

Chapter 1. Motivations

Quantum mechanics is an effective language that is used when we explore the nature at most fundamental levels. It has applications in almost all the branches of modern physics, including particle physics, nuclear physics, astrophysical physics, cosmology, condensed matter physics, etc.

We will introduce a bunch of new concepts beyond those in classical physics, which makes this a special course. Through this course, hopefully you will be excited to find that quantum mechanics not only successfully explains various natural phenomena at microscopic distances, but also makes further predictions that have been verified experimentally.

As the goal of this course, I hope you will

- Understand the basic concepts of quantum mechanics.
- Be able to set up the Schrödinger equation for a physics problem and solve for the corresponding wavefunctions and energy levels.
- Understand the statistical interpretation of physical observables.
- Understand the structure of the hydrogen atom.
- Understand the idea of spin.
- Be ready for the advanced quantum mechanics courses, PHYS 4707 and 4708.

Let us first set the clock back to the beginning of the 20th century. At that time, physicists were well trained with the knowledge of classical physics. Here is a list of things they knew well. First, physicists already understood classical mechanics, which is used to describe the motion of classical objects. In a nutshell, they knew how to use Newton's law $\vec{F} = m\vec{a}$ to derive the particle's position and momentum of a point-like particle as function of time. Second, the physicists knew the theory of electromagnetism, the Maxwell's equations, for describing physics systems involving electromagnetic forces. Third, the physicists also had the knowledge of thermal physics and statistical mechanics, developed by Boltzmann et al, as the law of physics system with many degrees of freedom.

At the same time, there had been many new findings on the experimental side, thanks to the advancement of technology. These curious physicists wanted to apply their knowledge of classical physics to explain the experimental results. But there seemed to be outstanding challenges. As evidence accumulated, they finally realized that some basic assumptions of classical physics have to be given up, and in particular, $\vec{F} = m\vec{a}$, fails under certain circumstances.

In this chapter, we will first go through the list of challenges to classical

physics, which finally lead to the introduction of quantum mechanics.

1.1. Blackbody Radiation

In thermal physics, blackbody is an object with certain temperature T and can radiate light at various frequencies. The energy density of the blackbody at each frequency have been measured experimentally.

There were two empirical formulae for describing blackbody radiation, obtained from the classical physics picture:

- Wien's law: $d\rho = c_1\nu^3 e^{-c_2\nu/T} d\nu$, where ν is the frequency, and c_1, c_2 are two fitting parameters.
- Rayleigh-Jeans law: $d\rho = (8\pi/c^3)kT\nu^2 d\nu$, where $c = 3 \times 10^8$ m/s is speed of light and $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant.

Both of them failed to give a complete explanation to the experimental data, as shown by the black points in the following plot. The Wien's law (blue curve) give a good fit at high frequencies, whereas the Rayleigh-Jeans law (magenta curve) only works for very low frequencies but blows up at high frequencies (the so called "ultraviolet catastrophe"). This was a big puzzle.

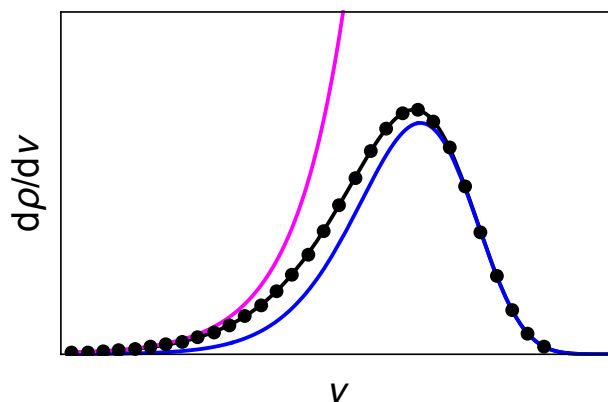


Fig. 1

To solve this puzzle, in 1900, Max Planck has made an important hypothesis which allows him to derive a formula that fits well for all the frequencies. In contrast to the classical physics picture where light is considered as a wave (the Maxwell equations are the wave equations for light), Planck assumes:

The energy carried by light is quantized (divided in parts). At given frequency ν , the energy carried by each quanta is equal to $E_\nu = h\nu$.

This is a remarkable assumption. It essentially gives a particle description

of light, where the quanta (particle carrying quantized energy of light) is often referred to as the photon. A new constant of nature is introduced here, h , is the Planck constant,

$$h = 6.62 \times 10^{-34} \text{ m}^2 \text{ kg/s} . \quad (1)$$

We consider the blackbody problem with the above assumption. At frequency ν , Boltzmann statistics tells us that the probability of finding n photons is proportional to $e^{-nh\nu/kT}$, where $n = 0, 1, 2, \dots$. The averaged total energy of photons at this frequency is

$$\bar{E}_\nu = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1} . \quad (2)$$

To derive the total energy at all frequencies, we need to sum up the degrees of freedom of light, including wave numbers and polarization. Consider a standing wave in a one dimensional (1D) box with size L_x , periodic condition requires $kL_x = n\pi$, where $n = 0, 1, 2, c \dots$ are non-negative integers. Summing over the possible wave number corresponds to the sum over n . In the large box limit ($L_x \rightarrow \infty$), the corresponding infinitesimal step is $dk = \Delta k = \pi/L_x$, where $\Delta n = 1$ is used. The sum over n thus becomes an integral, $\sum_n = \frac{L_x}{\pi} \int_0^{+\infty} dk = \frac{L_x}{2\pi} \int_{-\infty}^{+\infty} dk$. It is straightforward to generalize this to the three dimensional case.

As a result, the corresponding phase space of radiation is

$$2 \times \frac{1}{(2\pi)^3} \int d^3x \int d^3k = 2 \times \frac{1}{(2\pi)^3} V \int 4\pi\nu^2 d\nu , \quad (3)$$

where the prefactor 2 stands for two possible polarization (left- or right-handed) degrees of freedom of light. In the second step, we used the wave number $\vec{k} = (2\pi/\lambda)\hat{n} = (2\pi\nu/c)\hat{n}$, where \hat{n} is the unit vector along the \vec{k} direction. We have also assumed the blackbody radiation is homogeneous and isotropic.

With Eqs. (2) and (3), we can derive the energy density within the frequency interval $d\nu$,

$$\begin{aligned} d\rho &= 2 \left(\frac{2\pi}{c} \right)^3 \times \frac{1}{(2\pi)^3} 4\pi\nu^2 d\nu \bar{E}_\nu \\ &= \frac{8\pi h\nu^3 d\nu}{c^3} \frac{1}{e^{h\nu/kT} - 1} . \end{aligned} \quad (4)$$

This is the famous Planck's law. It fits the blackbody radiation spectrum very well. In Fig. 1, the Planck's law formula corresponds to the black curve which nicely fits the experimental data at every frequency.

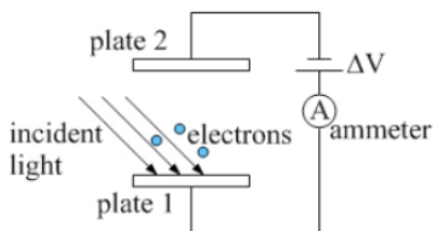
It is interesting to check the asymptotic behavior of Planck's law.

- At very high frequencies, $h\nu \gg kT$, we have $e^{h\nu/kT} - 1 \simeq e^{h\nu/kT}$, thus $\bar{E}_\nu \simeq h\nu e^{-h\nu/kT}$. This implies the probability of producing $n \geq 1$ photons is Boltzmann suppressed. In this case we obtain the Wien's law, which also fixes the parameters $c_1 = 8\pi h/c^3$, $c_2 = h/k$.
- At very low frequencies, $h\nu \ll kT$, we have $e^{h\nu/kT} - 1 \simeq h\nu/kT$, thus $\bar{E}_\nu \simeq kT$. This implies that the typical energy blackbody can radiate is dictated by its temperature regardless of the frequency. In this case, the Planck's law reduces to the Rayleigh-Jeans law.

The take home message of the above exercise is **energy of light is quantized**. The Planck's law marks the beginning of quantum physics.

1.2. Photoelectric effect

In 1887, Heinrich Hertz observed the photoelectric effect, using the experimental setup sketched below.



As the experimental finding, when a bunch of light is shined on the negative plate of a capacitor, electrons could absorb the energy of light and be freed from its binding with the plate. The resulting electron will travel to the positive plate and lead to a measured current at the ampere meter. This phenomenon only occurs when the frequency of light is high enough. Otherwise, no matter how long the light is shed to the plate, no electron will appear.

In 1905, Albert Einstein proposed a theory that explains the photoelectric effect. He makes use of Planck's hypothesis where each electron absorbs the energy of a photon (the quanta of light) for escaping the plate.¹ Assuming that the electron in the plate has a lower energy than those free ones, by an amount W , only when the photon energy is higher than W , can the electron be freed and generated the photoelectric phenomenon. In other words,

$$\nu > \frac{W}{h} . \quad (5)$$

¹In principle, there is also the probability for electron to absorb two or more photons, which could make it more energetic. However, the probability for more than one photon to be absorbed by the same electron is much more suppressed. This subtlety does not affect Einstein's explanation.

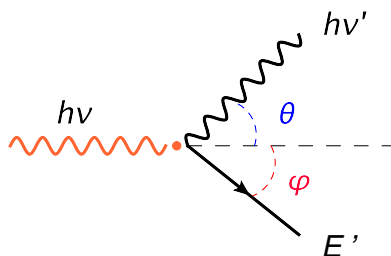
Clearly, this is strongly against the classical physics prediction where light is a continuous wave, in which case if it shines on an electron for long enough, the electron would accumulate large enough energy and be able to escape the plate (which does not happen in nature).

The photoelectric effect and its explanation provides a strong support of Planck's hypothesis on light quantization.

1.3. Compton Scattering

The Compton scattering experiment was carried out in 1920 which is another experimental evidence for the particle nature of the photon. In the experiment, X-ray with certain wavelength λ is shed through a metallic foil, resulting in an through-going X-ray component with the original wavelength λ , and a reflected component which a different frequency λ' . It was found that λ' is always larger than λ , and the larger the reflection angle the larger λ' is.

This phenomenon can be explained in terms of the particle nature of photon, assuming the light-electron scattering is described by the scattering of a photon particle carrying energy $h\nu = hc/\lambda$ with an electron at rest. The process is shown in the picture below, where the initial (orange line and point) and final (black lines) state photon, electron energies are labelled, in together with the scattering angle θ, φ .



We work out the kinematics based on energy and momentum conservation.

$$\begin{aligned} h\nu + mc^2 &= h\nu' + E' , \\ \frac{h\nu}{c} &= \frac{h\nu'}{c} \cos \theta + p' \cos \varphi , \\ \frac{h\nu'}{c} \sin \theta &= p' \sin \varphi , \end{aligned} \tag{6}$$

where m is the electron mass, and E', p' are the final state electron energy and momentum, respectively. They satisfy the dispersion relation $E'^2 = p'^2 c^2 + m^2 c^4$.

We first use the last two equations to remove the angle φ , which leads to

$$\left(\frac{h\nu}{c} - \frac{h\nu'}{c} \cos \theta \right)^2 + \left(\frac{h\nu'}{c} \sin \theta \right)^2 = p'^2 = \frac{E'^2}{c^2} - m^2 c^2 . \tag{7}$$

Next, we replace E' using the first equation and get

$$h\nu\nu'(1 - \cos\theta) = mc^2(\nu - \nu') . \quad (8)$$

Using the relation between frequency and wavelength for light, $\nu = c/\lambda$, we finally obtain

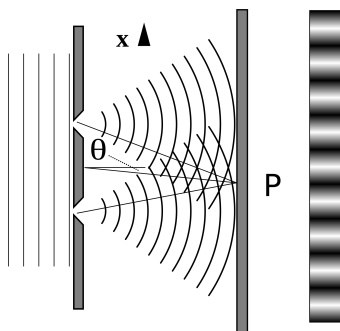
$$\lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta) . \quad (9)$$

Clearly, because $|\cos\theta| \leq 1$, λ' is always larger than λ , unless the scattering occurs at $\theta = 0$. In the latter case, there is no momentum transfer between the photon and electron – the photon simply travels along the original direction and $\lambda' = \lambda$ (This is also called forward scattering).

Moreover, for scattering angle $0 \leq \theta \leq \pi$, we have $1 \geq \cos\theta \geq -1$. Larger scattering angle yields smaller $\cos\theta$, and from Eq. (9) leads to larger difference between λ' and λ . These are exactly observed in Compton scattering.

1.4. Particle-Wave Duality

So far we have discussed several experimental findings that support the particle nature of light. On the other hand, in classical physics, light has been described as waves because of the interference effect it exhibited. A famous example of light interference is the double slit experiment carried out by Thomas Young in 1801. A schematic picture of the experimental setup is shown below. When a plane wave of light passes through two parallel slits separated by a distance d , one could observe the interference patterns (bright and dark lines) on the screen behind. This effect is most significant when the light wavelength λ is comparable to d .



In sharp contrast, the interference effect is not observed when $\lambda \ll d$. One example for this is the sunlight passing through the holes among tree leaves, where we see bright round spots on the ground that resembles the shape of the sun. In this case, one simply assumes the light is particle-like and travels in a straight line. The similar description is also used in optics when we describe the image of a candle behind a converging (diverging) lens.

The above comparison finally leads to the following dual description of light, which has both particle and wave nature. When the wavelength of light is comparable to (or larger than) the typical length scale of experiment (e.g. distance between double slits), the wave nature is most important and we must describe light using the wave equation. Alternatively, when the wavelength of light is much smaller than the typical experimental length scale, light should be considered as particles (photons) with energy quantized. The energy of each photon is equal to $h\nu = hc/\lambda$.

I cannot overemphasize the importance of this concept, which goes beyond classical physics. One must always bear the particle-wave duality in mind when analyzing natural phenomena, and make comparisons as mentioned above. In fact, such a duality not only applies to light, but also to all the other elementary particles, including the electron. The latter will be the focus of quantum mechanics, and the rest of this course.

1.5. Atomic Lines and the Bohr Model

As mentioned earlier, the beginning of 20th century has witnessed tremendous improvement in experimental technology. Physicists were able to probe matter at more fundamental levels. In particular, atoms are found to be not elementary, but composite with internal structures. Physicists discovered radioactivity, the α (Rutherford in 1899), β (Becquerel in 1896), γ (Villard in 1900) decays of nucleus, where the α, β, γ particles stand for ${}^4\text{He}$ nucleus, electron, and high energy photon, respectively. They have also learned to manipulate these particles experimentally.

In 1911, Ernest Rutherford did a very important experiment which is known as the Rutherford scattering. In the experiment, α particles are directed toward a gold foil as target. The goal of the experiment is to probe the structure of atoms by studying the scattering final states. It was found that most of the α particles simply travel through the target without any deflection, whereas very rare once in a while, large angle scatterings occur. The latter can be understood as α particle hit the gold nucleus which is much heavier. The experimental result shows that the nucleus only fills a very small size compared to atom, ² and most of the space of atom is empty. It is the electrons that fill up the ballpark space of an atom and fly around the nucleus. Therefore, the distribution of electron controls the properties of atoms. This also explains why in Compton scattering discussed earlier, the relevant process is photon-electron scattering.

The next big question following Rutherford's finding is how to describe the distribution of electrons?

²More quantitatively, a hydron atom has a radius around $1 \text{ \AA} = 10^{-8} \text{ cm}$. In contrast, the radius of its nucleus (made of a proton) is only around $1 \text{ fm} = 10^{-13} \text{ cm}$.

Here is another experimental input, called atomic lines. It was found by Johannes Rydberg back in 1888 that the wavelengths of light emitted by the hydrogen atom are not continuous but rather follows an empirical formula

$$\frac{1}{\lambda} = R \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad (10)$$

where $m = 1, 2, 3, \dots$, $n = 2, 3, 4, \dots$ are integers and $R \sim 10^7 \text{ m}^{-1}$ is the Rydberg constant. How to explain the discrete wavelength was a puzzle for atomic physics at that time.

These phenomena are apparently difficult to explain using classical physics. In fact, classical physics cannot even provide a consistent picture of atom. It is known that nucleus have positive electric charge whereas the electric charge of electron is negative. In classical physics, if the electron is attracted by the nucleus via the Coulomb force and orbits around the it, the electron will keep radiating away energy because it is accelerating. Eventually, the electron loses enough energy and falls onto the nucleus, and the atom will collapse. This does not happen in nature.

The above questions will find their answers in the rest of this course. It took more than one generation of physicists to fully figure out the theory behind atoms, which is quantum mechanics. This is a very exciting piece of history.

Let us first review Niels Bohr's try in 1913, where he took a phenomenological approach and proposed the Bohr's model, which lead to a remarkable success. The basic assumptions of Bohr's work are

- Electron stays on certain “orbits” around the nucleus with fixed radius r . The Coulomb's force balances the centrifugal force

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}, \quad (11)$$

where v is the orbiting velocity of electron.

- The orbiting of electron leads to an angular momentum, which is quantized

$$mvr = n\hbar, \quad (n = 1, 2, 3, \dots), \quad (12)$$

where on the right-hand side, $\hbar = h/(2\pi)$. The Planck constant is introduced as the unit of angular momentum quantization.

With the above two assumptions, and Eqs. (11) and (12), we can solve for r and v

$$r = \frac{4\pi\epsilon_0\hbar^2}{me^2} n^2, \quad v = \frac{e^2}{4\pi\epsilon_0\hbar} \frac{1}{n}. \quad (13)$$

We can further define the binding energy of electron on the n -th orbit

$$E_n = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2}. \quad (14)$$

This are already striking results. With one further assumption, this model can explain the Rydberg formula. The atomic lines are explained as the energy of radiated photon (quanta of light) when electron when the electron transits from one orbit (labelled by n) to another orbit (labelled by m), and only one photon is radiated in the process. This implies

$$E_\gamma = h\nu = E_n - E_m = \frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2} \left(\frac{1}{m^2} - \frac{1}{n^2} \right). \quad (15)$$

Using $\nu = c/\lambda$ and $h = 2\pi\hbar$, we derive

$$\frac{1}{\lambda} = \frac{me^4}{8\pi^2\varepsilon_0^2h^3c} \left(\frac{1}{m^2} - \frac{1}{n^2} \right). \quad (16)$$

This result has the same form as the empirical Rydberg formula, Eq. (10), and moreover, we derive the Rydberg constant in terms of constant of nature

$$R = \frac{me^4}{8\pi^2\varepsilon_0^2h^3c}. \quad (17)$$

The above shows how successful the Bohr model was.

This said, the Bohr model has left its assumptions unexplained. It paved the path forward, but is not yet a fundamental theory of atom. Clearly, Bohr's assumptions are not consistent with classical physics. As explained earlier, if the electron has a well-defined orbit around the nucleus, like in classical physics, there is no way for it not to undergo electromagnetic radiation continuously and finally fall to the nucleus. Atoms would not be stable, in contradiction with nature.

Here it is worth noting that the concept of orbit can be defined if electron is considered as a point-like particle, an object described simultaneously by its position \vec{r} and velocity $\dot{\vec{r}}$ in classical physics. Once the orbit is defined, a classical physicist can proceed to solve the Maxwell's equation to calculate the radiation rate.

From classical physics point of view, electron is a point-like particle. Even in today's experiments, we have not observed any internal structure of the electron. Moreover, electron carries unit electric charge so we can count the number of electrons using a Coulomb meter. There seems to be no reason not to assume electron is a point-like object.

Nonetheless, in order to make sense of Bohr's model, we have to give up the concept of orbit. In other words, electron inside the atom cannot be treated as a point-like particle anymore. By making analogy with the case of light, we could guess that the electron exhibits the wave nature inside the atom. In a nutshell, the electron forms a standing wave around the nucleus and this is why atoms could be stable.

The continuation along this guess leads to two fundamental concepts in quantum mechanics:

- Heisenberg’s uncertainty principle (1927). It states that we cannot measure \vec{r} and $\dot{\vec{r}}$ of electron in atom simultaneously well. The uncertainty in the measurements satisfy

$$\Delta r \cdot \Delta p \geq \frac{\hbar}{2}, \tag{18}$$

where $\vec{p} = m\dot{\vec{r}}$. We will give a rigorous definition of $\Delta r, \Delta p$ in Chapter 4.

- de Broglie matter wave (1924). It makes analogy to the case of light and assumes that electron also has the particle-wave duality. The wavelength of an electron with momentum p is

$$\lambda = \frac{h}{p}. \tag{19}$$

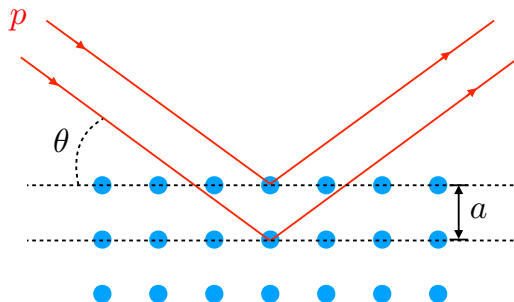
Inside atoms, the wave nature of electron is the most important. The size of atom is comparable to the wavelength of electron.

As we proceed further in this course, you will find that these two important concepts play their role in every case where the quantum mechanical effect is relevant.

1.6. The Wave Nature of Electron

Here we discuss two experiments that strongly support the existence of electron’s wave nature.

The Davisson–Germer experiment was done in 1923 – 27, where electrons are accelerated to a fixed energy (54 eV) and shed onto a nickel crystal. The reflected electron flux is observed at different reflection angles. The result shows interference effect, which is only explainable if electron is a wave. The experimental setup is illustrated by the following picture, where the blue dots are the positions of crystal lattice (nickel nucleus). The lattice spacing is a .



We assume that electron is a wave and consider the two paths shown by the red lines with arrows. Here, the angle between incoming electron direction and the lattice orientation is θ . It is straightforward to show that the lower path travels an extra distance of $\Delta L = 2a \sin \theta$. One would expect constructive (destructive) interference if ΔL is integer (half integer) times the electron wavelength. The constructive interference condition can be written as

$$\sin \theta = \frac{n\lambda}{2a} . \quad (20)$$

The electron wavelength can be found using de Broglie's assumption $\lambda = h/p \simeq h/\sqrt{2mE}$, where m is electron mass and $E = 54 \text{ eV}$. Using the Planck constant $h = 6.62 \times 10^{-34} \text{ m}^2 \text{ kg/s} = 4.1 \times 10^{-15} \text{ eV s}$ and $c = 3 \times 10^8 \text{ m/s}$, we find $\lambda \simeq 2 \times 10^{-10} \text{ m} = 2 \text{ \AA}$. The lattice spacing is roughly the size of atom, of order \AA . As a result, interference effects are observed at $\sin \theta \sim \mathcal{O}(1)$.

This is a strong support of the wave nature of electron. However, there is a subtlety. One could still ask: is each electron wave-like, or many electrons together forming a wave?

This question was finally addressed by a group of Italian physicists in 1976 in a double-slit experiment using electrons instead of photons. They managed to send electrons passing through the double slits one by one and record the position of electron when it reaches the screen (detector). Remarkably, the interference pattern predicted using the wave language is still found. This beautiful experiment excludes the possibility of many electrons together forming a matter wave. The only explanation left is that each individual electron behaves like a wave!

We conclude here by summarizing the particle-wave duality of the electron.

- Whether electron should be described as a particle or wave depends on the size of experiment. The wave aspect of electron is important if the de Broglie wavelength of electron is larger than the experimental length scale.
- We use the following quantities to describe the electron wave: ν (frequency), and λ (wavelength).
- We use the following quantities to describe the electron as a particle: E (energy), and p momentum.
- As the duality, Planck tells us $E = h\nu$, and de Broglie tells us $p = h/\lambda$.

1.7. $h \rightarrow 0$ and Classical Limit

Before closing this chapter, let us do a couple of fun exercises to appreciate how quantum physics is related to a non-zero Planck constant h .

As the first example, let us consider a pedestrian on the road. We can make a measurement his/her position and momentum. With the typical size and weight of human being,

$$\begin{aligned}\Delta x &\sim \text{meter}, & \Delta p &\sim \text{meter/second} \times 100 \text{ kg} \\ & & \Rightarrow \Delta x \Delta p &\sim 100 \text{ m}^2 \text{ kg/s}\end{aligned}\tag{21}$$

In contrast, the Planck constant is $h = 6.62 \times 10^{-34} \text{ m}^2 \text{ kg/s}$, which is much smaller than $\Delta x \Delta p$ of human. As a result, quantum mechanical effects are negligible at this length scale. We do not see much quantum physics in everyday life, and that is why physicists discovered classical physics first.

