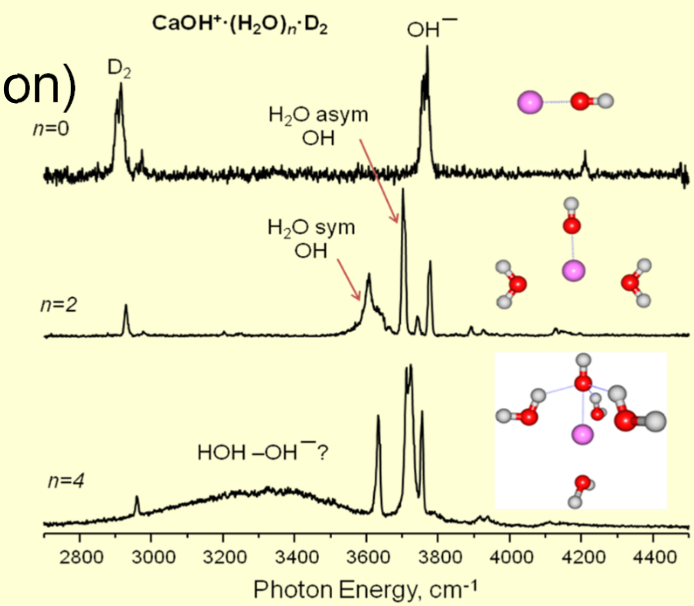
Chapter 1

Late 1800's – Several failures of classical (Newtonian) physics discovered

1905 – 1925 – Development of QM – resolved discrepancies between expt. and classical theory

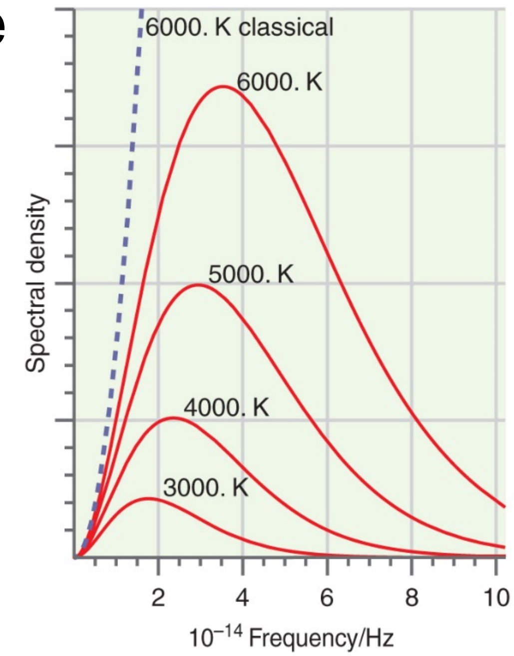
QM – Essential for understanding many phenomena in Chemistry, Biology, Physics

- photosynthesis + vision (electron excitation)
- vibrations/rotations (excitation of nuclear motion)
- magnetic resonance imaging
- radioactivity
- operation of transistors
- lasers (CD + DVD players)
- van der Waals interactions



(from M. Johnson, Yale University)

Problems where classical physics is inadequate



1. Blackbody Radiation

heated objects → light

Classical theory (Rayleigh-Jeans (1905)

spectral density =

$$\rho d\upsilon = \frac{8\pi\upsilon^2}{c^3}\overline{E}_{osc}d\upsilon$$

$$= \frac{8\pi\upsilon^2}{c^3}kTd\upsilon$$

Emits ∞ energy at all T

υ = frequency
ρ = spectral density (energy volume^{-1} frequency^{-1})
$\overline{E}_{osc}$ = average energy/osc
k = Boltzmann const.
c = speed of light

Planck: (1900)

$$\rho d\upsilon = \frac{8\pi h\upsilon^3}{c^3}\frac{1}{e^{h\upsilon/kT}-1}d\upsilon$$

originally determined by fitting experiment

Planck's constant: $h = 6.626x10^{-34}\ J \bullet s$

http://en.wikipedia.org/wiki/Planck's_constant

Planck later showed that his expression is consistent with the energies of the oscillators making up the blackbody object taking on discrete values $E = nh\upsilon\ ,\ \ n = 0,1,2,...$

$$\Rightarrow \overline{\text{E}} = \frac{h\upsilon}{e^{h\upsilon/kT} - 1}$$

T $\rightarrow$ 0 : 0

T $\rightarrow$ ∞ : kT — Classical result

Bottom result obtained using Taylor series of e^x for small x: $e^x = 1 + x + ...$

Derivation of Planck's result

Possible energies: *0, $h\upsilon$, $2h\upsilon$, $3h\upsilon$*, etc.

