}ESSENTIAL{

Baby Quantum Mechanics

for PHY 2A10

Zeroth Edition

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Preface

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Chapter 1

Electromagnetic radiation as Particles

1.1 Black-Body Radiation

Black-body is a hypothetical object from which electromagnetic radiation emanates solely due to the thermal motion of its charges. Any radiation that strikes it must be absorbed.

Max Plank in the year 1900 found the theory that explained black-body radiation. This resolved the problem of so-called ultraviolet catastrophe, that is in classical theory, a black-body would emit an arbitrarily high amount of energy at short wavelength as shown in Fig. 1.1. This also started the quantum age.

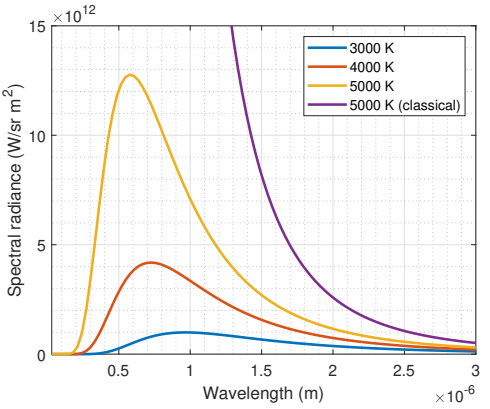

Figure 1.1: The black-body radiation graph compared with the classical model of Rayleigh and Jeans.

1.1.1 Spectral Energy Density

The goal of the theory of black-body radiation is to find the spectral energy density

$$dU = \text{ energy from } f \text{ to } f + df.$$

Let us define:

$$dN(f) \equiv \text{number of modes from } f \text{ to } f + df,$$

$$\overline{E(f)} \equiv \text{average energy for a wave of freq } f.$$

We can assume

$$dU \approx dN\overline{E}.$$

1.1.2 Counting Modes

First let us figure out what is dN, which is essentially a counting-mode problem.

One Dimension

Begin with considering a one-dimensional case as illustrated in Fig. 1.2: waves on a string from $x = 0$ to $x = L$ can be represented as

$$\Psi(x,t) = A \sin\left(\frac{n\pi x}{L}\right) \cos\left(2\pi f t\right), \tag{1.1}$$

where n is the number of antinodes. The wave equation is

$$\frac{\partial^2}{\partial t^2}\Psi(x,t) = c^2 \frac{\partial^2}{\partial x^2}\Psi(x,t), \tag{1.2}$$

where c is the velocity of the wave. So

$$f = \frac{cn}{2L}. \tag{1.3}$$

As the number of antinodes is the same as the number of modes as indicated in Fig. 1.2, $dn = dN(f)$, so

$$\frac{dN(f)}{df} = \frac{dN(f)/dn}{df/dn} = \frac{2L}{c}. \tag{1.4}$$

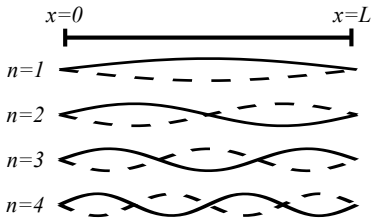

Figure 1.2: Counting modes in one dimension.

Three Dimensions

Now let us extend the above situation to the three-dimensional case.

$$\Psi(x,y,z,t) = A\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right) \sin\left(\frac{n_z\pi z}{L}\right)\cos\left(2\pi f t\right), \tag{1.5}$$

$$\frac{\partial^2}{\partial t^2}\Psi(x,t) = c^2\nabla^2\Psi(x,t). \tag{1.6}$$

We obtain

$$f = \frac{cn}{2L} \text{ with } n \equiv \sqrt{n_x^2+n_y^2+n_z^2}. \tag{1.7}$$

To count modes, consider an "antinode-number space" as shown in Fig. 1.3, which is an octant with axes n_x, n_y, and n_z. Then n becomes the "radius". The differential of the number of modes $dN(f)$ at the large n limit can be treated as a spherical shell of the octant with volume $\frac{1}{8}4\pi n^2 dn$. Therefore

$$\frac{dN(f)}{df} = \frac{dN(f)/dn}{df/dn} = \frac{\pi n^2 L}{c}. \tag{1.8}$$

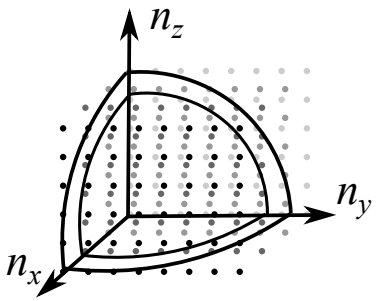

Figure 1.3: Counting modes in three dimensions.

In term of frequency f, we have

$$dN(f) = \frac{4\pi L^3}{c^3}f^2 df. \tag{1.9}$$

In addition, light can have two polarizations for each mode, which introduces a factor of two. The final form for density of states is thus

$$\boxed{dN(f) = \frac{8\pi L^3}{c^3} f^2 df}. \tag{1.10}$$

1.1.3 Average Energy

In statistical mechanics, the probability of an oscillator within an ensemble with energy E is given by

$$P(E) \propto \mathrm{e}^{-E/k_B T}, \tag{1.11}$$

where k_b is the Boltzmann constant. Thus, the average energy can be found via

$$\overline{E} = \frac{\sum EP(E)}{\sum P(E)} = \frac{\sum E\mathrm{e}^{-E/k_B T}}{\sum \mathrm{e}^{-E/k_B T}}. \tag{1.12}$$

Classically, there is no restriction on frequency (thus energy, as $E = hf$), so the summation turns into an integration

$$\overline{E} = \frac{\int_0^\infty E\mathrm{e}^{-E/k_B T}}{\int_0^\infty \mathrm{e}^{-E/k_B T}} = k_B T. \tag{1.13}$$

This result leads to the ultraviolet catastrophe, as the spectral energy density would blow up at high frequency. Max Planck solved the problem by claiming the electromagnetic radiation with frequency f is only allowed to have energy $E = nhf$. The new average energy is

$$\overline{E(f)} = \frac{\sum_{n=0}^\infty nhf\mathrm{e}^{-nhf/k_B T}}{\sum_{n=0}^\infty \mathrm{e}^{-nhf/k_B T}} = \frac{hf}{\mathrm{e}^{nhf/k_B T} - 1}. \tag{1.14}$$

1.1.4 Result

Classical:

$$dU(f) = k_B T \frac{8\pi V}{c^3} f^2 df. \tag{1.15}$$

Planck's spectral energy density:

$$\boxed{dU(f) = \frac{hf}{\mathrm{e}^{nhf/k_B T} - 1} \frac{8\pi V}{c^3} f^2 df}. \tag{1.16}$$

1.1.5 Application

Based on Planck's spectral energy density, we can derive the following laws.

Stefan-Boltzmann law

To find the intensity radiated by a black-body, we can integrate the spectral energy density.

$$I = \int \frac{c}{4\pi} dU = \sigma T^4, \tag{1.17}$$

here $\sigma = (2\pi^5 k_B^4)/(15c^2h^3) = 5.670 \times 10^{-8} W m^{-2} K^{-4}$.

Wien's displacement law

By solving $\partial(dU(\lambda)/\partial\lambda = 0$, we can find the peak wavelength of the radiation, which turns out to be

$$\lambda_{\text{peak}} T = 2.897 \times 10^{-3} m \cdot K. \tag{1.18}$$

Problems

1. (Conceptual) As mentioned in the video lecture, there are only three fundamental ways to produce light, what are they?
   (Hint: Quantized energy photon)

2. (Harris) For small z, e^z is approximately $(1 + z)$
   (a) Show Planck's spectral energy density agrees with the result of classical result in the limit of small frequency.
   (b) Show at high frequencies, Planck's result approaches zero.

