Part I

First-Principles Calculations

1 A Short Primer on Quantum Mechanics

Nanomechanics is part of both quantum physics and molecular physics. As this book is aimed at engineering students and engineers, whom we assume have no formal training in quantum physics, we begin our presentation with a short introduction of quantum mechanics, in order to provide the necessary background for later presentations.

1.1 Wave–Particle Duality: Law of Physics

Light and matter exhibit wave–particle duality, in other words, all matter and light have two manifestations: discreteness as the deterministic being and continuousness in the sense of probabilistic presence. In our current understanding, such wave–particle duality is the law of physics or first principle, because we do not know, at least to date, any other laws of universe that are more fundamental than it.

The relations between wave and particle properties of any object in the universe may be described by the de Broglie relations,

$$E = h\nu, \quad \text{and} \quad p = \frac{h}{\lambda}, \tag{1.1}$$

where h is the Planck constant, which is a universal constant of nature, and its value is $h = 6.63 \times 10^{-34}$ Js; λ is the matter wavelength; and ν is the matter wave frequency, which is the number of a repeating event, e.g., cycles or temporal wave number per unit time. The unit of frequency is hertz (Hz) (1 Hz means one wave cycle per second). The reciprocal of the frequency is period, which is the time duration of one wave cycle, i.e.,

$$T = \frac{1}{\nu}.$$

At first sight, many of us may experience difficulties understanding such wave–particle proposition because, in our common experience, a finite mass matter is always associated with the discrete particle, whereas the light wave is associated with the continuous electromagnetic field.

However, at the turn of the twentieth century, people had found several counterexamples or evidences that show either (1) light wave behaves like particles, and (2) matter exhibits wave properties.

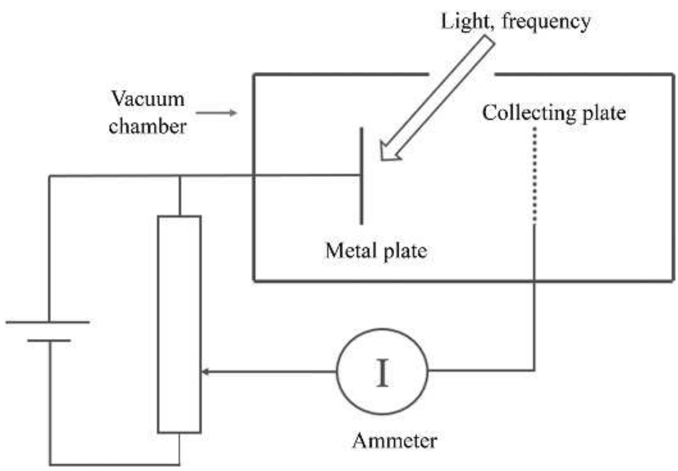

Figure 1.1 Illustration of photoelectric effect experiment

Two famous examples showing that light exhibits particle properties are: (1) photoelectric effect and (2) Compton effect.

1.1.1 Photoelectric Effect

In 1887, Heinrich Hertz found that when ultraviolet (UV) light is shone on a metal plate in a vacuum, and it emits charged particles (see Fig. 1.1), which were later shown to be electrons by J. J. Thomson (1899).

Based on classical electromagnetic theory, electric field $\mathbf{E}$ of light exerts force $F = -eE$ on electrons. As the intensity of light increases, the input energy to the metal plate increases as well, which may be absorbed by the electrons inside the metal plate, so that the kinetic energy of electrons inside the metal plate increases too. When the kinetic energy of the electrons reach a critical value, they may escape from the metal plate. From this perspective, electrons should be emitted whatever the frequency ν of light is, so long as $\mathbf{E}$ is sufficiently large; and for very low intensity, one may expect a time lag between light exposure and electron emission, because electrons need to absorb enough energy to escape from the metal plate.