Probability of having energy $nh\upsilon$ given by $p(n) = \dfrac{e^{-nh\upsilon/kT}}{\sum_n e^{-nh\upsilon/kT}}$

$e^{-E/kT}$ = Boltzmann factor

← normalization (sum over all levels)

$$\bar{E} = \sum E_n p(n) = \frac{\sum_{n=0}^{\infty} nh\upsilon e^{-nh\upsilon/kT}}{\sum_{n=0}^{\infty} e^{-nh\upsilon/kT}}$$

denominator $= 1 + e^{-h\upsilon/kT} + e^{-2h\upsilon/kT} + \ldots = 1 + x + x^2 + \ldots = \dfrac{1}{1-x} = \dfrac{1}{1-e^{-h\upsilon/kT}}$

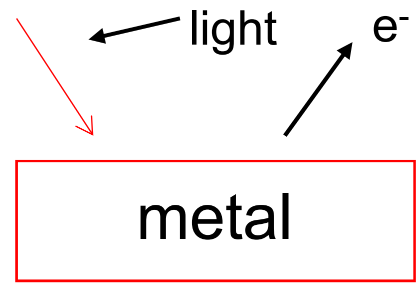
numerator = $h\upsilon\left[0 + e^{-h\upsilon/kT} + 2e^{-2h\upsilon/kT} + 3e^{-3h\upsilon/kT} + \ldots\right]$

$$= h\upsilon e^{-h\upsilon/kT}\left[1 + 2e^{-h\upsilon/kT} + 3e^{-2h\upsilon/kT} + \ldots\right] = \frac{h\upsilon e^{-h\upsilon/kT}}{\left(1-e^{-h\upsilon/kT}\right)^2}$$

$$\bar{E} = \frac{h\upsilon e^{-h\upsilon/kT}}{\left(1-e^{-h\upsilon/kT}\right)} = \frac{h\upsilon}{\left(e^{h\upsilon/kT}-1\right)}$$

avg. energy of mode of freq. $h\upsilon$

2. Photoelectric effect



expected behavior

- light is a wave, so each e^- absorbs small fraction of the energy
- e^- emitted at all υ, if intensity (I) great enough
- KE of ejected e^- > with > intensity

observed

- #e^- emitted $\propto$ intensity
- e^- emitted if $\upsilon > \upsilon_0$ (critical freq.)
- KE > with > υ, and independent of intensity

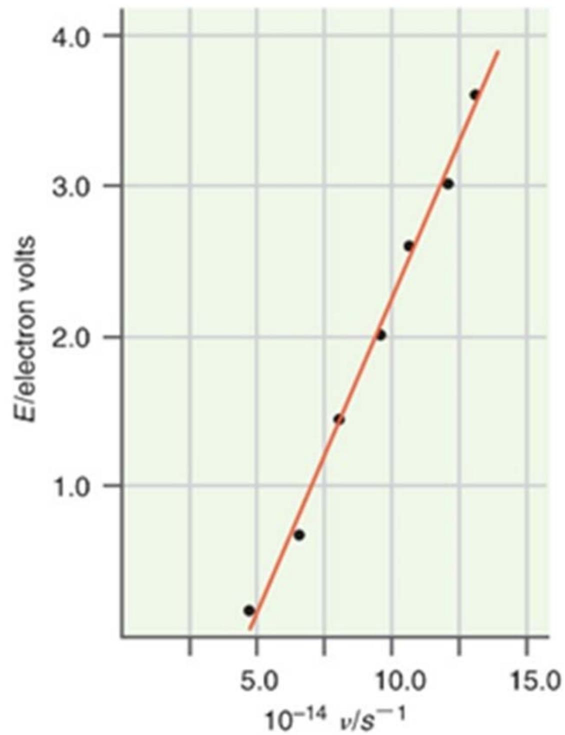
Explained by Einstein in 1905

light has energy $h\upsilon$ ($E = h\upsilon$) and acts particle-like, enabling its energy to be focused on one e^-

