

Chapter 11: Quantum Theory

11.1 Deviations of the real world from the classical approximation

11.1.1 Electromagnetic equilibrium energy distribution

Radiation Intensity M (energy/time/area) $\sim T^4$; and
radiation density ε (energy/volume) $\sim T^4$ (Tyndall¹, Stefan² 1879, Boltzmann³);

λ_{Max} (wavelength of maximum radiation intensity per wavelength) $\sim 1/T$ (Wien⁴ 1893)
at 1000 K: 2.9 μm ; at 6000 K: 480 nm Note: $\lambda \cdot \nu = c \leftrightarrow d/d\lambda = \nu^2/c \cdot d/d\nu$

for small ν : $d\varepsilon/d\lambda \sim \nu^4$ kT (Rayleigh⁵-Jeans⁶: ultraviolet catastrophe for large ν)

Planck 1900⁷: $d\varepsilon/d\lambda \sim \nu^5/(e^{h\nu/kT}-1)$ is fully correct in all these respects, basis:
emission and absorption is a quantized process – 'ladle sugar with a spoon'

11.1.2 Photoelectric effect

E_{kin} of photoelectron = $h\nu - A$, independent of intensity
(A = work function, ionization potential)

(Einstein⁸ 1905: radiation IS quantized – 'cube sugar')

$E_{\text{photon}} = h \cdot \nu = (h/2\pi) \cdot (2\pi \cdot \nu) = \hbar \cdot \omega = \omega$ in au

11.1.3 Size of atoms

all atoms are of the order of $1\text{\AA} = 10^{-10} \text{ m} = 100 \text{ pm}$ (Clausius⁹, Loschmidt¹⁰)

$\varepsilon_0 \cdot h^2/m_e \cdot e^2 = 1.66 \text{\AA} = \pi \cdot \text{Bohr}$ (A. Haas¹¹: 1910)

11.1.4 Bohr's model of H-atom and the periodic system (1913)¹²

Assumptions: Atomic and molecular transitions, states are discrete, stationary. Angular momentum is $n \cdot \hbar$, $n = 1, 2, \dots$ (two errors: rotation in 2d, smallest $n = 1$)

Then he could explain - a) some qualitative aspects and the basic order of the PS (Moseley¹³: atomic number = nuclear charge $\sim \sqrt{1/\lambda_{\text{x ray}}}$); - b) extremely accurately the spectra of H and He^+

¹ Tyndall, 1820-1893, Ireland : physicist

² Stefan, 1835-1893, Wien : physicist

³ Boltzmann, 1844-1906, Wien : statistical physical theories

⁴ Wien, 1864-1938, East Prussia – West Germany – Bavaria : physicist

⁵ Rayleigh, 1842-1919, England : physicist

⁶ Jeans, 1877-1946, England : scientist

⁷ Max Planck, 1858-1947, Kiel – Berlin – Göttingen : theory of radiation, thermodynamics, president of the German academy before and again after the war

⁸ Einstein, 1879-1955, Ulm – Zürich – Prag – Berlin – Princeton : Brown's motion, theory of physical invariants (so-called 'theory of relativity'), theories of photo-electric effect, of specific heat of solids, of gravitation, of space and time, interpretation of problems of quantum theory, initiated development and control of nuclear bombs

⁹ Clausius, 1822-1888, Prussia (Köslin, Bonn) : mechanical theory of heat and gases, defined the entropy

¹⁰ Loschmidt, 1821-1895, Austria : size of molecules \rightarrow Avogadro number; cyclic formula of benzene

¹¹ Arthur Haas, 1884-1941, Austria – Saxony – USA : atomic theory and its popularization

¹² Periodic System: J.L. Meyer (1830-1895, Tübingen : chemist) published a rather correct P.S. in his textbook of 1864 to systematize the chemical knowledge. D.I. Mendelejev (1834-1907, St. Petersburg : chemist) published a less correct P.S. in 1869 to predict unknown elements.