The actual experimental observation shows that the maximum kinetic energy of ejected electrons is independent of light intensity, but dependent on the frequency ν of the light. For $\nu < \nu_0$, i.e., for frequencies below a cutoff frequency, no electrons are emitted from the metal plate, and there is no time lag when the light intensity is low. However, the rate of ejection of electrons depends on light intensity.

To interpret the experimental results, Albert Einstein theorized that the energy distribution in light is discrete, or light travels in packets of discrete energy, which are referred to as *quanta*, and they are now called as *photons*,[1]

$$E = h\nu. \tag{1.2}$$

[1] Here, we adopt the hypothesis that the group of velocity of light is the velocity of photons.

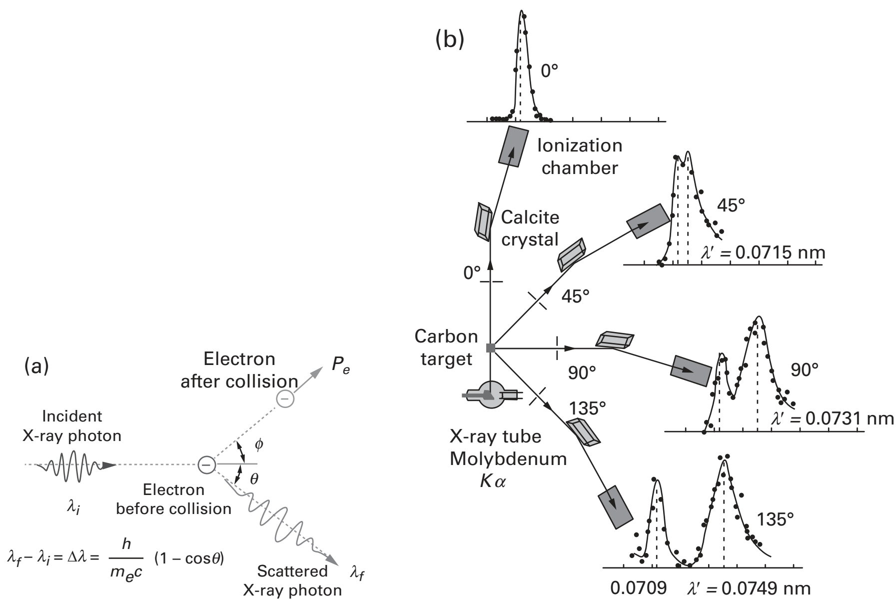

Figure 1.2 Compton scattering: (a) schematic illustration and (b) experimental observation

When an electron absorbs a single photon, it may leave the metal plate. The maximum kinetic energy of an emitted electron can then be expressed as

$$K_{max} = h\nu - \varphi,$$

where φ is the work function, which is the minimum energy needed for an electron to escape from the surface of the metal plate of a given metallic material. It is usually 2∼5 eV depending on the type of materials, and it may be written as $\varphi = h\nu_0$, so that we must have $\nu > \nu_0$ for the photoelectric effect to occur. Einstein's theory was later validated by the experiments conducted by Robert Andrews Millikan in 1914.

For his discovery of the law of the photoelectric effect, in 1921 Albert Einstein was awarded the Nobel Prize in Physics.

1.1.2 Compton Scattering

The second example is the so-called Compton scattering or the Compton effect, which is the light scattering due to the inelastic collision of photons and electrons. The experiment is illustrated in Fig. 1.2(a). In the experiment, a high-energy X-ray or gamma ray photon beam hits a target with electrons. In this case, classical theory predicts that when light is scattered on a free electron, the incident electromagnetic (EM) wave will shake the electron transversely, and the oscillating electron then radiates in all directions (except the exact direction of 90°). The classical theory predicts that there may be a change of the wavelength of the colliding photons due to the associated Doppler shift, when the light intensity is large.

