

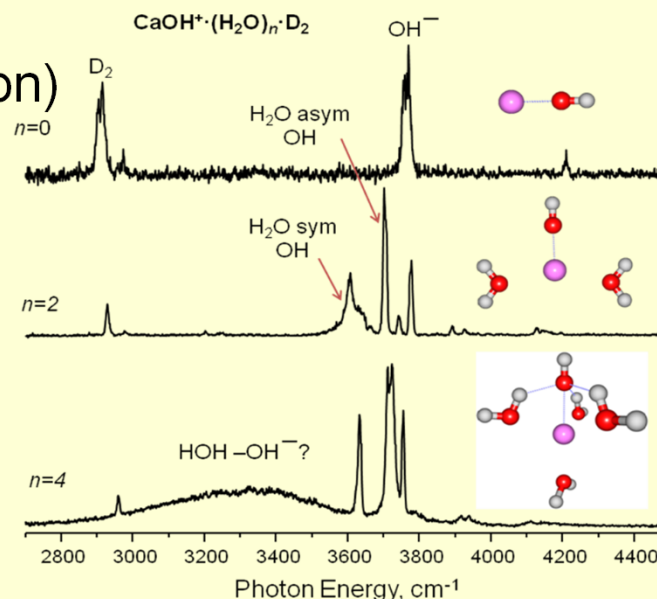
Chapter 1

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 =

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

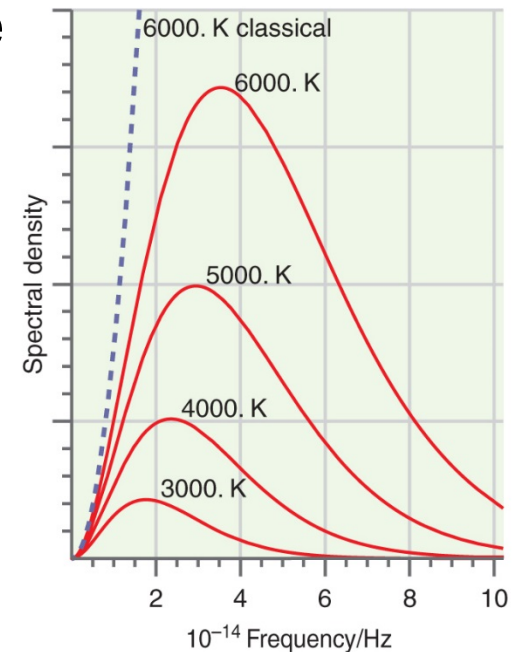
Emits ∞ energy at all T

Planck:
(1900)

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

ν = frequency
 ρ = spectral density (energy volume⁻¹ frequency⁻¹)
 \bar{E}_{osc} = average energy/osc
k = Boltzmann const.
c = speed of light

originally determined by fitting experiment



© 2013 Pearson Education, Inc.

Planck's constant: $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

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 $E = nh\nu$, $n = 0, 1, 2, \dots$

$$\Rightarrow \bar{E} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

$T \rightarrow 0 \rightarrow 0$

$T \rightarrow \infty \rightarrow kT$ Classical result

Bottom result obtained using Taylor series of e^x for small x :

$$e^x = 1 + x + \dots$$

Derivation of Planck's result

Possible energies: $0, h\nu, 2h\nu, 3h\nu, \dots$

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

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

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

normalization
(sum over all levels)

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

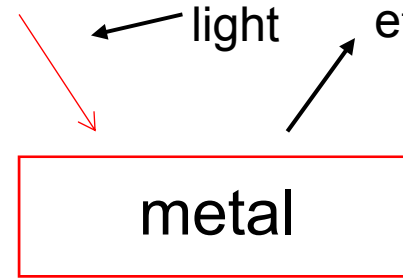
$$\text{denominator} = 1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots = 1 + x + x^2 + \dots = \frac{1}{1-x} = \frac{1}{1-e^{-h\nu/kT}}$$

$$\begin{aligned} \text{numerator} &= h\nu [0 + e^{-h\nu/kT} + 2e^{-2h\nu/kT} + 3e^{-3h\nu/kT} + \dots] \\ &= h\nu e^{-h\nu/kT} [1 + 2e^{-h\nu/kT} + 3e^{-2h\nu/kT} + \dots] = \frac{h\nu e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2} \end{aligned}$$

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

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

2. Photoelectric effect



expected behavior

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

observed

- #e⁻ emitted \propto I
- e⁻ emitted if $\nu > \nu_0$ (critical freq.)
- KE $>$ with $>$ ν , and independent of I