¹³ Moseley, 1887-1915 (WW1), England : physicist

11.1.5 Specific heat at low temperatures

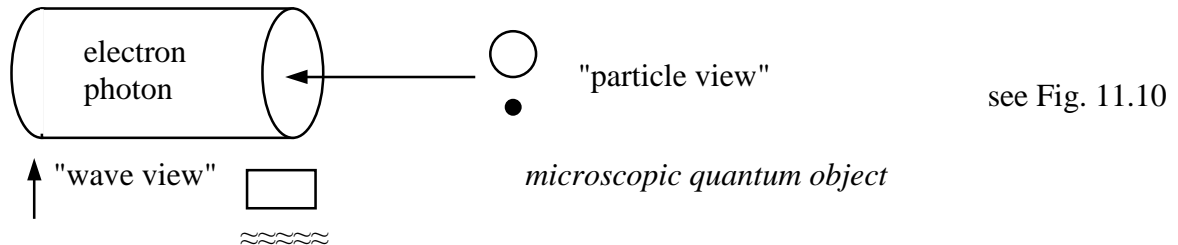
vibrating diatomic: $c \sim (h\nu/kT)^2 \cdot e^{-h\nu/kT}$ (Einstein)

condensed matter: $c \sim T^3$ (Debye)

but if $kT \gg$ excitable component of energy: $c_{\text{excitable component}} = R/2$

11.1.6 Prince de Broglie's idea (1924)¹⁴

Matter has both particle and wave properties: $\lambda = 2\pi\hbar/p = h/p$



11.2 Classical and Quantum Mechanical Principles

Heisenberg (1925)¹⁵, Schrödinger (1926)¹⁶, Born (1926)¹⁷: Beginning of the "complete theory of objective reality" = Quantum Mechanics

11.2.1 Concepts

■ **1) Macroscopic people perform macroscopic measurements.** Describe the human observations with "classical" concepts: m mass, e charge; x position, p momentum.

But: if one measures position, momentum, ... of mass, charge, ... one does not obtain a well defined sharp result. In general one obtains a **well defined distribution of results**.

The total reality is not as the macroscopic sector of the world seems to be.

So: Substance (mass = energy ≥ 0 ; charge is $<$ or $>$ 0 ;etc.) does **not have a sharp value** of position, velocity, ↗ , it has a **"smeared value"** distribution ↘ .

■ **2) Newton's¹⁸ mechanics & Maxwell's¹⁹ electrodynamics** are a good approximation for the world of "human dimensions".

def: $p = m \cdot dx/dt$, law: $F = dp/dt$, $F_{\text{conserv.}} = -dE_{\text{pot}}/dx$, with $E_{\text{pot}} = e_1 \cdot e_2 / 4\pi\epsilon_0 r$, $E_{\text{kin}} = p^2/2m$

Hamilton²⁰: $H = E_{\text{kin}} + E_{\text{pot}}$. $H(x,p,t)$ is constant in time for "conservative" forces and "closed systems".

¹⁴ **Duke de Broglie**, 1892-1987, France : theoretician

¹⁵ **Heisenberg**, 1901-1976, Germany : development and application of quantum mechanics in *abstract matrix form* to atoms, nuclei, elementary particles, magnetism, superconduction, cosmos; uncertainty concept; nuclear reactor

¹⁶ **Schrödinger**, 1887-1961, Austria - Schwaben - Schweiz - Schlesien - Preussen - England - Irland : Statistical theory, color TV, development and application of quantum mechanics in more concrete form of differential equations, gravitational and field theories

¹⁷ **Born**, 1882-1970, Germany - Scotland : theoretician, formulation and interpretation of quantum theory

¹⁸ **Newton**, 1643-1727, England : founded physics as a „fully developed science“; ‘Philosophiae naturalis principia mathematica’ = ‘Mathematical principles of science of nature’ 1687; mechanics with „Galilei-Newton-Relativity“; gravitation (Hooke); differential calculus (Leibniz); ‘Opticks’ including some chemical concepts

¹⁹ **Maxwell**, 1831-1879, Scotland - England : kinetic theory of gases, vector and tensor analysis, electromagnetic field theory

²⁰ **Hamilton**, 1805-1865, Ireland : improved the theory of mechanics and optics (extremal principles, Hamilton's energy function); invented the quaternions as a noncommutative extension of the complex numbers, which are now used to describe the spin

Newton's definition and law now read symmetrically : $\boxed{dx/dt = \partial H/\partial p \quad \text{and} \quad dp/dt = -\partial H/\partial x}$

(x, p) , (φ, ℓ) , (t, E) are classically conjugated pairs of variables.

Development, propagation in time is well determined: causality.

■ **3)** Classical observables \rightarrow linear, Hermitean operators:

$$x \rightarrow \mathbf{x}, p \rightarrow \mathbf{p}$$

The "smeared trajectories, smeared orbits" are called "wavefunctions, distribution amplitudes, state functions, state vectors, orbitals", they obey generalized laws: instead of classical laws for orbits, we have generalized laws for orbitals.

