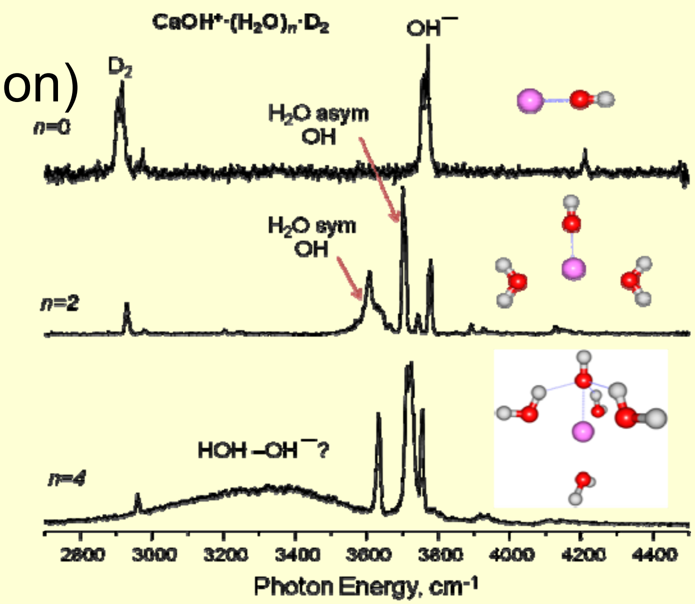
Chapter 1

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

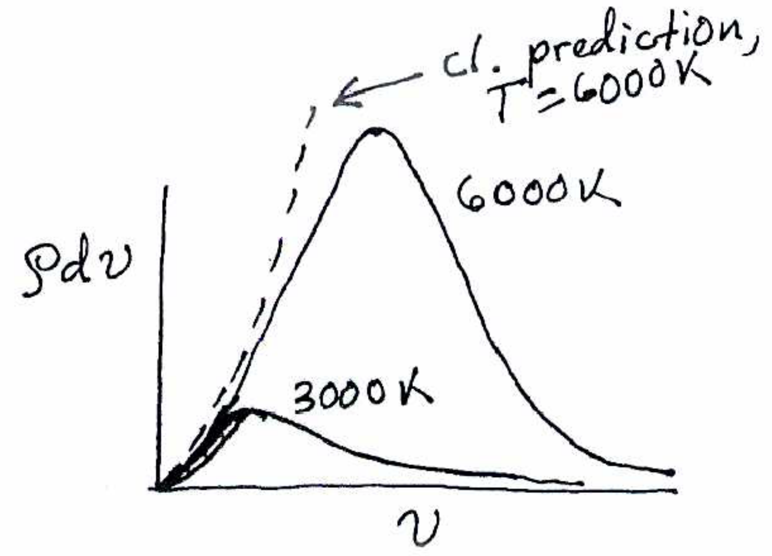
- photosynthesis + vision (electron excitation)
- vibrations/rotations (excitation of nuclear motion)
- magnetic resonance imaging
- radioactivity
- operation of transistors
- lasers (CD + DVD players)
- van der Waals interactions



Examples where classical Physics inadequate

1. Blackbody Radiation

heated objects → light



Classical theory
(Rayleigh-Jeans (1905)

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

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

Emits ∞ energy at all T

υ = frequency
ρ = density oscillators
$\bar{E}_{osc}$ = average energy/osc

Planck:
(1900)

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

originally by fitting experiment

Planck's constant: $h = 6.626 x 10^{-34} J \bullet s$

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

Planck later showed this is consistent with the energies of the oscillators making up the blackbody object taking on discrete values

$$E = nh\upsilon \ , \ \ n = 0, 1, 2, \ldots$$

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

T $\rightarrow$ 0: 0

T $\rightarrow$ ∞: kT

Classical result

Taylor series of e^x for small x: $e^x = 1 + x + \ldots$

Derivation of Planck result

Possible energies: *0, $h\upsilon$, $2h\upsilon$, $3h\upsilon$*, etc.
Probability of having energy $nh\upsilon$ given by Boltzmann factor

$$p(n) = \frac{e^{-nh\upsilon/kT}}{\sum_n e^{-nh\upsilon/kT}}$$

normalization
(sum overall 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 $= 1 + e^{-h\upsilon/kT} + e^{-2h\upsilon/kT} + \ldots = 1 + x + x^2 + \ldots = \frac{1}{1-x} = \frac{1}{1-e^{h\upsilon/kT}}$