Classical physics correspond to the limit $h \rightarrow 0$.

In the second example, we consider the very tiny atom. As some useful quantities to have in mind, ³the electron in the hydrogen atom features

$$\begin{aligned}\Delta x &\sim \text{\AA} = 10^{-10} \text{ m}, \\ m_e &\sim 10^{-30} \text{ kg}, \\ v &\sim c/137 \sim 10^6 \text{ m/s}, \\ &\Rightarrow \Delta x \Delta p \sim 10^{-34} \text{ m}^2 \text{ kg/s}\end{aligned}\tag{22}$$

In this case, $\Delta x \Delta p$ is comparable to the Planck constant h , and this is when quantum mechanical effects become very important.

As a conceptual experiment, if we really want to see the electron clearly inside the atom (which has a very small size Δx), we must shine the electron with light whose wavelength is smaller than the size of atom. The corresponding photon will be so energetic that it can easily transfer a large momentum to the electron (Δp), and kick it out of the atom. The smaller Δx is, the larger Δp would be given to the electron. Heisenberg's uncertainty principle, Eq. (18), states that the product $\Delta x \Delta p$ is always bounded from below.

■ The end.

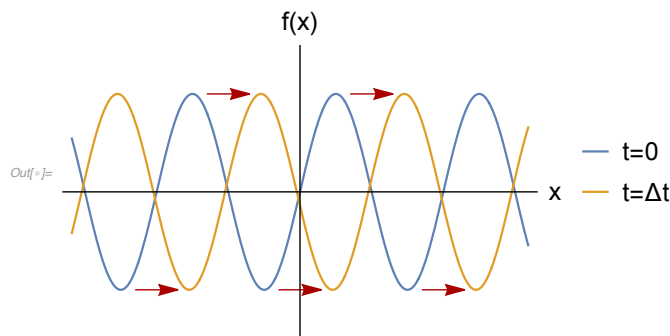
³You will understand why these numbers are what they are after this course.

Chapter 2. The Schrödinger Equation

Based on the discussions in the previous chapter, we have learned many experimental evidence for electron having both particle and wave nature. Inside atoms (small length scales), the wave nature of electron is playing a significant role.

If we accept that electron could behave like a wave, the Newton's law for point-like particle cannot be applied to describe both its \vec{r} and \vec{v} simultaneously. I.e., there is no sharp trajectories of the electron in the atom. We need another language for it.

Recall the definition of wave in classical physics, it is described by the amplitude function that spreads over the space and evolves with time, $f(\vec{r}, t)$. A wave satisfies certain wave equation. The simplest example is a plane wave moving in one space dimension, which satisfies the wave equation $(\partial^2/\partial t^2 - v^2\partial^2/\partial x^2)f(x, t) = 0$, where v is the speed of wave propagation. The plane wave solution with a fixed wavenumber is given by $f(x) = A \sin(kx - \omega t + \delta)$, where k is the wave number, $\omega = k/v$ is the angular frequency, and δ is the phase shift parameter. A picture of plane wave is shown below, at two different times $t = 0$ and $t = \Delta t$. As indicated by the red arrows, between the two time, the wave (peak and trough) moves to the right by a phase shift $\omega\Delta t$. All these are known in classical physics.



2.1. The equation

Back in 1924, right after de Broglie's work was published, in Zürich, Erwin Schrödinger was suggested by Debye to report on this work, and the latter made an important comment that *"to deal properly with waves, one had to have a wave equation"*. This leads to the discovery of the Schrödinger equation in 1925 as will be discuss below.

Schrödinger started by making analogy to classical physics, by introducing the wavefunction $\Psi(\vec{r}, t)$, similar to the amplitude of a classical wave. In the case

of plane wave,

$$\Psi(x, t) = Ae^{i(kx - \omega t)} . \quad (1)$$

Here we first work in one space dimension (1D), and make the generalization to three space dimensions (3D) later. And instead of using sin or cos which are real functions, the wavefunction Ψ is complex by definition. We will soon see why this choice is necessary.

When electron is described by a certain wavefunction Ψ , we sometimes also say that the electron is in the state Ψ .

Next, applying the particle-wave duality as discussed in previous chapter,

$$\begin{aligned} k &= \frac{2\pi}{\lambda} = \frac{2\pi}{h/p} = \frac{p}{\hbar} , \\ \omega &= 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar} , \end{aligned} \quad (2)$$

where p and E are the momentum and energy of electron, respectively. We introduce $\hbar = h/(2\pi)$ for simplicity. Inserting these relations in Eq. (1), we obtain

$$\Psi(x, t) = Ae^{i(px - Et)/\hbar} . \quad (3)$$

For non-relativistic electron $v \ll c$ (c is speed of light), it satisfies the dispersion relation

$$E = \frac{p^2}{2m} . \quad (4)$$

Together with the plane wavefunction, we can also write

$$\left(E - \frac{p^2}{2m} \right) \Psi(x, t) = 0 , \quad (5)$$

which is a trivial multiplication.

Next, taking advantage of the property of exponential, we find the relation

$$\begin{aligned} E e^{i(px - Et)/\hbar} &= i\hbar \frac{\partial}{\partial t} e^{i(px - Et)/\hbar} , \\ p e^{i(px - Et)/\hbar} &= -i\hbar \frac{\partial}{\partial x} e^{i(px - Et)/\hbar} , \\ p^2 e^{i(px - Et)/\hbar} &= -\hbar^2 \frac{\partial^2}{\partial x^2} e^{i(px - Et)/\hbar} . \end{aligned} \quad (6)$$

With these, we can rewrite Eq. (5) as a differential equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t) . \quad (7)$$

This is the Schrödinger equation for electron as a plane wave (without interactions or external potential).

It is important to note that this equation only works if the plane wave is described by the exponential Eq. (3). Had we used sin or cos functions instead, Eq. (7) would fail because it involves both single and double derivatives.¹

The next step question is what about electron in an atom. The simplest case is the hydrogen atom, where the nucleus is made of a single proton. The electron is not free and cannot be described by a plane wave. Instead, it feels an attractive Coulomb potential exerted by the proton. There is a potential energy that depends on the position of the electron. If there is a Schrödinger equation to describe such an electron, it must properly take into account of the potential energy.

In the 1D case, the Schrödinger equation in the presence of a potential energy becomes

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t) . \quad (8)$$

If the wavefunction were still described by the exponential form Eq. (3) (which is no true in general anymore), then using Eq. (6), we would obtain the dispersion relation $E = p^2/(2m) + V(x)$. However, this relation only holds for a point particle in classical physics. It is not appropriate in quantum mechanics because the Heisenberg uncertainty principle forbids the simultaneous knowledge of x and p .

In contrast, Eq. (8) still holds valid where E and p are no longer numbers but replaced by the derivative actions on the wavefunction

$$E \rightarrow i\hbar \frac{\partial}{\partial t} , \quad p \rightarrow -i\hbar \frac{\partial}{\partial x} , \quad p^2/(2m) \rightarrow -\hbar^2 \frac{\partial^2}{\partial x^2} . \quad (9)$$

Eq. (8) is the general Schrödinger equation in 1D. In the case of 3D, the Schrödinger equation takes the form

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) , \quad (10)$$

where $\vec{r} = (x, y, z)$ and $\vec{\nabla} = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ in Cartesian coordinates.

More generally, one should bear in mind that the potential energy function V could also depend on time t or even include the derivative operator $\vec{\nabla}$. We will not consider these possibilities in this course.

The Schrödinger equation is a first-order differential equation with respect to time. This means that once we know the function $\Psi(\vec{r}, 0)$ at time $t = 0$ (boundary condition), we can solve the equation to find the form of $\Psi(\vec{r}, t)$ at a latter time.

¹As we know, for $\sin x$ (or $\cos x$), taking derivative twice returns to the original function, up to a minus sign, but taking derivative once would yield $\cos x$ (or $\sin x$).

2.2. Statistical Interpretation

We will discuss various examples on how to solve the Schrödinger equation for the rest of this course, but first of all, we need to address what is the physical meaning of the wavefunction, $\Psi(\vec{r}, t)$.

Consider the electron double slit experiment again. What is measured in the experiment is the probability for electron to reach different positions on the screen. If the electron is fully described by the wavefunction, so is the corresponding prediction in probabilities. There must be a relationship between $\Psi(\vec{r}, t)$ and the probability $\rho(\vec{r})$.

By definition probability is a real number, whereas the wavefunction is complex in general. This suggests

$$\rho \neq \Psi . \quad (11)$$

As a strong evidence, if the double slit experiment is modified by closing one of the slits, we could measure the new probability of finding electron on the screen, ρ_1 or ρ_2 , depending on which of the two slits are left to be open. It is found that $\rho \neq \rho_1 + \rho_2$, due to the interference effect.

The correct explanation of the interference phenomenon is to define

$$\rho(\vec{r}, t) = |\Psi(\vec{r}, t)|^2 \equiv \Psi(\vec{r}, t)\Psi^*(\vec{r}, t) . \quad (12)$$

If the wavefunction for electron passing slit 1 (2) is called Ψ_1 (Ψ_2), we have $\rho_1 = |\Psi_1|^2$ and $\rho_2 = |\Psi_2|^2$. The total wavefunction when both slits are open is $\Psi(\vec{r}, t) = \Psi_1(\vec{r}, t) + \Psi_2(\vec{r}, t)$, thus

$$\rho = |\Psi_1(\vec{r}, t) + \Psi_2(\vec{r}, t)|^2 = \rho_1 + \rho_2 + 2\text{Re}(\Psi_1\Psi_2^*) . \quad (13)$$

The last term is nonzero and controls the interference effect as seen on the screen. This naturally explains why $\rho \neq \rho_1 + \rho_2$.

This explanation is also mathematically consistent with the classical physics explanation of Young's double slit experiment which sees the interference effect of light. There, the electromagnetic wave is described \vec{E} and \vec{B} fields, and the intensity (related to probability) is given by $\vec{E}^2 + \vec{B}^2$. \vec{E} and \vec{B} satisfy the wave equation for light (derived from the Maxwell equations).

As a more careful interpretation, because the space coordinate \vec{r} is continuous, the quantity $\rho(\vec{r}, t)$ defined in Eq. (12) is actually the probability density. The probability of find the electron in the infinitesimal volume $d^3\vec{r}$ is

$$\rho(\vec{r}, t)d^3\vec{r} = |\Psi(\vec{r}, t)|^2 d^3\vec{r} . \quad (14)$$

The unitarity condition for probability (i.e., total probability equal to 1) implies

$$\int |\Psi(\vec{r}, t)|^2 d^3\vec{r} = 1 . \quad (15)$$

This is the statistical interpretation of wavefunction presented by Max Born in 1926.

In quantum mechanics, the relevant question about the electron is no longer its exact trajectory, but other experimental observables, including the probability of find the electron at given position and time, the average of operators under certain electron state (to be defined below), etc. All these information are encoded in the wavefunction $\Psi(\vec{r}, t)$, which evolves according to the Schrödinger equation. To this end, it is important to know well how to solve this equation for various physics systems (with different forms of potential V). We will start with problems in 1D as warm up exercises in chapter 3, and then move on to higher dimensions.

2.3. Probability Current

Here let us calculate the time derivative of the probability density $\rho(\vec{r}, t) = |\Psi(\vec{r}, t)|^2$. Applying the Schrödinger equation,

$$\begin{aligned} \frac{d\rho(\vec{r}, t)}{dt} &= \Psi^*(\vec{r}, t) \frac{d\Psi(\vec{r}, t)}{dt} + \frac{d\Psi^*(\vec{r}, t)}{dt} \Psi(\vec{r}, t) \\ &= \Psi^*(\vec{r}, t) \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}) \Psi(\vec{r}, t) \right) \\ &\quad + \frac{1}{-i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^*(\vec{r}, t) + V^*(\vec{r}) \Psi^*(\vec{r}, t) \right) \Psi(\vec{r}, t) \quad (16) \\ &= -\frac{\hbar}{2mi} (\Psi^*(\vec{r}, t) \nabla^2 \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \nabla^2 \Psi^*(\vec{r}, t)) \\ &\quad + \frac{1}{i\hbar} (V - V^*) \Psi(\vec{r}, t) \Psi^*(\vec{r}, t) . \end{aligned}$$

Assuming the potential to be real, the above can be rewritten as

$$\frac{d\rho(\vec{r}, t)}{dt} = -\frac{\hbar}{2mi} \vec{\nabla} \cdot \left(\Psi^*(\vec{r}, t) \vec{\nabla} \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \vec{\nabla} \Psi^*(\vec{r}, t) \right) . \quad (17)$$

Define the probability current $\vec{j} = \frac{\hbar}{2mi} (\Psi^*(\vec{r}, t) \vec{\nabla} \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \vec{\nabla} \Psi^*(\vec{r}, t))$ which is a 3-vector, Eq. (17) can be written as

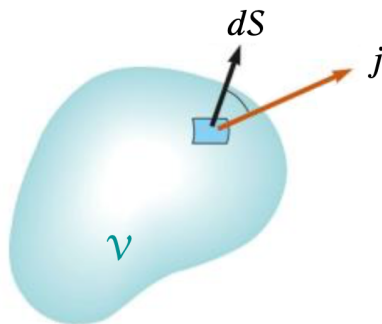
$$\frac{d\rho}{dt} + \vec{\nabla} \cdot \vec{j} = 0 . \quad (18)$$

There is a nice geometric explanation if we integrate this equation over a space volume \mathcal{V} ,

$$\int_{\mathcal{V}} d^3\vec{r} \left(\frac{d\rho}{dt} + \vec{\nabla} \cdot \vec{j} \right) = 0 . \quad (19)$$

Apply the Gauss's law, we obtain

$$\frac{d}{dt} \int_{\mathcal{V}} d^3\vec{r} \rho = - \oint_{\mathcal{S}} d\vec{S} \cdot \vec{j} . \quad (20)$$



The geometry meaning of this equation is shown in the above picture. $\int_{\mathcal{V}} d^3\vec{r} \rho$ can be interpreted as the total probability inside the volume \mathcal{V} . The rate for its change (time derivative) is equal to the net current flowing to the interior of the surface of this volume \mathcal{S} .² Importantly, when the net current is zero, the total probability is conserved.

2.4. Concept of Operators

Other than probability, we could construct other physical observables using the wavefunction. Here it is useful to introduce the concept of “operator” in quantum mechanics. In Eq. (9), we have already seen a few examples, where we replace the electron momentum \vec{p} with a derivative operator $-i\hbar\vec{\nabla}$. Such an operator acts on the wavefunction $\Psi(\vec{r}, t)$. Similarly, we also make the replacement for energy $E \rightarrow i\hbar\partial/\partial t$. This is also an operator. To generalize the idea, we can also consider the multiplication of space coordinate $\vec{r}\Psi(\vec{r}, t)$ as an operator acting on $\Psi(\vec{r}, t)$. The operator is \vec{r} itself.

We can also define combination of operators introduce above. An important one is the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) , \quad (21)$$

with which the Schrödinger equation can be written as

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = \hat{H} \Psi(\vec{r}, t) . \quad (22)$$

²In E&M, we have learned something similar involving the electric charge and the electric current.

From now on we will start to use the term “operator” in the discussions. Concrete examples include

$$\vec{r}, \quad V(\vec{r}), \quad \hat{p} = -i\hbar\vec{\nabla}, \quad \hat{H} = \hat{p}^2/(2m) + V(\vec{r}), \quad \dots \quad (23)$$

2.5. Average of Operators

Given the wavefunction $\Psi(\vec{r}, t)$ and an operator \hat{O} , we can evaluate the average of the operator under the state described by the wavefunction. The rule is

$$\langle \hat{O} \rangle = \int d^3\vec{r} \Psi^*(\vec{r}, t) \hat{O} \Psi(\vec{r}, t). \quad (24)$$

The effectiveness of this rule can be verified using two examples, $\hat{O} = \vec{r}$ and \hat{p} . The average of \vec{r}

$$\langle \vec{r} \rangle = \int d^3\vec{r} \Psi^*(\vec{r}, t) \vec{r} \Psi(\vec{r}, t) = \int d^3\vec{r} |\Psi(\vec{r}, t)|^2 \vec{r}, \quad (25)$$

is obviously what it should be, with $|\Psi(\vec{r}, t)|^2$ serving as the probability density.

To calculate the average of operator \hat{p} , we introduce the Fourier transformation of the wavefunction, where

$$\Psi(\vec{r}, t) = \int \frac{d^3\vec{p}}{(2\pi\hbar)^{3/2}} \tilde{\Psi}(\vec{p}, t) e^{i\vec{p}\cdot\vec{r}/\hbar}, \quad (26)$$

where $\tilde{\Psi}(\vec{p}, t)$ is the wavefunction in momentum space. It controls the probability of finding electron with certain momentum \vec{p} (instead of position, we cannot determine both). The inverse Fourier transformation is

$$\tilde{\Psi}(\vec{p}, t) = \int \frac{d^3\vec{r}}{(2\pi\hbar)^{3/2}} \Psi(\vec{r}, t) e^{-i\vec{p}\cdot\vec{r}/\hbar}, \quad (27)$$

The consistency between the two transformation Eqs. (26) and (27) can be verified by doing them one after the other,

$$\begin{aligned} \Psi(\vec{r}, t) &= \int \frac{d^3\vec{p}}{(2\pi\hbar)^{3/2}} \left(\int \frac{d^3\vec{r}'}{(2\pi\hbar)^{3/2}} \Psi(\vec{r}', t) e^{-i\vec{p}\cdot\vec{r}'/\hbar} \right) e^{i\vec{p}\cdot\vec{r}/\hbar} \\ &= \frac{1}{(2\pi\hbar)^3} \int d^3\vec{r}' \Psi(\vec{r}', t) \int d^3\vec{p} e^{i\vec{p}\cdot(\vec{r}-\vec{r}')/\hbar} \\ &= \frac{1}{(2\pi\hbar)^3} \int d^3\vec{r}' \Psi(\vec{r}', t) (2\pi\hbar)^3 \delta^3(\vec{r}-\vec{r}') \\ &= \int d^3\vec{r}' \Psi(\vec{r}', t) \delta^3(\vec{r}-\vec{r}') \\ &= \Psi(\vec{r}, t), \end{aligned} \quad (28)$$

where in the second line, we interchanged the order of two integrals; in the third line we did the $d^3\vec{p}$ integral by introducing the Dirac's δ -function; and the last step returns same result as the starting point. This confirms that the transformation Eq. (26) is indeed the inverse transformation of Eq. (27).

The Dirac's δ -function is a useful mathematical object. It is defined as

$$\delta(x - x_0) = \frac{1}{2\pi} \int dp e^{ip(x-x_0)} , \quad (29)$$

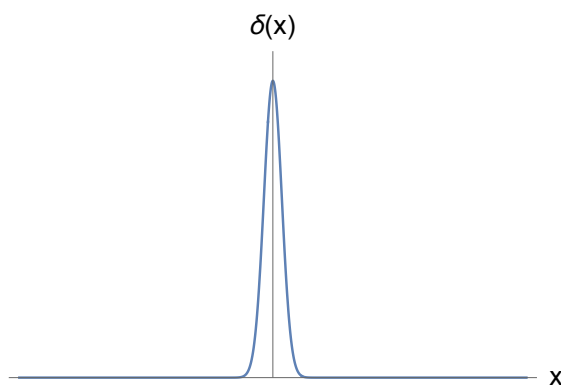
and satisfy the condition that for any function $f(x)$,

$$\int dx f(x) \delta(x - x_0) = f(x_0) . \quad (30)$$

As a result,

$$\int dx \delta(x - x_0) = 1 . \quad (31)$$

The value of $\delta(x - x_0)$ is zero anywhere except for the point $x = x_0$. At $x = x_0$, the value is infinitely large (positive). The form of δ -function is illustrated in the picture below, where one should think the height of the peak is infinitely large and the width of peak is infinitely narrow.



The three-dimensional δ function introduced in Eq. (28) is simply the product of three δ functions for each direction,

$$\delta^3(\vec{r} - \vec{r}') = \delta(x - x') \delta(y - y') \delta(z - z') . \quad (32)$$

With the above Fourier transformations, we proceed to evaluate the average

of operator \hat{p} ,

$$\begin{aligned}
\langle \hat{p} \rangle &= \int d^3\vec{r} \Psi^*(\vec{r}, t) (-i\hbar\nabla) \Psi(\vec{r}, t) \\
&= \int d^3\vec{r} \left(\int \frac{d^3\vec{p}''}{(2\pi\hbar)^{3/2}} \tilde{\Psi}^*(\vec{p}'', t) e^{-i\vec{p}'' \cdot \vec{r}/\hbar} \right) (-i\hbar\nabla) \left(\int \frac{d^3\vec{p}'}{(2\pi\hbar)^{3/2}} \tilde{\Psi}(\vec{p}', t) e^{i\vec{p}' \cdot \vec{r}/\hbar} \right) \\
&= \int d^3\vec{r} \left(\int \frac{d^3\vec{p}''}{(2\pi\hbar)^{3/2}} \tilde{\Psi}^*(\vec{p}'', t) e^{-i\vec{p}'' \cdot \vec{r}/\hbar} \right) \left(\int \frac{d^3\vec{p}'}{(2\pi\hbar)^{3/2}} \tilde{\Psi}(\vec{p}', t) \vec{p}' e^{i\vec{p}' \cdot \vec{r}/\hbar} \right) \\
&= \frac{1}{(2\pi\hbar)^3} \int d^3\vec{p}'' \tilde{\Psi}^*(\vec{p}'', t) \int d^3\vec{p}' \tilde{\Psi}(\vec{p}', t) \vec{p}' \int d^3\vec{r} e^{i(\vec{p}' - \vec{p}'') \cdot \vec{r}/\hbar} \\
&= \int d^3\vec{p}'' \tilde{\Psi}^*(\vec{p}'', t) \int d^3\vec{p}' \tilde{\Psi}(\vec{p}', t) \vec{p}' \delta^3(\vec{p}' - \vec{p}'') \\
&= \int d^3\vec{p}' |\tilde{\Psi}(\vec{p}', t)|^2 \vec{p}'
\end{aligned} \tag{33}$$

Making analogy with Eq. (25), it become clear that in the last line $|\tilde{\Psi}(\vec{p}', t)|^2$ can be interpreted as the probability density of finding electron having three-momentum \vec{p}' in the momentum space.

2.5. Ehrenfest Theorem

The theorem is named after Paul Ehrenfest's work in 1927, which evaluates the time evolution of the $\langle \hat{r} \rangle$, $\langle \hat{p} \rangle$ averages.

We first calculate the time derivative of $\langle \hat{r} \rangle$, where d/dt acts on the wavefunctions and we apply the The Schrödinger equation,

$$\begin{aligned}
\frac{d\langle \hat{r} \rangle}{dt} &= \frac{d}{dt} \int d^3\vec{r} \Psi^*(\vec{r}, t) \vec{r} \Psi(\vec{r}, t) \\
&= \int d^3\vec{r} \left(\Psi^*(\vec{r}, t) \vec{r} \frac{d\Psi(\vec{r}, t)}{dt} + \frac{d\Psi^*(\vec{r}, t)}{dt} \vec{r} \Psi(\vec{r}, t) \right) \\
&= \int d^3\vec{r} \left\{ \Psi^*(\vec{r}, t) \vec{r} \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}) \Psi(\vec{r}, t) \right) \right. \\
&\quad \left. + \frac{1}{-i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^*(\vec{r}, t) + V^*(\vec{r}) \Psi^*(\vec{r}, t) \right) \vec{r} \Psi(\vec{r}, t) \right\} \tag{34} \\
&= -\frac{\hbar}{2mi} \int d^3\vec{r} \vec{r} \cdot \vec{\nabla} \cdot \left(\Psi^*(\vec{r}, t) \vec{\nabla} \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \vec{\nabla} \Psi^*(\vec{r}, t) \right) \\
&= -\frac{\hbar}{2mi} \int d^3\vec{r} \partial_j \left\{ \vec{r} \left(\Psi^*(\vec{r}, t) \partial_j \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \partial_j \Psi^*(\vec{r}, t) \right) \right. \\
&\quad \left. - (\partial_j \vec{r}) \left(\Psi^*(\vec{r}, t) \partial_j \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \partial_j \Psi^*(\vec{r}, t) \right) \right\} ,
\end{aligned}$$

where we assume the potential term is real. In the last two steps, we integrate by parts, where $j = x, y, z$.

