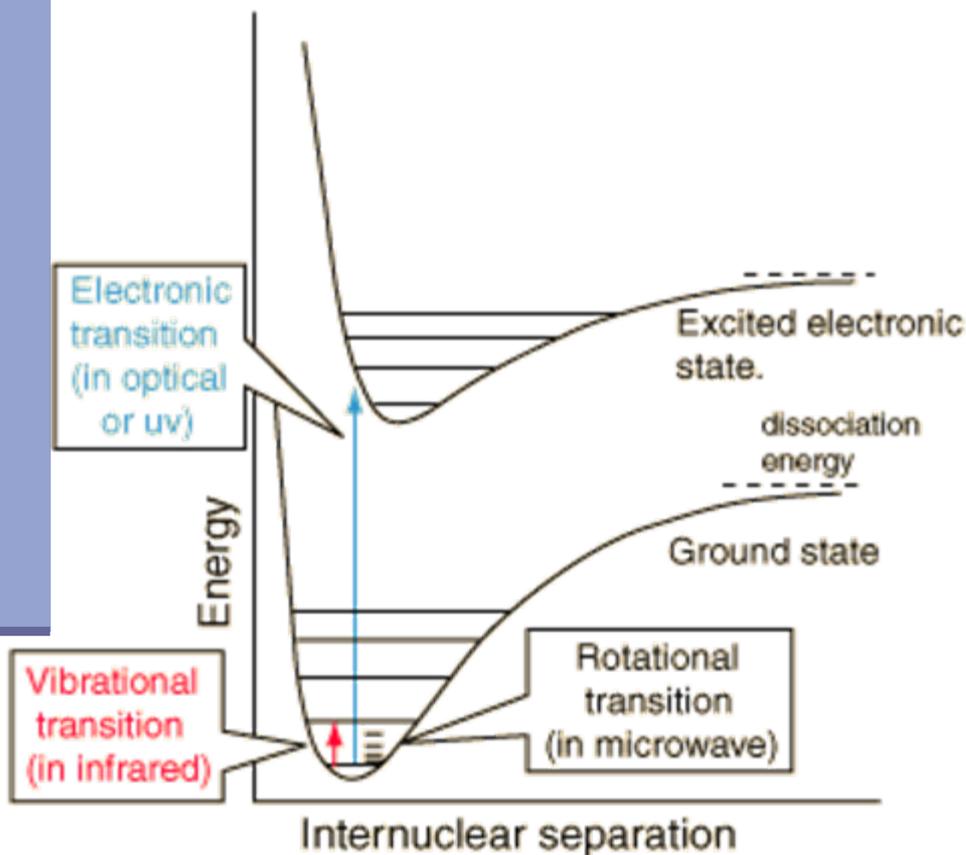**3.** Results are wrong even for atoms with **two** electrons – He spectrum!

Molecular spectra

Molecules are even more interesting – more degrees of freedom!
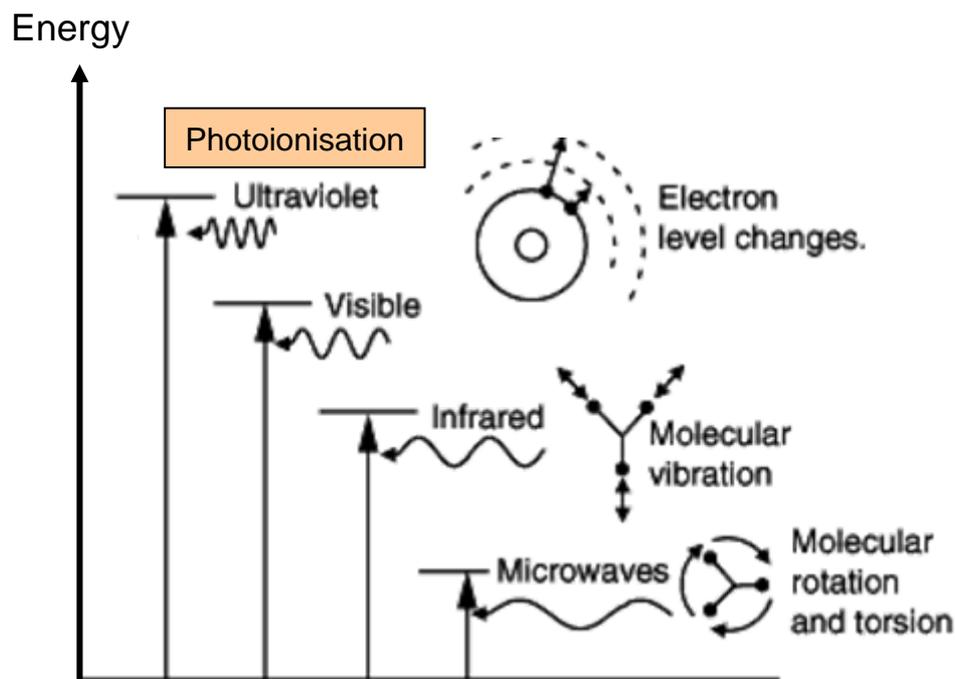
Energy

