Chapter 1. From Classical to Quantum Mechanics

Classical Mechanics (Newton): It describes the motion of a classical particle (discrete object).

$$F = ma = \frac{dp}{dt}, \quad p = m\upsilon = m\frac{dx}{dt}$$

F: force (N)
a: acceleration ($a = d\upsilon / dt = d^2x / dt^2$)
p: momentum (kg m/s)
x: position (m)

At every time instance, a particle has *definite position and momentum* $\{x(t), p(t)\}$ with well-defined energy:

$$E = \frac{p^2}{2m} + V(x)$$

where the potential gives rise to the force:

$$F = -\frac{dV(x)}{dx}$$

The state of a classical particle is specified by a point in the *phase space*: $\{x(t), p(t)\}$, and its evolution is called a *trajectory*.

Classical mechanics is deterministic.

<u>Classical Electrodynamics (Maxwell</u>**):** Four equations specify properties of an electromagnetic wave.

Light is electromagnetic wave with a speed of light with oscillating electric and magnetic fields. It differs from a Newtonian particle in that it fills the entire space and is continuous.

$$\lambda\nu = c, \qquad \tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

λ: wavelength (nm)
ν: frequency (Hz = s^{-1})
$\tilde{\nu}$: wave numbers (cm^{-1})
c: speed of light (3.0×10^{10} cm/s)

γ-ray x-ray UV visible IR radio wave
λ
ν ($\tilde{\nu}$)

Classical physics:

- energy is continuous,
- either wave or particle,
- position and momentum of a classical particle are well defined and measurable at the same time.

Blackbody radiation:

Blackbody is an object that absorbs and emits at all frequencies. An example is a heated metal.

Observations:

- independent of material
- radiation has continuous spectrum and a peak
- spectral peak changes with temperature

Rayleigh-Jeans law (classical electrodynamics theory)

$$\rho(\nu,T)=\frac{8\pi kT\nu^2}{c^3}$$

ρ: energy (spectral) density
k: Boltzmann constant (1.38×10^{-23} J/K)

Assumption: blackbody consists of a collection of oscillators (electrons, phonons, etc.) with arbitrary energies ($\propto kT$).

Fits the experimental curve well at low frequencies,
But when $\nu\to\infty$, $\rho\to\infty$ (ultraviolet catastrophe).

Planck's distribution (1900):

$$\rho = \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{e^{h\nu/kT} - 1}\right)$$

h: Planck's constant (6.626×10^{-34} Js)

When $\nu \to \infty$, $\rho \to 0$.

When $h\nu/kT << 1$, $\rho(\nu,T) = \dfrac{8\pi kT\nu^2}{c^3}$. $\quad (e^x \approx 1 + x)$

Assumption: energies of oscillators are *quantized*!

$$E = nh\nu \ , \Delta E = h\nu$$

Significance: for the first time, energy was assumed to be quantized!

The photoelectric effect

Electrons emit from metals when UV light is shone (1887 Hertz)

Observations:

- No e^- if $\nu < \nu_t$, even at high light intensity
- Above ν_t, e^- emitted even at low light intensity, but # of e^- increases with light intensity.
- Kinetic energy of e^- linearly proportional to ν.

Classically, e^- emission proportional to light intensity, not ν.

<u>Einstein's theory</u> (1905, *quantization of radiation field*)

$$\frac{1}{2}m_e\upsilon^2 = h\nu - \phi$$

Work function (E_{min} for e^- escape) $\phi = h\nu_t$.

Significance: light is made of *particles* called photons, each with $E = h\nu$!

Example: a 300 nm laser was used to knock out electrons from a metal. The velocity of the emitted electrons is about 8.1×10^5 m/s. Estimate the work function for the metal.

$$\phi = \frac{hc}{\lambda} - \frac{1}{2}m_e\upsilon^2 = -\frac{6.626\times10^{-34}\,Js\times3.0\times10^8\,m/s}{300\times10^{-9}\,m}$$

$$-\frac{9.1\times10^{-31}\,kg\times\left(8.1\times10^5\,m/s\right)^2}{2}$$

$$= 6.62\times10^{-19} - 2.99\times10^{-19} = 3.62\times10^{-19}\,J$$

Matter wave (1923, de Broglie)

Photon can behave either as a wave, which has wavelength, or a particle, which has momentum.

For photon:

$$E = mc^2 = h\nu$$

$$mc^2 = hc/\lambda \qquad (\lambda\nu = c)$$

so

$$\lambda = h/p \qquad (p = mc)$$

de Broglie reasoned that this might be true for all particles.

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

Matter-wave dualism: quantum objects may behave as either particles or waves.

Electron diffraction (1927, Davisson-Germer and Thomson)

Classically, e^- cannot interfere because it is a particle.

Conclusions:

i. electron can be wave-like (interference).

ii. crystal serves as grating if the lattice constant is comparable to λ.

Example: Calculate de Broglie wavelength for an e⁻ accelerated from rest thru a potential difference of 100 V

Kinetic energy

$$m_e \upsilon^2/2 \;=\; e\Delta\phi \qquad \text{or} \qquad \upsilon = (2e\Delta\phi/m_e)^{1/2}$$

and momentum

$$p \;=\; m_e \upsilon = (2m_e e\Delta\phi)^{1/2}$$

de Broglie wavelength

$$\begin{aligned}\lambda &= h/p \\ &= h/(2m_e e\Delta\phi)^{1/2} \\ &= \frac{6.626\times10^{-34}\,Js}{[(2\times9.109\times10^{-31}\,kg)(1.602\times10^{-19}\,C)(100.00V)]^{1/2}} \\ &= 1.23\times10^{-10}\,m = 1.23\times10^{-1}\,nm\end{aligned}$$

Crystal lattice const. is approx 0.1 nm, so e⁻ can be diffracted. Electronic wavelength can be controlled by electric field.

Double slit diffraction

Waves interfere, do particles?

The diffraction pattern confirms the wave nature of quantum particles.

Atomic spectrum

Rutherford's planetary model (1909) for atoms leads to an unstable atom since accelerate charges (electrons) emit continuous radiation, lose energy, and eventually collapse.

Observations:

- Stable atoms
- Line spectrum

For hydrogen, all lines can be described the Rydberg formula:

$$\tilde{\nu} = R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers ($n_1 < n_2$) and R_H = 109677 cm^{-1} is the Rydberg's constant.

Example: Origin of the Balmer (2→3 transitions) series

$$\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109677 cm^{-1}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 15232.9 cm^{-1}$$

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{15232.9 cm^{-1}} = 6.565 \times 10^{-5} cm = 656.5 nm$$

Bohr's atom model (1911)

Electron moves in an orbital associated with *quantized energy*. Transitions between orbitals correspond to absorption or emission

$$h\nu = |E_n - E_m|$$

and the quantized energies (E_n) can be obtained from semi-classical conditions:

$$2\pi r = n\lambda = n\frac{h}{p}, \quad \text{or} \quad m_e \upsilon r = nh/2\pi$$

Bohr's radius:

$$r = \frac{\varepsilon_0 h^2 n^2}{\pi m_e e^2} = 5.29 \times 10^{-11} m \quad (n=1)$$