3. (Harris) Show the expression of dU in terms of wavelength λ is

   $$\frac{dU}{d\lambda} = \frac{8\pi V h c}{\mathrm{e}^{hc/\lambda k_B T} - 1} \frac{1}{\lambda^5}. \tag{1.19}$$

   (Hint: $f = c/\lambda$, so $df = -(c/\lambda^2)d\lambda$)

4. Verify

   $$\overline{E(f)} = \frac{\sum_{n=0}^{\infty} nhf \mathrm{e}^{-nhf/k_B T}}{\sum_{n=0}^{\infty} \mathrm{e}^{-nhf/k_B T}} = \frac{hf}{\mathrm{e}^{nhf/k_B T} - 1}. \tag{1.20}$$

   (Hint: the denominator is a geometric series and the numerator is the derivative of a geometric series)

1.2 The Photoelectric Effect

The photoelectric effect refers to the phenomenon of light producing a flow of electricity upon a metal surface. The effect was first demonstrated by Heinrich Hertz in the 1880s. It is not well-explained until Albert Einstein proposed an explanation in 1905.

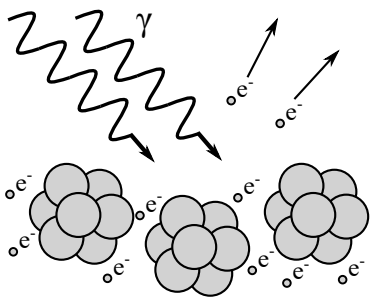

Figure 1.4: The photoelectric effect. Photons with sufficient energy strike on the metal surface, and knock out electrons.

1.2.1 Terminology and Main Results

- Work function ϕ: the minimum energy required to free an electron.
- Stopping potential: the potential difference that is just enough to stops electrons.
- Threshold wavelength: the maximum wavelength for which electrons are freed. Corresponding minimum frequency is the threshold frequency.
- New energy unit - electronvolt: an electronvolt (eV) is the amount of kinetic energy gained by a single electron accelerating through an electric potential difference of one volt in the vacuum. Conversion:

$$1 \text{ eV} = 1.602 \times 10^{-19} J. \tag{1.21}$$

The energy of a photon is

$$\boxed{E = hf}. \tag{1.22}$$

Each photon with sufficient energy is able to help one electron overcome the work function and bring it out of the metal surface. To conserve the energy, the maximum possible kinetic energy of an electron is

$$\boxed{K.E._{\max} = hf - \phi}. \tag{1.23}$$

1.2.2 The Production of X-Rays

- Bremsstrahlung: "braking radiation".
- Cutoff wavelength: minimum wavelength possible.

When producing X-rays, electrons are accelerated, smashed onto a target, and rapidly slow down. As it undergoes a large acceleration, powerful electromagnetic waves are created. Since electromagnetic waves can be quantized,

maximum energy (similarly maximum frequency or minimum wavelength) of produced X-rays can be calculated based on the maximum kinetic energy of electrons (See problem 4 for detail).

Problems

1. As a review for 1.1, What is the peak wavelength for black body radiation due to the human body?
   (Hint: Using Wein's law)

2. (Harris) Light of 300 nm wavelength strikes a metal plate, and photoelectrons are produced with a speed of 0.002c.
   (a) What is the work function of the metal?
   (b) What is the threshold wavelength then?

3. (Harris) A 940 kHz radio station broadcasts 40 kW power. How many photons are transmitted per second?

4. (Harris) A television picture tube accelerates electrons through a potential difference of 30,000 V. Find the cut-off wavelength for X-ray produced. (There is protection mechanisms shielding the X-ray. Also, this type of television is not that common nowadays.)

1.3 The Compton Effect

According to special relativity, a particle with zero mass should have momentum-energy relation given by

$$E = pc. \tag{1.24}$$

From the previous two sections, we assumed photon energy is determined by

$$E = hf. \tag{1.25}$$

Thus

$$p = \frac{h}{\lambda}. \tag{1.26}$$

1.3.1 Two-Particle Collision (Elastic)

- Before collision: A photon of wavelength λ approaches an electron at rest.
  - Photon: $E = h/\lambda$, $P = hc/\lambda$;
  - Electron: $E = 0$, $m_e c^2$.
- After collision: The electron scatters at speed of u, angle ϕ. A photon of wavelength λ' scatters at an angle θ.
  - Photon: $E = h/\lambda'$, $P = hc/\lambda$;

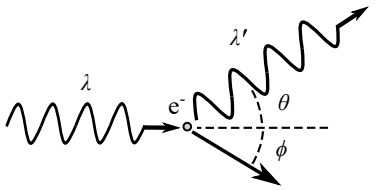

Figure 1.5: The Compton effect. The incident photon has wavelength λ. The scattered photon has wavelength λ' with scatter angle θ. The electron is scattered with angle ϕ.

  - Electron: $E = \gamma_u m_e u$, $P = \gamma_u m_e c^2$.

- Here $\lambda_u = 1/\sqrt{1 - u^2/c^2}$ is the Lorentz factor, as the electron is moving fast and relativistic correction needs to be considered.

- To solve for scattering angle, consider conservation of both energy and momentum.

  - Momentum
    - x-comp.: $\frac{h}{\lambda} = \frac{h}{\lambda'}\cos(\theta) + \gamma_u m_e u \cos(\phi)$;
    - y-comp.: $0 = \frac{h}{\lambda'}\sin(\theta) - \gamma_u m_e u \sin(\phi)$.

  - Energy
    - $h\frac{c}{\lambda} + m_e c^2 = h\frac{c}{\lambda'} + \gamma_u m_e c^2$.

- The result of the Compton effect by solving the above set of equations is

$$\boxed{\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos(\theta)).} \tag{1.27}$$

- The expression for ϕ is left as an exercise.

Problems

1. (Harris) An X-ray of unknown wavelength is directed at a carbon sample (source of electrons). An electron is scattered with a speed of 4.5×10^7 m/s at an angle of 60°. Determine the wavelength of the X-ray source.

2. (Harris) Obtain

$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos(\theta)), \tag{1.28}$$

   from

$$\begin{cases} \frac{h}{\lambda} = \frac{h}{\lambda'}\cos(\theta) + \gamma_u m_e u \cos(\phi), \\ 0 = \frac{h}{\lambda'}\sin(\theta) - \gamma_u m_e u \sin(\phi), \\ h\frac{c}{\lambda} + m_e c^2 = h\frac{c}{\lambda'} + \gamma_u m_e c^2. \end{cases} \tag{1.29}$$

(Hint: use $\cos^2(\phi) + \sin^2(\phi) = 1$)

3. (Harris) Show the scattering angles of the photon and the electron following

$$\cot\left(\frac{\theta}{2}\right) = \left(1 + \frac{h}{mc\lambda}\right)\tan(\phi). \tag{1.30}$$

1.4 Pair Production

In 1932, Carl D. Anderson observed particles that behave just like electrons but curved in the "wrong" direction under a magnetic field. These positively charged electrons are known as positrons.

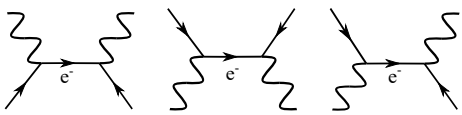

Figure 1.6: Feynman diagrams for electron scatterings. (a) electron-position annihilation; (b) electron-position pair production; (c) Compton scattering.

The minimum energy of a photon that is required to form a pair of particles can be determined using the rest mass energy of that pair.

The "time-reverse" process of pair production is pair annihilation, in which an electron-positron pair forms a pair of photons. This can be used in positron emission tomography (PET, check problem 2 for detail).