Not only are there electronic energy levels but there are also energy levels associated with nuclear motion i.e. vibrations and rotations.

Overview of molecular spectra

For diatomic molecules, electronic states represented by plots of potential energy as a function of internuclear distance.

Electronic transitions shown as vertical lines since the transition occurs so rapidly that the internuclear distance doesn't change during the excitation process (a good approximation!).

Vibrational transitions occur between different vibrational levels of the **same** electronic state.

Rotational transitions occur mostly between rotational levels of the same vibrational state. (although rotational transitions accompany both vibrational and electronic transitions)

Electronic transition (in optical or uv)

Excited electronic state.

dissociation energy

Ground state

Energy

Vibrational transition (in infrared)

Rotational transition (in microwave)

Internuclear separation
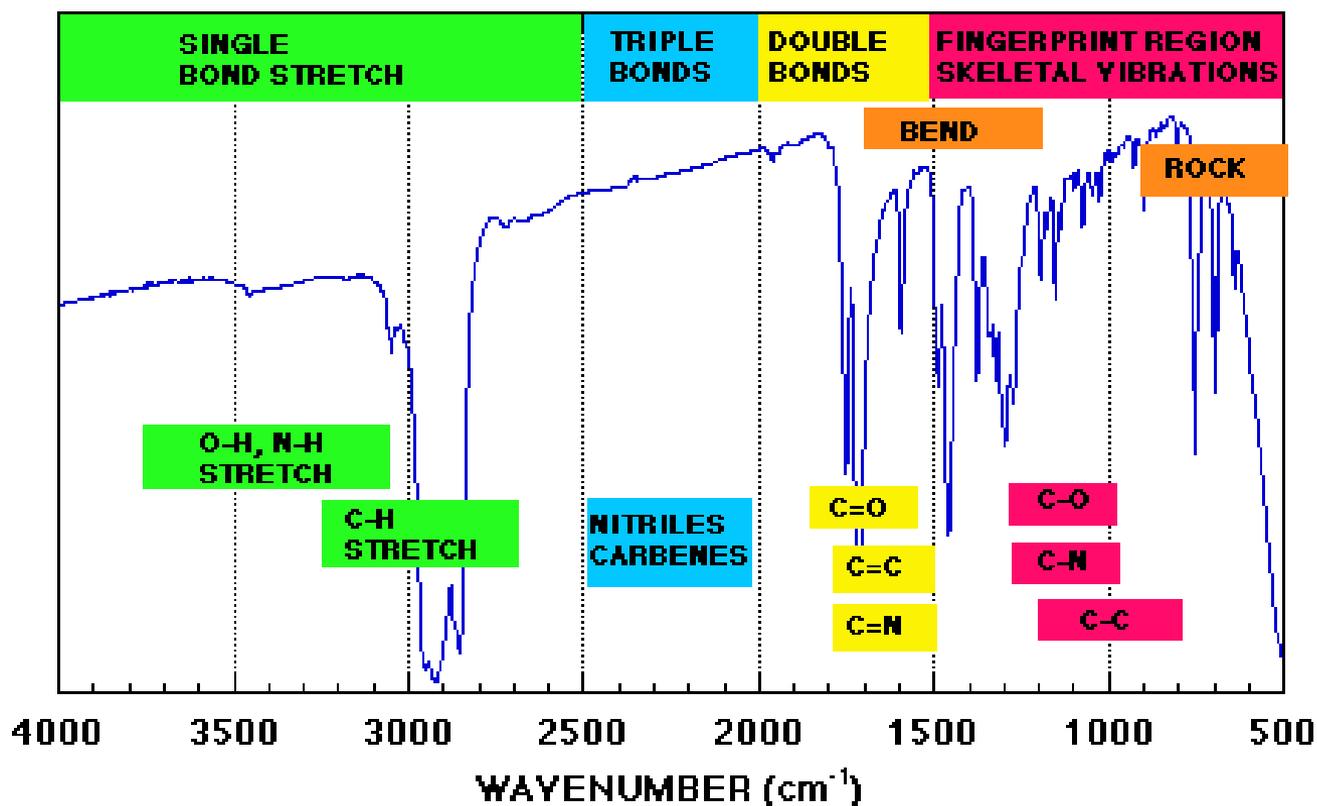
Some examples……..