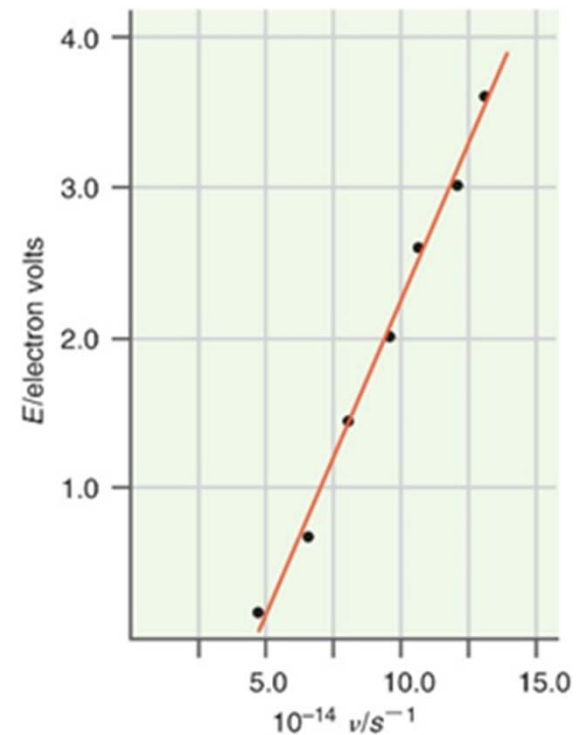
Explained by Einstein in 1905

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

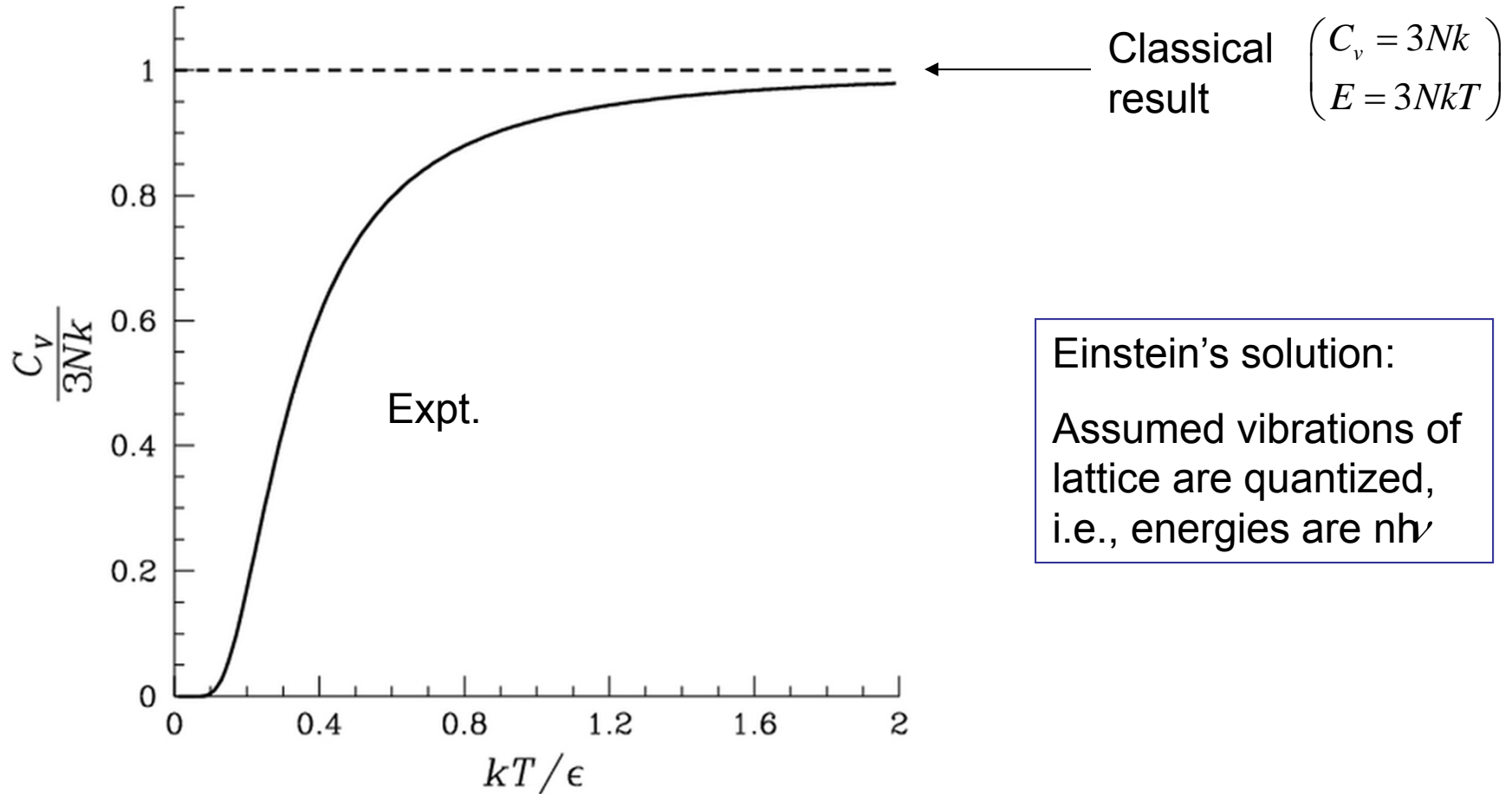
energy of ejected electron = $E_{el} = h\nu - \phi$,

