1. The Dawn of the Quantum Theory

How was science at the end of 19 century?

Chemistry
- periodic table of the elements and atomic weights
- molecular structure of compounds
- theory of chemical reactions

Physics
- generalization of Newtonian mechanics (= analytical mechanics)
- thermodynamics and the concept of entropy
- optics and electromagnetics

Physics of light: Maxwell's equations, Hertz's experiments of discharge → Light is electromagnetic wave.

At the beginning of 20 century,

The theory of relativity, Quantum theory → Big switch of the existing physics

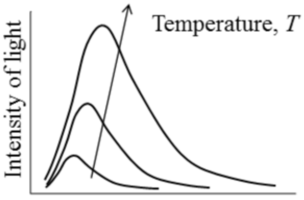
Quantum theory → Huge impact on chemistry, including
- atomic structure
- chemical bonding
- spectroscopy

1-1 Blackbody Radiation could not be Explained by Classical Mechanics.

Heated object emits light (= radiation).
Blackbody radiation law

$$\mathrm{d}\rho(\nu,T) = \rho_\nu(T)\mathrm{d}\nu = \frac{8\pi k_\mathrm{B}T}{c^3}\nu^2\,\mathrm{d}\nu$$

(Classical Rayleigh-Jeans law)
⟶ Ultraviolet catastrophe



1-2 Planck Used a Quantum Hypothesis to Derive the Blackbody Radiation Law.

Planck (1900) hypothesized that the electronic oscillation in a material is quantized ($E = h\nu$).

$$\Rightarrow \quad \mathrm{d}\rho(\nu,T) = \rho_\nu(T)\mathrm{d}\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\frac{h\nu}{k_\mathrm{B}T}}-1}\mathrm{d}\nu$$

Limit of $\dfrac{h\nu}{k_\mathrm{B}T} << 1$ gives Rayleigh-Jeans formula.

Wien's displacement law (empirical law): $\lambda_{\max}T = 2.90\times10^{-3}$ mK

Planck formula affords a coefficient 2.899×10^{-3} mK.

Blackbody radiation of 6000 K approximates the spectrum of sunlight.

1-3 Einstein Explained the Photoelectronic Effect with a Quantum Hypothesis.

Hertz (1887) found that metal surface emits electron when irradiated with light (= photoelectron effect).

→ Kinetic energy irrespective of the intensity of light
Threshold of frequency

Einstein (1905)
- explained photoelectronic effect using Planck formula.
- deduced that the emitted light is quantized (→photon).

$$KE = \frac{1}{2}mv^2 = h\nu - \phi$$

(ϕ is work function)

Table of work functions

Materials	ϕ / eV
Na	1.82
Au	4.69
GaAs	4.6
anthracene	4.71
Cu-phthalocyanine	4.56

1 eV = 1.602×10^{-19} J

1-4 The Hydrogen Atomic Spectrum Consists of Several Series of Lines.

Atoms at high temperature emits light (with specific frequency).

Balmer's empirical formula (for Hydrogen's emission spectrum line)

$$\nu = 8.2202 \times 10^{14} \times \left(1 - \frac{4}{n^2}\right) \text{ Hz}$$

excitations of n = 2 → n = 3, 4, 5・・・ (Balmer series)

1-5 The Rydberg Formula Accounts for All the Lines in the Hydrogen Atomic Spectrum.

Rydberg (~1887): $\tilde{\nu} = \frac{1}{\lambda} = 109680 \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1}$

→ Rydberg constant (R_H)

Similar formula can hold for other atomic spectrum line

$$\tilde{\nu} \propto \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1} \Rightarrow \text{Ritz's combination rule}$$

1-6 Louis de Broglie Postulated that Matter has Wavelike Properties

Physical description of light: wave-like, particle-like $\longrightarrow$ wave-particle duality

Einstein (theory of relativity)

$$\lambda = \frac{h}{p} \quad \left(p = \frac{h}{\lambda} = \frac{k}{2\pi} h = k\hbar \right)$$

de Broglie formula

$$\lambda = \frac{h}{m\upsilon} \text{ (de Broglie wavelenghth)}$$

Moving particle	λ / pm
100 V electron	120
Ra α ray	6.6×10^{-3}
golf ball	4.9×10^{-22}

1-7 de Broglie Waves are Observed Experimentally

X ray beam $\rightarrow$ X ray diffraction
electron beam $\rightarrow$ electron (beam) diffraction $\rightarrow$ TEM

Physical description of electron:
particle-like (J.J. Thomson, Nobel prize winner (1906))
wave-like (G.P. Thomson, Nobel prize winner (1937))

1-8 The Bohr Theory of the Hydrogen Atom can be Used to Derive the Rydberg Formula

Bohr's hydrogen atom model

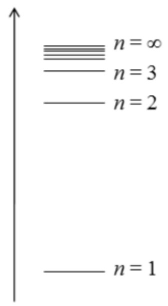
Balance of Coulombic force and centrifugal force

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m\upsilon^2}{r} \quad \Rightarrow \quad \text{classically forbidden (unsustainable motion)}$$

Introduction of non-classic condition

$$2\pi r = n\lambda \qquad (\lambda\text{: de Broglie wavelength})$$

$$m\upsilon r = n\hbar \qquad \text{(quantization of angular momentum)}$$



$$r = \frac{4\pi\varepsilon_0 \hbar^2 n^2}{me^2} = 5.292\times10^{-11}\ \text{m} \quad \text{(Bohr radius } (a_0))$$

$$E = -\frac{e^2}{8\pi\varepsilon_0 r} = -\frac{me^4}{8\pi\varepsilon_0^2 h^2}\frac{1}{n^2}$$

$$\Delta E = \frac{me^4}{8\pi\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu \qquad \text{(Bohr frequency condition)}$$

$\rightarrow$ 109737 cm^{-1} $\equiv R_\infty$ (*cf.* R_{H} = 109680 cm^{-1})

($2R_\infty$ is used as atomic unit of energy)

1-9 The Heisenberg Uncertainty Principle States the Position and the Momentum of a Particle Cannot be Specified Simultaneously with Unlimited Precision

Resolution of microscope $\Delta x \cong \lambda$ (wavelength of light)

Momentum of light $p = \dfrac{h}{\lambda}$ ⇒ partially transferred to electrons

$\Delta x \cdot \Delta p \geq h$ Uncertainty principle

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Conflict with Bohr theory

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Construction of new quantum theory