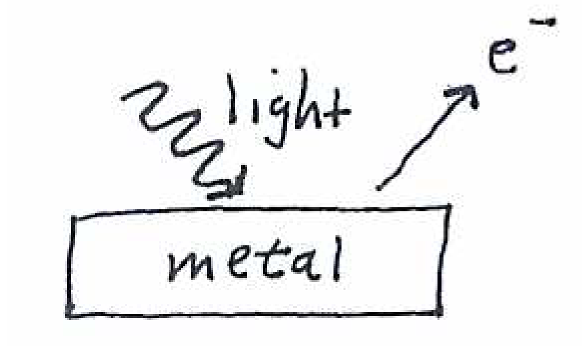
numerator $= h\upsilon\left[0 + e^{-h\upsilon/kT} + 2e^{-2h\upsilon/kT} + 3e^{-3h\upsilon/kT} + \ldots\right]$

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

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

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

2. Photoelectric effect



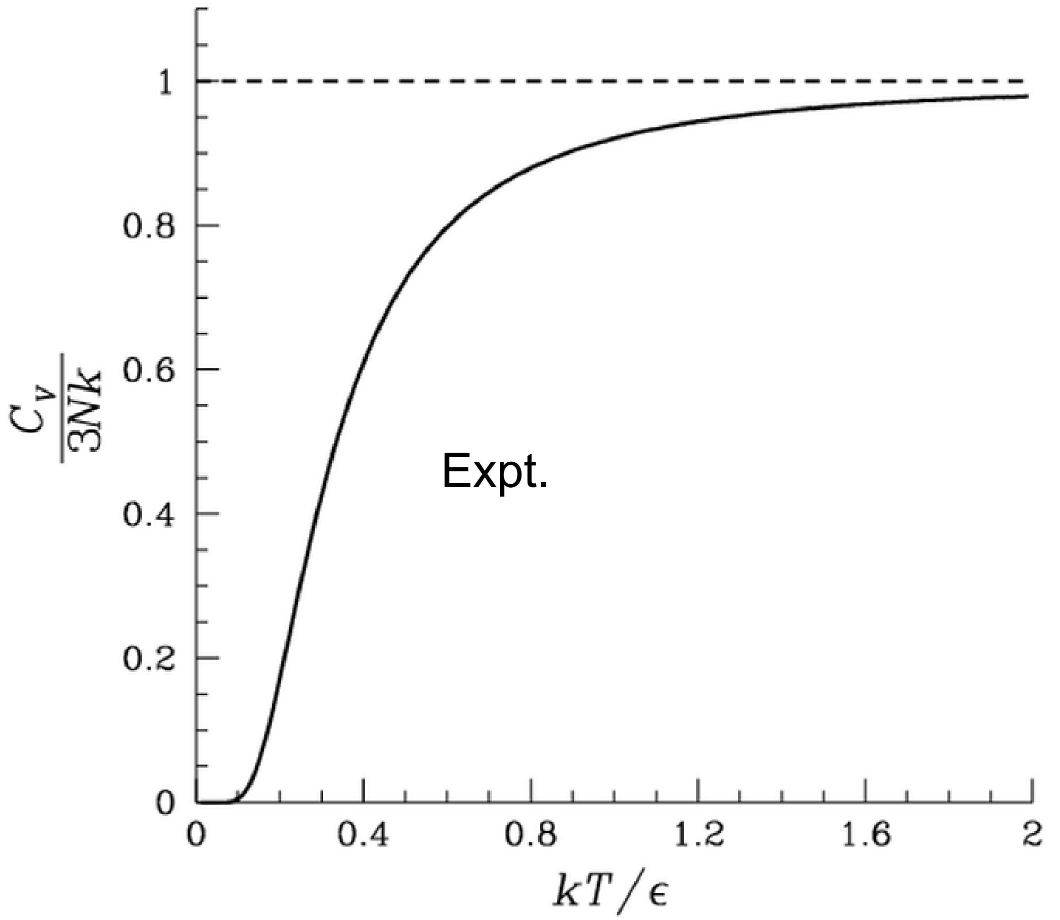
expected behavior	observed
• light is a wave, so each e^- absorbs small fraction of the energy	• #e^- emitted $\propto$ I
• e^- emitted at all υ, if intensity (I) great enough	• e^- emitted if $\upsilon > \upsilon_0$ (critical freq.)
• KE of ejected e^- > with I	• KE > with υ, and independent of I