Problems

1. (Harris) A stationary muon μ^- annihilates with a stationary antimuon μ^+ (same mass, 1.88×10^{28} kg. but opposite charge). The two disappear, replaced by electromagnetic radiation. (a) Why is it not possible for a single photon to result? (b) Suppose two photons result. Describe their possible directions of motion and wavelengths.

2. (Harris) In positron emission, an electron and positron annihilate, and two photons of a characteristic energy are detected. What is this energy, and what is the corresponding wavelength? The pair can be assumed to be essentially stationary before annihilation.

Chapter 2

Matter as Waves

2.1 Double Slit Experiment

2.1.1 Review

Double Slit Interference

Bright regions occur at angle θ for which

$$\boxed{\sin\theta = \frac{m\lambda}{d},} \tag{2.1}$$

where d is the distance between two slits, λ is the wavelength, and m is the order number (see above image for detail). Intensity of two-source interference follows

$$I = I_0 \cos^2 \frac{\phi}{2}, \tag{2.2}$$

where I_0 is the maximum possible total intensity, and ϕ is the relative phase between two source. It can be shown that for the case of double slit interference, the phase difference ϕ is $2\pi d \sin\theta/\lambda$. Therefore, consider the effect of two-slit interference only, the intensity profile is

$$\boxed{I(\theta) = I_0 \cos^2\left(\frac{\pi d \sin\theta}{\lambda}\right).} \tag{2.3}$$

Single Slit Diffraction

Angles of minimum intensity are at

$$\boxed{\sin\theta = \frac{m\lambda}{a},} \tag{2.4}$$

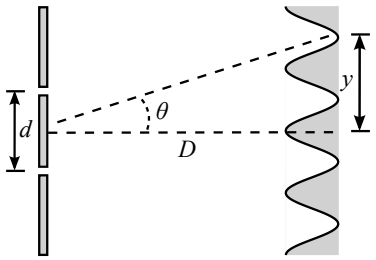

Figure 2.1: Double slit interference.

where a is the slit width, λ is the wavelength, and m is the order number. Similarly, the intensity profile with the effect of single-slit diffraction only can be found to be

$$\boxed{I = I_0 \ \mathrm{sinc}^2\left(\frac{\pi a \sin\theta}{\lambda}\right)}, \tag{2.5}$$

where the sinc function is defined as $\mathrm{sinc}\ x = \sin x/x$ for $x \neq 0$ and $\mathrm{sinc}\ 0 = 1$.

Fraunhofer Diffraction Equation

Combining above two results, that is, considering both effect of interference and diffraction, the intensity profile should be

$$\boxed{I(\theta) = I_0 \cos^2\left(\frac{\pi d \sin\theta}{\lambda}\right) \ \mathrm{sinc}^2\left(\frac{\pi a \sin\theta}{\lambda}\right).} \tag{2.6}$$

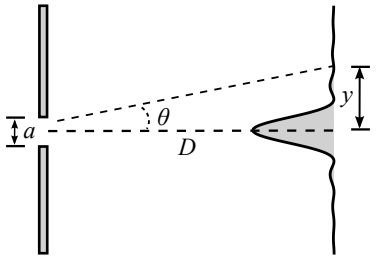

Figure 2.2: Single slit interference.

2.1.2 Bragg's Law

Interference can be used in studying crystal structure. X-rays are often used in a such case. Rays reflected from different layer of crystal gives the information about the crystal structure.

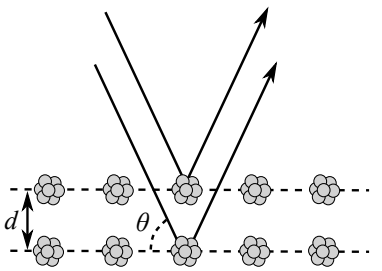

Figure 2.3: Bragg's law.

Constructive interference occurs at

$$2d\sin\theta = m\lambda.$$

Problem

1. Verify the phase difference (a) for double slit interference is $\pi d\sin\theta/\lambda$; (b) for single slit diffraction is $\pi a\sin\theta/\lambda$.
   (Hint: find the path difference first)

2.2 The Matter Wave

2.2.1 Wavelength

In 1924, Louis de Broglie hypothesized the matter wave. The wavelength associated with a massive object is given by

$$\boxed{\lambda = \frac{h}{p}.} \tag{2.7}$$

This relationship is true in general, even for relativistic cases. This contribution won for de Broglie the 1929 Nobel Prize.

2.2.2 Frequency

The frequency of a matter wave follows the same relationship as for electromagnetic radiation

$$\boxed{f = \frac{E}{h}.} \tag{2.8}$$

Recall that the wave number (or wave vector, which can be understand as "spatial frequency") and angular frequency are defined as $k = 2\pi/\lambda$ and

$\omega = 2\pi/T$ respectively, it would be convenient to define

$$\boxed{\hbar = \frac{h}{2\pi} \approx 1.055 \times 10^{-34} J \cdot s.} \tag{2.9}$$

Then the wave-particle properties can be linked via

$$\boxed{p = \frac{h}{\lambda} = \hbar k,} \tag{2.10}$$

$$\boxed{E = hf = \hbar\omega.} \tag{2.11}$$

Again, these two relations are true in general.

2.2.3 Velocity

The relation $v = f\lambda$ can be directly applied to find the speed of matter wave.

$$v_{phase} = f\lambda = \frac{E}{h}\frac{h}{p} = \frac{E}{p}. \tag{2.12}$$

However, we should notice that this is the velocity of the wave, or the phase velocity. The velocity of the particle, or the group velocity, can be found using energy and momentum.

Problems

1. (Harris) A Bragg diffraction experiment is conducted using a beam of electrons accelerated through a 1.0 kV potential difference.
   (a) If the spacing between atomic planes in the crystal is 0.1 nm. at what angles with respect to the planes will diffraction maxima be observed?
   (b) If a beam of X-rays produces diffraction maxima at the same angle as the electron beam. what is the X-ray photon energy?

2. (Harris) Classically and nonrelativistically, we say that the energy E of a massive free particle is just its kinetic energy.
   (a) With this assumption, show that the classical particle velocity $v_{particle}$ is $2E/p$.
   (b) Show that this velocity and that of the matter wave differ by a factor of 2.
   (c) In reality, a massive object also has internal energy no matter how slowly it moves, and its total energy E is γmc^2,
   where $\gamma \equiv 1/\sqrt{1-(v_{particle}/c)^2}$. Show that $v_{particle}$ is pc^2/E and that v_{wave} is $c^2/v_{particle}$. Is there anything wrong with v_{wave} ?

2.3 The Free-Particle Schrödinger Equation

The wave equation obeyed by matter-wave is the Schrödinger equation. For a single nonrelativistic massive particle, it can be expressed as

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\Psi(x,t)}{\partial t}. \tag{2.13}$$

In the next section, we are going to see how this expression is derived.

2.3.1 Derivation

Spatial Part

We begin with the simple energy relation

$$E_{total} = E_{kinetic} + E_{potential} = \frac{p^2}{2m} + U. \tag{2.14}$$

Now consider a generic complex wave equation

$$\Psi(x,t) = \mathrm{e}^{i(kx-\omega t)}. \tag{2.15}$$

Its second position derivative reads

$$\frac{\partial^2\Psi(x,t)}{\partial x^2} = (ik)^2\Psi(x,t) = -k^2\Psi(x,t). \tag{2.16}$$

Recall from Section 2.2 Matter Wave that $k = p/\hbar$,

$$\frac{\partial^2\Psi(x,t)}{\partial x^2} = -\left(\frac{p^2}{\hbar^2}\right)\Psi(x,t). \tag{2.17}$$

Notice that we have p^2 on the right-hand side, so if we reorganized the above form and plug it into the kinetic part of the energy relation at the beginning, we will get

$$\boxed{E\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\right)\Psi(x,t).} \tag{2.18}$$

This is called the time-independent Schrödinger equation.