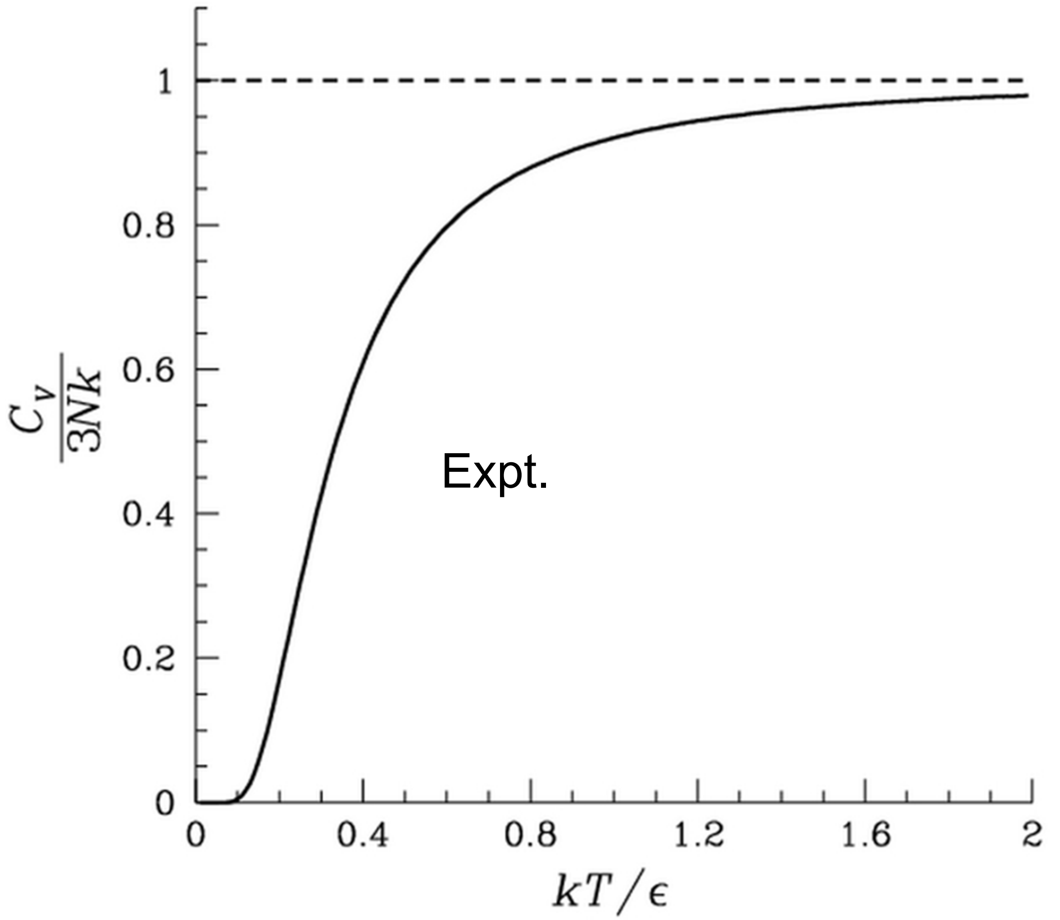
energy of ejected electron = $E_{el} = h\upsilon - \phi$,

ϕ = work function of metal (~IP)

$\Rightarrow$ critical frequency (implies critical energy) for production of photoelectrons



3. Heat capacity of solids (classical = 3R; actual $\rightarrow$ 0 as $T \rightarrow 0$) ($R = N_a k$)



Classical result $\begin{pmatrix} C_v = 3Nk \\ E = 3NkT \end{pmatrix}$

Einstein's solution:

Assumed vibrations of lattice are quantized, i.e., energies are $nh\nu$

Figure from Wikipedia

4. Wave-particle duality

- photoelectric effect $\Rightarrow$ light can behave as a particle
- diffraction of light $\Rightarrow$ light can behave as a wave

de Broglie (1924): particles have a wavelength:

$$\lambda = \frac{h}{p}$$

Demonstrated by diffraction of e^-, He, H_2 from crystalline surfaces

e^- with KE = 17 eV has λ = 3 Å, a typical lattice spacing in a crystal $\Rightarrow$ interference (diffraction)

large objects – baseballs, cars, etc., have de Broglie wavelengths too small to be detected

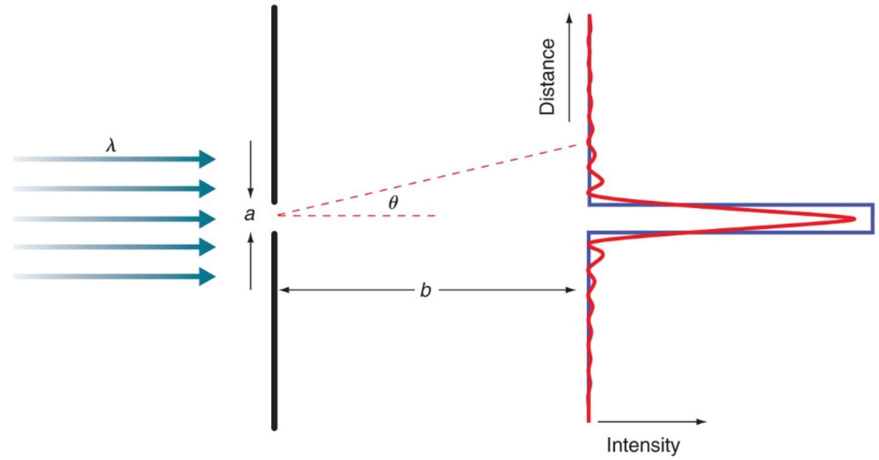
Baseball weighs ~0.14 kg; 100mph = 44.7m/s
$\lambda = 1.05\text{x}10^{-39} m$