UV/Visible/near IR spectroscopy

Example: Atmospheric absorption
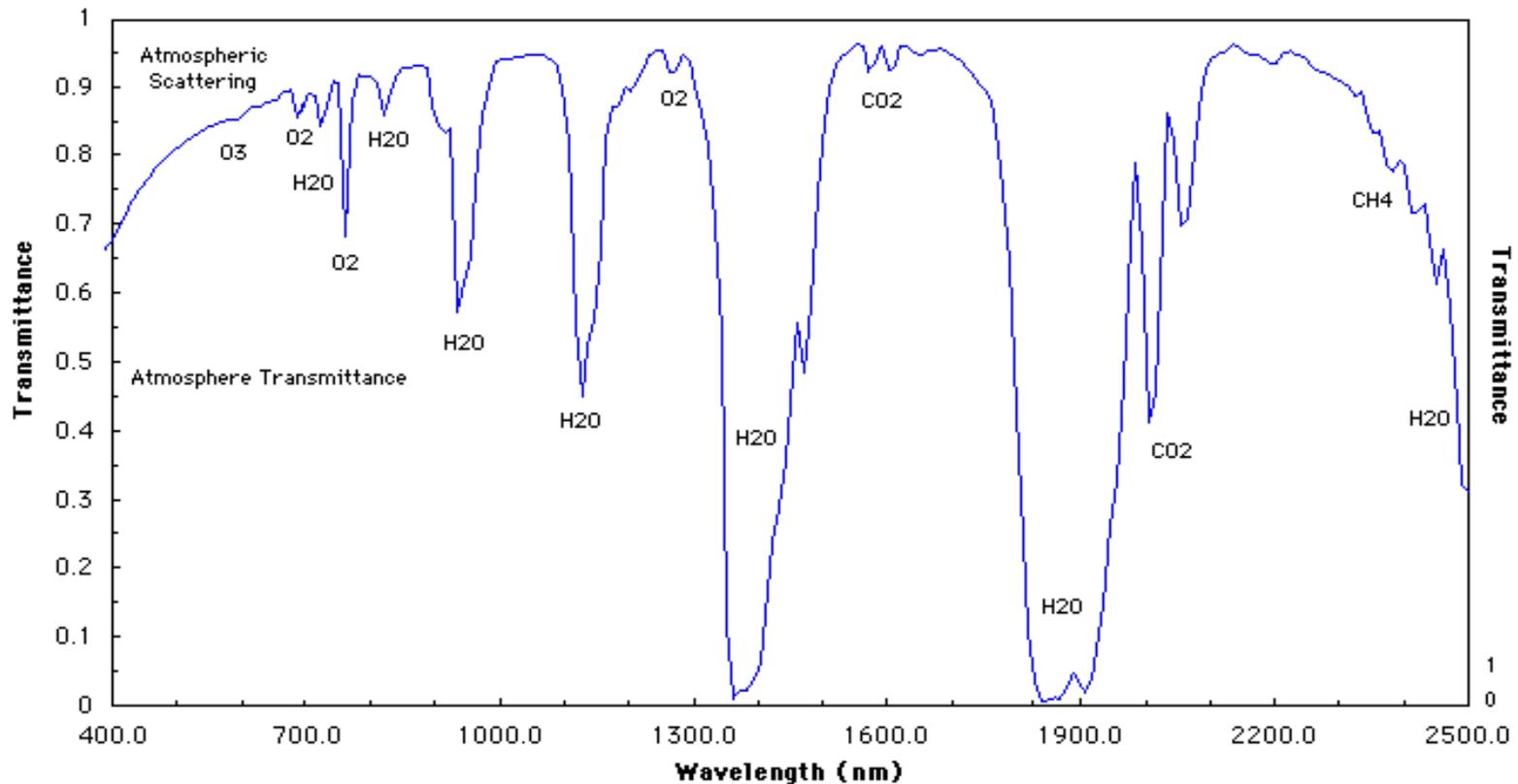
Atmospheric Profiling – the ozone hole is real!