Classical laws for observables \rightarrow laws of the operators: $E_{\text{kin}} \rightarrow 1/2m \cdot \mathbf{p} \cdot \mathbf{p}$,
 $E_{\text{pot}} \rightarrow e_1 e_2 / 4\pi\epsilon_0 \cdot \mathbf{r}^{-1}$

Complete description of a real, objective system by an intermediate quantity:
 trajectory \rightarrow wavefunction.

Compare the description of easily measurable electric, magnetic and gravitational forces by the "really existing" respective potential fields. - Plato's cave parable: we can easily see only the shadow on a screen (observations of particle motions) of the real world (wave function, potential)

Note: a single observation yields a single rational number, e.g. $\bar{B}_1(\vec{r}_0) = (\vec{\nabla} \times \vec{A})_{1\text{st component at } r_0}$ (where \vec{A} and $\vec{A} + \vec{\nabla} g$, g arbitrary function, are equivalent). The "real" object in classical electrodynamics in the potential field \vec{A} , which is a whole "gauge-equivalent" *set of functions*. The "real" object in the world is a complex "wavefunction", which can be multiplied by any complex number, for instance (a state vector space).

■ **4)** Theory shall be simple and applicable to reality. Therefore we introduce the following choices:

- Wavefunction shall be complex and analytic (differentiable): then many mathematical theorems apply.
- Operators shall be linear and Hermitean

11.2.2 Heisenberg's Uncertainty

A typical experiment: Accelerate an electron (e , m_e) by an electric potential difference V to determine velocity v_e and momentum p_e :

$$e \cdot V = m_e \cdot v_e^2/2 \quad p_e = m_e \cdot v_e \quad \text{classical mechanics \& electro-dynamics}$$

Then determine the position at a specified time with a microscope:

$$\Delta x_e > \lambda_{\text{ph}} \quad \lambda_{\text{ph}} \cdot v_{\text{ph}} = c_{\text{ph}} \quad \text{classical wave optics}$$

Now account for the two most basic new laws of physics:

$$\text{Einstein 1905:} \quad E = mc^2 \quad \text{equivalence (not convertibility !) of inertial and gravitational masses and energy}$$

$$E = h \cdot \nu \quad \text{quantisation of matter and energy}$$

$$\Rightarrow \text{For any observation: } \Delta x_e \cdot \Delta p_e > \lambda_{\text{ph}} \cdot p_{\text{ph}} = c_{\text{ph}}/v_{\text{ph}} \cdot m_{\text{ph}} c_{\text{ph}} = E_{\text{ph}}/v_{\text{ph}} = h$$

$$\text{Heisenberg 1927: always } \Delta a_{\text{exp}} \cdot \Delta b_{\text{exp}} > \Delta a_{\text{theo}} \cdot \Delta b_{\text{theo}} = \text{UP} > \hbar/2$$

a, b are a conjugated pair of observables. The uncertainty product UP depends on the system and its state (rule of thumb: $UP \sim n \cdot \hbar$ for n^{th} quantum state)

$UP = \hbar/2$ only for the ground state of a harmonic oscillator (diat. mol., el.mag. oscillation)

Δ is the variance (standard deviation) of repeated measurements on the same type of system in the same state:

$$x_i = \sum \bar{x} = \sum x_i / \sum 1 ; \Delta x = \sqrt{\sum (x_i - \bar{x})^2 / \sum 1}$$

Note: $\langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \geq \langle x^2 \rangle$ (equal sign only for choice of Zero so that $\langle x \rangle = \bar{x} = 0$)

A reliable scientist believes in measured values as $\bar{x} \pm (2 \text{ to } 3) \cdot \Delta x$, tabulated is $\bar{x} \pm \Delta x$.

Δ is obtained experimentally from an ensemble. But the Δ from an "absolutely accurate" measurement series on a "completely prepared" ensemble of equivalent systems is the quantum property of each single system!