Diffraction experiments

light incident on a single slit

$$\sin\theta = \frac{n\lambda}{a},$$

minima:
$n = \pm 1, \pm 2, \pm 3, \ldots$



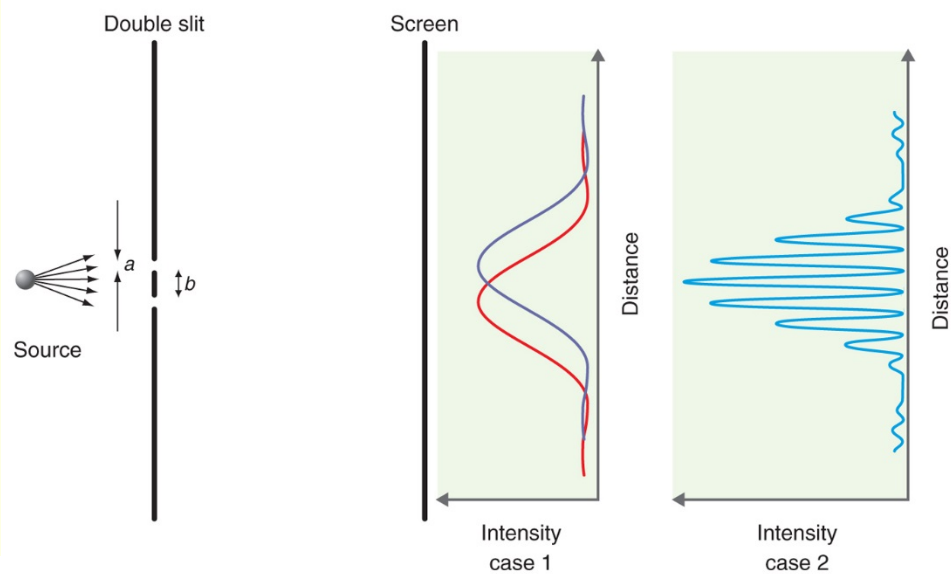
$\lambda \approx a$: well separated peaks
$\lambda \gg a$: can't see diffraction

double-slit expt. with e^-

the e^- goes through both slits!!

In 1977 the expt. was done with the He atoms $\Rightarrow$ Each atom goes through both slits!!

Comment on single flashes on screen (forces e^- back to particle nature)



