CHAPTER 11: Quantum Theory: Introduction and Principles

…Classical mechanics fails when applied to the transfers of very small quantities of energy and to objects of very small mass.

The failures of classical physics:

A. Newtonian mechanics failures

1. observation of black-body radiation
2. heat capacities
3. atomic and molecular spectra

B. Failures of classical electromagnetic waves theories

1. Compton scattering
2. photoelectric effect
3. optical spectra
4. two-slit experiment

<u>Discussions:</u>

(a) Black-body radiation.

An analysis of the data led Wilhelm Wien (in 1893) to formulate the Wien displacement law:

$T\lambda_{max} = \frac{c_2}{5}$, where $c_2 = 1.44$ cm K; c_2 is called the second radiation constant.

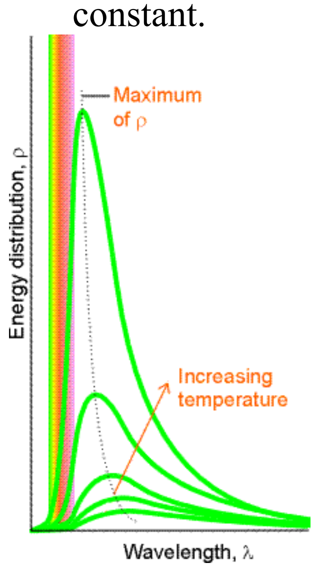

Fig. 1: The energy distribution in a black-body cavity at several temperatures. Note how the energy density increases in the visible region as the temperature is raised, and how the peak shifts to shorter wavelengths. The total energy density (the area under the curve) increases as the temperature is increased (as T^4).

A second feature of black-body radiation:

Josef Stefan 1879 determined the total energy density, ε:

$$\varepsilon = E/V = a\,T^4 \text{ : Stefan-Boltzman law}$$

…An alternative form of the law is in terms of the excitance, M, the power emitted by a region of surface divided by the area of the surface: … a measure of the brightness

$$M = \sigma T^4 \,;\ \sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$$

…The Stefan-Boltzmann law implies that 1 cm^2 of the surface of a black body at 1000K radiates about 6 W when all wavelengths of the emitted radiation are taken into account.

…It is to be noted that the Classical concept leads to the Rayleigh-Jeans equation:

$$d\varepsilon = \rho\, d\lambda \text{, where } \rho = \frac{8\pi k T}{\lambda^4} \quad \text{(The Rayleigh-Jeans equation)}$$

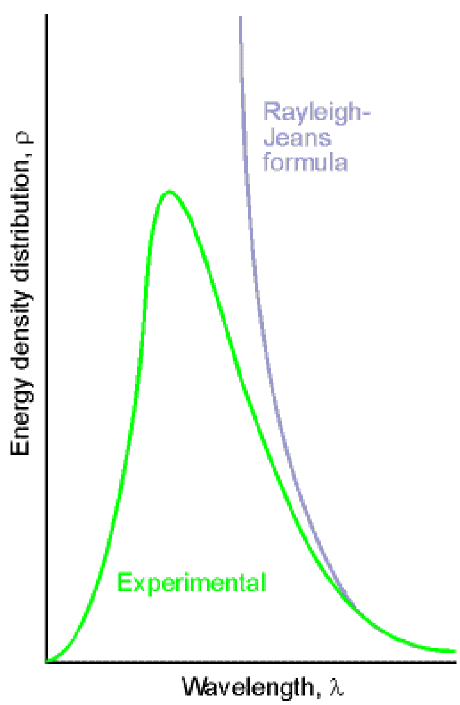

Fig. 2: The Rayleigh-Jeans law predicts an infinite energy density at short wavelengths. This prediction is called the ultraviolet catastrophe.

…The Rayleigh-Jeans equation predicts that oscillators of very short wavelength are strongly excited even at room temperature. …This leads to the so-called Ultraviolet Catastrophe.

(b) The Planck distribution.

…oscillators are quantized: $E = nh\nu$, where $n = 0, 1, 2, \ldots$

The resultant equation is:

$$d\varepsilon = \rho\, d\lambda$$

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right); \text{ Note as } T \Rightarrow 0,\ \rho \Rightarrow 0.$$

This expression fits the experimental observation.

(c) Heat capacities (for a monotonic solid).

Dulong and Petit's law: --mean energy of oscillation is KT for each atom's direction of displacement (degree of freedom).

$$U_m \text{ (molar internal energy)} = 3N_a\, kT = 3\ RT$$

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_V = 3R$$

(Note: equipartition theorem average energy per squared term in the energy is $\frac{1}{2}kT$.)

For heat capacities measured at low temperatures, Dulong and Petit's law is violated. Einstein in 1905 formulated correction:

$$U_m = \frac{3N_a h\nu}{e^{h\nu/kT} - 1}$$. Einstein quantitized atom's oscillations

$\therefore\ C_{V,m} = 3Rf$, where $f = \frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/2T} - 1}\right)$ and θ_E (is the Einstein temperature) $= h\nu/k$.

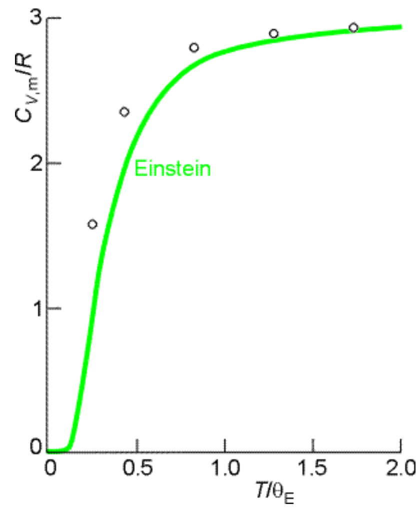

Fig. 3: Experimental low-temperature molar heat capacities and the temperature dependence predicted on the basis of Einstein's theory. His equation accounts for the dependence fairly well, but is everywhere too low.