Confining a system within Δx causes a momentum smearing $\Delta p > \hbar/2\Delta x$ and a kinetic energy $> \Delta p^2/2m = \hbar^2/8m \Delta x^2$ (zero point energy)

11.2.3 The general theory

■ a) A well defined subsystem of the world, e.g. an "isolated" molecule (but note: no system is really isolated, particularly when being investigated) is completely represented by its state vector $|\psi\rangle$.

a1) If $|\psi_1\rangle$ and $|\psi_2\rangle$ are states of system, $c_1|\psi_1\rangle + c_2|\psi_2\rangle$ is also a possible state (superposition principle). The two states need not have the same energy, etc.

a2) If the state $|\psi_1\rangle = |1\rangle$ is represented by a complex function $\psi(x)$ then the probability of measuring the discrete value x_i of the smeared property x is $W_i = |\psi(x_i)|^2$ (Born's probability interpretation).

■ b) Every directly measurable quantity a is represented by a linear Hermitean operator \mathbf{a} .

b1) In the special case where property a is "sharp", i.e. always has value a_0 , then the state $|\psi_{a_0}\rangle$ fulfills $\mathbf{a} \circ |\psi_{a_0}\rangle = |\psi_{a_0}\rangle \cdot a_0$

b2) The expectation value is $\bar{x} = \sum x_i \cdot W_i / \sum W_i = \langle \psi_i | \mathbf{x} | \psi_i \rangle / \langle \psi_i | \psi_i \rangle$.

Remember Dirac's convention: $\langle f | \mathbf{a} | g \rangle = \int_a^b dx \cdot f^*(x) \cdot \mathbf{a} \circ g(x)$

■ c) The basic law of nature is Heisenberg's commutator relation $[\mathbf{a}, \mathbf{b}] = i\hbar$; where a, b are classically conjugate properties.

$$\rightarrow \Delta a \cdot \Delta b > \hbar/2 \quad (\text{uncertainty relation})$$

$$\text{if } \mathbf{a} \cdot = a \cdot \text{ then } b = \pm i\hbar d/da$$

$$\rightarrow d\Psi/dt = \mathbf{H} \circ \Psi / i\hbar \quad \text{with } \mathbf{H} = \mathbf{E}_{\text{kin}} + \mathbf{E}_{\text{pot}} \quad (\text{time dependent Schrödinger equation})$$

Quantum causality: the time evolution of the state is well determined

(Since the measuring device is not known in every microscopic detail, the measuring result can only be predicted statistically)

c1) If the potential $V(x,t)$ does not depend on t explicitly (no external time dependent perturbation), *some* of the solutions of the Schrödinger equation are of the form

$$\Psi(x,t) = \psi(x) \cdot \chi(t) \quad \text{with} \quad \chi(t) = e^{-iEt/\hbar} \quad \text{and} \quad E, \psi(x) \text{ obey the time independent S.E.}$$

$$\mathbf{H}(x) \circ \psi(x) = \psi(x) \cdot E \quad (E = \text{eigenvalue of the energy operator } \mathbf{H})$$

Such states have a well defined energy ($\Delta E = 0$) and do not change properties in time (stationary). Of course there are also exist other states, varying in time.

11.3 Summary

11.3.1 Classical physics

$$\text{def: } \mathbf{p} = m \cdot \mathbf{v}, \quad \text{law: } F = dp/dt = -\Delta V, \quad \text{potential } V = e_1 e_2 / r, \quad T = p^2 / 2m, \quad H = V + T$$

definition of conjugated variables a, b : $\partial H / \partial a = db/dt$ ($x \& p, \phi \& \ell, t \& E$)

$$\text{basic law of motion:} \quad \partial H / \partial b = -da/dt$$

1-particle state: give a and b at t_0 : $a(t)$ & $b(t)$ determined by Newton-Hamilton's law (trajectory in phase space)

Virial theorem: For $T \sim p^2$ and $V \sim r^n$:

$$2T = nV \rightarrow T = n/(n+2) \cdot E, \quad V = 2/(n+2) \cdot E$$

Examples: Coulomb and gravitational forces: $T = -E = -0.5V$

Harmonic or Hook forces: $T = V = 0.5 E$

Also holds for expectation values quantum mechanically. Note: "One electron" in a many electron system 'sees' a complicated potential, then $T \approx -V \gg E$.