IR spectroscopy

Chemical identification - different molecules/groups have different vibrational frequencies – **see later notes on the simple harmonic oscillator.**

The Photoelectric effect

Light shining onto matter causes the emission of photoelectrons.

Note:
1. Photoelectrons are emitted instantly, whatever the intensity of the light.
2. There is a critical frequency below which no photoelectrons are emitted.
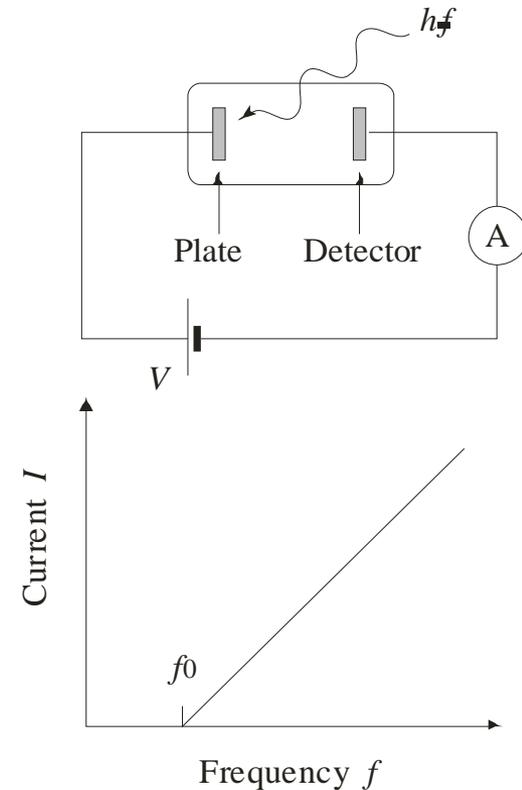**3.** Maximum kinetic energy of photoelectrons increases *linearly* with frequency.

Plate   Detector   A

$h f$

V

Current I

$f0$

Frequency f

Planck's photon picture: $E = hf$.