Next, we turn the integration of total derivative into a surface integral, and make a further assumption that on the surface with $\vec{r} \rightarrow \infty$, the wavefunction vanishes $\Psi(\infty) \rightarrow 0$. This allows us drop the surface integral and write

$$\begin{aligned} \frac{d\langle \hat{r} \rangle}{dt} &= -\frac{\hbar}{2mi} \left\{ \oint_{\infty} d\mathcal{S}_j \vec{r} \left(\Psi^*(\vec{r}, t) \partial_j \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \partial_j \Psi^*(\vec{r}, t) \right) \right. \\ &\quad \left. - \int d^3 \vec{r} (\partial_j \vec{r}) \left(\Psi^*(\vec{r}, t) \partial_j \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \partial_j \Psi^*(\vec{r}, t) \right) \right\} \quad (35) \\ &= \frac{\hbar}{2mi} \int d^3 \vec{r} (\partial_j \vec{r}) \left(\Psi^*(\vec{r}, t) \partial_j \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \partial_j \Psi^*(\vec{r}, t) \right). \end{aligned}$$

Using $\partial_j \vec{r}_i = \delta_{ij}$, we get

$$\frac{d\langle \hat{r} \rangle}{dt} = \frac{\hbar}{2mi} \int d^3 \vec{r} \left(\Psi^*(\vec{r}, t) \vec{\nabla} \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \vec{\nabla} \Psi^*(\vec{r}, t) \right). \quad (36)$$

We can perform another integration by parts for the second term and drop the surface term. It leads to

$$\begin{aligned} \frac{d\langle \hat{r} \rangle}{dt} &= \frac{1}{m} \int d^3 \vec{r} \Psi^*(\vec{r}, t) (-i\hbar \vec{\nabla}) \Psi(\vec{r}, t) \\ &= \frac{1}{m} \int d^3 \vec{r} \Psi^*(\vec{r}, t) \hat{p} \Psi(\vec{r}, t) \\ &= \frac{\langle \hat{p} \rangle}{m} \end{aligned} \quad (37)$$

The resulting relationship, $d\langle \hat{r} \rangle/dt = \langle \hat{p} \rangle/m$ has a classical physics correspondence. In the ($\hbar \rightarrow 0$) limit where the particle nature of electron is most important, we can interpret $\langle \hat{r} \rangle$ and $\langle \hat{p} \rangle$ as the position and momentum of a point-like electron. Clearly, $p = mv = mdx/dt$ holds in classical physics. On the other hand, when the wave nature of electron becomes important, we lose the definition of point-like particle. However, we can still talk about the operator average of position and momentum of the electron wave, and the relationship retains certain similarity to that in classical physics.

Next, we calculate the time derivative of $\langle \hat{p} \rangle$ in a similar fashion.

$$\begin{aligned}
\frac{d\langle \hat{p} \rangle}{dt} &= \frac{d}{dt} \int d^3\vec{r} \Psi^*(\vec{r}, t) \hat{p} \Psi(\vec{r}, t) \\
&= \int d^3\vec{r} \left(\Psi^*(\vec{r}, t) (-i\hbar \vec{\nabla}) \frac{d\Psi(\vec{r}, t)}{dt} + \frac{d\Psi^*(\vec{r}, t)}{dt} (-i\hbar \vec{\nabla}) \Psi(\vec{r}, t) \right) \\
&= \int d^3\vec{r} \left\{ \Psi^*(\vec{r}, t) (-\vec{\nabla}) \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}) \Psi(\vec{r}, t) \right) \right. \\
&\quad \left. + \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^*(\vec{r}, t) + V(\vec{r}) \Psi^*(\vec{r}, t) \right) \vec{\nabla} \Psi(\vec{r}, t) \right\}. \tag{38}
\end{aligned}$$

For the first term on the second line (in red color), we integrate by parts twice to let all the derivatives act on $\Psi(\vec{r}, t)$. This yields

$$\begin{aligned}
\frac{d\langle \hat{p} \rangle}{dt} &= \int d^3\vec{r} \left\{ \frac{\hbar^2}{2m} \Psi^*(\vec{r}, t) \vec{\nabla} \nabla^2 \Psi(\vec{r}, t) - \Psi^*(\vec{r}, t) \vec{\nabla} \left(V(\vec{r}) \Psi(\vec{r}, t) \right) \right. \\
&\quad \left. - \frac{\hbar^2}{2m} \Psi^*(\vec{r}, t) \nabla^2 \vec{\nabla} \Psi(\vec{r}, t) + V(\vec{r}) \Psi^*(\vec{r}, t) \vec{\nabla} \Psi(\vec{r}, t) \right\}. \tag{39}
\end{aligned}$$

Clearly, the two terms in blue color exactly cancel with each other. We can make a further simplification by expanding the derivative in the first line of Eq. (39), $\vec{\nabla} (V(\vec{r}) \Psi(\vec{r}, t)) = (\vec{\nabla} V(\vec{r})) \Psi(\vec{r}, t) + V(\vec{r}) \vec{\nabla} \Psi(\vec{r}, t)$, and get

$$\begin{aligned}
\frac{d\langle \hat{p} \rangle}{dt} &= - \int d^3\vec{r} \Psi^*(\vec{r}, t) \vec{\nabla} \left(V(\vec{r}) \right) \Psi(\vec{r}, t) \\
&= - \left\langle \vec{\nabla} V(\vec{r}) \right\rangle. \tag{40}
\end{aligned}$$

Like Eq. (37), there is also a classical physics correspondence if we take the point-like particle limit for electron ($\hbar \rightarrow 0$). In classical physics, the left-hand side reduces to the acceleration $dp/dt = ma$. Then the right-hand side need to be the force (recall $F = ma$), derivative of the potential at the particle's position. Using the above language, it should take the form

$$- \vec{\nabla} V(\langle \vec{r} \rangle). \tag{41}$$

Clearly, Eq. (41) is not strictly equal to Eq. (40). Only in the point-like particle limit, they approach to each other.

When the wave nature of the electron is important, the Eq. (40) derived above goes beyond the scope of classical physics. The fact that $d\langle \hat{p} \rangle/dt = -\langle \vec{\nabla} V(\vec{r}) \rangle \neq \vec{\nabla} V(\langle \vec{r} \rangle)$ indicates the break down of classical description of the electron when it is no longer particle like.

Eqs. (37) and (40) are called the Ehrenfest theorem. They are useful for calculating the time evolution of average position and momentum of the electron (as a wave) in quantum mechanics.

2.6. Time-independent Schrödinger Equation and Stationary State

Let us take a closer look at the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = \hat{H} \Psi(\vec{r}, t) . \quad (42)$$

We assume that the Hamiltonian operator does not explicitly depend on time t . In this case, it is possible to factorize the \vec{r} and t dependences in the wavefunction,

$$\Psi(\vec{r}, t) = \psi(\vec{r}) f(t) . \quad (43)$$

To show this, we insert Eq. (43) into the Schrödinger equation and get

$$i\hbar \psi(\vec{r}) \frac{\partial}{\partial t} f(t) = f(t) \hat{H} \psi(\vec{r}) , \quad (44)$$

or

$$i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = \frac{1}{\psi(\vec{r})} \hat{H} \psi(\vec{r}) , \quad (45)$$

Interestingly, the left-hand side of Eq. (45) only depend on time the time variable t , whereas the right-hand side only depends on the space coordinate \vec{r} . It is valid for any t or \vec{r} . The only way for this equation to hold is if both sides are equal to a constant of t and \vec{r} , which is denoted by E . This observation leads to equations,

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} f(t) &= E f(t) , \\ \hat{H} \psi(\vec{r}) &= E \psi(\vec{r}) . \end{aligned} \quad (46)$$

The first equation is easy to solve, which gives

$$f(t) = f(0) e^{-iEt/\hbar} . \quad (47)$$

This allows us to write

$$\Psi_E(\vec{r}, t) = \psi_E(\vec{r}) f(0) e^{-iEt/\hbar} = \Psi_E(\vec{r}, 0) e^{-iEt/\hbar} . \quad (48)$$

Here we added a subscript $_E$ to remember that the solution is related to the constant E introduce above. In this case, $\Psi_E(\vec{r}, t)$ is often called a stationary state. Although evolving with time, its energy always remains in tact.

The second equation of (46) is an eigenvalue equation for the Hamiltonian operator. It is an ordinary different equation. It is also a linear equation, which

in general can be solved to derive the form of the spatial part of the wavefunction $\psi(\vec{r})$. Because the Hamiltonian operator is the sum of kinetic energy and potential energy operators, the physical meaning of E is nothing but the total energy of the electron in state $\Psi_E(\vec{r}, t)$.

Given a specific Hamiltonian \hat{H} , the possible values of energy E is not unique. A given physics system (with certain form of the potential term V) could have different states with different energy eigenvalues. All these information can be found by solving $\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$. See upcoming chapters for explicit examples.

2.7. Superposition of States

If E is an eigenvalue of the Hamiltonian operator \hat{H} , we showed above that

$$\Psi_E(\vec{r}, t) = \psi_E(\vec{r})e^{-iEt/\hbar}, \quad (49)$$

is a solution to the original time-dependent Schrödinger equation. However, this is not yet the general form of wavefunction.

The Hamiltonian could have more than one eigenvalue and eigenstates, E_i and ψ_i , where $i = 1, 2, 3, \dots$. A general wavefunction can be a linear combination (superposition) of these states,

$$\Psi(\vec{r}, t) = \sum_i c_i \psi_i(\vec{r}) e^{-iE_i t/\hbar}, \quad (50)$$

where c_i are complex coefficients. They are properly chosen so that the wavefunction is properly normalized.

As an explicit example, we consider two energy levels E_1 and E_2 , and the wavefunction

$$\Psi(\vec{r}, t) = \cos \theta \psi_1(\vec{r}) e^{-iE_1 t/\hbar} + \sin \theta \psi_2(\vec{r}) e^{-iE_2 t/\hbar}. \quad (51)$$

The corresponding probability density of find electron at position \vec{r} at time t is

$$\begin{aligned} \rho(\vec{r}, t) &= |\Psi(\vec{r}, t)|^2 \\ &= \cos^2 \theta |\psi_1(\vec{r})|^2 + \sin^2 \theta |\psi_2(\vec{r})|^2 + 2\text{Re}(\cos \theta \sin \theta e^{-i(E_1 - E_2)t/\hbar}) \\ &= \cos^2 \theta |\psi_1(\vec{r})|^2 + \sin^2 \theta |\psi_2(\vec{r})|^2 + 2\psi_1(\vec{r})\psi_2(\vec{r}) \cos \theta \sin \theta \cos[(E_1 - E_2)t/\hbar], \end{aligned} \quad (52)$$

where it is assumed that $\psi_{1,2}(\vec{r})$ are real functions for simplicity.

Due to the presence of last term, for $E_1 \neq E_2$, the probability density is an oscillating function of time.

In this classical limit $\hbar \rightarrow 0$, the cosine term above becomes very fast oscillating. Experimentally, we could only measure the time averaged effect of this term,³ which is 0. In this case, quantum effect disappears (or is not manifest).

This implies, if we want to observe the quantum mechanics effect, we must design the experiment with sufficiently small energy difference $E_1 - E_2$ such that we have enough time to make the probability measurement. In the extreme limit $E_1 = E_2$, ρ becomes time independent. One can do the experiment as slowly as he/she wants and still obtain the same result reliably.

The time-dependent probability is a pure quantum mechanical effect and has wide applications in modern physics. A famous example is the neutrino oscillation phenomenon (Nobel Prize Physics 2015).

■ The end.

³Experimental results are always the one averaged over the smallest time interval between which you can check your watch.

Chapter 3. Solving 1D Problems

In this chapter, we solve several 1D Schrödinger equation problem, for different physics setups, i.e., forms of potential V . These exercises will give an idea of what are most relevant quantities in the context of quantum mechanics, and how to derive them using the wavefunctions. We will also discuss the implication of the Heisenberg uncertainty principle using a concrete example. Finally, these 1D problems serve as a warm up for solving the 3D Schrödinger equation that is relevant for the hydrogen atom.

First of all, we present a few simple and useful theorems, which apply not only in 1D but also for higher dimensions.

- If $\psi(x)$ is a stationary state solution to the Schrödinger equation (assuming the potential is real)

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right) \psi(x) = E\psi(x) . \quad (1)$$

then $\psi^*(x)$ is also the solution to the same equation.

- For given energy eigenvalue E , there is always a real wavefunction solution to the Schrödinger equation. Given the first theorem, clearly we can take the linear combinations

$$\varphi(x) = c_1(\psi(x) + \psi^*(x)), \quad \chi(x) = -ic_2(\psi(x) - \psi^*(x)) , \quad (2)$$

where the coefficients $c_{1,2}$ are real numbers chosen to make the wavefunctions properly normalized. Both are real functions and eigenfunctions of \hat{H} with energy E .

- If the potential term is invariant under parity transformation $V(x) = V(-x)$ and $\psi(x)$ is a solution to the with energy E , then so is $\psi(-x)$ with the same energy E . This can be easily verified by defining $x' = -x$ in the above Schrödinger equation. This also implies that we can take the linear combinations

$$f(x) = c_1(\psi(x) + \psi(-x)) , \quad g(x) = c_2(\psi(x) - \psi(-x)) , \quad (3)$$

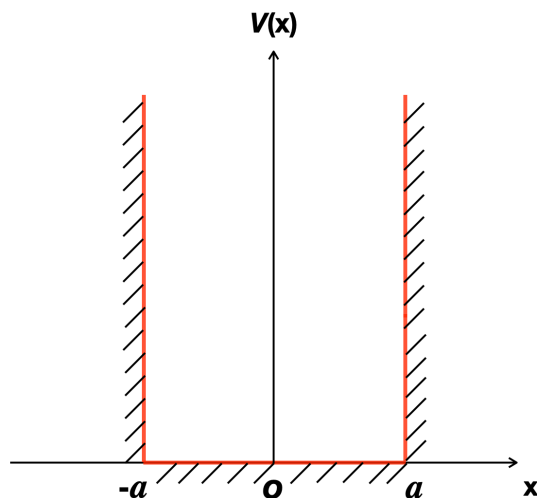
such that $f(-x) = f(x)$, $g(-x) = -g(x)$. They are called parity even and odd wavefunctions, respectively. Again, the coefficients $c_{1,2}$ are chosen to make the wavefunctions properly normalized.

3.1. Infinite Square Well and Bound States

In the first 1D problem, the electron lives in an infinite square well, with a potential of the form

$$V(x) = \begin{cases} +\infty & x < -a \\ 0 & -a \leq x \leq a \\ +\infty & x > a \end{cases} \quad (4)$$

as shown in the following plot.



Outside the potential well, $V = +\infty$. If we are interested in finite energy solution to the Schrödinger equation, Eq. (1), the only possibility is that $\psi(x) = 0$ for $x > a$ or $x < -a$. The wavefunction of the electron is only nonzero within the potential, which is called a bound state. It also implies that at the boundary of the well,

$$\psi(a) = \psi(-a) = 0 . \quad (5)$$

Inside the potential well, the potential vanishes, thus the time-independent Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x) . \quad (6)$$

This is the free electron equation. Generic forms of its solutions are

$$\psi(x) = A \sin(kx) + B \cos(kx) , \quad (7)$$

or

$$\psi(x) = Ae^{ikx} + Be^{-ikx} , \quad (8)$$

for $-a \leq x \leq a$, where

$$k = \sqrt{\frac{2mE}{\hbar^2}} . \quad (9)$$

We can proceed with either Eq. (7) or (8). Here we choose to proceed with Eq. (7), motivated by that the potential considered here is even under parity. The sine and cosine functions remain invariant up to a sign under the parity transformation.

Applying the boundary conditions Eq. (5), we obtain

$$\begin{aligned} A \sin(ka) + B \cos(ka) &= 0, \\ -A \sin(ka) + B \cos(ka) &= 0. \end{aligned} \quad (10)$$

Both condition must hold implies that both $A \sin(ka)$ or $B \cos(ka)$ must be zero. We are not interested in the case where $A = B = 0$ because the corresponding wavefunction is trivially 0. The alternatively choices are

$$\begin{aligned} \text{case 1 : } \quad A &= 0, \quad \cos(ka) = 0, \\ \text{case 2 : } \quad B &= 0, \quad \sin(ka) = 0. \end{aligned} \quad (11)$$

We consider these two cases separately.

In case 1, $\psi(x) = B \cos(kx)$, where k is given by Eq. (9). The requirement $\cos ka = 0$ then implies

$$ka = \sqrt{\frac{2mE}{\hbar^2}} a = \left(n + \frac{1}{2}\right) \pi, \quad (12)$$

where n is any integer.

Interestingly, this implies that the energy eigenvalue E must be discrete (quantized)

$$E_n = \frac{\left(n + \frac{1}{2}\right)^2 \pi^2 \hbar^2}{2ma^2} = \frac{(2n + 1)^2 \pi^2 \hbar^2}{8ma^2}. \quad (13)$$

We are still yet to determine the coefficient B , which is fixed by the normalization condition of the wavefunction,

$$\begin{aligned} 1 &= \int_a^a dx |\psi(x)|^2 = |B|^2 \int_a^a dx \cos^2(kx) = |B|^2 \int_a^a dx \frac{1 + \cos(2kx)}{2} \\ &= \frac{|B|^2}{2} \left(2a + \frac{\sin(2ka) - \sin(-2ka)}{2k}\right) = |B|^2 a. \end{aligned} \quad (14)$$

This implies $|B| = \sqrt{1/a}$ (we drop the arbitrary phase which is not physical). The wavefunction in this case is

$$\psi_n = \sqrt{\frac{1}{a}} \cos\left(\sqrt{\frac{2mE_n}{\hbar^2}} x\right) = \sqrt{\frac{1}{a}} \cos\left(\frac{(n + 1/2)\pi x}{a}\right). \quad (15)$$

The corresponding energy eigenvalue is given by Eq. (13).

In case 2, the wavefunction is $\psi(x) = A \sin(kx)$, and $\sin(ka) = 0$ implies

$$ka = \sqrt{\frac{2mE}{\hbar^2}} a = n\pi, \quad (16)$$

where n is any integer.

Again, this implies energy quantization

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{(2n)^2 \pi^2 \hbar^2}{8ma^2}. \quad (17)$$

The corresponding wavefunction is

$$\psi_n = \sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{a}\right). \quad (18)$$

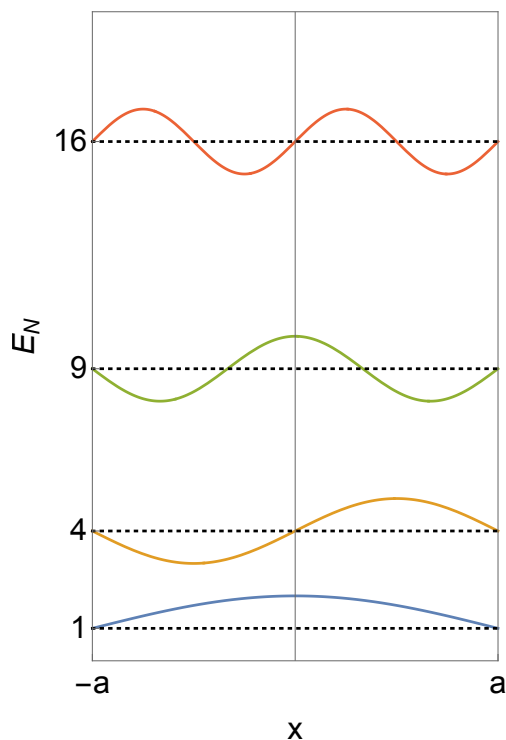
Clearly, in this case, we are not interested in $n = 0$ otherwise the wavefunction is again 0 everywhere.

Summarizing the energy spectrum Eqs. (13) and (17), we can write in general

$$E_N = \frac{N^2 \pi^2 \hbar^2}{8ma^2}, \quad (19)$$

where $N = 1, 2, 3, \dots$. When N is an odd (even) integer, the corresponding wavefunction is parity even (odd).

The following picture illustrates the energy levels and shape of wavefunctions for the infinite square well. E_N is plotted in unit of $\pi^2 \hbar^2 / (8ma^2)$.

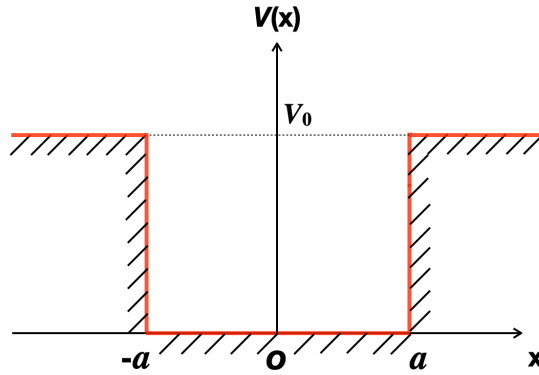


3.2. Finite Square Well

Next, we consider the finite square well problem, with a potential of the form

$$V(x) = \begin{cases} V_0 & x < -a \\ 0 & -a \leq x \leq a \\ V_0 & x > a \end{cases} \quad (20)$$

as shown in the following plot.



We consider the bound state solution of the finite square well, with energy $0 < E < V_0$, and the wavefunction.

We first consider outside the potential well, with $|x| > a$. In this region the Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = -(V_0 - E) \psi(x) . \quad (21)$$

Because V_0 is a constant and $V_0 > E$, the general solution is

$$\psi(x) = Ae^{-\beta x} + Be^{\beta x} , \quad (22)$$

where

$$\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} . \quad (23)$$

Requiring the wavefunction to be finite everywhere including $x \rightarrow \pm\infty$, we obtain

$$\psi(x) = \begin{cases} Ae^{-\beta x} & x < -a \\ Be^{\beta x} & x > a \end{cases} \quad (24)$$

The wavefunction damps to zero at $x \rightarrow \pm\infty$. By definition, a bound state is localized near some finite value of x .

Inside the potential well, the Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x) , \quad (25)$$

which is the same equation as the infinite square well problem for $-a \leq x \leq a$. As we already learned earlier, because the potential is parity invariant, we can choose the wavefunction to be even or odd under parity, with forms

$$\psi(x) = C \sin(kx) \quad \text{or} \quad C \cos(kx) , \quad (26)$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} . \quad (27)$$

We will discuss these two cases separately.

The next step is to match the wavefunction forms at the boundary of potential $x = \pm a$. Here are two important requirements to satisfy

- Wavefunction must be continuous and finite anywhere, so is the corresponding probability distribution.
- The first derivative of the wavefunction is continuous even if the potential has a jump, as long as the jump is not infinitely large. This can be shown by integrating the general Schrödinger equation Eq. (1) between the interval from $x = a - \varepsilon$ to $x = a + \varepsilon$, assuming at $x = a$ the potential has a non-continuity ΔV ,

$$-\frac{\hbar^2}{2m} \left(\psi'(a - \varepsilon) - \psi'(a + \varepsilon) \right) + \varepsilon \left(V(a - \varepsilon) + V(a + \varepsilon) \right) = 2\varepsilon E \psi(a) . \quad (28)$$

Taking the limit $\varepsilon \rightarrow 0$ and use the fact that the energy E , wavefunction, and potential $V(x)$ are all finite, we get

$$\lim_{\varepsilon \rightarrow 0} \left(\psi'(a - \varepsilon) - \psi'(a + \varepsilon) \right) \rightarrow 0 . \quad (29)$$

We apply the above two conditions to the matching in the finite square well problem.