However, in the Compton scattering experiment, one can observe the change of the wavelength of the scattering light even when the light intensity is very small, which is called the Compton shift. The shift of the wavelength can be calculated by treating the collision of the photon and electron as the elastic collision of two billiard balls. That is, the photon behaves like a particle and, hence, the photon–electron collision obeys the energy conservation and momentum conservation,

$$h\nu + m_e c^2 = h\nu' + \left(p_e^2 c^2 + m_e^2 c^4\right)^{1/2} \quad \text{and} \quad \mathbf{p}_\nu = \mathbf{p}_{\nu'} + \mathbf{p}_e. \tag{1.3}$$

Note that $(p_e^2 c^2 + m_e^2 c^4)^{1/2} = mc^2$ is Einstein's relativistic energy, which can be derived from Einstein relations,

$$E = mc^2,\ m = \frac{m_e}{\sqrt{1 - v^2/c^2}},\ \text{and}\ p = mv,\ \rightarrow\ p^2c^2 = -m_e^2 c^4 + (mc^2)^2$$

and m_e in Eq. (1.3) is the electron's static mass.

From Eq. (1.3), one can find that

$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos\theta) \geq 0. \tag{1.4}$$

In Fig. 1.2(b), one finds the shifted wavelength measurement at different angles. Note that for every fixed angle, there is also an unshifted peak, that is due to collision of the X-ray photon and the core of the atom (the nucleus of the atom plus the immobile electrons) because in that case, based on Eq. (1.3), one can find that

$$\lambda' - \lambda = \frac{h}{m_c c}(1 - \cos\theta) \sim 0,\ \ m_c \gg m_e. \tag{1.5}$$

The Compton effect is a strong evidence that the continuous electromagnetic waves may behave like particles. For the discovery of the Compton effect, Arthur Holly Compton earned the 1927 Nobel Prize in Physics.

On the other hand, discrete matter may also behave like continuous waves. In the following, we consider a well-known double-slit diffraction experiment of matter waves.

1.1.3 Interference of Matter Waves

The double-slit experiment was originally performed by Thomas Young in 1801 in demonstrating the wave nature of light, in which an incoming coherent plane wave is directly hitting a thin plate with two slits, one can observe the wave interference pattern on the screen behind the double-slit plate as shown in Fig. 1.3(b).

On the other hand, if the incoming object is not light, but a beam of particles such as electrons, atoms, or even molecules, what would we expect the measurement result on the back screen to be? A natural expectation on the results of double-slit diffraction of matter waves is depicted in Fig. 1.3(a). However, on the contrary, for matter particle waves, the particle density on the back screen has the same interference pattern as the light wave. Interference pattern produced by a beam of C_{60} molecules is shown in Fig. 1.4, which demonstrates the wave–particle duality of C_{60} molecules. It should be

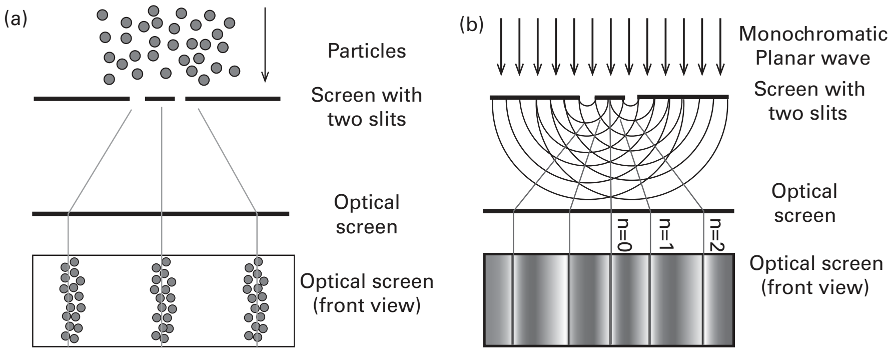

Figure 1.3 Double-slit experiment: (a) expected result for particles and (b) experimental observation