The photon supplies the energy available, $\phi = hf_0$ (ionisation energy / work function)
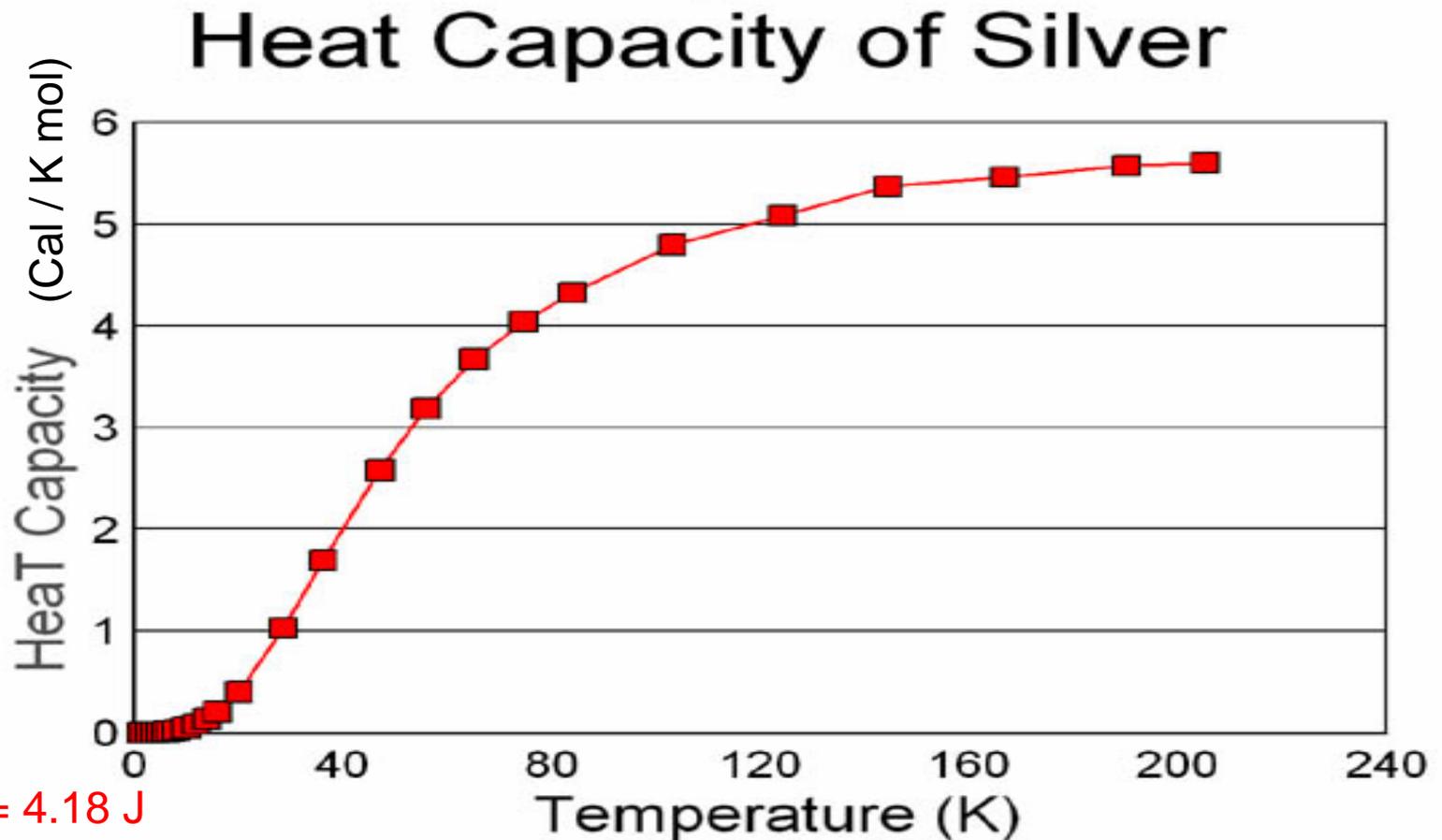For $f < f_0$, not enough energy to ionise.
For $f > f_0$, $h\nu_c$ used in ionisation, the rest is carried off by the electron as kinetic energy:
$KE_{max} = hf - \phi$.

Heat capacities of monatomic solids

Some typical data…

* I cal = 4.18 J

Classical calculation - Equipartition

Treat atoms as a classical harmonic oscillator: $E = KE + PE = \dfrac{p_x^2}{2m} + \dfrac{1}{2}kx^2$

Equipartition: Every quadratic energy term contributes $1/2kT$ to the average energy, $<E>$.

$$\langle E \rangle = \left\langle \frac{p_x^2}{2m} \right\rangle + \left\langle \frac{1}{2}kx^2 \right\rangle = \frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T \quad \text{in 1 dimension}$$

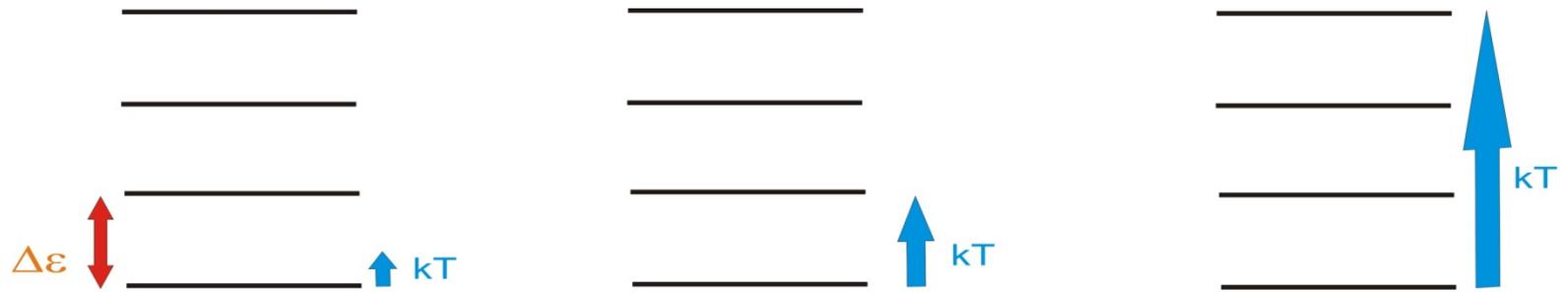Atoms vibrate in 3d: $\langle E \rangle_{3d} = 3k_B T$