In case 1, we consider $\psi(x) = C \cos(kx)$ for $-a \leq x \leq a$. At $x = a$, the matching conditions are

$$\begin{aligned} Ae^{-\beta a} &= C \cos(ka) , \\ -\beta Ae^{-\beta a} &= -kC \sin(ka) . \end{aligned} \quad (30)$$

The matching conditions at $x = -a$ give the same equations. Dividing both sides of these two equations, we obtain

$$\beta = k \tan(ka) . \quad (31)$$

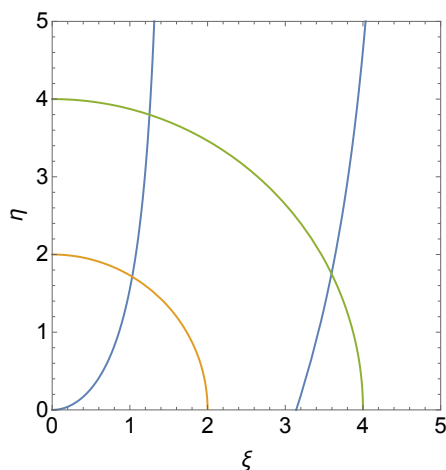
In addition, from the original definitions of k and β , they satisfy

$$\beta^2 + k^2 = \frac{2mV_0}{\hbar^2} . \quad (32)$$

With Eqs. (31) and (32) we can solve for β and k . To make a further simplification, we define $\xi = ka$, $\eta = \beta a$. They satisfy the equations

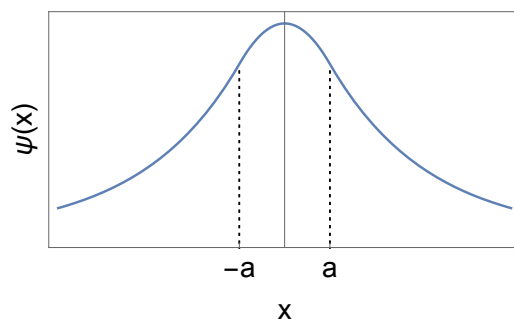
$$\begin{aligned}\xi \tan \xi &= \eta, \\ \xi^2 + \eta^2 &= \frac{2mV_0a^2}{\hbar^2}.\end{aligned}\quad (33)$$

We plot these two equations in the η versus β plane. The blue curves corresponds to $\eta = \xi \tan \xi$, whereas depending on the value of $2mV_0a^2/\hbar^2$, the condition $\xi^2 + \eta^2 = 2mV_0a^2/\hbar^2$ corresponds to the circles with different radii.



The intersections between the two curves indicates the allowed values of η , ξ , or k and β , and in turn the allowed energy eigenvalue E . Clearly, there is always at least one intersection point.

For $\sqrt{2mV_0a^2/\hbar^2} < \pi$, there is only one solution. The corresponding values of ξ, η has to be solved numerically. We discuss some qualitative features here. Following the assumption that $E < V_0$, and the definition of k in Eq. (27), we find $ka < \pi$. This tells that inside the potential well, $-a \leq x \leq a$, the wavefunction $C \cos(ka)$ only covers less than half of the period of cosine function. Thus the wavefunction must take the following form. It is parity even.



It is interesting to examine the $V_0 \rightarrow +\infty$ limit, in which case we recover the infinite square well. In this case, $\eta \rightarrow +\infty$, and the first equation of Eq. (33) reduces to $\xi \tan \xi = +\infty$, which is satisfied if

$$\xi = \left(n + \frac{1}{2}\right) \pi \quad \Rightarrow \quad E_n = \frac{\pi^2 \hbar^2}{2ma^2} \left(n + \frac{1}{2}\right)^2 . \quad (34)$$

This limiting result is consistent with what was found in Eq. (13).

In case 2, the wavefunction is parity odd, and has the form $\psi(x) = C \sin(kx)$ for $-a \leq x \leq a$ and the matching conditions at $x = a$ are

$$\begin{aligned} Ae^{-\beta a} &= C \sin(ka) , \\ -\beta Ae^{-\beta a} &= kC \cos(ka) . \end{aligned} \quad (35)$$

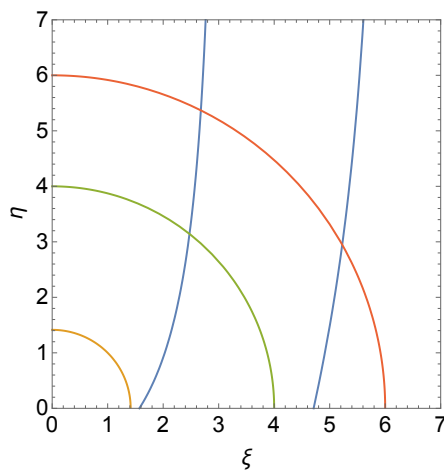
Again, defining $\xi = ka$, $\eta = \beta a$ we obtain

$$\eta = -\xi \cot \xi , \quad (36)$$

along with the circle condition

$$\xi^2 + \eta^2 = \frac{2mV_0a^2}{\hbar^2} . \quad (37)$$

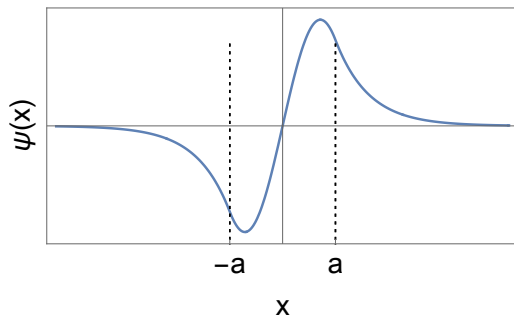
The intersection of curves represented by Eqs. (36) and (37) is shown in the plot below.



Clearly, in this case, the existence of an intersection point is not guaranteed. For example, if the circle is small (like the orange one), there is no intersection, thus no solution to parity odd wavefunction. The condition for parity odd wavefunction to exist is

$$\sqrt{\frac{2mV_0a^2}{\hbar^2}} > \frac{\pi}{2} , \quad \text{or} \quad V_0 \geq \frac{\pi^2 \hbar^2}{8ma^2} . \quad (38)$$

The potential barrier must be high enough for such solutions to exist. The plot below shows an example of the parity odd wavefunction.



Again it is interesting to examine the $V_0 \rightarrow \infty$ ($\eta \rightarrow \infty$) limit. In this case, Eq. (36) implies $\cot \xi = -\infty$, thus

$$\xi = n\pi \quad \Rightarrow \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, \quad (39)$$

which is consistent with the result in Eq. (17).

In summary, the finite square well can accommodate two class of wavefunctions, which are parity even or odd. There is always at least one parity even state, whereas the potential barrier needs to be sufficiently high (see Eq. (38)) in order for the parity odd state to exist. We did not discuss the derivation of coefficients A (or B) and C in the wavefunctions, which is straightforward by requiring $\int_{-\infty}^{+\infty} dx |\psi(x)|^2 = 1$. The integral is will not blow up because $\psi(x)$ approaches to zero exponentially as x approaches to plus or minus infinity.

3.3. 1D Harmonic Oscillator

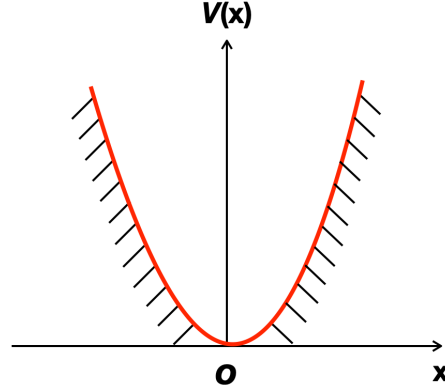
The harmonic oscillator problem is very an important example. Indeed, the study of theoretical physics involves solving the harmonic oscillator problem many times using various methods.

The potential for 1D harmonic oscillator takes the form

$$V(x) = \frac{1}{2} kx^2. \quad (40)$$

Let us first have a telegraphic review of how we solved the harmonic oscillator problem in classical physics. Assuming the electron is a point particle described by is position x and velocity \dot{x} simultaneously, we obtain the force from the potential $F = -dV/dx = -kx$. Using Newton's law, $F = ma$, we get $m\ddot{x} = -kx$. The general solution is $x = A \sin(\omega t + \delta)$, where $\omega = \sqrt{k/m}$, A is the amplitude of

the oscillation, and δ is a phase shift depending on the initial condition. With this solution we can derive the total energy of the harmonic oscillator, which is the sum of kinetic and potential energies, $E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 A^2$. Because A is a free parameter, we can change it continuously, and make it as small as possible in classical physics. We are allowed to set $A = 0$, which simply means the oscillator has no motion, thus $E = 0$.



Next, we will see the above picture changes drastically in quantum mechanics.

The time-independent Schrödinger equation in this case is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + \frac{1}{2} m \omega^2 x^2 \psi(x) = E \psi(x) . \quad (41)$$

A picture of the potential is shown in the picture above. Clearly, at infinity $x \rightarrow \pm\infty$, the potential energy blows up, implying that the wavefunction there must vanish,

$$\psi(x \rightarrow \pm\infty) \rightarrow 0 . \quad (42)$$

Physically, it means that the probability of finding the electron at infinity is zero.

We first simplify this equation by defining $\xi = \sqrt{m\omega/\hbar} x$ and $\lambda = 2E/\hbar\omega$, and divide each term in Eq. (41) by a factor of $-\hbar\omega/2$. Using $\frac{d^2}{d\xi^2} = \frac{\hbar}{m\omega} \frac{d^2}{dx^2}$, we get

$$\frac{d^2}{d\xi^2} \psi + (\lambda - \xi^2) \psi = 0 . \quad (43)$$

There is no obvious solution to this equation. We first examine the asymptotic behavior of this equation. For $\xi \rightarrow \pm\infty$, the above equation is approximately,

$$\frac{d^2}{d\xi^2} \psi - \xi^2 \psi \simeq 0 . \quad (44)$$

The approximately solution to this equation is

$$\psi \simeq C e^{\pm \xi^2/2} . \quad (45)$$

We must keep the minus sign in the exponential for ψ to remain finite.

We then define

$$\psi = e^{-\xi^2/2} u(\xi) , \quad (46)$$

which holds for all ξ , and plug it into general equation Eq. (43) to derive the equation for $u(\xi)$

$$\frac{d^2 u}{d\xi^2} - 2\xi \frac{du}{d\xi} + (\lambda - 1)u = 0 . \quad (47)$$

This is a special equation called the Hermite's equation. It can be solved with the series expansion of $u(\xi)$

$$u(\xi) = \sum_{j=0}^{\infty} c_j \xi^j . \quad (48)$$

This allows us to derive

$$\begin{aligned} \xi \frac{du}{d\xi} &= \sum_{j=0}^{\infty} j c_j \xi^j , \\ \frac{d^2 u}{d\xi^2} &= \sum_{j=0}^{\infty} j(j-1) c_j \xi^{j-2} = \sum_{j=2}^{\infty} j(j-1) c_j \xi^{j-2} = \sum_{j'=0}^{\infty} (j'+1)(j'+2) c_{j'} \xi^{j'} , \end{aligned} \quad (49)$$

where in the last step, we introduced $j' = j - 2$. Plugging these expansions in Eq. (47), we derive the recursion relation

$$c_{j+2} = \frac{2j - \lambda + 1}{(j+1)(j+2)} c_j . \quad (50)$$

For general values of λ , $u(\xi)$ is still an infinite series.

To make progress, we consider again the $|\xi| \rightarrow \infty$ behavior of the function $u(\xi)$. As an infinite series, it typically blows up at $|\xi| \rightarrow \infty$. This can be understood with the following argument. At large ξ , the sum is dominated by high power terms with $j \gg 1$. For very large j , the recursion relation becomes approximately

$$c_{j+2} \simeq \frac{1}{(j/2)} c_j . \quad (51)$$

This behavior implies that at very large ξ ,

$$u(\xi) \sim \sum_j \frac{1}{(j/2)!} \xi^j = \sum_{j'} \frac{1}{j'!} \xi^{2j'} = e^{\xi^2} . \quad (52)$$

This is an approximation because it works well for $j \gg 1$ but is not exact for $j \sim \mathcal{O}(1)$. But it is a sufficiently good approximation because the sum, if infinite, is dominated by the large j terms.

Plugging Eq. (52) back in Eq. (47), we find that $\psi \simeq e^{\xi^2/2}$ will blow up at $\xi \rightarrow \infty$ (or $x \rightarrow \infty$). This is clearly not the desired behavior for a wavefunction. The only way out is to make $u(\xi)$ a polynomial. In other words, the sum over j in Eq. (48) does not go to $j \rightarrow \infty$ but is truncated at a term with finite powers of ξ .

Observing the recursion relation Eq. (50), we find this is possible for special choices of λ values

$$\lambda = 2n + 1, \quad (n = 0, 1, 2, \dots). \quad (53)$$

Remember that λ is related to the energy eigenvalue E , the above condition implies that the energy spectrum of 1D harmonic oscillator is also quantized,

$$E_n = \frac{\hbar\omega}{2}\lambda = \hbar\omega \left(n + \frac{1}{2} \right). \quad (54)$$

The corresponding finite series $u(\xi)$ with the sum over j from 0 up to n is the Hermite polynomial. It has the general form

$$\begin{aligned} H_n(\xi) = & (2\xi)^n - n(n-1)(2\xi)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!}(2\xi)^{n-4} \\ & + \dots + (-1)^{[n/2]} \frac{n!}{[n/2]!} (2\xi)^{n-2[n/2]}. \end{aligned} \quad (55)$$

where $[n/2] = n/2$ for n as an even integer, and $[n/2] = (n-1)/2$ for n as an odd integer. The Hermite polynomial satisfies the normalization condition

$$\int_{-\infty}^{+\infty} d\xi e^{-\xi^2} H_m(\xi) H_n(\xi) = \sqrt{\pi} 2^n n! \delta_{mn}. \quad (56)$$

With the Hermite polynomial, we can derive the properly normalized wavefunction for 1D harmonic oscillator

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n \left(\sqrt{m\omega/\hbar} x \right) e^{-\frac{m\omega}{2\hbar} x^2}. \quad (57)$$

For the ground state $n = 0$, we have the energy eigenvalue

$$E_0 = \frac{1}{2} \hbar\omega, \quad (58)$$

and the wavefunction

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2}. \quad (59)$$

This result is in sharp contrast to classical physics expectation. We find a non-zero lowest energy for 1D harmonic oscillator. Quantum mechanics forbids the continuous reduction of the oscillation amplitude to as small as we want.

3.4. The Role of Heisenberg Uncertainty Principle

The Heisenberg uncertainty principle ($\Delta x \Delta p \geq \hbar/2$) plays an important role in understanding the above result for 1D harmonic oscillator. Early on, we have introduced Δx and Δp as the uncertainties in the position and momentum measurements. Here we give a strict definition of them.

$$\begin{aligned}(\Delta x)^2 &= \langle (\hat{x} - \langle \hat{x} \rangle)^2 \rangle , \\ (\Delta p)^2 &= \langle (\hat{p} - \langle \hat{p} \rangle)^2 \rangle ,\end{aligned}\tag{60}$$

where $\langle \hat{O} \rangle$ means taking average of an operator \hat{O} under certain state.

Let us consider the ground state of 1D harmonic oscillator. The wavefunction is given by Eq. (59). It is an even function of x . Clearly, $\langle x \rangle = 0$. It is also easy to verify that $\langle \hat{p} \rangle = 0$. Therefore,

$$\begin{aligned}\Delta x &= \sqrt{\langle \hat{x}^2 \rangle} = \sqrt{\int_{-\infty}^{+\infty} dx x^2 \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{m\omega}{\hbar}x^2}} = \frac{\hbar}{2m\omega} , \\ \Delta p &= \sqrt{\langle \hat{p}^2 \rangle} = \sqrt{\int_{-\infty}^{+\infty} dx \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{m\omega}{2\hbar}x^2} \left(-i\hbar\frac{d}{dx}\right)^2 e^{-\frac{m\omega}{2\hbar}x^2}} = \frac{m\hbar\omega}{2} ,\end{aligned}\tag{61}$$

This leads to

$$\Delta x \Delta p = \hbar/2 ,\tag{62}$$

which marginally satisfies the uncertainty principle.

Physically, we can understand this result as the following. If we reduce the amplitude of oscillation, controlled by Δx , to sufficiently small values, the uncertainty principle implies that the uncertainty in Δp is large. In other words, the kinetic energy is large. It is impossible to make both the potential energy and kinetic energy as small as we want. Effectively, this interplay leads to a lower bound on the energy, $E_0 > 0$.

3.5. Plane Wave and Normalization

Here we consider the very simple case of free Schrödinger equation, with $V = 0$ for all x ,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x) .\tag{63}$$

As discussed in chapter 3.1, we can adopt either Eq. (7) or (8) as the solution to this equation. Here we consider the exponential form,

$$\psi(x) = C e^{\pm ipx/\hbar} , \quad p = \sqrt{2mE} .\tag{64}$$

Combining this with the time-dependent factor, the full wavefunction takes the form

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} = Ce^{i(\pm px - Et)/\hbar} . \quad (65)$$

For \pm sign, this could be interpreted as a plane wave propagating to the $\pm\hat{x}$ direction.

In contrast, if we choose the sine and cosine forms for the stationary state, they correspond to standing wave solutions.

In the absence of a potential energy at $x \rightarrow \pm\infty$, it is more meaningful to consider the propagating wave solutions because there is no boundary for holding any standing wave.

Let us proceed to consider the plane wave moving in the $+\hat{x}$ direction

$$\psi(x) = Ce^{ipx/\hbar} . \quad (66)$$

We are interested in finding its coefficient C . If we use the normalization condition as before,

$$\int_{-\infty}^{+\infty} dx |\psi(x)|^2 = 1 , \quad (67)$$

we find that the integral on the left-hand side is actually infinite in this case,

$$\int_{-\infty}^{+\infty} dx |C|^2 = +\infty \times |C|^2 , \quad (68)$$

which would require $C = 0$. It seems we are running into trouble here.

The consistent solution is to regularize the integral by considering the integration over a 1D box $-L/2 \leq x \leq L/2$, and let $L \rightarrow +\infty$ later. In this case, we have

$$\int_{-L/2}^{L/2} dx |\psi(x)|^2 = 1 \quad \Rightarrow \quad |C| = \sqrt{\frac{1}{L}} . \quad (69)$$

Therefore, the plane wavefunction is

$$\psi(x, t) = \sqrt{\frac{1}{L}} e^{ipx/\hbar} . \quad (70)$$

Of course, if we set $L \rightarrow +\infty$ this wavefunction still vanishes. However, in quantum mechanics, we are interested in physical quantities that are measurable. We do not directly measure the wavefunction. Instead, we could measure the average of operators under a given wavefunction. These quantities are still well defined.

For example, if we evaluate the average of momentum operator under the state Eq. (70), we get

$$\begin{aligned}\langle \hat{p} \rangle &= \int_{-L/2}^{L/2} dx \psi^*(x) \hat{p} \psi(x) = \frac{1}{L} \int_{-L/2}^{L/2} dx e^{-ipx/\hbar} \left(-i\hbar \frac{d}{dx} \right) e^{ipx/\hbar} \\ &= \frac{p}{L} \int_{-L/2}^{L/2} dx = p ,\end{aligned}\tag{71}$$

which is a finite result. We can always set $L \rightarrow +\infty$ after this averaging, which does not affect the final result at all.

Alternatively, sometimes in the literature people consider another way of normalizing the wavefunction

$$\psi_p(x, t) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} .\tag{72}$$

In this case, the wavefunction satisfies the orthogonality and normalization condition

$$\int_{-\infty}^{+\infty} dx \psi_p^*(x) \psi_{p'}(x) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dx e^{i(p'-p)x/\hbar} = \delta(p - p') .\tag{73}$$

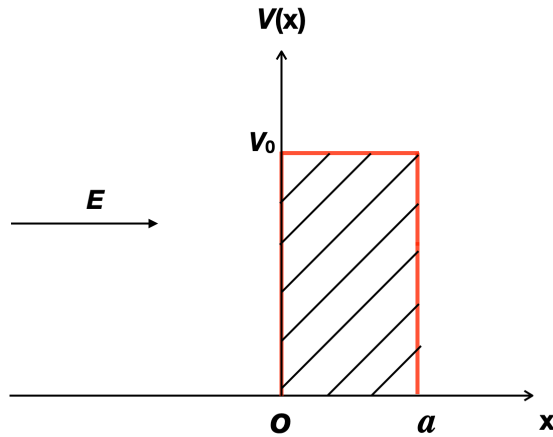
If one chooses to use such a wavefunction for the plane wave, we must redefine the operator averaging as

$$\langle \hat{O} \rangle = \frac{\int_{-\infty}^{+\infty} dx \psi_p^*(x) \hat{O} \psi_p(x)}{\int_{-\infty}^{+\infty} dx \psi_p^*(x) \psi_p(x)} .\tag{74}$$

In this case, both the numerator and denominator will be infinite when $L \rightarrow +\infty$, but the ratio will hold finite.

To summarize, one is allowed to use either Eq. (70), or (72), or any other normalization choices, for the plane wavefunction, as long as we calculate the physical observables in a correspondingly consistent way. Their difference is only a matter of convention.

3.6. Penetration of Finite Barrier



Here we discuss the barrier penetration problem. Imagine that we make an experiment by accelerating an electron to a fixed energy $E > 0$ and let it travel in the $+\hat{x}$ direction. It encounters a potential barrier which lies at $0 \leq x \leq a$. As a result, part of the electron is reflected back (travel in the $-\hat{x}$ direction) and part of the electron could continue to travel in the $+\hat{x}$ direction behind the barrier. This is a 1D scattering problem. A picture of the potential barrier is shown above. We assume the height of barrier $V_0 > E$.

In the $x < 0$ and $x > a$ regions, the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x) . \tag{75}$$

Because this is a scattering problem, there is no standing wave. We choose the exponential form for its solutions,

$$\psi(x) = \begin{cases} Ce^{ikx} + De^{-ikx} & x < 0 \\ Ee^{ikx} & x > a \end{cases} \tag{76}$$

where $k = \sqrt{2mE/\hbar^2}$. Physically, in the $x < 0$ region, there are both the incoming plane wave traveling in the $+\hat{x}$ direction and the reflected plane wave in the $-\hat{x}$ direction. The wavefunction is a superposition of the two. In contrast, in the $x > a$ region, there is only the forward going wave in the $+\hat{x}$ direction. Nothing is coming from $+\infty$.

Recall the probability current introduced in chapter 2.3. In the 1D case, it takes the form

$$\vec{j} = \frac{\hbar}{2mi} \left(\psi^*(x) \frac{d}{dx} \psi(x) - \psi(x) \frac{d}{dx} \psi^*(x) \right) . \tag{77}$$

With the above components of the wave, Ce^{ikx} , De^{-ikx} , Ee^{ikx} , we find

$$\begin{aligned} \text{Incoming flux : } j_0 &= \frac{\hbar k}{m} |C|^2, \\ \text{Reflected flux : } j_R &= \frac{\hbar k}{m} |D|^2, \\ \text{Transmitted flux : } j_T &= \frac{\hbar k}{m} |E|^2. \end{aligned} \quad (78)$$

We define the reflection and transmission coefficients, which are physical observables,

$$R = \frac{j_R}{j_0} = \frac{|D|^2}{|C|^2}, \quad T = \frac{j_T}{j_0} = \frac{|E|^2}{|C|^2}. \quad (79)$$

Conservation of probability requires

$$T + R = 1. \quad (80)$$

Because R and T only depend on the ratio of coefficients in the wavefunction, we are free to set $C = 1$, such that $R = |D|^2$, $T = |E|^2$.

In the region $0 \leq x \leq a$, the potential is nonzero and larger than the energy, thus the Schrödinger equation takes the form

$$\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = (V_0 - E) \psi(x), \quad (81)$$

whose solution is

$$\psi(x) = Ae^{\beta x} + Be^{-\beta x}, \quad (82)$$

where $\beta = \sqrt{2m(V_0 - E)}/\hbar$.

Next, we match the wavefunctions in different regions at the boundaries $x = 0, a$. Because the jump in the potential value is finite, both the wavefunction and its first derivative must be continuous. This has been discussed in chapter 3.2.