ϕ = work function of metal (\sim IP)

\Rightarrow critical frequency for production of photoelectrons



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



Einstein's solution:
Assumed vibrations of lattice are quantized, i.e., energies are $n h \nu$

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 $\lambda = 3 \text{ \AA}$, a typical lattice spacing in a crystal \Rightarrow interference (diffraction)

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

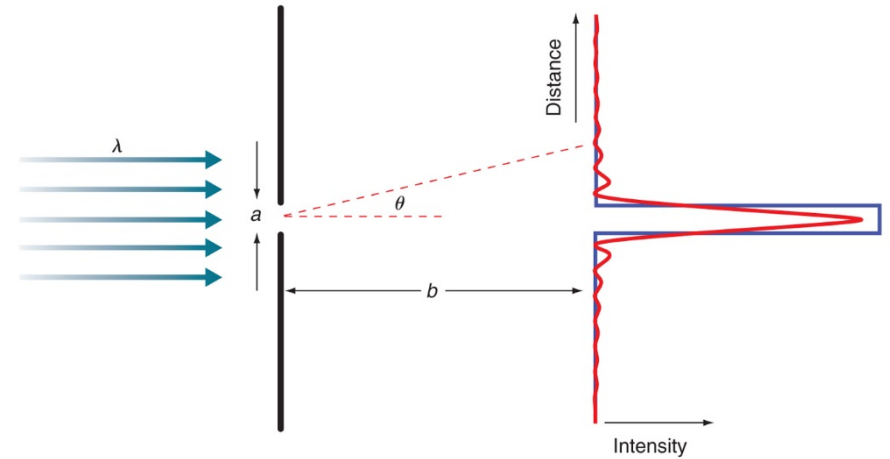
Diffraction experiments

light incident on a single slit

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

minima:

$$n = \pm 1, \pm 2, \pm 3, \dots$$



© 2013 Pearson Education, Inc.

$\lambda \approx a$: well separated peaks

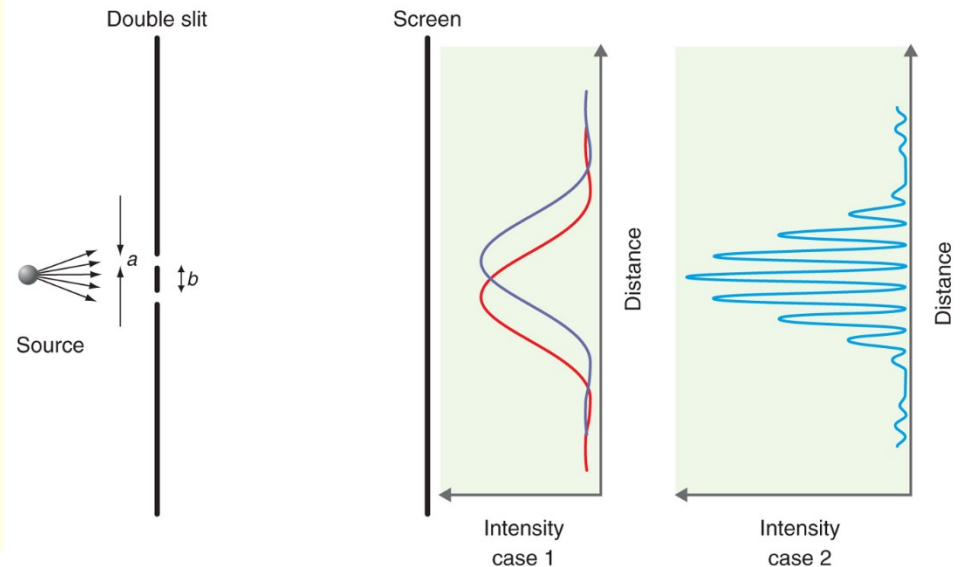
$\lambda \gg a$: can't see diffraction

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)



© 2013 Pearson Education, Inc.