Temporal Part

Next, let's consider the time derivative

$$\frac{\partial\Psi(x,y)}{\partial t} = -i\omega\Psi(x,t). \tag{2.19}$$

Also from Section 2.2 Matter Wave, we have $E = \hbar\omega$, thus

$$E\Psi(x,t) = i\hbar\frac{\partial\Psi(x,y)}{\partial t}. \tag{2.20}$$

The Whole Picture

Combining the above two parts together, what we get is

$$\boxed{i\hbar\frac{\partial\Psi(x,y)}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\right)\Psi(x,t).} \tag{2.21}$$

2.3.2 Probability Density

By the Copenhagen interpretation, the wave function itself does not have any meaning, but the modules square at a certain time and position of it represents the probability of the particle appearing in that time and position.

$$P(x,t) = |\Psi(x,t)|^2 = |\mathrm{Re}\Psi(x,t)|^2 + |\mathrm{Im}\Psi(x,t)|^2 = \Psi(x,t)^*\Psi(x,t). \tag{2.22}$$

Chapter 3

Bound States

3.0 Bound States

3.0.1 Stationary States

From the previous chapter:

$$\boxed{i\hbar\frac{\partial\Psi(x,t)}{\partial t}=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U\right)\Psi(x,t).} \tag{3.1}$$

To solve this equation, a standard technique is the separation of variables. Let assume

$$\Psi(x,t)=\psi(x)\phi(t). \tag{3.2}$$

Then we have

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2}{\partial x^2}\psi(x)+U(x)=i\hbar\frac{1}{\phi(t)}\frac{\partial}{\partial t}\phi(t)=C. \tag{3.3}$$

The Temporal Part

$$i\hbar\frac{1}{\phi(t)}\frac{\partial}{\partial t}\phi(t)=C. \tag{3.4}$$

General solution:

$$\phi(t)=\mathrm{e}^{-i(C/\hbar)t}. \tag{3.5}$$

It turned out that $C=E$, so

$$\Psi(x,t)=\psi(x)\mathrm{e}^{-i(E/\hbar)t}. \tag{3.6}$$

Notice:

$$\Psi^*(x,t)\Psi(x,t)=\psi^*(x)\mathrm{e}^{i(E/\hbar)t}\psi(x)\mathrm{e}^{-i(E/\hbar)t}=\psi^*(x)\psi(x). \tag{3.7}$$

The probability density function is time-independent. That is why the phrase "stationary state" is used.

The Spatial Part

Since $C = E$, the spatial part reduces to the time-independent Schrödinger Equation,

$$\boxed{E\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\right)\Psi(x,t).} \tag{3.8}$$

3.0.2 Well-Behaved Function

- Normalizable

$$\int_{\text{all space}} |\Psi(x,t)|^2 dx = 1. \tag{3.9}$$

- Smoothness - C^1

3.1 Case 1: The Infinite Well

Inside the well, the potential is zero, so we have

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x), \text{ for } 0 \le x \le L. \tag{3.10}$$

General solution

$$\psi(x) = A\sin(kx), \tag{3.11}$$

where we define $k \equiv \sqrt{2mE/\hbar^2}$. Applying boundary condition $\psi(L) = 0$ gives

$$A\sin(kL) = 0. \tag{3.12}$$

Therefore

$$kL = n\pi, \forall n \in \mathbb{Z}. \tag{3.13}$$

This result implies that

$$\begin{cases} E = \frac{n^2\pi^2\hbar^2}{2mL^2}, \\ \\ \psi(x) = A\sin\left(\frac{n\pi x}{L}\right). \end{cases} \tag{3.14}$$

Applying normalization condition gives

$$\int_{\text{all space}} |\Psi(x,t)|^2 dx = \int_0^L \left(A\sin\frac{n\pi x}{L}\right)^2 dx = 1. \tag{3.15}$$

The integral equals $A^2L/2$, so we have

$$A = \sqrt{\frac{2}{L}}. \tag{3.16}$$

And here is the final result

$$\boxed{\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, & \text{for } 0 \le x \le L \\ 0, & \text{else} \end{cases}} \tag{3.17}$$

and

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}.} \tag{3.18}$$

Problem

1. Suppose now the infinite well is at $|x| < a/2$, determine the allowed energies and corresponding wave functions.

3.2 Case 2 The Finite Well

This time, let us consider a potential

$$U(x) = \begin{cases} 0 & 0 \le x \le L, \\ U_0 & x \le 0 \text{ or } x \ge L. \end{cases} \tag{3.19}$$

Now the time-independent Schrödinger equation can be expressed as

$$\frac{d^2}{dx^2}\psi(x) = \frac{2m\left(U(x) - E\right)}{\hbar^2}\psi(x). \tag{3.20}$$

For simplicity, let us divide the whole space into three regions: region (I) $x \le 0$, region (II) $0 \le x \le L$, and region (III) $x \ge L$, and name the wave equations inside those three regions $\psi_{\mathrm{I}}(x)$, $\psi_{\mathrm{II}}(x)$, and $\psi_{\mathrm{III}}(x)$ respectively.

3.2.1 Region II

As $U(x) = 0$ for $0 \le x \le L$, the equation becomes

$$\frac{d^2}{dx^2}\psi(x) = -k^2\psi(x), \tag{3.21}$$

where $k = \sqrt{2mE/\hbar^2}$. As the differential equation is the same as that of the infinite well, we have the same general solution

$$\begin{aligned}\psi_{\mathrm{II}} =& A'\mathrm{e}^{ikx} + B'\mathrm{e}^{-ikx} \\ =& A\sin(kx) + B\cos(kx).\end{aligned} \tag{3.22}$$

3.2.2 Region I and Region III

The differential equation can be rewritten as

$$\frac{d^2}{dx^2}\psi(x) = \alpha^2\psi(x), \tag{3.23}$$

where $\alpha = \sqrt{2m(U_0 - E)/\hbar^2}$. Consider the waves inside the well, i.e. $E < U_0$, so that α is real. The general solution is

$$\psi = C\mathrm{e}^{\alpha x} + D\mathrm{e}^{-\alpha x}. \tag{3.24}$$

The wave function should not diverge, i.e. $\psi(x) \to 0$ as $x \to \pm\infty$. Therefore we have

$$\boxed{\psi_{\mathrm{I}} = C\mathrm{e}^{\alpha x},} \tag{3.25}$$

$$\boxed{\psi_{\mathrm{III}} = D\mathrm{e}^{-\alpha x}.} \tag{3.26}$$

3.2.3 Boundary Conditions

As stated before, wave equations should be C^1 functions. Therefore, wave functions and their derivatives should match at $x = 0$ and $x = L$.

x=0

- $\psi(x)$ continuous

$$\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0) \Rightarrow \boxed{C = B}. \tag{3.27}$$

- $d\psi(x)/dx$ continuous

$$\frac{d}{dx}\psi_{\mathrm{I}}(0) = \frac{d}{dx}\psi_{\mathrm{II}}(0) \Rightarrow \boxed{\alpha C = kA}. \tag{3.28}$$

x=L

- $\psi(x)$ continuous

$$\psi_{\mathrm{II}}(L) = \psi_{\mathrm{III}}(L) \Rightarrow \boxed{A\sin(kL) + B\cos(kL) = D\mathrm{e}^{-\alpha L}}. \tag{3.29}$$

- $d\psi(x)/dx$ continuous

$$\frac{d}{dx}\psi_{\mathrm{II}}(L) = \frac{d}{dx}\psi_{\mathrm{III}}(L) \Rightarrow \boxed{kA\cos(kL) - kB\sin(kL) = -\alpha D\mathrm{e}^{-\alpha L}}. \tag{3.30}$$

Plugging the first two conditions into the last two equations yields

$$\begin{cases} \frac{\alpha}{k}C\sin(kL) + C\cos(kL) = D\mathrm{e}^{-\alpha L}, \\ k\frac{\alpha}{k}C\cos(kL) - kC\sin(kL) = -\alpha D\mathrm{e}^{-\alpha L}, \end{cases} \tag{3.31}$$

which can be further simplified to

$$\boxed{2\cot(kL) = \frac{k}{\alpha} - \frac{\alpha}{k}.} \tag{3.32}$$

The distance at which the amplitude of the wave become 1/e of its original value (the amplitude at the boundary) is called the penetration depth. It is given by

$$\delta = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(U_0 - E)}}. \tag{3.33}$$

Problem

1. Study the case where potential energy is given by

$$U(x) = \begin{cases} \infty & x \le 0 \\ 0 & 0 < x < L \\ U_0 & x \ge L. \end{cases} \tag{3.34}$$

3.3 Case 3 The Simple Harmonic Oscillator

Let's consider the case of a simple harmonic oscillator.

