A. Planck’s Theory of Radiation

- In 1901, Max Planck published a “quantum” theory of radiation which explains the known spectral distribution of black body radiators. His “quantum hypothesis” can be used to explain the heat capacities of diatomic molecules and solids. Planck’s quantum hypothesis can be constructed as follows.

- Assume as before the black body is composed of a large number of oscillators whose energies obey the harmonic oscillator equation:

\[ E = \frac{p^2}{2m} + \frac{\kappa x^2}{2} \]  \hspace{1cm} (2.1)

- The frequency of the harmonic oscillation is given in terms of the constants \( m \) and \( \kappa \) as

\[ \omega = 2\pi \nu = \sqrt{\frac{\kappa}{m}} \] \hspace{1cm} (2.2)

- Rearrange the equation for the harmonic oscillator as follows:

\[ a = \sqrt{2mE} \quad \text{and} \quad b = \sqrt{\frac{2E}{\kappa}} \] \hspace{1cm} (2.3)

- Now \( \frac{p^2}{a^2} + \frac{x^2}{b^2} = 1 \) is the equation of an ellipse with semi-axes \( a \) and \( b \), and so the trajectory of a harmonic oscillator (i.e. the set of points \((p,x)\) for all time) can be represented in momentum-coordinate space as an ellipse...
• Classically, when an oscillating atom emits radiation, its trajectory is modified as the momentum and the amplitude of displacement change. The energy emitted by an oscillator has no restricted values. But Planck assumed that in the black body, oscillator trajectories are restricted in such a way that only certain trajectories are possible.

• Only certain trajectories being allowed means that only ellipses with certain values of a and b may exist. The area of an ellipse is \( \pi ab \) and we can express this quantum restriction by saying

\[
nh = \pi ab = \pi (2mE)^{1/2} \left( \frac{2E}{k} \right)^{1/2} = \frac{2E}{\sqrt{k/m}} = \frac{E}{v},
\]

where \( v \) is the oscillator frequency. The constant \( h \) is Planck’s constant, and \( n \) is an integer. It follows that the energy of an oscillator is restricted by the rule \( E=nhv \), where \( n=0,1,2,3\ldots \)

• If an oscillator emits energy, it must pass from \( E=(n+1)hv \), say, to \( E=nhv \), which restricts energy changes to \( \Delta E=hv \).

• This means that energy is emitted into the cavity of the black body in discrete amounts or quanta. These energy “particles” are called photons.

B. Summary of Planck’s Quantum Theory of Radiation
• The intensity of radiation is still governed by the equation

\[
I(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle E \rangle,
\]

but Planck’s quantum hypothesis changes the expression for the average energy

\[
\langle E \rangle = \frac{hv}{e^{hv/kT} - 1} \tag{2.4}
\]

• Later in the course we will show how to obtain this result. For now

\[
I(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle E \rangle = \frac{8\pi\nu^2}{c^3} \frac{hv}{e^{hv/kT} - 1} = \frac{8\pi\nu^2}{c^3} \frac{h}{e^{hv/kT} - 1} \tag{2.5}
\]

• By fitting the equation for \( I(\nu, T) \) to data, Planck determined that the constant \( h=6.626\times10^{-34} \) J-sec. The constant \( h \) is now called Planck’s constant.

• At high temperature such that \( kT>>hv \), Planck’s Radiation Law must converge to the classical law, Jean’s Law.

C. The Wave-Particle Duality
• In 1925, deBroglie proposed an explanation for why an electron does not decay from a Bohr orbit. Recalling Planck’s hypothesis that radiation is quantized in particles of energy \( E=hv \) with momentum, deBroglie hypothesized that electrons have wavelengths. If the wavelength of an electron wave orbiting a nucleus is an integral
multiple of the length of the orbit, a standing electron wave results (see diagram below). deBroglie’s equation states that within a Bohr orbit: \( n\lambda = 2\pi R; \quad n = 1, 2, 3\ldots \)

- Using Bohr’s expression for the quantization of angular momentum

\[
mVR = \frac{nh}{2\pi} \Rightarrow 2\pi R = n\lambda = \frac{nh}{mV} \Rightarrow \lambda = \frac{h}{mV} = \frac{h}{p}
\]

(2.6)

- DeBroglie’s particle wave hypothesis can be used to obtain quantized energy expressions for very simple problems.