11.3.2 Quantum physics

$$\text{Basis: } \Delta E = \hbar \cdot \nu = \hbar \omega \quad \lambda = 2\pi/p \quad E = mc^2 \quad \Delta x = \lambda \quad \lambda \cdot \nu = c \rightarrow \Delta x \cdot \Delta p \sim \hbar$$

Concepts: observable variable \rightarrow linear (!), Hermitean (!) operator

orbit, trajectory \rightarrow orbital, wavefunction, state vector $|\Psi_i(a)\rangle = |\Phi_i(b)\rangle = |i\rangle$

definition of commutator $[\mathbf{a}, \mathbf{b}] = \mathbf{a} \cdot \mathbf{b} - \mathbf{b} \cdot \mathbf{a}$ basic law $[\mathbf{a}, \mathbf{b}] = i\hbar \cdot$

a-representation: $\Psi(a,t) \leftrightarrow$ Fourier transformation $\leftrightarrow \Phi(b,t)$

$$\mathbf{a} \rightarrow \mathbf{a} = a \cdot \quad \text{and} \quad \mathbf{b} \rightarrow \mathbf{b} = -i\hbar \cdot \partial / \partial a$$

$$\text{examples: } \Psi(x,t), \quad \mathbf{x} = x \cdot \quad \text{and} \quad \mathbf{p} = -i\hbar \cdot d/dx;$$

$$\mathbf{E} = \mathbf{H} = V(x) \cdot -1/2m \cdot d^2/dx^2 = i\hbar \cdot d/dt$$

Eigenvalues of Hermitean operators are real. Eigenfunctions of different eigenvalues are orthogonal

$$\Delta a \cdot \Delta b \approx n \cdot \hbar > \hbar/2$$

$$d\Psi/dt = \mathbf{H} \circ \Psi(x,t) / i\hbar$$

If $dV/dt = 0$, there exist stationary states:

$$\Psi(x,t) = \psi(x) \cdot e^{-iEt/\hbar} \quad \text{with} \quad E, \psi(x) \quad \text{from} \quad \mathbf{H} \circ \psi(x) = \psi(x) \cdot E$$

Eigenvalues d of operator \mathbf{d} are the possible measured results

Eigenfunctions of d have a sharp observable variable value d : $d_0 = \bar{d} = \langle \psi | \mathbf{d} | \psi \rangle / \langle \psi | \psi \rangle, \quad \Delta d = 0$.

Learning objectives

After careful study of this chapter you should be able to:

(1) List the characteristics of *black-body radiation* and explain how *Planck's hypothesis* of the quantization of energy explains them, Section 13.2(a).

(2) Explain how the characteristics of the *heat capacities* of solids at low temperatures conflict with classical physics but are explained by the quantum theory, Section 13.2(b).

(3) Describe the experimental features of the *photoelectric effect*, Section 13.2(c), and show how the quantum theory accounts for them in terms of *photons*, eqn (13.2.6).

(4) Describe the features of the *Compton effect* and explain how quantum theory accounts for them, Section 13.2(d).

(5) Summarize the evidence for the *wave-nature of matter*, Section 13.2(e), and state the *de Broglie relation*, eqn (13.2.8).

(6) Explain why *atomic and molecular spectra* provide evidence for quantization, Section 13.2(f).

(7) Write the *Schrödinger equation* for a general potential energy, eqn (13.3.1).

(8) Show that the solutions of the Schrödinger equation for a free particle lead to the de Broglie relation, eqns (13.3.2–4).

(9) Describe the relation between the *curvature* of the wavefunction and the *kinetic energy* of the

particle it describes, Section 13.3(a).

(10) State the *Born interpretation* of the wavefunction, Section 13.3(b).

(11) Justify and write the *normalization condition*, eqn (13.3.7), and *normalize* a wavefunction, Example 13.3.

(12) List the conditions that must be satisfied by a wavefunction for it to be acceptable, and explain how these lead to quantization, Section 13.3(c).

(13) Explain what is meant by an *operator*, an *eigenvalue equation*, an *eigenvalue*, and an *eigenfunction*, eqn (13.4.3).

(14) Explain the relation between *operators* and *observables*, eqn (13.4.4).

(15) Write the operator for the *linear momentum*, eqn (13.4.5), and the *position* of a particle.

(16) Write the wavefunctions for a particle in a definite state of linear momentum, Section 13.4(a).

(17) Explain the term *superposition* and its interpretation, Section 13.4(b).

(18) Explain the significance of an *expectation value*, Section 13.4(b), and calculate its value for a given wavefunction, Example 13.6.

(19) State the *uncertainty principle*, eqn (13.4.8), and justify it in terms of a superposition of wavefunctions, Section 13.4(c).

(20) Explain the meaning of the expression *complementary observables*, Section 13.4(c).