The Prehistory of Quantum Chemistry

	Matter			Energy
ancient civilizations	discrete matter			
Dalton	atoms	1803		
Avogadro	molecules	1811		
		1900	Planck	discrete energy
		1905-6	Einstein	heat capacities photoelectric effect
Rutherford	nuclear model of the atom	1909-11		
		1913	Bohr	discrete energy levels in atoms
but…		1905	Einstein	mass-energy equivalence!

Everything seemed fine at the time...

Our future discoveries must be looked for in the sixth decimal place.

Michelson, 1894
Nobel Laureate

… until a Catastrophe

Problems:

- Black-body radiation
- Heat capacities
- The photoelectric effect
- Atomic line spectra

The Development of Quantum Chemistry

Matter Energy

de Broglie	1924	wave nature of matter
Heisenberg	1926-7	matrix mechanics
Schrödinger	1926-7	wave mechanics
Dirac	1928	relativistic quantum mechanics
Pauling	1928	chemical bonds

The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

Dirac, 1929

This changed when computers came into use for solving these equations and quantum chemistry emerged as a new branch of chemistry.

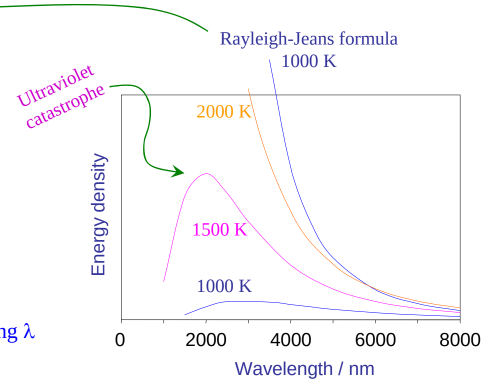
$\Rightarrow$ The 1998 Nobel Prize in Chemistry

Black-body Radiation

A black body absorbs all radiation which falls on it (no reflection).

It emits radiation according to its temperature.

Classical theory: $\rho = \dfrac{8\pi kT}{\lambda^4}$



Planck was able to predict the experimental finding of a maximum in the energy emitted at different wavelengths:

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right) \rightarrow \frac{8\pi kT}{\lambda^4} \text{ at long } \lambda$$

Planck's Quantum Hypothesis

- Light comes in "packets" of $\varepsilon = h\nu$

  $E\ (= U) = q\varepsilon \quad q = 0,1,2,\ldots$

- These packets of energy are subject to statistics.

  The observable is an average:

$$\bar{U} = \sum_q (q\varepsilon)\,\mathrm{Prob}(q\varepsilon) = \frac{\sum_q (q\varepsilon)e^{-q\varepsilon/kT}}{\sum_q e^{-q\varepsilon/kT}}$$

$$\Rightarrow \quad \bar{U} = \frac{\varepsilon}{e^{\varepsilon/kT}-1} \rightarrow kT \quad \text{when } \varepsilon \ll kT$$

the classical limit

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Heat Capacities of Solids

Planck's ideas were extended to the heat capacity of solids by Einstein.

For a crystal of N atoms:

$$C_V = 3N\frac{dU}{dT} = 3Nk\left(\frac{\varepsilon}{kT}\right)^2 \frac{e^{\varepsilon/kT}}{\left(e^{\varepsilon/kT}-1\right)^2} \quad \to 3R \quad \text{when } \varepsilon \ll kT$$

3-D vibrations

Dulong and Petit

$Nk = R$, the gas constant

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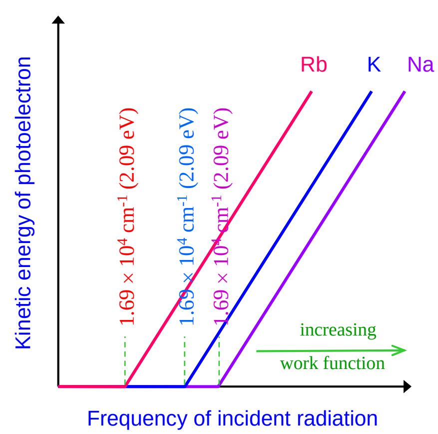
The Photoelectric Effect

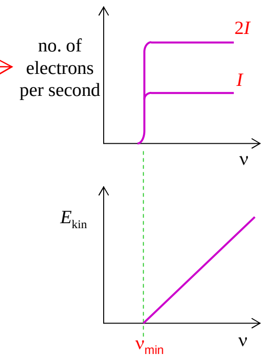
When high frequency radiation (UV and up) falls on a metal surface, electrons are emitted.



The Photoelectric Effect – 2

Three observations must be explained:

- no emission below ν_{min}.
- Above ν_{min} the emission current depends on light intensity I, not ν.
- The kinetic energy of the emitted electrons depends linearly on $(\nu - \nu_{min})$.



Einstein showed that these are consistent with Planck's hypothesis of the quantization of radiation.

Light of frequency ν is considered as a stream of photons, each with energy $h\nu$. A photon is annihilated on collision with an electron and gives up its energy.

Part is used to overcome the binding energy to the metal, the remainder appears as kinetic energy.

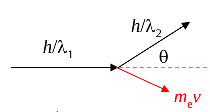
$$h\upsilon_{min} = \phi(\mathrm{M})$$

$$h\upsilon = \phi(\mathrm{M}) + \tfrac{1}{2}mv^2$$

Wave - Particle Duality

Compton Effect

If a beam of light (X-rays) falls on a stream of electrons, it is scattered and the frequency is shifted.



The shift depends on scattering angle only: $\lambda_2 - \lambda_1 = \dfrac{h}{m_e c}(1 - \cos\theta)$

which is exactly the result expected from conservation of momentum and energy for a photon of momentum h/λ .

Laser Cooling

Nowadays atomic and particle physicists use lasers to "cool" particle beams.

=> Light behaves like particles.

Electron Diffraction

Electrons (and other particles) can be diffracted by crystals or thin foils.

=> Particles behave like light.

De Broglie relation

$$p = h / \lambda$$

Compare with Einstein's expression from the Special Theory of Relativity: $E^2 = p^2c^2 + m^2c^4$

Apply this to a "particle" of zero mass $E = pc$

and substitute $E = h\upsilon = hc / \lambda$

and we arrive at de Broglie's relation: $p = h / \lambda$