Example: For a particle in a box, the length of the box \( L \) must equal an integral multiple of half deBroglie wavelengths: \( n\left(\frac{\lambda}{2}\right) = L \), \( n = 1, 2, 3\ldots \)

But \( \lambda = \frac{h}{p} \) so

\[
n\left(\frac{\lambda}{2}\right) = \frac{nh}{2p} = L \Rightarrow p = \frac{h}{\lambda} = \frac{nh}{2L}
\]

(2.7)

- The energy is then

\[
E_n = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{nh}{2L}\right)^2 = \frac{n^2h^2}{8mL^2}
\]

(2.8)

- Now define \( \Delta E = E_{n+1} - E_n \)

\[
\Delta E = \frac{h^2}{8mL^2} \left( (n + 1)^2 - n^2 \right) = \frac{(2n + 1)h^2}{8mL^2}
\]

(2.9)

\( L \) is the path length associated with the motion. If \( L \) is very large, \( \Delta E \) becomes very small. If \( L \) becomes small the energy level splitting becomes large. Basically, (18.4) means that the larger the distance associated with the motion the smaller the quantization
effect. This explains why translational and rotational motions are not strongly quantized and obey the equipartition theorem while vibrational motions are quantized and at low temperature do not obey the equipartition theorem.

D. The Classical Wave Equation

• DeBroglie’s hypothesis of a wave-particle duality, brought to bear on the problem of atomic-level mechanics an impressive computational machinery built up in classical physics to treat wave mechanics. Specifically the wave function becomes an important tool in quantum mechanics. Here we review classical wave mechanics with a view to familiarize the reader with the idea of wave functions, eigenfunctions, and eigenvalues.

• In classical mechanics, wave functions are obtained by solving a differential equation. For example, the one-dimensional wave equation for a vibrating string with linear mass $\rho$ (units of kg/m) and tension $T$ (units of force) is

$$\frac{\partial^2 \Psi (x,t)}{\partial x^2} - \frac{\rho}{T} \frac{\partial^2 \Psi (x,t)}{\partial t^2} = 0$$

(2.10)

, where the wave velocity is given by $c = \sqrt{\frac{T}{\rho}}$. In this problem the wave function $\Psi(x,t)$ quantifies the vertical displacement of the string as a function of $x$ and $t$.

Any wave function of the form

$$\Psi_n(x,t) = A_n \cos(2\pi \nu_n t) \sin(\frac{2\pi x}{\lambda_n})$$

(2.11)

is a solution of the wave equation, where the specific forms for the wave frequency $\nu_n$ and the wavelength $\lambda_n$ are determined by the details of the problem. For example, for a harmonically vibrating string, fixed at $x=0$ and $x=L$ (i.e. $\Psi(0,t) = \Psi(L,t) = 0$). These boundary conditions impose the following requirements on the frequency and wavelength:

$$\nu_n = \frac{nc}{2L} \text{ and } \lambda_n = \frac{2L}{n} \text{ for } n = 1, 2, 3...$$

(2.12)

The frequencies $\nu_n$ are the harmonic frequencies of the vibrating string.

• Superposition: Any linear combination of wave functions

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t)$$

(2.13)
where $c_n$ is a constant, is also a solution to the wave equation.

- **Separation of Variables:** The solution in Equation (3.2) to the Wave equation (3.1) is obtained by a process called separation of variables. One assumes the wave function has a special form

$$\Psi(x,t) = \psi(x)f(t)$$

(2.14)

- Equation (3.5) is substituted into Equation (3.1):

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} - \frac{\rho \partial^2 \Psi(x,t)}{T \partial t^2} \Rightarrow \frac{\partial^2 \psi(x)f(t)}{\partial x^2} = \frac{\rho \partial^2 \psi(x)f(t)}{T \partial t^2}$$

$$f(t)\frac{\partial^2 \psi(x)}{\partial x^2} = \psi(x)\frac{\rho \partial^2 f(t)}{T \partial t^2} \Rightarrow \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} = \frac{\rho}{T} \frac{\partial^2 f(t)}{f(t) \partial t^2}$$

(2.15)

- The last expression in Equation (3.6) has all the $x$ variables on the left and all the $t$ variables on the right. This can only be so if the lhs and rhs are equal to a constant

$$\frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} = \frac{\rho}{T} \frac{\partial^2 f(t)}{f(t) \partial t^2} = -\alpha$$

(2.16)

The wave equation has been separated into two equations which can be solved separately:

$$\frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} = -\alpha \Rightarrow \frac{\partial^2 \psi(x)}{\partial x^2} + \alpha \psi(x) = 0$$

(2.17)

and

$$\frac{\rho}{T} \frac{1}{f(t)} \frac{\partial^2 f(t)}{\partial t^2} = -\alpha \Rightarrow \frac{\partial^2 f(t)}{\partial t^2} + \frac{\alpha T}{\rho} f(t) = 0$$

(2.18)

- A wave function that is independent of time is called a stationary wave. Equation (3.8) is the differential equation for a stationary wave is

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \alpha \psi(x) = 0$$

(2.19)

where $\alpha$ is a constant. If the boundary conditions are $\psi(0) = \psi(L) = 0$ any function of the form

$$\psi_n(x) = \sin\left(\frac{n\pi x}{L}\right)$$

(2.20)

is a solution if $\alpha_n = \left(\frac{n\pi}{L}\right)^2$. Any linear combination of functions of the form (3.11) is also a solution.