Explained by Einstein in 1905

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

$E_{el} = h\upsilon - \phi$, ϕ = work function of metal (~IP)

3. Heat capacity of solids (classical = 3R; actual → 0 as T → 0)



Classical result

Einstein solution:

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

Figure from Wikipedia

4. Spectra of atoms + molecules – discrete lines

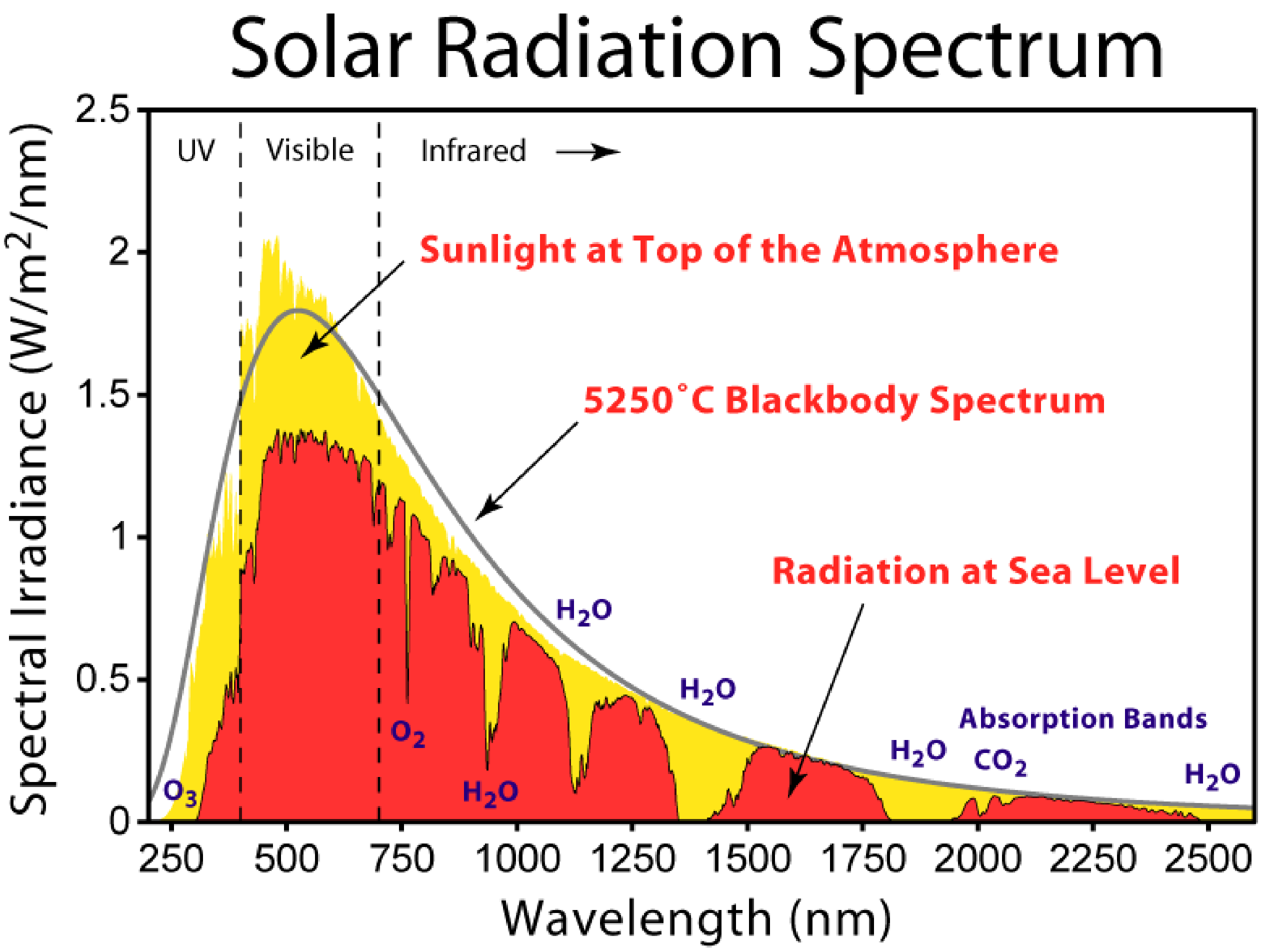
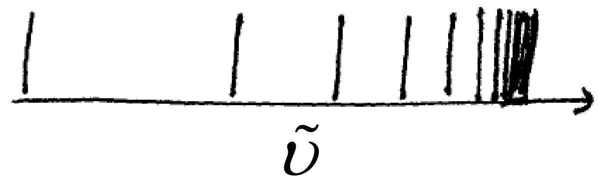