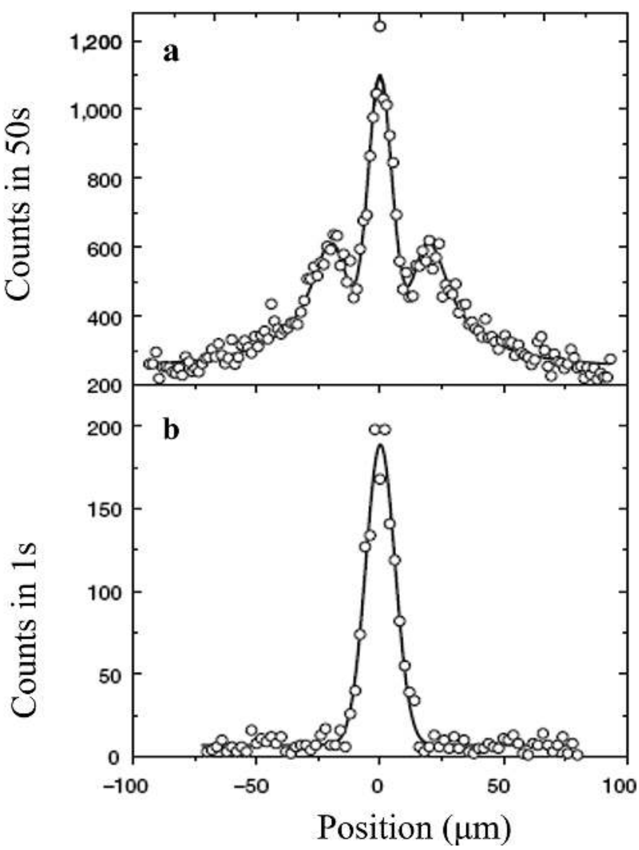

Figure 1.4 Interference pattern produced by C_{60} molecules: (a) experimental recording (open circles) and the fitting curve by using the Kirchhoff diffraction theory (continuous line) – the expected zeroth and first-order maxima can be clearly seen. The details of the theory are discussed in the text; and (b) the molecular beam profile without the grating in the path of the molecules (Arndt et al. (1999))

noted that the position of the matter wave is uncertain, and it is a wave of probability distribution, and it is sometimes called the de Broglie wave. One of the consequences of this probabilistic wave is the uncertainty principle, which is sometimes called the Heisenberg principle. The principle asserts that there is a fundamental limit to the precision with which certain pairs of physical properties of a particle can be simultaneously determined, such as position x and momentum p,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2},$$

where $\hbar = \frac{h}{2\pi} = 1.05457172610^{-34}$Js is the reduced Planck constant and σ_x, σ_p are standard deviation of position and momentum.

The quantum mechanics uncertainty principle indicates that the more precise the momentum of a particle is determined, the less precise its position can be known, and vice versa. In other words, for a fixed precision of momentum, the precision of the position is bounded below. This is to say that as random variables, position and momentum are intrinsically related, and the product of their variances has a low bound.

To close this section, we note that not only light and matter exhibit wave–particle duality, antimatter also exhibits wave–particle duality.

1.2 Schrödinger Equation

The partial different equation that governs the matter wave motion is called the Schrödinger equation.

1.2.1 A Short Heuristic Derivation

Since this is not a quantum mechanics book but an introduction to nanomechanics to engineers, we derived the Schrödinger equation in a heuristic manner.

Before we get into mathematical derivations, we first make the following assumptions:

1. The total energy E of a particle is

$$E = T + V = \frac{p^2}{2m} + V.$$

This is the energy expression for a classical particle with mass m where the total energy E is the sum of the kinetic energy T, and the potential energy V (which can vary with position, and time). p and m are the momentum and the mass of the particle, respectively.