The correction of the assumption that all atoms oscillate with the same frequency leads to the Debye formula:

$$C_{V,m} = 3Rf \text{ , where } f = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)} dx$$

where θ_D is the maximum value of the oscillation. $\theta_D = h\nu/k$ is the Debye temperature.

(d) Atomic and Molecular Spectra.

…The most compelling evidence for quantitization

C. Wave-particle duality

The above establishes that the energies of the electromagnetic field and the oscillating atoms are quantized.

(a) The particle character of electromagnetic radiation

(1) spectra

(2) photoelectric effect

(3) Compton scattering

(4) two slit experiment

(b) The wave character of particles

Note: de Broglie relation: $\lambda = h/p$

That is, a particle with a high linear momentum has a short wavelength. Macroscopic bodies have such high momenta (even when they are moving slowly) that their wavelengths are undetectably small, and the wave-like properties cannot be observed.

D. The Schrödinger equation

In 1926, the Austrian physicist Erwin Schrödinger proposed (for the time-independent) system

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

$$\hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-34}\ \text{J} \cdot \text{s}$$

More generally (e.g., in three-dimensions):

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi = E\psi} \quad ;\text{ where } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Note: The time-dependent Schrödinger equation is

$$\boxed{H\psi = i\hbar\frac{\partial\psi}{\partial t}}$$

* Note: quantization enters in and by itself. No need for inspired insight!!

E. The Born interpretation of the wavefunction

The Born interpretation of the wavefunction focuses on the square of the wavefunction (or the sqare modulus, $|\psi|^2 = \psi^*\psi$). It states that the value of $|\psi|^2$ at a point is proportional to the probability of finding the particle at that point.

(a) Normalization

$|\psi|^2$ can be normalized such that the proportionality of the Born interpretation becomes an equality. That is define N, such that

$$N\int \psi^*\psi\, dx = 1$$

(b) Quantization (How does it arise?)

The Born interpretation puts severe restrictions on the acceptability of wavefunctions. The principal constraints are that ψ must not be infinite over any finite region. Also, the wavefunction must be singled-valued.

The Schrödinger equation itself also implies some mathematical restrictions: the second derivative of ψ must be well-defined (function continuous), with continuous slope.

Thus, ψ must be continuous, have continuous slope, be single-valued, and be finite everywhere (except at spikes).

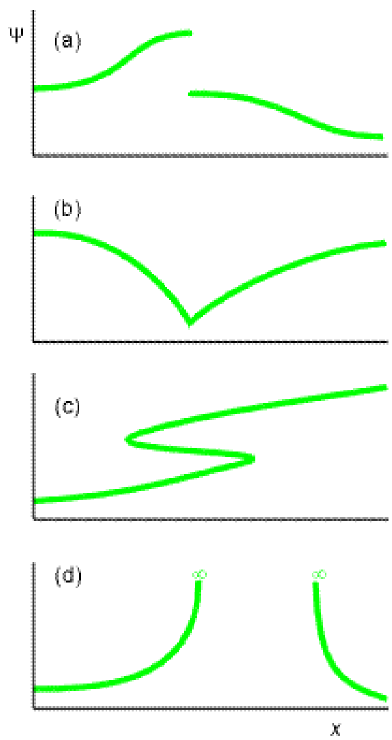

Fig. 4: The wavefunction must satisfy stringent conditions for it to be acceptable. (a) Unacceptable because it is not continuous; (b) unacceptable because its slope is discontinuous; (c) unacceptable because it is not single-valued; (d) unacceptable because it is infinite over a finite region.

Quantum Mechanical Principles

F. The information in a wavefunction

(1) Operators

$\hat{\Omega}\Psi = \omega\Psi$

Observables, ω, are represented by operators, $\hat{\Omega}$, built from the following position and momentum operators:

$$\hat{x} = x \quad \text{and} \quad \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$$

$$\text{Note: } \boxed{\hat{p}_x^2 = -\hbar^2 \frac{d^2}{dx^2}}$$

(2) Superpositions and expectation values

$\Psi = c_1\psi_1 + c_2\psi_2 + \cdots \quad = \sum_k c_k\psi_k$ (…e.g., the two-slit experiment)

$\langle\Omega\rangle = \int \Psi^* \hat{\Omega}\Psi \, d\tau$; sometimes written as $\overline{\Omega}$ (average value).

…an expectation value is a weighted average of a large number of observations of a property.

G. The uncertainty principle

It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

For example $\Delta p \cdot \Delta q \geq \frac{\hbar}{2}$, where

$$\Delta p = \left\{\langle p^2\rangle - \langle p\rangle^2\right\}^{1/2} \quad \text{and} \quad \Delta q = \left\{\langle q^2\rangle - \langle q\rangle^2\right\}^{1/2}$$

The Heisenberg uncertainty principle is more general than that above. It applies to any pair of observables called <u>complementary observables</u>, which are defined in terms of the properties of their operators:

$\hat{\Omega}_1\hat{\Omega}_2 \neq \hat{\Omega}_2\hat{\Omega}_1$ (i.e., they do not <u>commute</u>).

Note: $\Delta p^2 = \overline{(p - \overline{p})^2} = \overline{\left(p^2 - 2p\overline{p} + \overline{p}^2\right)} = \overline{p^2} - 2\overline{p}\,\overline{p} + \overline{p}^2 = \overline{p^2} - \overline{p}^2$

where $\overline{p^2} \equiv \langle p^2 \rangle$ and $\overline{p} \equiv \langle p \rangle$

…Also, mention <u>correspondence principle</u> …