For a spring-mass system, we have the potential energy $U(x) = 1/2\kappa x^2$, where κ is the spring constant. Insert the potential energy into the time-independent Schrödinger equation, we have

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + \frac{1}{2}\kappa x^2\psi(x) = E\psi(x). \tag{3.35}$$

Solving this differential equation is beyond the scope of this series. However, we can still guess and check the simplest solution, a Gaussian. Actually, a Gaussian does satisfy the above differential equation. Start with $\psi(x) = A\exp\left(-ax^2\right)$, and plug back into the differential equation. The result is that $a = \sqrt{m\kappa}/2\hbar$. Then applying the normalization condition gives $A = (m\kappa/\pi^2\hbar^2)^{1/8}$.

Actually this Gaussian is the first eigen equation

$$\psi_0(x) = (m\kappa/\pi^2\hbar^2)^{1/8} \exp\big(-(\sqrt{m\kappa}/2\hbar)x^2\big), \tag{3.36}$$

and its corresponding eigen energy is $E_0 = \hbar/2\sqrt{\kappa/m}$. It turns out that the complete eigen equations and eigen energies are

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega_0}{\pi\hbar}\right)^{1/4} \exp\big(-m\omega_0 x^2/2\hbar\big) H_n\left(\sqrt{\frac{m\omega_0}{\hbar}}x\right), \tag{3.37}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0. \tag{3.38}$$

Here $\omega_0 = \sqrt{\kappa/m}$ is the natural frequency, and H_n is the Hermite functions (physics), which is defined as

$$H_n(z) = (-1)^n \mathrm{e}^{z^2} \frac{d^n}{dz^n}\left(\mathrm{e}^{-z^2}\right). \tag{3.39}$$

* Ladder Operator Method

Notice that the eigen energies are equally separated by $\hbar\omega_0$, thus it is convenient to work in the energy basis, instead of using real space wave functions. Introducing the energy eigenstates $|n\rangle$, and define following operators:

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right), \tag{3.40}$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right). \tag{3.41}$$

Here the subscription under ω is omitted for simplicity. Pay attention that here $\hat{x}$ and $\hat{p}$ are operators as well, and if were applied to wave functions, they could be expressed as $\hat{x} = x$, and $\hat{p} = -i\hbar\frac{\partial}{\partial x}$.

One can check the effect of applying a or $a^\dagger$ to an eigen wave equation is to turn it into another eigen wave equation with eigen energy either increased or decreased by $\hbar\omega$. Thus, in energy basis, we have

$$a^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle, \tag{3.42}$$

$$a |n\rangle = \sqrt{n}\,|n-1\rangle. \tag{3.43}$$

Notice that

$$a^\dagger a |n\rangle = a^\dagger\sqrt{n}\,|n-1\rangle = n\,|n\rangle. \tag{3.44}$$

Therefore, we can define number operator as $N = a^\dagger a$. Then, the Hamiltonian can be expressed as

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right). \tag{3.45}$$

3.4 Expectation Values, and Uncertainties

3.4.1 Expectation Values

As discussed before, $|\psi(x)|^2$ can be treated as probability density. Thus, the probability of finding the particle at an interval (a, b) is given by an integral

$$P = \int_a^b |\psi(x)|^2 dx. \tag{3.46}$$

We may also find the expectation value of quantity with position dependence via

$$\overline{f(x)} = \int_{\text{all space}} f(x)|\psi(x)|^2 dx, \tag{3.47}$$

or more precisely,

$$\overline{O} = \int_{\text{all space}} \psi^*(x)\hat{O}\psi(x)dx, \tag{3.48}$$

if the observable is described by an operator.

3.4.2 Uncertainties

Uncertainty ΔO can be defined as

$$(\Delta O)^2 = \overline{(O - \overline{O})^2}, \tag{3.49}$$

which can be simplified to be

$$\begin{aligned} \overline{(O - \overline{O})^2} &= \overline{(O^2 + \overline{O}^2 - 2O\overline{O})} \\ &= \overline{O^2} + \overline{O}^2 - 2\overline{O}^2 \\ &= \overline{O^2} - \overline{O}^2. \end{aligned} \tag{3.50}$$

Thus, to find uncertainties, we normally find $\overline{O}$ and $\overline{O^2}$ first using

$$\overline{O} = \int_{\text{all space}} \psi^*(x)\hat{O}\psi(x)dx, \tag{3.51}$$

$$\overline{O^2} = \int_{\text{all space}} \psi^*(x)\hat{O}^2\psi(x)dx. \tag{3.52}$$

3.4.3 The Uncertainty Principle

In short, the uncertainty principle can be expressed as

$$\Delta x \Delta p \geq \frac{\hbar}{2}. \tag{3.53}$$

The detailed derivation can be found in Appendix I.

Chapter 4

Unbound States

4.1 The Potential Step

Suppose we have a potential step

$$U(x) = \begin{cases} 0 & x < 0, \\ U_0 & x > 0. \end{cases} \tag{4.1}$$

If there was a wave traveling from left to right, we need to consider the following two scenarios (i) $E > U_0$, and (ii) $E < U_0$.

4.1.1 (i) $E > U_0$

Similar to the finite well case, let the wavefunction at where $U(x) = 0$ be $\psi_I(x)$, and the wavefunction at where $U(x) = U_0$ be $\psi_{II}(x)$. To solve the wavefunction, we start with time-independent Schrödinger Equation as usual. For $\psi_I(x)$, we have

$$\frac{d^2}{dx^2}\psi_I(x) = -\frac{2mE}{2\hbar}\psi_I(x). \tag{4.2}$$

Let $k^2 = 2mE/2\hbar$, then we have a general solution

$$\psi_I(x) = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx}. \tag{4.3}$$

For $\psi_{II}(x)$, we have

$$\frac{d^2}{dx^2}\psi_{II}(x) = -\frac{2m(E-U_0)}{2\hbar}\psi_{II}(x). \tag{4.4}$$

Let $k'^2 = 2m(E-U_0)/2\hbar$, and a solution can be

$$\psi_{II}(x) = C\mathrm{e}^{ik'x}. \tag{4.5}$$

We can treat terms in the form $\exp(+ikx)$ as waves propagate to the right, and terms in the form $\exp(-ikx)$ as waves propagate to the left. The reason why there are two terms in $\psi_I(x)$ but only one term in $\psi_{II}(x)$ is as followed:

- Force and potential are related by $F = -\nabla U$. Thus, the abrupt change of potential at $x = 0$ causes a force behaving like a Dirac-delta function.
- This force can change the propagation direction of the wave that is initially traveling to the right, or it can let the wave pass through and change its other properties instead.
- Thus, in the region $x < 0$, there is a "reflected" wave traveling to the left.
- In the region $x > 0$, $U(x)$, again, is a constant, so there is no additional force that can reflect the "transmitted" wave.