Figure from Wikipedia

4. Spectra of atoms + molecules – discrete lines

spectrum H atom



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

Rydberg series

n_1, n integers, $n = n_1+1,\ n_1+2,\ n_1+3,\ \ldots$

$R_H = 109{,}677.581\ \text{cm}^{-1}$

We will return to this

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:

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

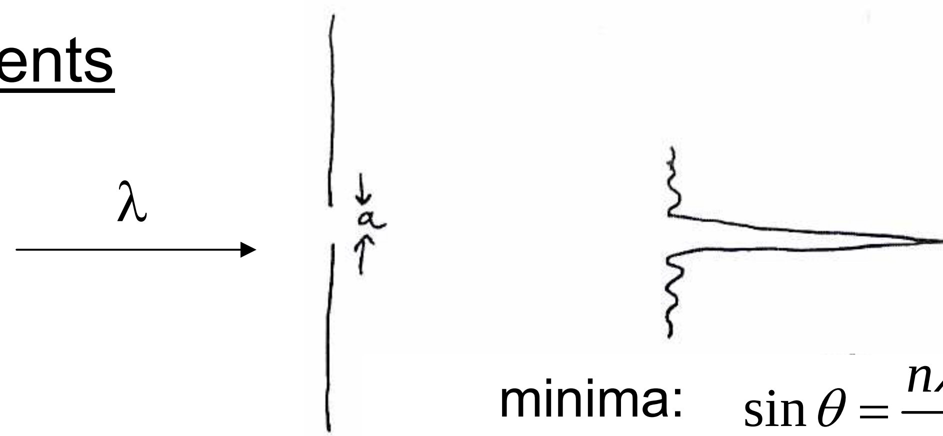
Demonstrated by diffraction of e^-, He, H_2 from crystalline surfaces

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

<u>Diffraction experiments</u>

light incident on a single slit



minima: $\sin\theta = \dfrac{n\lambda}{a}$, n = ±1, ±2, ±3, …

well separated peaks when

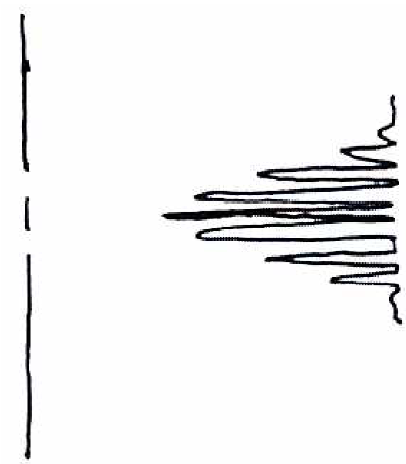
$\lambda \approx$ a

λ>> 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!!



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 + time)
(position, momentum)
are conjugate variables

We will come back to these considerations.