The **average energy**, $<E>$ is just the **internal energy** of the system , U, and so:

$$U = 3k_B T \qquad \text{and} \qquad C_V(T) = \left(\frac{\partial U}{\partial T} \right)_V = 3k_B$$

i.e. C_v is **independent of temperature** and has a value of 3R (~25 J K $^{-1}$ mol^{-1}) for all monatomic solids. This is known as the Dulong-Petit law.

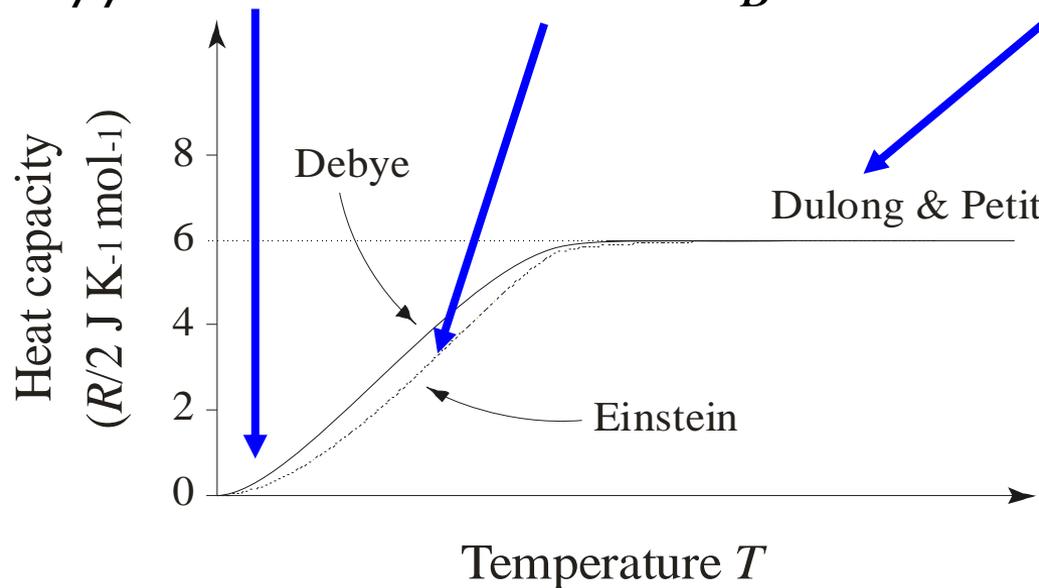This classical calculation works well at "high temperatures" but fails at low T.

Quantisation is the answer….

$$\Delta\varepsilon\rangle\rangle kT$$

$$\Delta\varepsilon \approx k_B T$$

$$\Delta\varepsilon\langle\langle kT$$

$\Delta\varepsilon$ kT

kT

kT

1. What matters is size of $\Delta\varepsilon$ compared to kT

2. Each solid has a unique $\Delta\varepsilon \Rightarrow C_v(T)$ "cuts-on" at different T but has same shape for all.

Heat capacity (R/2 J K$_{-1}$ mol$_{-1}$)

Debye

Dulong & Petit

Einstein

8

6

4

2

0

Temperature T

Take home message……

Energy is quantised

Evidence: Atomic + molecular spectra

Photoelectric effect

T-dependence of heat capacities

+ others…..

Quantisation is observable in the macroscopic thermodynamic properties of matter.

e.g. $C_V(T) \Rightarrow H(T), S(T)$ etc……

cf) Kirchoff's Law