5. Spectra of atoms + molecules – discrete lines

Solar Radiation Spectrum

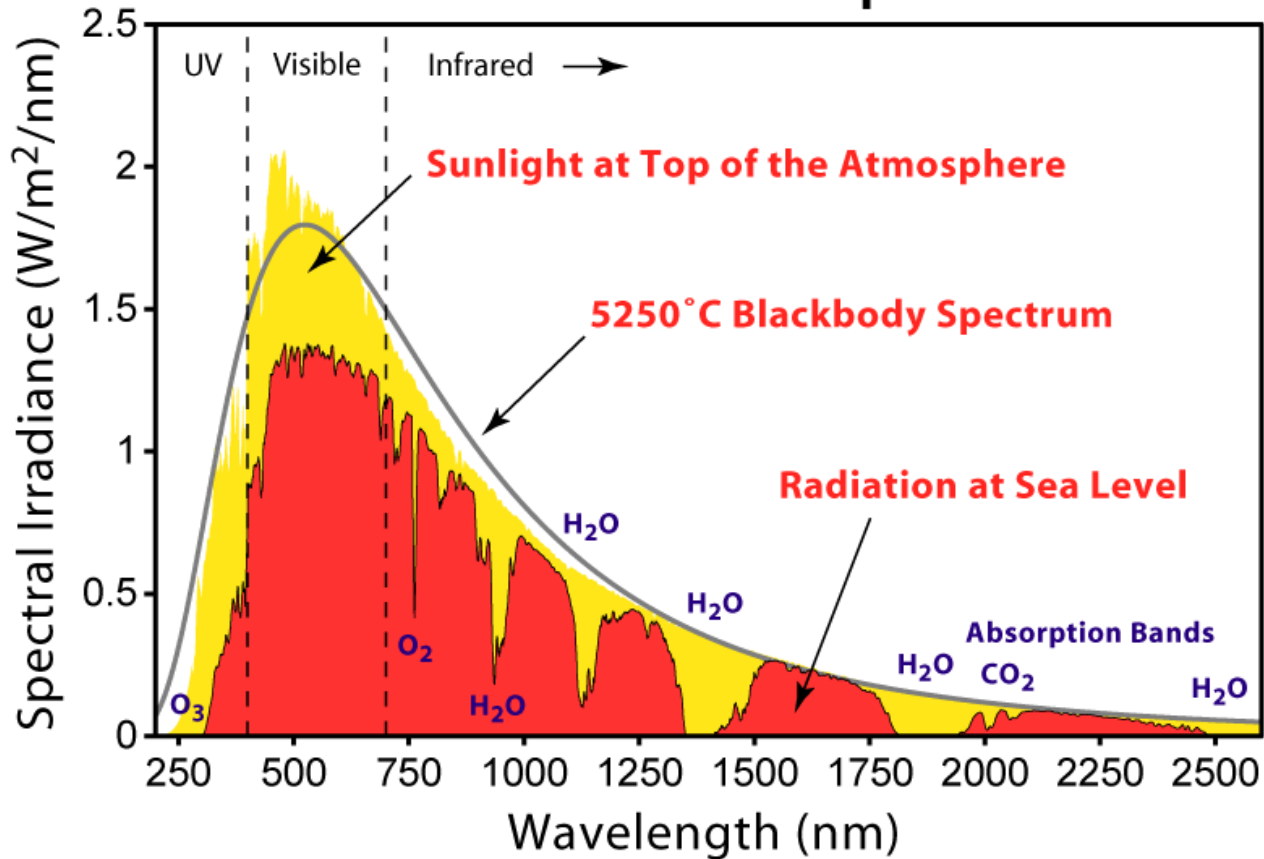


Figure from Wikipedia

spectrum H atom



$$\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n^2} \right) \quad \text{Rydberg series}$$

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

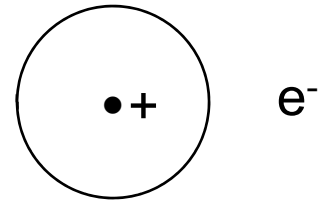
$$R_H = 109,677.581 \text{ cm}^{-1} \longrightarrow 13.6 \text{ eV}$$

(1 eV = 8066 cm⁻¹)

Explained by Bohr model (1911)

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r}$$

Coulomb force centrifugal force



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

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

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

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

Valid solutions: the wave perfectly fits in

$$\rightarrow r = \frac{4\pi\epsilon_0 \hbar^2 n^2}{m_e e^2}$$

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

$$= \frac{-e^2}{8\pi\epsilon_0 r} = \frac{-m_e e^2}{8\epsilon_0^2 \hbar^2 n^2}, \quad n = 1, 2, 3$$

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

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e n^2 \hbar^2}{m_e^2 r^3}$$

$$r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{e^2 m_e}$$

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.