5. Spectra of atoms + molecules – discrete lines

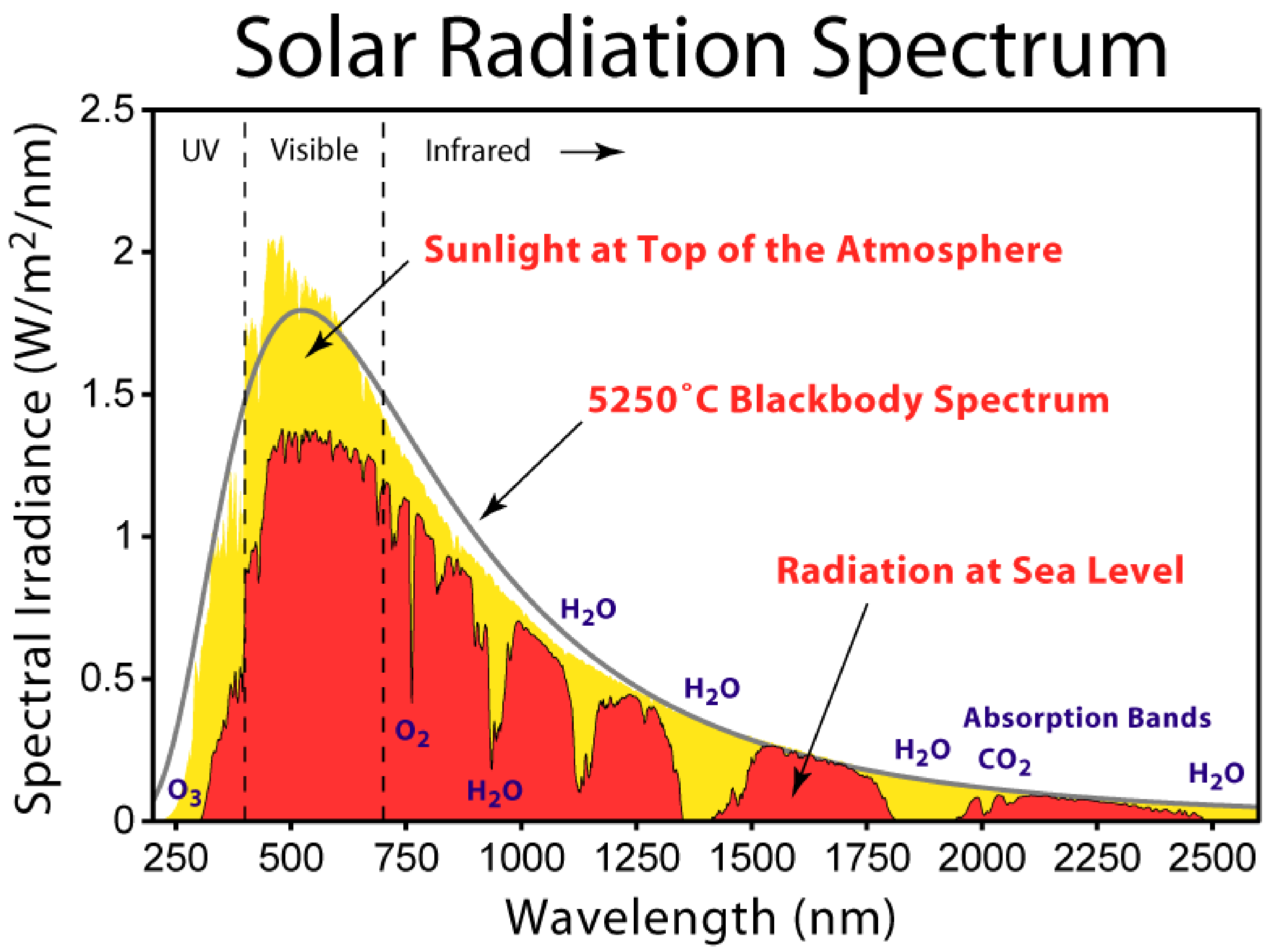


Figure from Wikipedia

spectrum H atom

$$\tilde{\upsilon} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n^2} \right)$$

Rydberg series

n_1, n integers, n = n_1+1, n_1+2, n_1+3, …

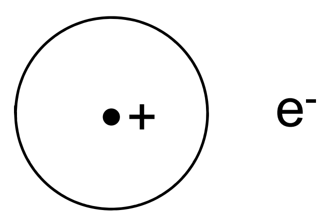
R_H = 109,677.581 cm^{-1} ⟶ 13.6 eV
(1 eV = 8066 cm^{-1})

Explained by Bohr model (1911)

$$\frac{e^2}{4\pi\varepsilon_o r^2} = \frac{m_e \mathrm{v}^2}{r}$$

Coulomb force

centrifugal force



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

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

Bohr based his result on the correspondence Principle, rather than the de Broglie relation, which wasn't proposed until several years later.

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See plato.Stanford.edu/entries/bohr~correspondence/)

Valid solutions: the wave perfectly fits in the "orbit"

$$\rightarrow r = \frac{4\pi\varepsilon_0 \hbar^2 n^2}{m_e e^2}$$

$$E_{tot} = E_{kinetic} + E_{pot}$$

$$= \frac{-e^2}{8\pi\varepsilon_0 r} = \frac{-m_e e^2}{8\varepsilon_0^2 h^2 n^2}, \quad n = 1, 2, 3$$

$$\mathrm{v} = \frac{n\hbar}{m_e r}$$

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e n^2 \hbar^2}{m_e^2 r^3}$$

$$r = \frac{4\pi\varepsilon_0 n^2 \hbar^2}{e^2 m_e}$$

gives the definition of Rydberg's constant

Summary:

- energy + oscillators are quantized
- wave-particle duality
- de Broglie relationship
- these ideas paved the way for QM

NOTE: Frequencies of a guitar string are "quantized" (and guitars are clearly Classical)

Quantization comes from boundary conditions

Fourier transforms:
(frequency $\leftrightarrow$ time)
(position $\leftrightarrow$ momentum)
are conjugate variables

We will come back to these considerations.