With the reasoning above, we can denote terms of wavefunctions as incident wave, reflected wave, and transmitted wave

$$\psi_{inc} = A\mathrm{e}^{ikx},\ \psi_{ref} = B\mathrm{e}^{-ikx}, \psi_{trans} = C\mathrm{e}^{ik'x}. \tag{4.6}$$

Applying boundary conditions

$$\begin{cases} \psi_I(0) = \psi_{II}(0), \\ \psi_I'|_{x=0} = \psi_{II}'|_{x=0}, \end{cases} \tag{4.7}$$

gives following relationship between amplitudes

$$\begin{cases} A + B = C, \\ k(A - B) = k'C. \end{cases} \tag{4.8}$$

We can define two physical quantities: transmission probability T and reflection probability R as

$$T = \frac{\text{transmition per time}}{\text{reflection per time}}, \tag{4.9}$$

$$R = \frac{\text{reflection per time}}{\text{reflection per time}}. \tag{4.10}$$

Here we can multiply velocities to numerator and denominator to ensure those terms are "per time". Then, as $v = p/m = \hbar k/m$, we are able to use wavevector k to force those terms to be "per time" as desired. Thus, T and R can be expressed as

$$T = \frac{|\psi_{trans}|^2 k'}{|\psi_{inc}|^2 k} = \frac{C^* C k'}{A^* A k}, \tag{4.11}$$

$$R = \frac{|\psi_{ref}|^2 k}{|\psi_{inc}|^2 k} = \frac{B^* B}{A^* A}. \tag{4.12}$$

With the relationship between amplitudes, the above relation becomes

$$T = \frac{4kk'}{(k+k')^2}, \tag{4.13}$$

$$R = \frac{(k-k')^2}{(k+k')^2}. \tag{4.14}$$

In terms of U_0 and E,

$$\boxed{T = 4\frac{\sqrt{E(E-U_0)}}{(\sqrt{E}+\sqrt{E-U_0})^2},} \tag{4.15}$$

$$\boxed{R = 4\frac{(\sqrt{E}-\sqrt{E-U_0})^2}{(\sqrt{E}+\sqrt{E-U_0})^2}.} \tag{4.16}$$

4.1.2 (ii) $E < U_0$

When $E < U_0$, the wave equation ψ_{II} becomes

$$\psi_{II}(x) = C\mathrm{e}^{-\alpha x}, \tag{4.17}$$

where

$$\alpha = \sqrt{\frac{2m(U_0-E)}{\hbar^2}}, \tag{4.18}$$

and the term with positive exponent ignored. The reason is that as a well behaved function, the function should converge as $x \to +\infty$. Again, applying boundary conditions gives

$$\begin{cases} A + B = C, \\ k(A-B) = -\alpha C. \end{cases} \tag{4.19}$$

It turns out that in this case $R = 1$ and $T = 0$. However, this does not imply that there is no possibility to find a particle at $x > 0$, as $|\psi_{II}|$ still has a value greater than 0.

4.2 The Potential Barrier

Consider a potential barrier:

$$U = \begin{cases} 0 & x < 0 \text{ or } x > L \\ U_0 & 0 < x < L. \end{cases} \tag{4.20}$$

As discussed in Section 4.1, we can see that the wavefunction propagates in both direction in regions where $x < 0$, and $0 < x < L$, but it only travels to the right in the region where $x > L$.

(i) $E > U_0$

Let the $\psi_I(x)$ be the wavefunction to the left of the barrier, ψ_{II} be the wavefunction inside the barrier, and ψ_{III} be the wavefunction to the right of the barrier. Using the result from Section 4.1 directly, we have

$$\begin{cases} \psi_I(x) = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx}, \\ \psi_{II}(x) = C\mathrm{e}^{ik'x} + D\mathrm{e}^{-ik'x}, \\ \psi_{III}(x) = F\mathrm{e}^{ikx}, \end{cases} \tag{4.21}$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \text{ and } k' = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}. \tag{4.22}$$

Applying boundary conditions

$$\begin{cases} \psi_I(0) = \psi_{II}(0), \\ \psi_I'|_{x=0} = \psi_{II}'|_{x=0}, \\ \psi_{II}(L) = \psi_{III}(L), \\ \psi_{II}'|_{x=L} = \psi_{III}'|_{x=L}, \end{cases} \tag{4.23}$$

gives

$$\begin{cases} A + B = C + D, \\ k(A-B) = k'(C-D), \\ C\mathrm{e}^{ik'L} + D\mathrm{e}^{-ik'L} = F\mathrm{e}^{ikL}, \\ ik'(C\mathrm{e}^{ik'L} + D\mathrm{e}^{-ik'L}) = ikF\mathrm{e}^{ikL}. \end{cases} \tag{4.24}$$

Similar to Section 4.1, we can find the reflection and transmission probabilities as following

$$R = \frac{\sin^2(k'L)}{\sin^2(k'L) + 4k'^2k^2/(k^2-k'^2)^2}, \tag{4.25}$$

$$T = \frac{4k'^2k^2/(k^2-k'^2)^2}{\sin^2(k'L) + 4k'^2k^2/(k^2-k'^2)^2}, \tag{4.26}$$

Or in terms of E and U_0

$$\boxed{R = \frac{\sin^2[\sqrt{2m(E-U_0)}L/\hbar]}{\sin^2[\sqrt{2m(E-U_0)}L/\hbar] + 4(E/U_0)/[(E/U_0)-1]},} \tag{4.27}$$

$$\boxed{T = \frac{4(E/U_0)/[(E/U_0)-1]}{\sin^2[\sqrt{2m(E-U_0)}L/\hbar] + 4(E/U_0)/[(E/U_0)-1]}.} \tag{4.28}$$

Notice the reflection probability can be 0, when

$$\frac{\sqrt{2m(E-U_0)}}{\hbar}L = n\pi. \tag{4.29}$$

This occurs when the waves that are reflected at $x = 0$ and at $x = L$ destructively interfere in the region where $x < 0$. A classical analogy can be thin-film interference.

(ii) $E < U_0$

Inside the barrier, the wavefunction now becomes

$$\psi_{II}(x) = Ce^{\alpha x} + De^{-\alpha x}, \tag{4.30}$$

where $\alpha = \sqrt{2m(U_0 - E)/\hbar^2}$.

With procedures similar as case (i), the reflection and transmission probabilities in this case are

$$\boxed{R = \frac{\sinh^2[\sqrt{2m(E-U_0)}L/\hbar]}{\sinh^2[\sqrt{2m(E-U_0)}L/\hbar] + 4(E/U_0)/[(E/U_0)-1]},} \tag{4.31}$$

$$\boxed{T = \frac{4(E/U_0)/[(E/U_0)-1]}{\sinh^2[\sqrt{2m(E-U_0)}L/\hbar] + 4(E/U_0)/[(E/U_0)-1]}.} \tag{4.32}$$

Notice that even when particle have insufficient energy to overcome the potential barrier, it still has probability to transmit through. This is referred to as tunneling.

Chapter 5

Quantum Mechanics in 3D

5.1 The 3D Infinite Well

Recall the Schödinger Equation in one dimension is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)+U(x)\Psi(x,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,t). \tag{5.1}$$

It is not hard to imagine that for a three-dimensional case, the Schödinger Equation (in the Cartesian coordinate) becomes

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z,t)+U(x,y,z)\Psi(x,y,z,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t), \tag{5.2}$$

or more generally

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(r,t)+U(r)\Psi(r,t)=i\hbar\frac{\partial}{\partial t}\Psi(r,t). \tag{5.3}$$

We can still use the same trick - separation of variable - to isolate spatial and temporal parts. The time independent part, or the spatial part, reads

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r)+U(r)\Psi(r)=E\psi(r). \tag{5.4}$$

The derivation is similar to a one-dimensional case (see Section 2.3 for detail).