The matching condition at $x = 0$ is

$$\begin{aligned} 1 + D &= A + B, \\ ik(1 - D) &= \beta(A - B). \end{aligned} \quad (83)$$

We can solve A, B in terms of D ,

$$\begin{aligned} A &= \frac{1}{2} \left(\left(1 + \frac{ik}{\beta} \right) + D \left(1 - \frac{ik}{\beta} \right) \right), \\ B &= \frac{1}{2} \left(\left(1 - \frac{ik}{\beta} \right) + D \left(1 + \frac{ik}{\beta} \right) \right). \end{aligned} \quad (84)$$

The matching condition at $x = a$ is

$$\begin{aligned} Ee^{ika} &= Ae^{\beta a} + Be^{-\beta a} , \\ ikEe^{ika} &= \beta(Ae^{\beta a} - Be^{-\beta a}) . \end{aligned} \quad (85)$$

We can solve A, B in terms of E ,

$$\begin{aligned} A &= \frac{E}{2} \left(1 + \frac{ik}{\beta} \right) e^{ika-\beta a} , \\ B &= \frac{E}{2} \left(1 - \frac{ik}{\beta} \right) e^{ika+\beta a} . \end{aligned} \quad (86)$$

Eqs. (84) and (86) together leads to coupled equations for D and E

$$\begin{aligned} \left(1 + \frac{ik}{\beta} \right) + D \left(1 - \frac{ik}{\beta} \right) &= E \left(1 + \frac{ik}{\beta} \right) e^{ika-\beta a} , \\ \left(1 - \frac{ik}{\beta} \right) + D \left(1 + \frac{ik}{\beta} \right) &= E \left(1 - \frac{ik}{\beta} \right) e^{ika+\beta a} . \end{aligned} \quad (87)$$

They allow us to find the transmission coefficient (also called tunneling rate)

$$\begin{aligned} T &= \left| \frac{2i\beta k e^{-ika}}{(k^2 - \beta^2) \sinh(\beta a) + 2i\beta k \cosh(\beta a)} \right|^2 \\ &= \frac{4\beta^2 k^2}{(k^2 - \beta^2)^2 \sinh^2(\beta a) + 4\beta^2 k^2 \cosh^2(\beta a)} \\ &= \left(1 + \frac{(k^2 + \beta^2)^2}{4\beta^2 k^2} \sinh^2(\beta a) \right)^{-1} . \end{aligned} \quad (88)$$

Plugging the definitions for β and k in terms of the input parameters, we get

$$T = \frac{1}{1 + \frac{1}{4\frac{E}{V_0} \left(1 - \frac{E}{V_0} \right)} \sinh^2 \left(\frac{\sqrt{2m(V_0 - E)}a}{\hbar} \right)} . \quad (89)$$

Interestingly, we find that even if $V_0 > E$, there is still a non-zero transmission coefficient. Physically, it implies the incoming electron is able to tunnel through the potential barrier. This is a pure quantum mechanical effect, which is strictly forbidden in classical physics.

It is also useful to check the classical limit $\hbar \rightarrow 0$. In this case, the argument of the sinh function in the denominator becomes infinity. As a result, $T \rightarrow 0$. Correspondingly, the reflection coefficient $R \rightarrow 1$ in this case. All the incoming electron get reflected.

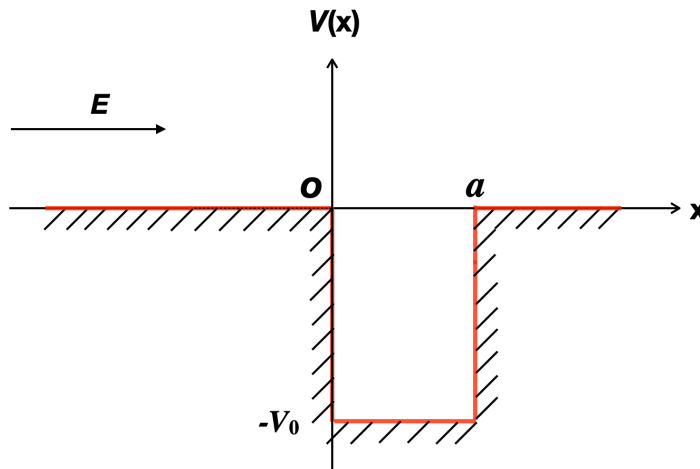
We could also consider the very high barrier limit $V_0 \gg E$, and $mV_0a^2 \gg 1$. In this case, we find

$$T \simeq \frac{16E}{V_0} \exp\left(-\frac{\sqrt{8mV_0a^2}}{\hbar}\right). \quad (90)$$

The tunneling rate is exponentially suppressed.

3.7. Scattering with Potential Well

We continue to explore the scattering problem, similar to the setup of chapter 3.6. But this time we consider a potential well instead of barrier.



In this case, the wavefunction in the three regions can be written as

$$\psi(x) = \begin{cases} e^{ikx} + De^{-ikx} & x < 0 \\ Ae^{ik'x} + Be^{-ik'x} & 0 \leq x \leq a \\ Ee^{ikx} & x > a \end{cases} \quad (91)$$

where $k = \sqrt{2mE/\hbar^2}$ and $k' = \sqrt{2m(V_0 + E)/\hbar^2}$.

We could repeat the derivation as chapter 3.6 but with the replacement $\beta \rightarrow ik'$ everywhere. Applying this replacement in the tunneling rate result, Eq. (88), and use $\sinh(iz) = i \sin z$, we obtain

$$T = \frac{1}{1 + \frac{(k^2 - k'^2)^2}{4k^2 k'^2} \sin^2(k'a)} = \frac{1}{1 + \frac{\sin^2(\sqrt{2m(V_0 + E)a^2/\hbar^2})}{4\frac{E}{V_0}(1 + \frac{E}{V_0})}}. \quad (92)$$

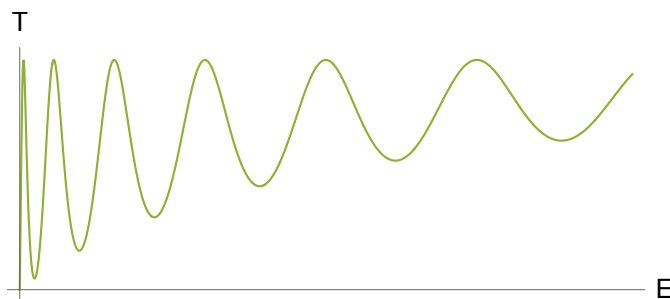
It is interesting to notice that the sine function is zero when

$$\sqrt{\frac{2m(V_0 + E)a^2}{\hbar^2}} = n\pi, \quad \Rightarrow \quad E = E_n = -V_0 + \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad (93)$$

where n is an integer. Because we assumed $E > 0$, it requires $n > \sqrt{2mV_0a^2/(\pi^2\hbar^2)}$. In this case, the tunneling rate $T = 1$. The electron wave fully tunnels through the potential well.

This is called resonant tunneling effect. It occurs when the incoming electron energy is chosen to satisfy Eq. (93).

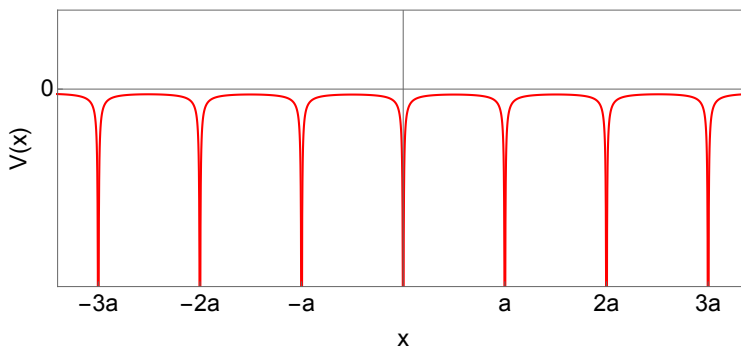
More generally, the energy dependence of the tunneling rate is shown in the plot below.



3.8. 1D Lattice Potential

As the last example discussed in this chapter, we consider the 1D lattice problem. Its results are very useful for condensed matter physics for studying conductors and insulators.

The 1D crystal lattice is an array of atoms, with the position of nuclei (carrying positive electric charge) placed along the array, equally spaced. The source a periodic attractive Coulomb potential for the electrons, as shown in the following picture.

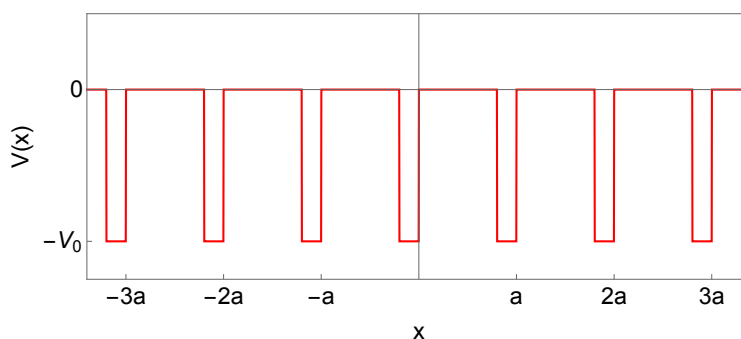


We are interested in the energy of electrons given the above potential. In crystals, there can be two types of electrons. The valence electrons have energy $E < 0$. They are tightly bounded to one of the nuclei and their wavefunctions are highly localized within the Coulomb potential dip around that nucleus. The free

electrons have energy $E > 0$. Their wavefunctions have a much broader spread across many nuclei. The latter is relevant for conducting the electric current.

We are interested in the wavefunction and allowed energy eigenvalues for the free electrons ($E > 0$).

The Schrödinger equation with the above periodic Coulomb potential is rather complicated to solve. Let us make approximations that retain the qualitative features and allow us to proceed deriving the result analytically. Consider the following alternative potential as an approximation.



This is called the Kronig-Penney potential. It is still periodic, but using finite squared wells to replace the Coulomb potentials. The depth of each well is V_0 . The width of each well is b ($0 < b < a$).

Because the potential of the Schrödinger equation is periodic, $V(x) = V(x+a)$, if $\psi(x)$ is a solution to this Schrödinger equation, it is simple to show that $\psi(x+a)$ is also the solution with the same energy eigenvalue.

Based on this, we present an important theorem called the Bloch's theorem. It states that $\psi(x)$ and $\psi(x+a)$ are related to each other by

$$\psi(x+a) = e^{iRa}\psi(x) . \tag{94}$$

where R is a real free parameter.

Given Bloch's theorem, it is sufficient for us to consider the wavefunction in three regions, $-b < x < 0$, $0 < x < a - b$ and $a - b < x < a$.

In the region $0 < x < a - b$, the potential vanished, the wavefunction is that for a free electron

$$\psi(x) = Ae^{ikx} + Be^{-ikx} , \tag{95}$$

where $k = \sqrt{2mE/\hbar^2}$.

In the region $-b < x < 0$, the potential $V = -V_0$ is a constant, the wavefunction takes the form

$$\psi(x) = Ce^{i\beta x} + De^{-i\beta x} , \tag{96}$$

where $\beta = \sqrt{2m(V_0 + E)/\hbar^2}$.

The matching conditions at $x = 0$ lead to (both ψ and ψ' are continuous)

$$\begin{aligned} C &= \frac{1}{2} \left(\left(1 + \frac{k}{\beta}\right) A + \left(1 - \frac{k}{\beta}\right) B \right) , \\ D &= \frac{1}{2} \left(\left(1 - \frac{k}{\beta}\right) A + \left(1 + \frac{k}{\beta}\right) B \right) . \end{aligned} \quad (97)$$

In the region $a - b < x < a$, we use the Bloch's theorem. The wavefunction is related to the one in the region $-b < x < 0$,

$$\psi(x) = e^{iRa} \left(C e^{i\beta(x-a)} + D e^{-i\beta(x-a)} \right) . \quad (98)$$

Next, consider the matching condition at $x = a - b$, which are

$$\begin{aligned} A e^{ik(a-b)} + B e^{-ik(a-b)} &= e^{iRa} \left(C e^{-i\beta b} + D e^{i\beta b} \right) , \\ k A e^{ik(a-b)} - k B e^{-ik(a-b)} &= e^{iRa} \left(-\beta C e^{i\beta b} - \beta D e^{i\beta b} \right) . \end{aligned} \quad (99)$$

Because we already solved C, D in terms of A, B in Eq. (97). Plugging Eq. (97) into (99), we obtain a coupled linear equation for A and B , of the form

$$\begin{cases} M_{11}A + M_{12}B = 0 \\ M_{21}A + M_{22}B = 0 \end{cases} \quad (100)$$

where M_{ij} are made of parameters in the model. In order for these homogeneous linear equations to have a solution, the determinant of the coefficient matrix must vanish,

$$\det \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = 0 . \quad (101)$$

After a straightforward (but a bit tedious) simplification, we can get

$$\cos(k(a-b)) \cos(\beta b) + \frac{k^2 + \beta^2}{2k\beta} \sin(k(a-b)) \sin(\beta b) = \cos(Ra) . \quad (102)$$

We still do not know what R is, but we know that $|\cos(Ra)| \leq 1$. This constrains the combination of parameters on the left-hand side.

As a further approximation, we consider the narrow and deep potential well limit, $b \rightarrow 0$, $V_0 \rightarrow +\infty$ but hold the product bV_0 finite and nonzero.

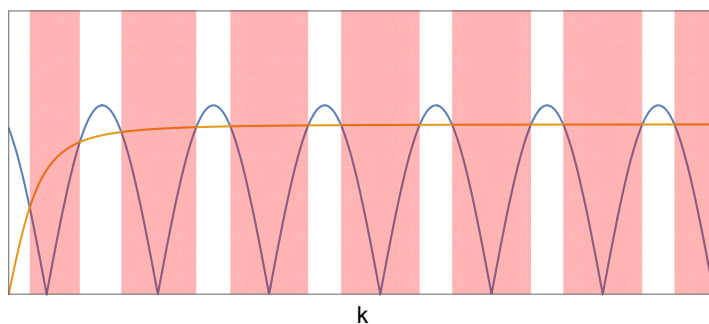
In this case, we have $kb \rightarrow 0$ and $\beta b \rightarrow 0$, and the condition for the left-hand side of Eq. (102) to be less or equal than 1 becomes

$$\left| \cos(ka) + \frac{\beta^2 b}{2k} \sin(ka) \right| \leq 1 . \quad (103)$$

Plugging in the approximate relation $\beta \simeq \sqrt{2mV_0/\hbar^2}$, we get

$$\left| \cos \left(ka + \arctan \left(\frac{mbV_0}{k\hbar^2} \right) \right) \right| \leq \frac{1}{\sqrt{1 + \left(\frac{mbV_0}{k\hbar^2} \right)^2}} . \quad (104)$$

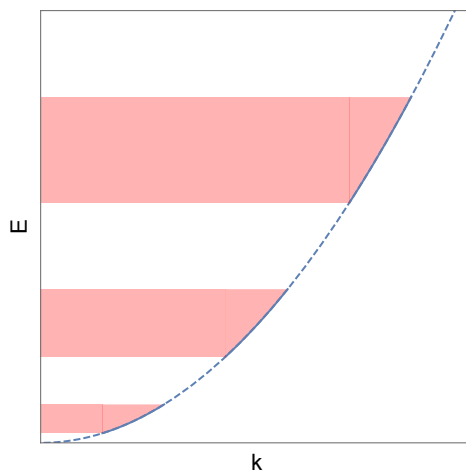
Consider each side of Eq. (104) as a function of k , we plot them below. The allowed value of k corresponds to the regions where the blue curves lies below the orange curve. We highlight them using the red shaded regions.



Because k is related to the energy eigenstate

$$E = \frac{k^2\hbar^2}{2m} . \quad (105)$$

The above allowed regions for k implies the allowed energy values of free electron in crystals form energy bands, as shown in the picture below.



For $0 < \arctan (mbV_0/(k\hbar^2)) < \pi/2$, there exists an energy gap from $E = 0$ to the first allowed energy band. This energy gap is very important for determining whether a material is a metal or insulator.

In order to conduct electric current, a fraction of electrons inside the crystal must be free electrons with positive energy $E > 0$. This could be achieved if electron absorbs energy from thermal effects. If the energy gap is too large for electron to become free, the crystal is an insulator. In the opposite case, it is a conductor. All insulators become conductors at sufficiently high temperatures.

■ The end.

Chapter 4. Formalism

In the last chapter, we have done quite a few examples in 1D. In this chapter, we will discuss formalisms, on the structure of solutions to the Schrödinger equation. For simplicity, most of the discussions will be based on 1D. It is straightforward to generalize then to the 3D case. With these tools, we will get better prepared for exploring the 3D case that is relevant for the real world (solving the hydrogen atom).

4.1. Linear Operators

The Schrödinger equation is a linear equation for the wavefunction, which means if Ψ_1 and Ψ_2 are both solutions to the same Schrödinger equation, so is their sum. To write down the Schrödinger equation, we have introduced a bunch of operators so far, including \hat{x} , \hat{p} , \hat{H} , etc. They are linear operators. When linear operators act on wavefunctions, they satisfy the following properties

$$\begin{aligned}\hat{O}(c_1\Psi_1 + c_2\Psi_2) &= c_1\hat{O}\Psi_1 + c_2\hat{O}\Psi_2, \\ (\hat{O}_1 + \hat{O}_2)\Psi &= \hat{O}_1\Psi + \hat{O}_2\Psi, \\ (\hat{O}_1 + \hat{O}_2)\Psi &= (\hat{O}_2 + \hat{O}_1)\Psi, \\ (\hat{O}_1 + (\hat{O}_2 + \hat{O}_3))\Psi &= ((\hat{O}_1 + \hat{O}_2) + \hat{O}_3)\Psi,\end{aligned}\tag{1}$$

where $c_{1,2}$ are complex numbers.

An operator acts on “everything” on its right-hand side.

When an operator on a state Ψ , it ends up as a new state $\Psi' = \hat{O}\Psi$ (here \prime does not mean derivative).

We introduce the unit operator \hat{I} , such that $\hat{I}\Psi = \Psi$ for any Ψ . This way, the multiplication of any complex number c with a wavefunction Ψ can be understood as an operator proportional to the unit operator, $c\hat{I}$, acting on Ψ . In the coordinate space, where wavefunction is a function of coordinate x , the position operator $\hat{x} = x\hat{I}$.

Two operators are identical to each other if $\hat{O}_1\Psi = \hat{O}_2\Psi$ for any Ψ . In this case, we can drop the wavefunction and simply write $\hat{O}_1 = \hat{O}_2$.

The product of two operators acting on a wavefunction is defined as $(\hat{O}_1\hat{O}_2)\Psi = \hat{O}_1(\hat{O}_2\Psi)$, where the two operators act on Ψ one by one, following the same order as they are written.

In general, the product of two operators cannot trivially interchange order,

$\hat{O}_1\hat{O}_2 \neq \hat{O}_2\hat{O}_1$. As a result, we can introduce the commutator of two operators,

$$[\hat{O}_1, \hat{O}_2] = \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1 . \quad (2)$$

For example, in 1D case,

$$\begin{aligned} [\hat{x}, \hat{p}]\Psi(x) &= \hat{x}\hat{p}\Psi(x) - \hat{p}\hat{x}\Psi(x) = x(-i\hbar)\frac{d}{dx}\Psi(x) - (-i\hbar)\frac{d}{dx}(x\Psi(x)) \\ &= (-i\hbar)[x\Psi'(x) - (\Psi(x) + x\Psi'(x))] = i\hbar\Psi(x) . \end{aligned} \quad (3)$$

This holds for any wavefunction Ψ . From the definition of identical operators above, we conclude, $[\hat{x}, \hat{p}] = i\hbar\hat{I} = i\hbar$.

To become familiar with the use of operators, it is useful to work out the following exercises

$$\begin{aligned} [\hat{x}, \hat{p}^2] &= 2i\hbar\hat{p} , \\ [\hat{x}, \hat{p}^n] &= ni\hbar\hat{p}^{n-1} , \\ [\hat{x}^m, \hat{p}] &= mi\hbar\hat{x}^{m-1} . \end{aligned} \quad (4)$$

In general, the commutator of operators satisfy the following properties

$$\begin{aligned} [\hat{O}_1, \hat{O}_2] &= -[\hat{O}_2, \hat{O}_1] , \\ [\hat{O}_1, \hat{O}_1] &= 0 , \\ [\hat{O}_1, c\hat{I}] &= 0 , \\ [\hat{O}_1, \hat{O}_2 + \hat{O}_3] &= [\hat{O}_1, \hat{O}_2] + [\hat{O}_1, \hat{O}_3] , \\ [\hat{O}_1, \hat{O}_2\hat{O}_3] &= \hat{O}_2[\hat{O}_1, \hat{O}_3] + [\hat{O}_1, \hat{O}_2]\hat{O}_3 , \\ [\hat{O}_1\hat{O}_2, \hat{O}_3] &= \hat{O}_1[\hat{O}_2, \hat{O}_3] + [\hat{O}_1, \hat{O}_3]\hat{O}_2 , \\ [\hat{O}_1, [\hat{O}_2, \hat{O}_3]] &+ [\hat{O}_2, [\hat{O}_3, \hat{O}_1]] + [\hat{O}_3, [\hat{O}_1, \hat{O}_2]] = 0 . \end{aligned} \quad (5)$$

We can also define a function of linear operator, which is understood in terms of Taylor expansion,

$$f(\hat{O}) = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} \hat{O}^n . \quad (6)$$

As an example, consider a function $f(x) = e^{ax}$ and $\hat{O} = d/dx$, then

$$\begin{aligned} f(\hat{O}) &= e^{a\frac{d}{dx}} = \sum_{n=0}^{\infty} \frac{a^n}{n!} \frac{d^n}{dx^n} , \\ e^{a\frac{d}{dx}}\Psi(x) &= \sum_{n=0}^{\infty} \frac{a^n}{n!} \frac{d^n\Psi(x)}{dx^n} = \Psi(x+a) . \end{aligned} \quad (7)$$

This means $e^{a\frac{d}{dx}}$ is a shift operator.

4.2. 1D Harmonic Oscillator: Algebraic Method

Here we discuss a concrete example to illustrate how useful the concept of linear operator could be. We consider the same 1D Harmonic oscillator problem as discussed in Chapter 3.3. The time-independent Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2x^2\right)\psi(x) = E\psi(x). \quad (8)$$

We have already seen the straightforward way of solving this differential equation, where for $\psi(x \rightarrow \pm\infty)$ to vanish requires the energy E to take discrete values. Here, we discuss another approach.

Note $\hat{p} = -i\hbar\frac{d}{dx}$, the Hamiltonian can be written as $\hat{H} = \frac{1}{2m}(\hat{p}^2 + m^2\omega^2x^2)$.

Let us define two operators

$$\hat{a}_{\pm} = \frac{1}{\sqrt{2m\omega\hbar}}(\mp i\hat{p} + m\omega x). \quad (9)$$

It is interesting to find they satisfy the commutation relation (using $[x, \hat{p}] = i\hbar$)

$$[\hat{a}_-, \hat{a}_+] = 1. \quad (10)$$

More interestingly,

$$\begin{aligned} \hat{a}_-\hat{a}_+ &= \frac{1}{2m\omega\hbar}(i\hat{p} + m\omega x)(-i\hat{p} + m\omega x) \\ &= \frac{1}{2m\omega\hbar}(\hat{p}^2 + m^2\omega^2x^2 - im\omega[x, \hat{p}]) \\ &= \frac{1}{2m\omega\hbar}(\hat{p}^2 + m^2\omega^2x^2 + m\omega\hbar) \\ &= \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}. \end{aligned} \quad (11)$$

In other words,

$$\hat{H} = \hbar\omega\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\right). \quad (12)$$

Similarly, we can also show that

$$\hat{H} = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right). \quad (13)$$

Even more interestingly,

$$\begin{aligned} [\hat{a}_+, \hat{H}] &= \hbar\omega\left[\hat{a}_+, \hat{a}_+\hat{a}_- + \frac{1}{2}\right] = \hbar\omega\hat{a}_+[\hat{a}_+, \hat{a}_-] = -\hbar\omega\hat{a}_+, \\ [\hat{a}_-, \hat{H}] &= \hbar\omega\hat{a}_-. \end{aligned} \quad (14)$$

So far, we have found a bunch of interesting relationships among the operators. They are purely algebraic manipulations. There is no physics yet.

Next, we discuss their physics implications. Suppose there is a wavefunction ψ_n is a solution of the time-independent Schrödinger equation with energy E_n , i.e., $\hat{H}\psi_n = E_n\psi_n$.

Consider another state of the form $\hat{a}_+\psi_n$. We ask the question whether it is an energy eigenstate of \hat{H} . To see this, we act \hat{H} on this state,

$$\begin{aligned}\hat{H}\hat{a}_+\psi_n &= \left(\hat{a}_+\hat{H} - [\hat{a}_+, \hat{H}]\right)\psi_n = \left(\hat{a}_+\hat{H} + \hbar\omega\hat{a}_+\right)\psi_n \\ &= E_n\hat{a}_+\psi_n + \hbar\omega\hat{a}_+\psi_n = (E_n + \hbar\omega)\hat{a}_+\psi_n.\end{aligned}\quad (15)$$

This tells us $\hat{a}_+\psi_n$ is indeed an eigenstate of \hat{H} , with energy eigenvalue $E_n + \hbar\omega$. The acting of operator \hat{a}_+ raises the energy of a state by fixed amount $\hbar\omega$. Because of this property, \hat{a}_+ is often referred to as the “raising operator”.