2. Einstein's light quanta hypothesis (1905) asserts that the energy E of a photon is proportional to the frequency ν (or angular frequency, $\omega = 2\pi\nu$) of the corresponding electromagnetic wave:

$$E = h\nu = \hbar\omega.$$

3. The de Broglie hypothesis (1924) states that any particle can be associated with a wave, and that the momentum p of the particle is related to the wavelength λ (or wave number k) of such a wave by:

$$p = \frac{h}{\lambda} = \hbar k.$$

Expressing p and wavelength k as vectors, we have

$$\mathbf{p} = \hbar\mathbf{k}.$$

4. The three assumptions discussed earlier allow one to derive the governing equation for plane waves only. To extend those assumptions to general situations will require the superposition principle, and thus, one must separately postulate that the Schrödinger equation is linear.

Schrödinger's main idea was to express the phase of the matter wave as a complex phase factor so that the matter wave probability function has the following form:

$$\Psi(\mathbf{r}, t) = A \exp i(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad \text{where } \mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z, \tag{1.6}$$

where $\mathbf{k}$ is the wave number and ω is the angular frequency.

Considering that Eq. (1.6) is the intrinsic form of the wave function, we have

$$\frac{\partial}{\partial t}\Psi = -i\omega\Psi$$

and then

$$E\Psi = h\nu\Psi = \hbar\omega\Psi = i\hbar\frac{\partial}{\partial t}\Psi. \tag{1.7}$$

Similarly, for spatial derivatives, we have

$$\frac{\partial}{\partial x}\Psi = ik_x\Psi, \quad \text{and} \quad \frac{\partial^2}{\partial x^2}\Psi = -k_x^2\Psi.$$

We then have

$$p_x^2\Psi = (\hbar k_x)^2\Psi = -\hbar^2\frac{\partial^2}{\partial x^2}\Psi$$

and hence

$$\mathbf{p}^2\Psi = \left(p_x^2 + p_y^2 + p_z^2\right)\Psi - \hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi = -\hbar^2\nabla^2\Psi.$$

Recalling the Assumption 1 on total energy,

$$E = T + V = \frac{p^2}{2m} + V \;\Rightarrow\; E\Psi = (T+V)\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \tag{1.8}$$

and combining Eqs. (1.7) and (1.8), we obtain the standard form of time-dependent Schrödinger equation for a single particle as,

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t), \tag{1.9}$$

where m is the mass of the particle, $-\frac{\hbar^2}{2m}\nabla^2$ is said to be the kinetic energy operator, and $V(\mathbf{r},t)$ is the potential energy of the particle at position $\mathbf{r}$ and at time t.

In passing, we note that the Schrödinger equation, i.e., Eq. (1.9), is a second-order, homogeneous, linear partial differential equation.

1.2.2 Wave Function

Further examining the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r},t)\Psi$$

we find that

$$E = T + V = \frac{\mathbf{p}\cdot\mathbf{p}}{2m} + V(\mathbf{r},t) \;\Rightarrow\; -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t),$$

which may be viewed as a differential operator, and we name the energy differential operator as *Hamiltonian operator* or simply “Hamiltonian,”

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t). \tag{1.10}$$

Max Born made a physical interpretation of the wave function $\Psi(\mathbf{r},t)$: The probability of finding the particle in a small volume $\delta\Omega$ at position $\mathbf{r}$ and time t is equal to $|\Psi(\mathbf{r},t)|^2\delta\Omega = \Psi(\mathbf{r},t)\Psi^*(\mathbf{r},t)\delta\Omega$. In other words, $|\Psi(\mathbf{r},t)|^2$ is the probability distribution of finding the particle in the location $\mathbf{r}$ at time t. Since the total probability to find the particle in the space should be one, i.e.,

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r},t)|^2 d\Omega = 1$$

and a wave function that satisfies this condition is said to be normalized. Suppose that we have a solution of Eq. (1.9), which is not normalized,

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r},t)|^2 d\Omega = C,$$

we can then normalize it by choosing

$$\Psi(\mathbf{r},t) = \frac{1}{\sqrt{C}}\Psi(\mathbf{r},t).$$