Now let's consider a simple model - a three dimensional infinite well. It is not very easy to visualize such a potential, but mathematically, the potential energy can be

$$U(x,y,z)=\begin{cases}0 & 0<x<L_x, 0<y<L_y, 0<z<L_z,\\ \infty & \text{otherwise.}\end{cases} \tag{5.5}$$

Wavefunctions can only exist in those region where potential equals to zero, thus this problem is also called particle in the box.

To find the wavefunctions inside the "box", we can separation of variable again, and let

$$\psi(x,y,z) = X(x)Y(y)Z(z). \tag{5.6}$$

Plugging the above form into time-independent Schödinger equation gives

$$\frac{1}{X(x)}\frac{\partial^2}{\partial^2 x}X(x) + \frac{1}{Y(y)}\frac{\partial^2}{\partial^2 y}Y(y) + \frac{1}{Z(z)}\frac{\partial^2}{\partial^2 z}Z(z) = -\frac{2mE}{\hbar^2}. \tag{5.7}$$

As the right-hand side is a constant that dose not depend on x, y,or z, terms on the left-hand side must be constants as well. So we have

$$\frac{\partial^2}{\partial^2 x}X(x) = C_x X(x), \tag{5.8}$$

$$\frac{\partial^2}{\partial^2 y}Y(y) = C_y Y(y), \tag{5.9}$$

$$\frac{\partial^2}{\partial^2 z}Z(z) = C_z Z(z). \tag{5.10}$$

which has general solution (after applying boundary conditions. Detailed calculation is similar to one-dimensional scenario in Section 3.1)

$$X(x) = A_x \sin\frac{n_x \pi x}{L_x}, \tag{5.11}$$

$$Y(y) = A_y \sin\frac{n_y \pi y}{L_y}, \tag{5.12}$$

$$Z(z) = A_z \sin\frac{n_z \pi z}{L_z}, \tag{5.13}$$

where A_x, A_y, and A_z are normalization factors to be determined. Therefore, the complete spatial wave function is

$$\psi_{n_x,n_y,n_z}(x,y,z) = A \sin\frac{n_x \pi x}{L_x}\sin\frac{n_y \pi y}{L_y}\sin\frac{n_z \pi z}{L_z}, \tag{5.14}$$

with corresponding eigen energy

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{\pi^2\hbar^2}{2m}. \tag{5.15}$$

5.1.1 Degeneracy

Suppose we have

$$L_x = L_y = L_z = L. \tag{5.16}$$

There are states with same eigen energy as show in Table.

Energy levels with multiple states are said to be degenerate, otherwise they are nondegenerate. In the case when $E = 6\pi^2\hbar^2/2mL^2$, we say degeneracy = 3.

5.1.2 Splitting of Energy Levels

Degeneracy usually results from symmetry. For more complicated situation, we can, for example, impose an external field to break symmetry, and to split originally degenerate energy levels. In this simple case, we can make L_x, L_y, and L_z not equal to each other.

5.2 The Bohr Model of an Atom

Niels Bohr proposed the Bohr model of an atom in 1913, which agreed well with experimental evidence at that time. He won the 1922 Nobel Prize "for his services in the investigation of the structure of atoms and of the radiation emanating from them". Now let us take a close look at the Bohr Model.

In the Bohr model, electrons are in a circular orbit around the nucleus. In this case, the centripetal force is provided by the electron-magnetic attraction between the electron itself and the nucleus. Suppose the distance between electron and nucleus is r, and the speed of the electron is v. For a Hydrogen atom, we have

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2}. \tag{5.17}$$

Here $m = 9.109 \times 10^{-31}\ kg$ is the electron mass, $\varepsilon_0 = 8.854 \times 10^{12}\ C^2N^{-1}m^{-2}$ is the vacuum permittivity, and $e = 1.602 \times 10^{-19}\ C$ is the charge of electron. In other words, we can write the expression as

$$v = \sqrt{\frac{e^2}{4\pi\varepsilon_0 m}\frac{1}{r}}. \tag{5.18}$$

The energy of the electron in this case can also be found simply by adding its kinetic energy and potential energy. Since we have the expression for its speed v, the kinetic part is pretty easy. The electric potential is also not hard to find. After simplification, the result would just be

$$E = -\frac{e^2}{8\pi\varepsilon_0 r}. \tag{5.19}$$

n_x,n_y, n_z	E_{n_x,n_y,n_z} $[\pi^2\hbar^2/2mL^2]$
1,1,1	3
2,1,1	
1,2,1	
1,1,2	6
1,2,2	
2,1,2	
2,2,1	9
...	...

5.2.1 Angular Momentum

As a short detour, let us take a moment to analyze the angular momentum. Classically, we have angular momentum

$$L = mvr. \tag{5.20}$$

Here Bohr made an assumption much like the one Planck did when solving the problem of Black-body radiation. Planck assumed that energy has the smallest indivisible part which equals hf. Bohr also assumed that the angular momentum also has such a smallest indivisible portion which is $\hbar = h/2\pi$. Therefore,

$$L = mvr = n\hbar. \tag{5.21}$$

An alternative interpretation is that, we can treat the electron as a wavefunction circling around the orbit (wave-particle duality). Because the wavefunction has to be smooth, we require the circumference of the orbital to be an integer multiplication of wavelength:

$$2\pi r = n\lambda. \tag{5.22}$$

From the Section 2.2, we know the wavelength of a matter-wave follows

$$\lambda = \frac{h}{p} = \frac{h}{mv}. \tag{5.23}$$

Therefore, combining the above two expressions gives

$$2\pi r = n\frac{h}{mv} \tag{5.24}$$

$$\begin{aligned} mvr &= n\frac{h}{2\pi} \\ &= n\hbar = L. \end{aligned} \tag{5.25}$$

The same result yields pretty naturally.

With the above results, we can find out the radius r to be

$$\boxed{r = \frac{(4\pi\varepsilon_0)\hbar^2}{me^2}n^2}. \tag{5.26}$$

We can notate constants in front as $a_0 = (4\pi\varepsilon_0)\hbar^2/me^2 \approx 0.0529\ nm$, which is known as the Bohr radius. With this expression for radius r, the energy can be written as

$$\begin{aligned} \boxed{E = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2}} \\ = -13.6\text{ eV}\frac{1}{n^2}. \end{aligned} \tag{5.27}$$

5.3 The Schrödinger Equation for a Central Force

A central force is a force that points from the particle directly towards (or away from) a fixed point in space, the center, and whose magnitude only depends on the distance of the object to the center, r. Therefore, the potential only depends on the distance from the center

$$\nabla U(r) = -F(r). \tag{5.28}$$

Since the potential is spherically symmetric if we place the center at the origin or the coordinate system, it would be convenient to work in the spherical coordinate system.