Similarly, we could show

$$\hat{H}\hat{a}_-\psi_n = (E_n - \hbar\omega)\hat{a}_-\psi_n. \quad (16)$$

The acting of operator \hat{a}_- lowers the energy of a state by fixed amount $\hbar\omega$. \hat{a}_- is often referred to as the “lowering operator”.

As another physics input, we know that for potential energy of the form $V(x) = m\omega^2x^2/2$, the energy eigenvalues of the physical system is bounded from below. This means there must exist a state with the lowest energy (the ground state), ψ_0 . The fact that there exist no state with lower energy implies

$$\hat{a}_-\psi_0 = 0. \quad (17)$$

Using the definition of the \hat{a}_- operator, Eq. (9), we have

$$\left(\hbar\frac{d}{dx} + m\omega x\right)\psi_0(x) = 0. \quad (18)$$

This is a quite simple equation and can be solved by rewriting it into

$$\frac{d \ln \psi_0(x)}{dx} = -\frac{m\omega}{\hbar}x, \quad (19)$$

which leads to

$$\psi_0(x) = C \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \quad (20)$$

The coefficient C can be determined by the normalization condition $\int_{-\infty}^{+\infty} dx |\psi_0(x)|^2 = 1$. This leads to

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \quad (21)$$

Acting the Hamiltonian operator on this wavefunction, we can find the corresponding energy eigenvalue

$$E_0 = \frac{1}{2}\hbar\omega . \quad (22)$$

Excited states can be obtained by acting the raising operator \hat{a}_+ on the ground state wavefunction. The corresponding energy eigenvalue increase by $\hbar\omega$ per \hat{a}_+ action. Therefore

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega . \quad (23)$$

All result are consistent with the findings in Chapter 3.3.

Because each \hat{a}_+ action increase the energy by $\hbar\omega$, we could consider this action adds one quanta (a particle for the harmonic oscillator) to the system. Each particle carries energy $\hbar\omega$. The ground state ψ_0 is the state with zero particle, whereas ψ_n is considered as a state with n particles in the system.

4.3. Heisenberg Uncertainty Principle (another remark)

Here is a useful remark based on the 1D harmonic oscillator problem which we have solved using two methods so far. One important finding is that the ground state energy is nonzero, $E_0 = \hbar\omega/2$. This is in sharp contrast with classical physics description where E_0 can be made as close to zero as possible.

Such a difference can be understood (qualitatively) using the Heisenberg uncertainty principle. Without solving any differential equation, we could already derive a rough estimate of the ground state energy.

Given the potential energy $V(x) = m\omega^2x^2/2$ which is minimized at $x = 0$, to reduce the energy, the electron had better be as close to the origin as possible. This agrees with the intuition from classical physics. However, in quantum mechanics we can only talk about the average of the electron's position operator, $\langle\hat{x}\rangle$. Because of the wave nature, the electron has a spread around the origin which we call Δx . The corresponding potential energy is roughly

$$V \simeq \frac{1}{2}m\omega^2(\Delta x)^2 . \quad (24)$$

On the other hand, due to the uncertainty principle, when Δx is smaller, the uncertainty of its momentum (spread in the momentum space) Δp becomes higher, $\Delta p \geq \hbar/(2\Delta x)$. By approximating the average of the momentum operator $\langle\hat{p}\rangle$ by Δp , kinetic energy of the electron is

$$T \simeq \frac{(\Delta p)^2}{2m} \geq \frac{\hbar^2}{8m(\Delta x)^2} . \quad (25)$$

Clearly, if we set Δx to zero, the kinetic energy will blow up.

The total energy is the sum of kinetic and potential energies

$$E = T + V \gtrsim \frac{1}{2}m\omega^2(\Delta x)^2 + \frac{\hbar^2}{8m(\Delta x)^2} . \quad (26)$$

To find the ground state energy, we minimize E with respect to Δx , which leads to

$$E \gtrsim 2\sqrt{\frac{1}{2}m\omega^2(\Delta x)^2 \times \frac{\hbar^2}{8m(\Delta x)^2}} = \frac{1}{2}\hbar\omega . \quad (27)$$

This gives the correct form of ground state energy. It also gives the correct value of $\Delta x = \sqrt{\hbar/(2m\omega)}$, as found in Chapter 3.3. This is a useful trick and illustrates the practical implication of Heisenberg uncertainty principle.

In research, it is often useful to take this kind of intuitive approach to estimate the result, before doing any concrete calculations.

4.4. Hermitian Operators and Physical Observables

We first introduce the Dirac's "bra" and "ket" notation of states, by rewriting

$$\begin{aligned} \psi(x) &\rightarrow |\psi\rangle , \\ \psi^*(x) &\rightarrow \langle\psi| , \end{aligned} \quad (28)$$

and rewriting the overlapping integral as an inner product

$$\int dx \psi_1^*(x)\psi_2(x) \rightarrow \langle\psi_1|\psi_2\rangle . \quad (29)$$

The "bra" and "ket" notation has the following properties

$$\begin{aligned} \langle\psi|\psi\rangle &> 0 , \\ \langle\psi_1|\psi_2\rangle &= \langle\psi_2|\psi_1\rangle^* = \langle\psi_2^*|\psi_1^*\rangle , \\ \langle\psi_1|c_2\psi_2 + c_3\psi_3\rangle &= c_2\langle\psi_1|\psi_2\rangle + c_3\langle\psi_1|\psi_3\rangle , \\ \langle c_1\psi_1 + c_2\psi_2|\psi_3\rangle &= c_1^*\langle\psi_1|\psi_3\rangle + c_2^*\langle\psi_2|\psi_3\rangle . \end{aligned} \quad (30)$$

The action of an operator on a state is denoted as

$$\hat{O}\psi(x) \rightarrow \hat{O}|\psi\rangle = |\hat{O}\psi\rangle . \quad (31)$$

As a result,

$$\int dx \psi_1^*(x)\hat{O}\psi_2(x) \rightarrow \langle\psi_1|\hat{O}|\psi_2\rangle . \quad (32)$$

The attractive feature of Dirac's "bra" and "ket" notation is not only simplicity. Moreover, it helps to take the discussion to an abstractive level. The ket $|\psi\rangle$ contains all the information about the state. It is not a function of coordinate x .

The wavefunction in coordinate space $\psi(x)$ could be defined as an inner product $\langle x|\psi\rangle$, where the bra $\langle x|$ is the conjugate of the ket $|x\rangle$. The latter corresponds to an electron state at rest, located at position x .

With the Dirac's notation, we proceed to define the complex conjugate of an operator, denoted as \hat{O}^* , where we simply take the complex conjugate for all the complex numbers in the operator (i.e., all $i \rightarrow -i$, i is the imaginary unit). For example, $\hat{x}^* = \hat{x}$, $\hat{p}^* = (-i\hbar\frac{d}{dx})^* = i\hbar\frac{d}{dx} = -\hat{p}$. It is obvious that $(\hat{O}_1\hat{O}_2)^* = \hat{O}_1^*\hat{O}_2^*$. When acting on bra and ket states, we can write

$$|\hat{O}\psi\rangle^* = \hat{O}^*|\psi\rangle^* = \left(\hat{O}|\psi\rangle\right)^* = \langle\hat{O}\psi|. \quad (33)$$

Next, we define a very important transformation to operator, the Hermitian conjugation, denoted as \hat{O}^\dagger . The formal definition in terms of bra and ket states is, for any ψ_1, ψ_2 ,

$$\langle\psi_1|\hat{O}^\dagger|\psi_2\rangle \equiv \langle\hat{O}\psi_1|\psi_2\rangle. \quad (34)$$

In the language of integral, this means

$$\int dx \psi_1^*(x) \hat{O}^\dagger \psi_2(x) = \int dx \left(\hat{O}\psi_1(x)\right)^* \psi_2(x) = \int dx \left(\hat{O}^*\psi_1(x)^*\right) \psi_2(x), \quad (35)$$

in the last two steps, it is understood that \hat{O} or \hat{O}^* only acts on the wavefunction on its right-hand side within the big bracket.

The Hermitian conjugate of the product of two operators is equal to the product of each but with the opposite order,

$$(\hat{O}_1\hat{O}_2)^\dagger = \hat{O}_2^\dagger\hat{O}_1^\dagger. \quad (36)$$

It is straightforward to prove this based on the definition of Hermitian conjugation,

$$\begin{aligned} \text{first : } & \langle\psi_1|(\hat{O}_1\hat{O}_2)^\dagger|\psi_2\rangle = \langle\hat{O}_1\hat{O}_2\psi_1|\psi_2\rangle, \\ \text{second : } & \langle\psi_1|\hat{O}_2^\dagger\hat{O}_1^\dagger|\psi_2\rangle = \langle\psi_1|\hat{O}_2^\dagger|\hat{O}_1^\dagger\psi_2\rangle = \langle\hat{O}_2\psi_1|\hat{O}_1^\dagger\psi_2\rangle = \langle\hat{O}_2\psi_1|\hat{O}_1^\dagger|\psi_2\rangle \\ & = \langle\hat{O}_1\hat{O}_2\psi_1|\psi_2\rangle. \end{aligned} \quad (37)$$

Because the right-hand side of the two lines are equal to each other, we conclude $\langle\psi_1|(\hat{O}_1\hat{O}_2)^\dagger|\psi_2\rangle = \langle\psi_1|\hat{O}_2^\dagger\hat{O}_1^\dagger|\psi_2\rangle$. This relation holds for any ψ_1, ψ_2 , thus $(\hat{O}_1\hat{O}_2)^\dagger = \hat{O}_2^\dagger\hat{O}_1^\dagger$ is proven.

Next, we define the Hermitian operator, which satisfy $\hat{O}^\dagger = \hat{O}$. As a result

$$\langle\psi_1|\hat{O}|\psi_2\rangle \equiv \langle\hat{O}\psi_1|\psi_2\rangle, \quad (38)$$

holds for any ψ_1, ψ_2 , or more explicitly,

$$\int dx \psi_1^*(x) \hat{O} \psi_2(x) = \int dx \left(\hat{O}^*\psi_1(x)^*\right) \psi_2(x) = \left(\int dx \psi_2^*(x) \hat{O} \psi_1(x)\right)^*. \quad (39)$$

Hermitian operators play a very important role in quantum mechanics. Many of the operators introduced for writing down the Schrödinger equation are Hermitian operators, including \hat{x} , \hat{p} , \hat{p}^2 , $V(x)$, \hat{H} .

Here we show that \hat{p} is Hermitian, which is less trivial than for \hat{x} . Using the integral form,

$$\begin{aligned} \int dx \psi_1^*(x) \hat{p} \psi_2(x) &= \int dx \psi_1^*(x) (-i\hbar) \frac{d}{dx} \psi_2(x) \\ &= (-i\hbar) \left(\int dx \frac{d}{dx} (\psi_1^*(x) \psi_2(x)) - \int dx \psi_2(x) \frac{d}{dx} \psi_1^*(x) \right), \end{aligned} \quad (40)$$

where in the last line, we integrate by parts. Assuming that $\psi_{1,2}(x \rightarrow \infty) = 0$, we can drop the first term which amounts to a surface integral,

$$\int dx \psi_1^*(x) \hat{p} \psi_2(x) = i\hbar \int dx \psi_2(x) \frac{d}{dx} \psi_1^*(x) = \left(\int dx \psi_2(x) \hat{p} \psi_1^*(x) \right)^* , \quad (41)$$

This is consistent with the definition in Eq. (39). Thus, $\hat{p}^\dagger = \hat{p}$ is Hermitian. As a further result, $(\hat{p}^2)^\dagger = (\hat{p}\hat{p})^\dagger = \hat{p}^\dagger \hat{p}^\dagger = \hat{p}^2$. Thus \hat{p}^2 is also a Hermitian operator.

Here are a few theorems about Hermitian operators.

- If \hat{O}_1, \hat{O}_2 are both Hermitian operators, so is their sum $\hat{O}_1 + \hat{O}_2$.
- If \hat{O}_1, \hat{O}_2 are both Hermitian operators, their product $\hat{O}_1 \hat{O}_2$ is not always Hermitian unless $[\hat{O}_1, \hat{O}_2] = 0$.
- If \hat{O}_1, \hat{O}_2 are both Hermitian operators, so is $i[\hat{O}_1, \hat{O}_2]$.
- For a Hermitian operator \hat{O} , its average value under any state is a real number, $\langle \psi | \hat{O} | \psi \rangle \in \mathbb{R}$.

It is straightforward to prove this.

$$\langle \psi | \hat{O} | \psi \rangle^* = \langle \psi | \hat{O} \psi \rangle^* = \langle \hat{O} \psi | \psi \rangle = \langle \psi | \hat{O} | \psi \rangle . \quad (42)$$

- If for any state, the average value of an operator is always real, then such an operator must be Hermitian.

To prove this, we first choose an arbitrary state ψ , the average of operator \hat{O} under this state being real means

$$\langle \hat{O} \psi | \psi \rangle = \langle \psi | \hat{O} \psi \rangle . \quad (43)$$

Next, we consider $\psi = \psi_1 + c\psi_2$ where c is any complex number. Insert this expression in Eq. (43) and expand, we find,

$$\begin{aligned} \text{Left-hand side} &= \langle \hat{O} \psi_1 | \psi_1 \rangle + |c|^2 \langle \hat{O} \psi_2 | \psi_2 \rangle + c \langle \hat{O} \psi_1 | \psi_2 \rangle + c^* \langle \hat{O} \psi_2 | \psi_1 \rangle , \\ \text{Right-hand side} &= \langle \psi_1 | \hat{O} \psi_1 \rangle + |c|^2 \langle \psi_2 | \hat{O} \psi_2 \rangle + c \langle \psi_1 | \hat{O} \psi_2 \rangle + c^* \langle \psi_2 | \hat{O} \psi_1 \rangle . \end{aligned} \quad (44)$$

Because Eq. (43) also applies for ψ_1 and ψ_2 . The first two terms in each line of Eq. (44) are equal to each other. For the remaining parts to be equal, we need

$$c(\langle \hat{O}\psi_1|\psi_2\rangle - \langle \psi_1|\hat{O}\psi_2\rangle) = c^*(\langle \psi_2|\hat{O}\psi_1\rangle - \langle \hat{O}\psi_2|\psi_1\rangle) . \quad (45)$$

As stated earlier, this must be valid for any value of c . In particular, we can choose $c = 1$ and i , which imply that the terms in the bracket on both side of Eq. (46) must vanish. i.e.,

$$\langle \hat{O}\psi_1|\psi_2\rangle = \langle \psi_1|\hat{O}\psi_2\rangle , \quad (46)$$

for any ψ_1, ψ_2 . This is nothing but the definition of an Hermitian operator.

Before moving on, let us do a concrete exercise to better understand how Hermitian conjugation of an operator works. We consider the 1D harmonic oscillator, again. In the algebraic method discussed Chapter 4.2, we introduced the raising and lowering operators in Eq. (9),

$$\hat{a}_\pm = \frac{1}{\sqrt{2m\omega\hbar}}(\mp i\hat{p} + m\omega x) . \quad (47)$$

Clearly, because \hat{p} and x are Hermitian operators, with the extra i in front of \hat{p} , \hat{a}_\pm are not Hermitian operators. Instead, we have

$$\hat{a}_+^\dagger = \hat{a}_- , \quad \hat{a}_-^\dagger = \hat{a}_+ . \quad (48)$$

The exercise here is to consider the n -th excited state, in the ket notation $|\psi_n\rangle = C_n \hat{a}_+^n |\psi_0\rangle$, and find the normalization factor C_n by imposing the normalization condition, $\langle \psi_n|\psi_n\rangle = 1$.

$$\langle \psi_n|\psi_n\rangle = |C_n|^2 \langle \hat{a}_+^n \psi_0|\hat{a}_+^n \psi_0\rangle = |C_n|^2 \langle \psi_0|\hat{a}_-^n \hat{a}_+^n |\psi_0\rangle , \quad (49)$$

where in the last step, we apply the definition of Hermitian conjugation of operator \hat{a}_+^n . Because $\hat{a}_- |\psi_0\rangle = 0$, and obvious thing to do is to move \hat{a}_- across the \hat{a}_+^n operators. To do so, we first note

$$\begin{aligned} [\hat{a}_-, \hat{a}_+^n] &= \hat{a}_- \hat{a}_+^n - \hat{a}_+^n \hat{a}_- \\ &= \hat{a}_- \hat{a}_+^n - \hat{a}_+ \hat{a}_- \hat{a}_+^{n-1} + \hat{a}_+ \hat{a}_- \hat{a}_+^{n-1} - \hat{a}_+^2 \hat{a}_- \hat{a}_+^{n-2} + \hat{a}_+^2 \hat{a}_- \hat{a}_+^{n-2} - \dots \\ &\quad - \hat{a}_+^{n-1} \hat{a}_- \hat{a}_+ + \hat{a}_+^{n-1} \hat{a}_- \hat{a}_+ - \hat{a}_+^n \hat{a}_- \\ &= [\hat{a}_-, \hat{a}_+] \hat{a}_+^{n-1} + \hat{a}_+ [\hat{a}_-, \hat{a}_+] \hat{a}_+^{n-2} + \dots + \hat{a}_+^{n-1} [\hat{a}_-, \hat{a}_+] \\ &= n \hat{a}_+^{n-1} . \end{aligned} \quad (50)$$

As a result,

$$\hat{a}_- \hat{a}_+^n = \hat{a}_+^n \hat{a}_- + [\hat{a}_-, \hat{a}_+^n] = \hat{a}_+^{n-1} (\hat{a}_+ \hat{a}_- + n) , \quad (51)$$

and Eq. (49) becomes

$$\begin{aligned} \langle \psi_n|\psi_n\rangle &= |C_n|^2 \langle \psi_0|\hat{a}_-^{n-1} \hat{a}_+^{n-1} (\hat{a}_+ \hat{a}_- + n) |\psi_0\rangle \\ &= n |C_n|^2 \langle \psi_0|\hat{a}_-^{n-1} \hat{a}_+^{n-1} |\psi_0\rangle . \end{aligned} \quad (52)$$

By iteration, we will eventually obtain

$$\langle \psi_n | \psi_n \rangle = n! |C_n|^2 \langle \psi_0 | \psi_0 \rangle . \quad (53)$$

Requiring it to normalize to 1 leads to

$$C_n = \frac{1}{\sqrt{n!}} . \quad (54)$$

The n -th excited ket state takes the form

$$|\psi_n\rangle = \frac{1}{\sqrt{n!}} \hat{a}_+^n |\psi_0\rangle . \quad (55)$$

In coordinate space, using the explicit form of \hat{a}_+ and $\psi_0(x)$ (see Eqs. (9) and (21)), we can reproduce the same correctly normalized wavefunction $\psi_n(x)$ as derived in Chapter 3.3.

4.5. Matrix Representation of States and Operators

So far, we have learned that in quantum mechanics, wavefunctions (solutions to the Schrödinger equation with a given Hamiltonian) are used to describe a state of electron, and physical observables correspond to Hermitian operators (that act on wavefunctions). Experimental measurement of an observable is the average of the corresponding operator under a given state. These are the basic tools for doing calculations in quantum mechanics.

As discussed in Chapter 2, a general wavefunction can be a superposition of many states. We use the bra and ket notation here.

$$|\Psi\rangle = \sum_n c_n |\psi_n\rangle e^{iE_n t/\hbar} , \quad (56)$$

where $|\psi_i\rangle$ are the energy eigenstates of the Hamiltonian, and c_i are a set of coefficients (can be complex numbers). To be concrete, you can think of 1D harmonic oscillator as example. In this case, the index $n = 0, 1, 2, \dots$ labels the different energy levels, with $E_n = \hbar\omega(n + 1/2)$.

The above Eq. (56) states something very profound. The energy eigenstates of the 1D harmonic oscillator (with $n = 0, 1, 2, \dots$) form a complete set. Any wavefunction that is the solution to the same (time-dependent) Schrödinger equation can always be written as a linear combination of these energy eigenstates.

Here is an interesting theorem. If two eigenstates of the same Hamiltonian carry different energy eigenvalues, they must be orthogonal to each other, i.e., if $E_m \neq E_n$, then $\langle \psi_m | \psi_n \rangle = 0$. This can be easily proved by noting that \hat{H} is a Hermitian operator, thus $\langle \hat{H} \psi_m | \psi_n \rangle = \langle \psi_m | \hat{H} \psi_n \rangle$, applying the time-independent

Schrödinger equation $\hat{H}|\psi_{m,n}\rangle = E_{m,n}|\psi_{m,n}\rangle$, we get $(E_m - E_n)\langle\psi_m|\psi_n\rangle = 0$. Therefore, if $E_m - E_n \neq 0$, $\langle\psi_m|\psi_n\rangle$ must vanish. (This proof can be generalized to any Hermitian operator, not only the Hamiltonian.)

This theorem tells us that every two eigenstates of the 1D harmonic oscillator are orthogonal to each other, because none of them are degenerate in energy. (We will address the degenerate case in the Chapter 4.6.)

The complete and orthogonal set of energy eigenstates of a given Hamiltonian is usually referred to as the Hilbert space. We could further simplify Eq. (56) by absorbing the phase factor into the coefficient c_n and write

$$|\Psi\rangle = \sum_n c_n |\psi_n\rangle, \quad (57)$$

where

$$c_n = \langle\psi_n|\Psi\rangle. \quad (58)$$

We can verify this by taking the inner product of $\langle\psi_n|$ with both sides.

Next, we consider an operator \hat{O} acting on $|\Psi\rangle$, which can be considered as another state $|\Psi'\rangle = \hat{O}|\Psi\rangle = |\hat{O}\Psi\rangle$. We can still expand it as a linear combination of states from the Hilbert space

$$\hat{O}|\Psi\rangle = \sum_n c_n \hat{O}|\psi_n\rangle = \sum_n c_n |\hat{O}\psi_n\rangle = \sum_n c_n \sum_m o_{mn} |\psi_m\rangle, \quad (59)$$

where in the last step, we expand $|\hat{O}\psi_n\rangle$ in the Hilbert space again, and

$$o_{mn} = \langle\psi_m|\hat{O}|\psi_n\rangle. \quad (60)$$

When \hat{O} acts on an Hilbert space state

$$\hat{O}|\psi_n\rangle = \sum_m o_{mn} |\psi_m\rangle. \quad (61)$$

Consider the most special case where $\hat{O} = \hat{I}$ is a unit operator,

$$\begin{aligned} \hat{I}|\Psi\rangle &= \sum_n c_n \hat{I}|\psi_n\rangle \\ &= \sum_n c_n \sum_m \langle\psi_m|\hat{I}|\psi_n\rangle |\psi_m\rangle \\ &= \sum_n c_n \sum_m |\psi_m\rangle \langle\psi_m|\psi_n\rangle \\ &= \sum_n c_n \left(\sum_m |\psi_m\rangle \langle\psi_m| \right) |\psi_n\rangle, \end{aligned} \quad (62)$$

where in the last step, we are allowed to consider $\sum_m |\psi_m\rangle\langle\psi_m|$ inside the bracket to be an operator. Comparing it with the first line, we find an interesting (and useful) way to writing the unit operator

$$\hat{I} = \sum_n |\psi_n\rangle\langle\psi_n|. \quad (63)$$

This sum must go through every state that belongs to the Hilbert space.

With Eqs. (58) and (60), we are ready to present the matrix representation of states and operators. The basic idea is that all the information of Ψ and \hat{O} are contained in the coefficients c_n and o_{mn} , respectively. The Hilbert space states are already defined once the Hamiltonian is known.

Under the matrix representation, state and operator take the following form

$$|\Psi\rangle \rightarrow C = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \\ \vdots \end{pmatrix}, \quad \hat{O} \rightarrow O = \begin{pmatrix} o_{11} & o_{12} & \cdots & o_{1n} & \cdots \\ o_{21} & o_{22} & \cdots & o_{2n} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ o_{m1} & o_{m2} & \cdots & o_{mn} & \cdots \\ \vdots & \vdots & \cdots & \vdots & \ddots \end{pmatrix}, \quad (64)$$

where state corresponds to a column matrix, and operator corresponds to a square matrix. Depending on the number of states in the Hilbert space, the dimensions of these matrices can be infinite.

o_{mn} is often called the matrix element.

With the above matrices, Eq. (57) can be rewritten as a row matrix of Hilbert states times the column matrix Eq. (64),

$$|\Psi\rangle = (|\psi_1\rangle \quad |\psi_2\rangle \quad \cdots \quad |\psi_n\rangle \quad \cdots) C, \quad (65)$$

Eq. (61) can be rewritten as

$$\hat{O}|\psi_n\rangle = (|\psi_1\rangle \quad |\psi_2\rangle \quad \cdots \quad |\psi_n\rangle \quad \cdots) O, \quad (66)$$

and Eq. (59) can be rewritten as

$$\hat{O}|\Psi\rangle = (|\psi_1\rangle \quad |\psi_2\rangle \quad \cdots \quad |\psi_n\rangle \quad \cdots) OC. \quad (67)$$

The multiplication of matrices follow the same rules as those for linear operators introduced earlier. In particular,

$$\begin{aligned} \hat{O}_1\hat{O}_2|\psi_n\rangle &= \hat{O}_1 \left((|\psi_1\rangle \quad |\psi_2\rangle \quad \cdots) O_2 \right) \\ &= \hat{O}_1 (|\psi_1\rangle \quad |\psi_2\rangle \quad \cdots) O_2 \\ &= (|\psi_1\rangle \quad |\psi_2\rangle \quad \cdots) O_1 O_2. \end{aligned} \quad (68)$$

The Hermitian conjugation of an operator also corresponds a square matrix. The matrix element is

$$o_{mn}^\dagger = \langle \psi_m | \hat{O}^\dagger | \psi_n \rangle = \langle \hat{O} \psi_m | \psi_n \rangle = \langle \psi_n | \hat{O} \psi_m \rangle^* = o_{nm}^* . \quad (69)$$

The matrix for the Hermitian conjugate operator \hat{O}^\dagger corresponds to taking the transpose and complex conjugate to the matrix for the original operator \hat{O} .

For a Hermitian operator $\hat{O} = \hat{O}^\dagger$. This implies $o_{mn}^\dagger = o_{nm}^*$. The corresponding matrix is called a Hermitian matrix.

Historically, due to the similarity of the algebra of operator-station action and matrix, quantum mechanics is also called matrix mechanics.

As a concrete example, we consider the energy eigenstates of of 1D harmonic oscillator, $\{|\psi_0\rangle, |\psi_1\rangle, |\psi_2\rangle, \dots\}$, forming a Hilbert space. Let us write down the matrix representation for the operators $\hat{a}_\pm, \hat{x}, \hat{p}, \hat{H}$.

From Eq. (55), we already know $|\psi_n\rangle = \frac{1}{\sqrt{n!}} \hat{a}_+^n |\psi_0\rangle$. As a result,

$$\begin{aligned} \hat{a}_+ |\psi_n\rangle &= \sqrt{n+1} \frac{1}{\sqrt{(n+1)!}} \hat{a}_+^{n+1} |\psi_0\rangle = \sqrt{n+1} |\psi_{n+1}\rangle , \\ \hat{a}_- |\psi_n\rangle &= \frac{1}{\sqrt{n!}} \hat{a}_- \hat{a}_+^n |\psi_0\rangle = \frac{1}{\sqrt{n!}} (\hat{a}_+^{n-1} (\hat{a}_+ \hat{a}_- + n)) |\psi_0\rangle = \sqrt{n} |\psi_{n-1}\rangle , \end{aligned} \quad (70)$$

where in the second line we used Eq. (51). With these, we can obtain the matrix element for \hat{a}_\pm ,

$$\begin{aligned} \langle \psi_m | \hat{a}_+ | \psi_n \rangle &= \sqrt{n+1} \langle \psi_m | \psi_{n+1} \rangle = \sqrt{n+1} \delta_{mn} , \\ \langle \psi_m | \hat{a}_- | \psi_n \rangle &= \sqrt{n} \langle \psi_m | \psi_{n-1} \rangle , \end{aligned} \quad (71)$$

which allows us to write, in the basis of $\{|\psi_0\rangle, |\psi_1\rangle, |\psi_2\rangle, \dots\}$,

$$a_- = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & \cdots & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & \cdots & 0 & \cdots \\ 0 & 0 & 0 & 0 & \ddots & \vdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \sqrt{n} & \cdots \\ 0 & 0 & 0 & 0 & \cdots & 0 & \ddots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad a_+ = \begin{pmatrix} 0 & 0 & 0 & 0 & \cdots & 0 & \cdots \\ \sqrt{1} & 0 & 0 & 0 & \cdots & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & \cdots & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \ddots & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \cdots \\ 0 & 0 & 0 & \cdots & \sqrt{n} & 0 & \ddots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (72)$$

Next, using the inverse relation of Eq. (9),

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}_+ + \hat{a}_-), \quad \hat{p} = i\sqrt{\frac{\hbar m\omega}{2}} (\hat{a}_+ - \hat{a}_-), \quad (73)$$

we get the matrix representations for \hat{x} and \hat{p} ,

$$x = \sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \ddots \\ \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix}, \quad p = i\sqrt{\frac{\hbar m\omega}{2}} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & \cdots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \ddots \\ \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix}. \quad (74)$$

Finally, the Hamiltonian $\hat{H} = \hbar\omega(\hat{a}_+\hat{a}_- + 1/2)$ has the matrix representation

$$H = \hbar\omega \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & \cdots \\ 0 & \frac{3}{2} & 0 & 0 & \cdots \\ 0 & 0 & \frac{5}{2} & 0 & \cdots \\ 0 & 0 & 0 & \frac{7}{2} & \ddots \\ \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix}, \quad (75)$$

which is a diagonal matrix, as expected. The diagonal matrix elements are the corresponding energy eigenvalues.

4.6. Common Eigenstates and Conserved Quantities

Here we consider the case when there are energy degenerate states as the solution to the same Schrödinger equation. Barring accidental case, degeneracy among states usually occurs when there is an operator \hat{O} (not the unit operator) that commutes with the Hamiltonian \hat{H} , i.e., $[\hat{O}, \hat{H}] = 0$.

This can be seen by assuming that $|\psi\rangle$ is an eigenstate of \hat{H} with energy E . Next, we consider the state resulting from \hat{O} acting on $|\psi\rangle$, which we call $|\psi'\rangle = \hat{O}|\psi\rangle$. It is straightforward to show that $|\psi'\rangle$ is also the eigenstate of \hat{H} with energy E . Indeed,

$$\hat{H}|\psi'\rangle = \hat{H}\hat{O}|\psi\rangle = \hat{O}\hat{H}|\psi\rangle = \hat{O}(E|\psi\rangle) = E\hat{O}|\psi\rangle = E|\psi'\rangle. \quad (76)$$

Next, we show that such an operator \hat{O} , if it is Hermitian, can help to distinguish energy degenerate states.

If there are n energy degenerate states for a Hamiltonian, $\{|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_n\rangle\}$, and we manage to find an operator \hat{O} satisfying $[\hat{O}, \hat{H}] = 0$. We can calculate the matrix form of \hat{O} in this basis (which is a subspace of the Hilbert space if $|\psi_1\rangle, \dots, |\psi_n\rangle$ are not all the energy eigenstates of \hat{H}).

$$O = \begin{pmatrix} o_{11} & o_{12} & \cdots & o_{1n} \\ o_{21} & o_{22} & \cdots & o_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ o_{n1} & o_{n2} & \cdots & o_{nn} \end{pmatrix}, \quad (77)$$

where the matrix element $o_{ij} = \langle \psi_i | \hat{O} | \psi_j \rangle$.

If \hat{O} is a Hermitian operator, then O is a Hermitian matrix, $O^\dagger = O$. It is not diagonal matrix in general. As a mathematical theorem (will not be proved here), any Hermitian matrix can be diagonalized with a unitary matrix U ,

$$UOU^\dagger = \begin{pmatrix} \tilde{o}_1 & 0 & 0 & 0 \\ 0 & \tilde{o}_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & \tilde{o}_n \end{pmatrix} \equiv \text{diag}\{\tilde{o}_1, \tilde{o}_2, \dots, \tilde{o}_n\}, \quad (78)$$

where a unitary matrix satisfies the condition, $UU^\dagger = U^\dagger U = I_{n \times n}$, and $\det U = 1$. An analogue of unitary matrix is the orthogonal matrix which can be used for diagonalizing a real symmetric matrix, as we learned in linear algebra.

Because UOU^\dagger is still a Hermitian matrix, its diagonal elements $\tilde{o}_1, \tilde{o}_2, \dots, \tilde{o}_n$ must all be real numbers.

We can rewrite Eq. (78) as $O = U^\dagger \text{diag}\{\hat{o}_1, \hat{o}_2, \dots, \hat{o}_n\}U$. In terms of components,

$$o_{ij} = \sum_{k=1}^n U_{ik}^\dagger \hat{o}_k U_{kj}. \quad (79)$$

Let us also define a new basis using the above unitary matrix

$$(|\phi_1\rangle \quad |\phi_2\rangle \quad \dots \quad |\phi_n\rangle) = (|\psi_1\rangle \quad |\psi_2\rangle \quad \dots \quad |\psi_n\rangle) U^\dagger, \quad (80)$$

where $|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_n\rangle$ are linear combinations of states in the original basis $|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_n\rangle$. In terms of components, $|\phi_i\rangle = \sum_{j=1}^n U_{ji}^\dagger |\psi_j\rangle$.

Moreover, because $|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_n\rangle$ are linear combinations of energy degenerate states $|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_n\rangle$, with energy E . It is obvious that they are still degenerate with energy equal to E , i.e., $\hat{H}|\phi_i\rangle = E|\phi_i\rangle$ for $i = 1, 2, \dots, n$.

In the new basis

$$\hat{O}|\phi_i\rangle = \sum_{j=1}^n U_{ji}^\dagger \hat{O}|\psi_j\rangle = \sum_{j=1}^n U_{ji}^\dagger \sum_{k=1}^n o_{kj} |\psi_k\rangle. \quad (81)$$

Insert Eq. (79) in the last step, we get

$$\begin{aligned} \hat{O}|\phi_i\rangle &= \sum_{j=1}^n U_{ji}^\dagger \sum_{k=1}^n \sum_{l=1}^n U_{kl}^\dagger \hat{o}_l U_{lj} |\psi_k\rangle \\ &= \sum_{k=1}^n \sum_{l=1}^n \tilde{o}_l U_{kl}^\dagger |\psi_k\rangle \left(\sum_{j=1}^n U_{lj} U_{ji}^\dagger \right). \end{aligned} \quad (82)$$

The last bracket gives δ_{li} because U is unitary ($UU^\dagger = I_{n \times n}$). As a result,

$$\hat{O}|\phi_i\rangle = \tilde{o}_i \sum_{k=1}^n U_{ki}^\dagger |\psi_k\rangle = \tilde{o}_i |\phi_i\rangle. \quad (83)$$

In the last step, we have shown that $|\phi_i\rangle$ is an eigenstate of Hermitian operator \hat{O} with eigenvalue \tilde{o}_i . This applies to all the states $|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_n\rangle$ in the new basis.

Summarizing the above discussions, we have shown that if there are energy degenerate states ($|\psi_i\rangle$) of a Hamiltonian, and if there exists a Hermitian operator \hat{O} that commutes with \hat{H} , then it is always possible to write down linear combination of the degenerate states ($|\phi_i\rangle$) such that they are eigenstates of both \hat{H} and \hat{O} ,

$$\hat{H}|\phi_i\rangle = E|\phi_i\rangle, \quad \hat{O}|\phi_i\rangle = \tilde{o}_i|\phi_i\rangle. \quad (84)$$

for $i = 1, 2, \dots, n$.

$|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_n\rangle$ are called common eigenstates of \hat{H} and \hat{O} .

Generically, the eigenvalues of \hat{O} are not identical, $\tilde{o}_1 \neq \tilde{o}_2 \neq \dots \neq \tilde{o}_n$. If so, we can use the eigenvalues \tilde{o}_i ($i = 1, 2, \dots, n$) to distinguish the $|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_n\rangle$ states which have identical energy eigenvalue E .

One could still ask the further question what if some of the \hat{O} eigenvalues are still degenerate, e.g., $\tilde{o}_1 = \tilde{o}_2$? In this case, the typical answer is we could find another Hermitian operator \hat{O}' satisfying $[\hat{O}', \hat{H}] = [\hat{O}', \hat{O}] = 0$. We can find common eigenstates of \hat{H} , \hat{O} and \hat{O}' . The eigenvalues $\tilde{o}'_1, \tilde{o}'_2$, if different from each other, can be used to further distinguish the states. — In fact, this is exactly what happens in nature. We will see a concrete example when solving the hydrogen atom in the next chapter.

The last remark we want to make is about conservation laws. If there is a Hermitian operator \hat{O} that commutes with the Hamiltonian, then the average of this operator under any state is time invariant (conserved). To prove this, we calculate $d\langle\Psi|\hat{O}|\Psi\rangle/dt$ and apply the Schrödinger equation,

$$\begin{aligned} \frac{d}{dt}\langle\Psi|\hat{O}|\Psi\rangle &= \left\langle \frac{d\Psi}{dt} \middle| \hat{O}|\Psi\rangle + \langle\Psi|\hat{O} \middle| \frac{d\Psi}{dt} \right\rangle = -i\hbar\langle\hat{H}\Psi|\hat{O}|\Psi\rangle + i\hbar\langle\Psi|\hat{O}|\hat{H}\Psi\rangle \\ &= i\hbar\langle\Psi|[\hat{O}, \hat{H}]|\Psi\rangle = 0. \end{aligned} \quad (85)$$

This result implies, if we manage to find the common eigenstate of \hat{H} and \hat{O} , then the eigenvalues characterize this state, E and \tilde{o} , are always constant of time, although the state itself in general evolves with time.

■ The end.

Chapter 5. Hydrogen Atom

In this chapter, we discuss Schrödinger equation and its solutions in three space dimensions (3D). The goal is to first derive the wavefunction and energy levels for the hydrogen atom. With these results, we will be able to give a fundamental explanation of the atom lines and the Rydberg formula. We will make comparison with the phenomenological Bohr model. Toward the end of this chapter, we briefly discuss what happens when the hydrogen atom is exposed to an external magnetic field.

5.1. Schrödinger Equation with Central Potential

Compared to the 1D case, we make the following changes to the Schrödinger equation in the 3D case

$$\begin{aligned}x &\rightarrow \vec{r} = (x, y, z) , \\ \hat{p} &\rightarrow \hat{\vec{p}} = -i\hbar\vec{\nabla} = -i\hbar(\partial/\partial x, \partial/\partial y, \partial/\partial z) , \\ \hat{p}^2 &\rightarrow \hat{\vec{p}}^2 = -\hbar^2\nabla^2 = -\hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) .\end{aligned}\tag{1}$$

The Schrödinger equation reads

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\Psi(\vec{r}, t) .\tag{2}$$

We continue to assume the potential V to be real and time-independent.

Consider the stationary state solution with fixed energy E ,

$$\Psi(\vec{r}, t) = \psi(\vec{r})e^{-iEh/\hbar} ,\tag{3}$$

where $\psi(\vec{r})$ satisfies the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r}) .\tag{4}$$

In the following, we will focus on the special case where the potential term $V(\vec{r})$ only depends on the magnitude r . This is called a central (centrifugal) potential. The Coulomb potential for electron inside the hydrogen atom belongs to this class, where $V(r) = -e^2/(4\pi\epsilon_0 r)$.

In the presence of a central potential, it is most convenient to write down the Schrödinger equation in spherical coordinates, which is related to Cartesian

coordinates as

$$\begin{aligned}x &= r \sin \theta \cos \phi , \\y &= r \sin \theta \sin \phi , \\z &= r \cos \theta .\end{aligned}\tag{5}$$

Correspondingly, we can convert the derivatives with respect to x, y, z into derivatives with respect to r, θ, ϕ ,

$$\begin{aligned}\frac{\partial}{\partial x} &= \sin \theta \cos \phi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \phi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \phi}{r \sin \theta} \frac{\partial}{\partial \phi} , \\ \frac{\partial}{\partial y} &= \sin \theta \sin \phi \frac{\partial}{\partial r} + \frac{\cos \theta \sin \phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos \phi}{r \sin \theta} \frac{\partial}{\partial \phi} , \\ \frac{\partial}{\partial z} &= \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} .\end{aligned}\tag{6}$$

It is a bit tedious but straightforward to show that

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} .\tag{7}$$

We can now rewrite Hamiltonian operator as

$$\hat{H} = -\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hbar^2}{2mr^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + V(r) .\tag{8}$$

5.2. Orbital Angular Momentum Operators

In classical physics, the orbital angular momentum is defined as $\vec{r} \times \vec{p}$. In quantum mechanics, it corresponds to operators

$$\hat{\vec{L}} = \vec{r} \times \hat{\vec{p}} ,\tag{9}$$

which is a Hermitian operator.

In terms of its components in Cartesian coordinates

$$\begin{aligned}\hat{L}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) , \\ \hat{L}_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) , \\ \hat{L}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) .\end{aligned}\tag{10}$$

These operators satisfy the following commutation properties

$$\begin{aligned}
[\hat{L}_i, r_i] &= [\hat{L}_i, \hat{p}_i] = 0 , \\
[\hat{L}_i, r_j] &= i\hbar\varepsilon_{ijk}r_k , \\
[\hat{L}_i, \hat{p}_j] &= i\hbar\varepsilon_{ijk}\hat{p}_k , \\
[\hat{L}_i, \hat{L}_j] &= i\hbar\varepsilon_{ijk}\hat{L}_k ,
\end{aligned} \tag{11}$$

where $i, j, k = x, y, z$. Based on the above relations, we can further derive

$$[\hat{L}_i, \vec{r}^2] = [\hat{L}_i, \hat{p}^2] = [\hat{L}_i, \vec{r} \cdot \hat{p}] = 0 . \tag{12}$$

We can define the vector product of angular momentum operators and show

$$\hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}} . \tag{13}$$

This relation could be proved in terms of components,

$$\begin{aligned}
(\hat{\vec{L}} \times \hat{\vec{L}})_i &= \varepsilon_{ijk}\hat{L}_j\hat{L}_k = \frac{1}{2}\varepsilon_{ijk}[\hat{L}_j, \hat{L}_k] = \frac{1}{2}\varepsilon_{ijk}(i\hbar\varepsilon_{jkl}\hat{L}_k) \\
&= \frac{i\hbar}{2}(\varepsilon_{ijk}\varepsilon_{jkl})\hat{L}_k = i\hbar\delta_{il}\hat{L}_k = i\hbar\hat{L}_i .
\end{aligned} \tag{14}$$

Next, we write down the angular momentum operators in Eq. (10) in terms of spherical coordinates

$$\begin{aligned}
\hat{L}_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) , \\
\hat{L}_y &= i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) , \\
\hat{L}_z &= -i\hbar\frac{\partial}{\partial\phi} ,
\end{aligned} \tag{15}$$

and

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) . \tag{16}$$

Comparing this with Eq. (8), we find that the operator $\hat{\vec{L}}^2$ is part of the Hamiltonian (kinetic energy),

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{2mr^2}\hat{\vec{L}}^2 + V(r) . \tag{17}$$

As an important observation, $\hat{\vec{L}}^2$ is an operator that takes derivatives with respect to the angular coordinates θ, ϕ . Thus,

$$[\hat{\vec{L}}^2, \partial/\partial r] = [\hat{\vec{L}}^2, r] = [\hat{\vec{L}}^2, V(r)] = 0 . \tag{18}$$

As a result,

$$[\hat{L}^2, \hat{H}] = 0 . \quad (19)$$

Eq. (19) is a remarkable relation if we recall the discussion in chapter 4.6. We have found an operator that commutes with Hamiltonian. This implies that if there are energy degenerates of the Hamiltonian, we will be able to use \hat{L}^2 to distinguish these states. They will be assigned different quantum numbers (eigenvalues) under \hat{L}^2 .

As further step, it is crucial to note that \hat{L}_z also commutes with \hat{H} , and more over

$$[\hat{L}_z, \hat{L}^2] = [\hat{L}_z, \hat{H}] = [\hat{L}^2, \hat{H}] = 0 . \quad (20)$$

Therefore, both \hat{L}^2 and \hat{L}_z can be used to distinguish energy degenerate states.

Because $[\hat{L}_x, \hat{L}_z], [\hat{L}_y, \hat{L}_z] \neq 0$, there are no more angular momentum operators that can be added to Eq. (20). There, we chose \hat{L}_z instead of \hat{L}_x, \hat{L}_y as a convention.

We will make the above statement more quantitative next.

5.3. Spherical Harmonics

We solve the time-independent Schrödinger equation with the Hamiltonian given in Eq. (17),

$$\left(-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{2mr^2} \hat{L}^2 + V(r) \right) \psi(\vec{r}) = E\psi(\vec{r}) . \quad (21)$$

We mention again that \hat{L}^2 only takes derivatives with respect to θ, ϕ and does not involve r . This motivate us to factorize the wavefunction as

$$\psi(\vec{r}) = R(r)Y(\theta, \phi) . \quad (22)$$

Inserting this into Eq. (21), we obtain

$$-\frac{\hbar^2}{2m} Y(\theta, \phi) \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R(r) + \frac{1}{2mr^2} R(r) \hat{L}^2 Y(\theta, \phi) + V(r) R(r) Y(\theta, \phi) = E R(r) Y(\theta, \phi) . \quad (23)$$

Dividing each term by $\frac{\hbar^2}{2mr^2} R(r) Y(\theta, \phi)$ and with some reorganization, we obtain

$$\frac{1}{R(r)} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R(r) + \frac{2mr^2}{\hbar^2} (E - V(r)) = \frac{1}{\hbar^2} \frac{1}{Y(\theta, \phi)} \hat{L}^2 Y(\theta, \phi) . \quad (24)$$

The left-hand side of this equation is a function of coordinate r , whereas the right-hand side is a function of coordinates θ, ϕ . The equation holds for any value of

r, θ, ϕ . This is only possible if both sides are equal to a constant number λ . The value of λ and the functions R, Y are still to be determined. In spite of these unknowns, Eq. (24) is separated into two equations

$$\begin{aligned} \hat{L}^2 Y(\theta, \phi) &= -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi) , \\ \frac{d}{dr} r^2 \frac{d}{dr} R(r) + \frac{2mr^2}{\hbar^2} (E - V(r)) R(r) &= \lambda R(r) . \end{aligned} \quad (25)$$

The normalization condition for $\psi(\vec{r})$

$$\int d^3 \vec{r} |\psi(\vec{r})|^2 = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 dr |\psi(\vec{r})|^2 = 1 , \quad (26)$$

can also be separated into two conditions

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta |Y(\theta, \phi)|^2 = \int_0^\infty r^2 dr |R(r)|^2 = 1 , \quad (27)$$

We first solve the first equation in Eq. (25), whose solution holds for any form of the central potential. We make a further factorization

$$Y(\theta, \phi) = P(\theta)Q(\phi) , \quad (28)$$

and reorganize Eq. (25) as

$$\frac{1}{P(\theta)} \sin \theta \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} P(\theta) + \lambda \sin^2 \theta = -\frac{1}{Q(\phi)} \frac{d^2}{d\phi^2} Q(\phi) . \quad (29)$$

Using a similar argument that the left- (right-)hand side only depends on θ (ϕ), both sides must be equal to another constant, which we call m^2 . This yields two equations

$$\begin{aligned} \frac{d^2}{d\phi^2} Q(\phi) + m^2 Q(\phi) &= 0 , \\ \sin \theta \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} P(\theta) + (\lambda \sin^2 \theta - m^2) P(\theta) &= 0 . \end{aligned} \quad (30)$$

The first normalization condition Eq. (27) can be further separated as

$$\int_0^{2\pi} d\phi |Q(\phi)|^2 = \int_0^\pi \sin \theta d\theta |P(\theta)|^2 = 1 , \quad (31)$$

The first equation of Eq. (30) is rather simple to solve, the general solution is

$$Q(\phi) \propto e^{im\phi} . \quad (32)$$

Periodic condition in the ϕ direction, $Q(\phi) = Q(\phi + 2\pi)$ implies m must be an integer,

$$m = 0, \pm 1, \pm 2, \dots \quad (33)$$

The normalization condition further fully determines the form of $Q(\phi)$,

$$Q(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (34)$$

To solve the second equation of Eq. (30), we define $\xi = \cos \theta$ (thus $-1 \leq \xi \leq 1$), which leads to

$$(1 - \xi)^2 \frac{d^2 P}{d\xi^2} - 2\xi \frac{dP}{d\xi} + \left(\lambda - \frac{m^2}{1 - \xi^2} \right) P = 0 \quad (35)$$

This is a special differential equation called the associated Legendre equation. For it to have a regular solution (no divergence) everywhere in $-1 \leq \xi \leq 1$, we need

$$\lambda = \ell(\ell + 1) \quad (36)$$

where ℓ is a positive integer

$$\ell = 1, 2, 3, \dots \quad (37)$$

For given ℓ , the range of m is restricted to

$$m = -\ell, -(\ell - 1), \dots, 0, \dots, (\ell - 1), \ell \quad (38)$$

When the above conditions are fulfilled, the function $P = P_\ell^m(\cos \theta)$ is a finite polynomial. As a few examples,

$$\begin{aligned} P_0^0(\cos \theta) &= 1, & P_1^0(\cos \theta) &= \cos \theta, & P_1^{\pm 1}(\cos \theta) &= \mp \sin \theta, \\ P_2^0(\cos \theta) &= \frac{1}{2}(3 \cos^2 \theta - 1), & P_2^1(\cos \theta) &= -3 \sin \theta \cos \theta, & P_2^2(\cos \theta) &= 3 \sin^2 \theta. \end{aligned} \quad (39)$$

More generally, $P_\ell^m(\cos \theta)$ satisfy the following conditions

$$\begin{aligned} P_\ell^{-m}(\cos \theta) &= (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(\cos \theta), \\ \int_0^\pi \sin \theta d\theta P_\ell^m(\cos \theta) P_{\ell'}^m(\cos \theta) &= \frac{2}{2\ell + 1} \frac{(\ell + m)!}{(\ell - m)!} \delta_{\ell\ell'}. \end{aligned} \quad (40)$$

The normalization Eq. (31) then fully determines the form $P(\theta)$ in terms of the Legendre polynomial

$$P(\theta) = (-1)^m \sqrt{\frac{2\ell + 1}{2} \frac{(\ell - m)!}{(\ell + m)!}} P_\ell^m(\cos \theta) \quad (41)$$

With the solutions Eqs. (34) and (41), we introduce the spherical harmonic functions

$$Y_{\ell m}(\theta, \phi) = (-1)^m \sqrt{\frac{2\ell + 1}{4\pi} \frac{(\ell - m)!}{(\ell + m)!}} P_{\ell}^m(\cos \theta) e^{im\phi} . \quad (42)$$

Useful properties of the spherical harmonics are

$$\begin{aligned} Y_{\ell m}(\theta, \phi) &= (-1)^m Y_{\ell, -m}(\theta, \phi) , \\ \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta Y_{\ell m}^*(\theta, \phi) Y_{\ell' m'}(\theta, \phi) &= \delta_{\ell \ell'} \delta_{m m'} , \\ \hat{L}^2 Y_{\ell m}(\theta, \phi) &= \ell(\ell + 1) \hbar^2 Y_{\ell m}(\theta, \phi) , \\ \hat{L}_z Y_{\ell m}(\theta, \phi) &= m \hbar Y_{\ell m}(\theta, \phi) . \end{aligned} \quad (43)$$

$Y_{\ell m}(\theta, \phi)$ is the common eigenstate of \hat{L}^2 and \hat{L}_z . We can label it with the corresponding quantum numbers

$$\ell, \quad m , \quad (44)$$

where ℓ is referred to as the orbital (or azimuthal) quantum number, and m is the magnetic quantum number. We will see the meaning of these names later in this chapter.