5.3.1 The Spherical Coordinate System

A quick review for the spherical coordinate system:

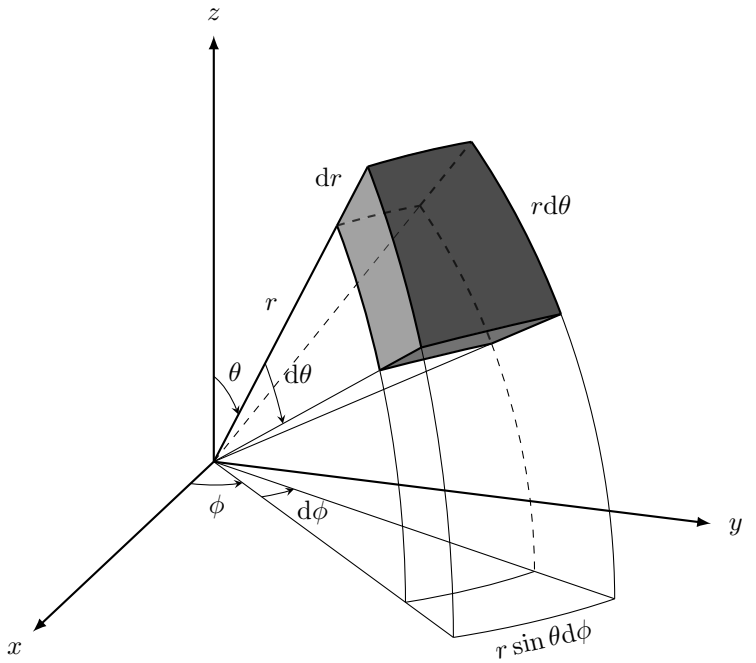

Figure 5.1: The spherical coordinate system (figure generated using TikZ, code by @Alexander Tsagkaropoulos, available on `https://tex.stackexchange.com/questions/159445/draw-in-cylindrical-and-spherical-coordinates/159452`).

Coordinate transformations between Cartesian coordinate system and spherical coordinate system are as followed

$$\begin{cases} x = r\sin\theta\cos\phi, \\ y = r\sin\theta\sin\phi, \\ z = r\cos\theta; \end{cases} \quad \begin{cases} r = \sqrt{x^2+y^2+z^2}, \\ \theta = \cos^{-1}(z/\sqrt{x^2+y^2+z^2}), \\ \phi = \tan^{-1}(y/x). \end{cases} \tag{5.29}$$

The Volume differential in spherical coordinates is

$$dV = r^2\sin\theta dr d\theta d\phi. \tag{5.30}$$

The Solid angle differential is

$$d\Omega = \sin\theta d\theta d\phi. \tag{5.31}$$

The Laplace operator is [1] [2]

$$\nabla^2 = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \csc^2\theta\frac{\partial^2}{\partial\phi^2}\right]. \tag{5.32}$$

Therefore, the Schrödinger equation in spherical coordinate system for a central force is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r,\theta,\phi) + U(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi), \tag{5.33}$$

with ∇^2 expressed above. The next step is to study this partial differential equation.

5.3.2 Separation of Variable

First, rearrange this partial differential equation so that (except the wave-function $\psi(r,\theta,\phi)$) terms or operators with θ and ϕ dependence are on one side, and terms or operators with r dependence are on the other side.

$$\begin{aligned} &\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\psi(r,\theta,\phi) + \csc^2\theta\frac{\partial^2}{\partial\phi^2}\psi(r,\theta,\phi) \\ &= \left[-\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(E-U(r))\right]\psi(r,\theta,\phi). \end{aligned} \tag{5.34}$$

Now apply the separation of variable, and let

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi). \tag{5.35}$$

Then the differential equation becomes

[1] Brian Dolan, Lecture notes for Differential Equations and Complex Analysis (MP469), available on http://www.thphys.nuim.ie/Notes/MP469/Laplace.pdf.

[2] WolframMathWorld, Laplace's Equation–Spherical Coordinates, available on https://mathworld.wolfram.com/LaplacesEquationSphericalCoordinates.html.

$$R\Phi \csc\theta \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + R\Theta\csc^2\theta\frac{\partial^2\Phi}{\partial\phi^2}$$
$$= -\Theta\Phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(E-U(r))R\Theta\Phi. \tag{5.36}$$

Dividing both sides by $R\Theta\Phi$ gives

$$\frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\csc^2\theta\frac{\partial^2\Phi}{\partial\phi^2}$$
$$= -\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(E-U(r)). \tag{5.37}$$

As one side depends on θ and ϕ, the other side depends on r, the only possibility is that they both equal to a constant, C.

$$\begin{cases} \frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\csc^2\theta\frac{\partial^2\Phi}{\partial\phi^2} = C \\ -\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(E-U(r)) = C \end{cases}. \tag{5.38}$$

The first equation can be further separated.

$$\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - C\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}. \tag{5.39}$$

With the same reasoning, the above form can only equal to another constant, D. Thus, we now turn a partial differential equation into three ordinary differential equations as following

$$\begin{cases} -\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(E-U(r)) = C, \\ \frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - C\sin^2\theta = D, \\ -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = D. \end{cases} \tag{5.40}$$

We will see the solutions of the above differential equations in the next section.

5.4 Central Force Cont. and the Hydrogen Atom

In the previous section, we have converted the partial differential equation of a central force to a set of ordinary differential equations. Now let us analyze them.

5.4.1 The Azimuthal Equation

The first and the simplest one is the azimuthal equation.

$$\frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = -D\Phi(\phi). \tag{5.41}$$

It is not hard to tell the general solution is

$$\Phi(\phi) = \mathrm{e}^{\pm i\sqrt{D}\phi}. \tag{5.42}$$

One way to interpret the physical meaning of the azimuthal equation $\Phi(\phi)$ is that it represents the amplitude of the wave function with ϕ dependence. Therefore, it is in a sense the projection of the wave on the ϕ space. Then the following analysis would be similar to the Bohr model as discussed in Section 5.2.

Now let us treat the azimuthal equation $\Phi(\phi)$ as a wave function that is constrained in a ring. $\sqrt{D}$ needs to be an integer in order to make it smooth. Thus, rewrite the equation as

$$\boxed{\Phi(\phi) = \mathrm{e}^{im_l\phi}, m_l = 0, \pm 1, \pm 2...} \tag{5.43}$$

m_l is the so-called magnetic quantum number.

Now we have a set of eigen solutions. The next question is: do we have an operator that is compatible[3] with this basis so that we have a set of eigenvalues? It turned out that one of them is the L_z operator. It measures the projection of angular momentum vector on the z-axis, and we have

$$\boxed{L_z = m_l\hbar}. \tag{5.44}$$

This form should look familiar, and the reasoning behind it is similar to that of the Bohr model. The difference is that, in the Bohr model, we said we know the angular momentum vector L, but here we say we only know the z-component L_z.

In reality, we can never precisely know the angular momentum vector L. If we know the angular momentum vector L, we can set up the coordinate system so that the angular momentum L aligns with z-axis. Then the motion of the particle is in the xy-plane, which means we precisely know this particle has zero z-component of velocity and z-component of zero momentum, but this would violet the Uncertainty Principle.

5.4.2 The Polar Equation

To solve the polar solution (also the radio solution) analytically is beyond the scope of this series. To those who might be interested, rather detailed steps can be found in [4]. Here only the most important results are listed.

[3] Generally, we say two operators are compatible if they commute, i.e. $[A, B] = AB - BA = 0$. In this specific case, we can treat $\partial^2/\partial\phi^2$ as an operator, it is commute with $L_z = -i\hbar\partial/\partial\phi$.

[4] Hydrogen Atom Wave Equation, AHBETE, available on https://ahbete.github.io/archive/MA436.pdf.

We have the polar equation

$$\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}\Theta\theta) - C\sin^2\theta\Theta(\theta) = m_l^2\Theta(\theta). \tag{5.45}$$

It can be shown that the constrain for the constant C is that,

$$\boxed{C = -l(l+1), l \in \mathbb{N}}. \tag{5.46}$$

Here l is the angular quantum number. Also, once a specific l is picked, m_l can only be

$$\boxed{m_l = 0, \pm1, ..., \pm l}. \tag{5.47}$$

The physical quantity associated with the angular quantum number l is the length of the angular momentum vector.

$$L^2 = l(l+1)\hbar^2 \text{ or } |L| = \sqrt{l(l+1)}\hbar. \tag{5.48}$$

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