Since we already know that $Y_{\ell m}(\theta, \phi)$ is a spherical harmonic function, once the values of ℓ and m are given, the angular part of the wavefunction is fully determined.

Based on the discussion of chapter 4.6, if a wavefunction living in central potential has a particular set of quantum numbers ℓ and m , then it always possesses these numbers when evolving with time. They are conserved quantum numbers.

$Y_{\ell m}(\theta, \phi)$ is not the eigenstate of \hat{L}_x or \hat{L}_y . It does not have a fixed quantum number under these two operators. This is because $[\hat{L}_x, \hat{L}_z]$, $[\hat{L}_y, \hat{L}_z] \neq 0$. When they act on $Y_{\ell m}(\theta, \phi)$, we have the following relations

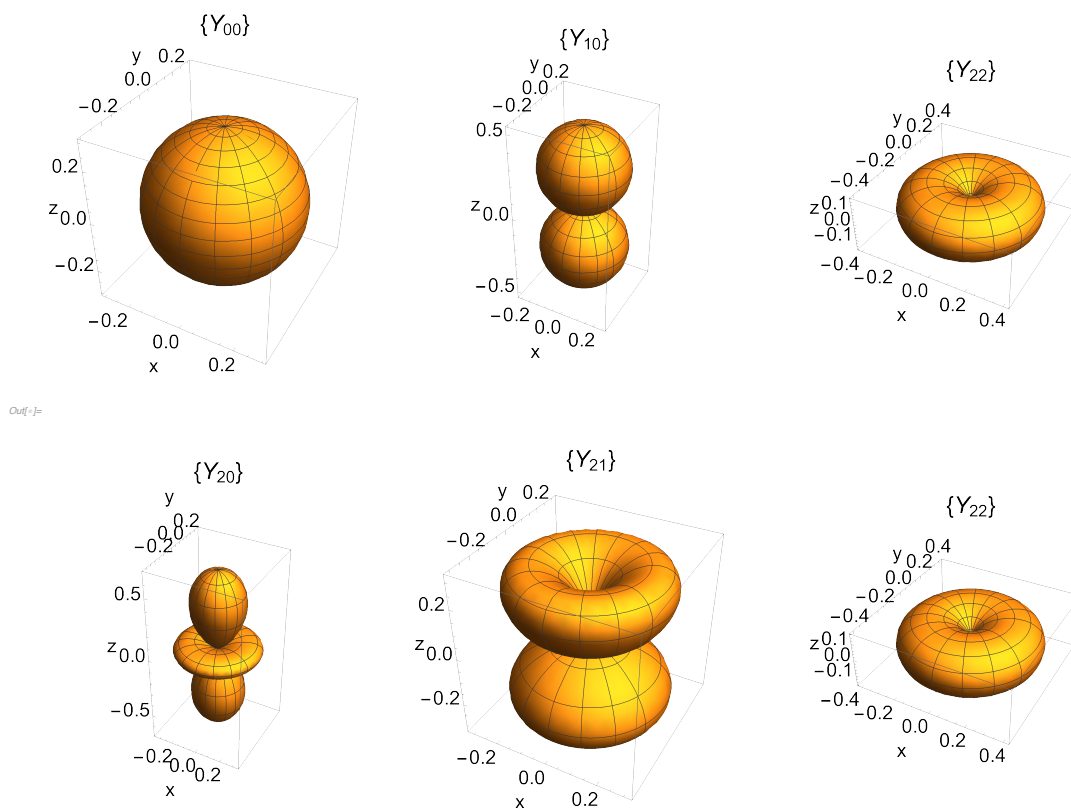
$$\begin{aligned} \hat{L}_{\pm} Y_{\ell m}(\theta, \phi) &= \hbar \sqrt{\ell(\ell + 1) - m(m \pm 1)} Y_{\ell, m \pm 1}(\theta, \phi) \\ &= \hbar \sqrt{(\ell \pm m + 1)(\ell \mp m)} Y_{\ell, m \pm 1}(\theta, \phi) , \end{aligned} \quad (45)$$

where

$$\hat{L}_{\pm} \equiv \hat{L}_x \pm i \hat{L}_y = i \hbar e^{\pm i\phi} \left(\mp i \frac{\partial}{\partial \theta} + \cot \theta \frac{\partial}{\partial \phi} \right) , \quad (46)$$

are also called raising and lower operators (in terms of changing the magnetic quantum number m).

In the following picture, we show how the spherical harmonic functions look (for $\ell \leq 2$) in 3D space. In a given direction (θ, ϕ) , the distance of from surface to the origin is given by $|Y_{\ell m}(\theta, \phi)|$.



5.4. The Hydrogen Atom

Our next task will be to solve the second equation of Eq. (25). To this end, we need to decide on the form of the central potential $V(r)$. We focus on the case of the hydrogen atom, which is a bound state made of a proton with $+e$ electric charge and an electron with $-e$ electric charge. They feel the attractive Coulomb potential from each other. In reality, the proton is about 2000 times heavier than the electron. Therefore, as a good approximation, we can put the proton at the origin of spherical coordinates (which barely moves), and the electron's position is described by \vec{r} . In this case,

$$V(r) \simeq -\frac{e^2}{4\pi\epsilon_0 r} . \quad (47)$$

We can do better than this. In general, we describe the proton's position with \vec{r}_2 and electron's position with \vec{r}_1 . They both could have a kinetic energy. Their Hamiltonian in quantum mechanics is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + V(r) , \quad (48)$$

where $\vec{\nabla}_{1,2} = \partial/\partial\vec{r}_{1,2}$, and $V(r)$ is given by Eq. (47) and $r = |\vec{r}_1 - \vec{r}_2|$.

We redefine coordinate

$$\vec{r} = \vec{r}_1 - \vec{r}_2, \quad \vec{R} = \frac{m\vec{r}_1 + M\vec{r}_2}{m + M}, \quad (49)$$

where m (M) is the mass of electron (proton). \vec{R} is the center of mass of the electron-proton system.

In terms of r and R , we have

$$\begin{aligned} \vec{\nabla}_1 &= \vec{\nabla} + \frac{m}{m + M} \vec{\nabla}_R, \\ \vec{\nabla}_2 &= -\vec{\nabla} + \frac{m}{m + M} \vec{\nabla}_R, \end{aligned} \quad (50)$$

where $\vec{\nabla} = \partial/\partial\vec{r}$ and $\vec{\nabla}_R = \partial/\partial\vec{R}$.

The Hamiltonian can be written as

$$\hat{H} = \left(-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) + \left(-\frac{\hbar^2}{2(m + M)} \nabla_R^2 \right), \quad (51)$$

where $\mu = mM/(m + M)$ is the reduced mass of the electron-proton system. Numerically, $\mu \simeq m$ is very close to the electron mass. The Hamiltonian is separated into two uncoupled parts, describing the relative motion of electron and proton, and the overall motion of center-of-mass frame that has no external potential, respectively. The resulting wavefunction factorizes into the product

$$\psi(\vec{r})f(\vec{R}), \quad (52)$$

where $f(\vec{R})$ is a plane wave

$$f(\vec{R}) = \frac{1}{\sqrt{V}} e^{i\vec{K}\cdot\vec{R}}, \quad (53)$$

and $\psi(\vec{r})$ satisfies the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi(\vec{r}) = E\psi(\vec{r}). \quad (54)$$

In chapter 5.3, we have derived that

$$\psi(\vec{r}) = R(r)Y_{\ell m}(\theta, \phi), \quad (55)$$

where $Y_{\ell m}(\theta, \phi)$ is the spherical harmonic function. The equation for $R(r)$ is the second equation in Eq. (25) but with the replacement $m \rightarrow \mu$ (to be strict)

$$\frac{d}{dr} r^2 \frac{d}{dr} R(r) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R(r) = \ell(\ell + 1)R(r). \quad (56)$$

5.5. The Radial Wavefunction and Energy Levels

We proceed to solve Eq. (56).

Define $\chi(r) = rR(r)$, we find

$$\frac{d\chi}{dr} = R + r \frac{dR}{dr}, \quad \frac{d^2\chi}{dr^2} = \frac{1}{r} \frac{d}{dr} r^2 \frac{d}{dr} R(r). \quad (57)$$

Thus, the equation for χ is

$$\frac{d^2}{dr^2} \chi(r) + \frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \chi(r) = \frac{\ell(\ell+1)}{r^2} \chi(r). \quad (58)$$

Next, we clean up the constant factors \hbar, e, ϵ_0 by a rescaling of the coordinate r into $\tilde{r} = Ar$ (A is decided below). The differential equation for $\chi(\tilde{r})$ is

$$\chi''(\tilde{r}) + \left(\frac{2\mu E}{A^2 \hbar^2} + \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 A \tilde{r}} - \frac{\ell(\ell+1)}{\tilde{r}^2} \right) \chi(\tilde{r}) = 0, \quad (59)$$

where $''$ means $d^2/d\tilde{r}^2$. We choose $A = \mu e^2 / (4\pi\epsilon_0 \hbar^2)$ and further define $\tilde{E} = \mu E / (A^2 \hbar^2)$. This leads to

$$\chi''(\tilde{r}) + \left(2\tilde{E} + \frac{2}{\tilde{r}} - \frac{\ell(\ell+1)}{\tilde{r}^2} \right) \chi(\tilde{r}) = 0, \quad (60)$$

We first examine the asymptotic behavior of this equation near the origin. For $\tilde{r} \rightarrow 0$, the equation is approximately

$$\chi''(\tilde{r}) - \frac{\ell(\ell+1)}{\tilde{r}^2} \chi(\tilde{r}) \sim 0, \quad (61)$$

whose solutions are $\chi = A\tilde{r}^{\ell+1} + B\tilde{r}^{-\ell}$. Because $\ell \geq 0$ (see Eq. (37)), for the wavefunction not to blow up at origin, we must have $B = 0$, thus $\chi \propto \tilde{r}^{\ell+1}$ as $\tilde{r} \rightarrow 0$.

Next, we examine the behavior at infinity. For $\tilde{r} \rightarrow +\infty$, the equation of χ is approximately

$$\chi''(\tilde{r}) + 2\tilde{E}\chi(\tilde{r}) = 0, \quad (62)$$

whose solution is $\chi \propto Ae^{\sqrt{-2\tilde{E}}\tilde{r}} + Be^{-\sqrt{-2\tilde{E}}\tilde{r}}$. Because E is a real number, for the wavefunction not to blow up at infinity, we must have $A = 0$, thus $\chi(\tilde{r}) \propto e^{-\sqrt{-2\tilde{E}}\tilde{r}}$ as $\tilde{r} \rightarrow +\infty$.

Motivated by these behaviors, we define

$$\chi(\tilde{r}) = \tilde{r}^{\ell+1} e^{-\sqrt{-2\tilde{E}}\tilde{r}} u(\tilde{r}). \quad (63)$$

We further define $\beta = \sqrt{-2\tilde{E}}$ $\xi = 2\beta\tilde{r}$. The equation for \tilde{u} can be written as

$$\xi \frac{d^2 u}{d\xi^2} + (2(\ell + 1) - \xi) \frac{du}{d\xi} - \left(\ell + 1 - \frac{1}{\beta} \right) u = 0 . \quad (64)$$

This is a special differential equation called the confluent hypergeometric equation.

We can insert the series expansion $u = \sum_{j=0}^{\infty} c_j \xi^j$ into the above equation and derive the recursion relation among the coefficients c_j ,

$$c_{j+1} = \frac{j + \ell + 1 - 1/\beta}{(j + 1)(j + 2\ell + 2)} c_j . \quad (65)$$

In order for this polynomial to be finite, it must be truncated at some finite power of ξ term. This implies that $n_r = -(\ell + 1 - 1/\beta)$ have to be non-negative integers, i.e., $n_r = 0, 1, 2, \dots$.

It is useful to define the principle quantum number n , which is also an integer,

$$n = \frac{1}{\beta} = n_r + \ell + 1 . \quad (66)$$

Possible values of n is $n = 1, 2, 3, \dots$, and correspondingly, the range of orbital quantum number ℓ satisfies $0 \leq \ell \leq (n - 1)$.

Because β is related to the energy eigenvalue E (recall $\beta = \sqrt{-2\tilde{E}}$ and $\tilde{E} = \mu E / (A^2 \hbar^2)$), we find that the energy of the system must be quantized. The energy eigenvalues are

$$E_n = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} , \quad (67)$$

which agrees with the prediction of Bohr's model discussed in chapter 1.5. Here we derive this result from the more fundamental Schrödinger equation.

$|E_n| = -E_n$ is often called the binding energy of the n -th level of hydrogen atom. The ground state corresponds to $n = 1$, $\ell = m = 0$.

It is useful to introduce the fine-structure constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0 c \hbar} = \frac{1}{137} , \quad (68)$$

where c is the speed of light. This allows us to rewrite the energy as

$$E_n = -\frac{\mu \alpha^2 c^2}{2n^2} = -\frac{1}{n^2} \times 13.6 \text{ eV} . \quad (69)$$

Another useful quantity we can define is the Bohr radius

$$a = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = \frac{\hbar}{\mu c \alpha} = 0.529 \text{ \AA} . \quad (70)$$

The Bohr radius describe the de Broglie wavelength of electron inside the hydrogen atom (see Eq. (82) below), which dictates the size of the atom. The corresponding typical momentum of the electron is $p \sim h/a \sim \mu\alpha c$. Because μ is roughly the electron mass, we could interpret the factor αc as the typical velocity of electron when it orbits around the proton. This velocity $v = c/137 \ll c$ implies that electron is non-relativistic in the hydrogen atom.

One could apply the Heisenberg uncertainty principle and derive an estimate of the ground state binding energy Eq. (67), in a similar fashion as chapter 4.3.

In the classical limit, $\hbar \rightarrow 0$, we have $a \rightarrow 0$, $E_n \rightarrow -\infty$. There is no bound state with finite energy in the classical limit. This is consistent with the classical physics picture where the electron will continue losing energy by radiating light and eventually fall on to the proton.

With the Bohr radius, we could also write the energy eigenstate as

$$E_n = -\frac{\hbar^2}{2n^2\mu a^2} . \quad (71)$$

There is a remarkable feature about the energy eigenvalue given in Eq. (67) (or equivalently, Eqs. (69) and (71)). It only depends on the principle quantum number n , but not the other quantum numbers of ℓ, m of the state, implying the presence of degeneracy.

The degeneracy is most obvious if we write down the wavefunction explicitly. The properly normalized radial wavefunction (which is a real function) for hydrogen atom with quantum numbers (n, ℓ) is,

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right) . \quad (72)$$

where $L_{n-\ell-1}^{2\ell+1}$ is the associated Laguerre polynomial. In terms of series expansion in r (or ξ), its coefficients satisfy the recursion relation Eq. (65).

More formally, the finite solution to Eq. (64) is

$$u = {}_1F_1(-n+\ell+1, 2\ell+2, \xi) = {}_1F_1\left(-n+\ell+1, 2\ell+2, \frac{2r}{na}\right) , \quad (73)$$

where ${}_1F_1(a, b, z)$ is the confluent hypergeometric function of the first kind, and we have used $\xi = 2\beta\tilde{r} = 2(1/n)(r/a)$. For $a = -n+\ell+1$ is zero or a negative integer, and $b = 2\ell+2$ is also an integer, confluent hypergeometric function reduces to the associated Laguerre polynomial,

$$u = {}_1F_1\left(-n+\ell+1, 2\ell+2, \frac{2r}{na}\right) = \frac{(2\ell+1)!(n-\ell-1)!}{(n+\ell)!} L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right) . \quad (74)$$

5.6. The Total Wavefunction

Together with angular wavefunction, the spherical harmonics, the total wavefunction is

$$\psi_{n\ell m}(\vec{r}) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right) Y_{\ell m}(\theta, \phi). \quad (75)$$

As an example, the ground state wavefunction is simply

$$\psi_{100}(\vec{r}) = \sqrt{\frac{1}{\pi a^3}} e^{-r/a}, \quad (76)$$

and in more details

$$R_{10}(r) = \frac{2}{a^{3/2}} e^{-r/a}, \quad Y_{00}(\theta, \phi) = \sqrt{\frac{1}{4\pi}}. \quad (77)$$

To summarize, the hydrogen atom wavefunction is characterized by three quantum numbers, n, ℓ, m ,

- Principle quantum number n , with range

$$n = 1, 2, 3, \dots$$

- Orbital quantum number ℓ . For given n , the range is

$$\ell = -n, -(n-1), \dots, 0, \dots, (n-1), n.$$

- Magnetic quantum number m . For given ℓ , the range is

$$m = -\ell, -(\ell-1), \dots, 0, \dots, (\ell-1), \ell.$$

For given n , there are in total

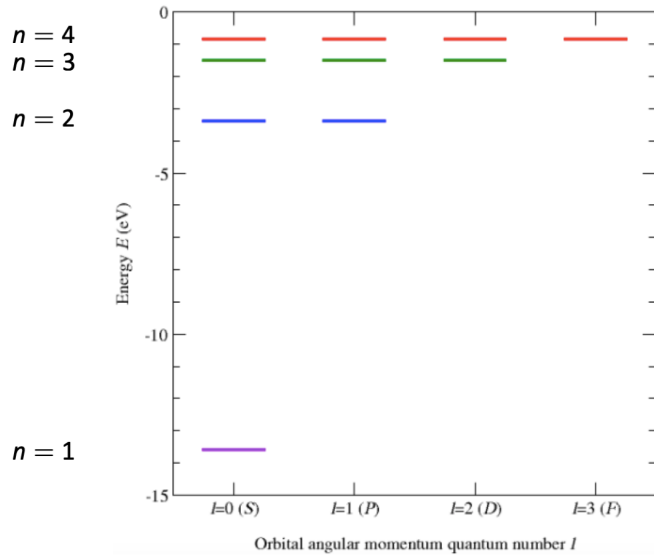
$$\sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} 1 = n^2, \quad (78)$$

different states having the same energy eigenvalue $E_n = -13.6 \text{ eV}/n^2$. The degree of degeneracy is n^2 .

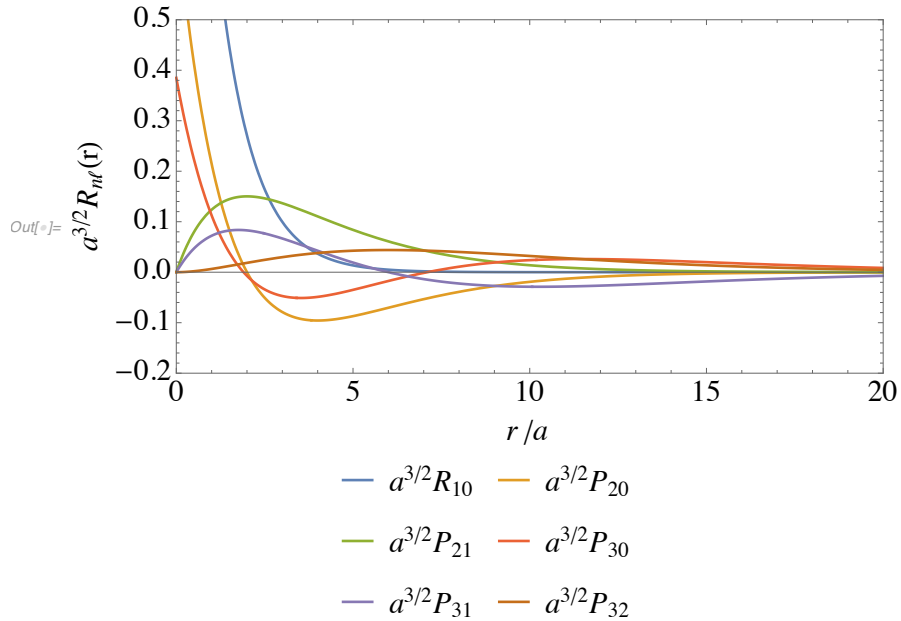
Given the quantum numbers n, ℓ, m , the wavefunction of the hydrogen atom is completely fixed. Of course one needs to know to insert these quantum numbers into the corresponding spherical harmonic function and Laguerre polynomial. From now on, it is assumed that we are already educated and know this procedure. As a result, we can use the Dirac's ket notation to represent the hydrogen wavefunction Eq. (75),

$$\psi_{n\ell m}(\vec{r}) \longrightarrow |n\ell m\rangle. \quad (79)$$

The following picture illustrates the hydrogen states and their degeneracy. The horizontal axis labels n , and the vertical axis labels ℓ . Each colored line has a $(2\ell + 1)$ -fold degeneracy due to choices of m .



The following plots show the radial wavefunction Eq. (72) for the lowest few states of hydrogen atom, with $n \leq 3$ and $\ell \leq n - 1$. A few features that are worth noting. For $R_{n\ell}$, the wavefunction vanishes at $r = 0$ for $\ell > 0$. The principle quantum number n counts the number of zero points of the radial wavefunction.



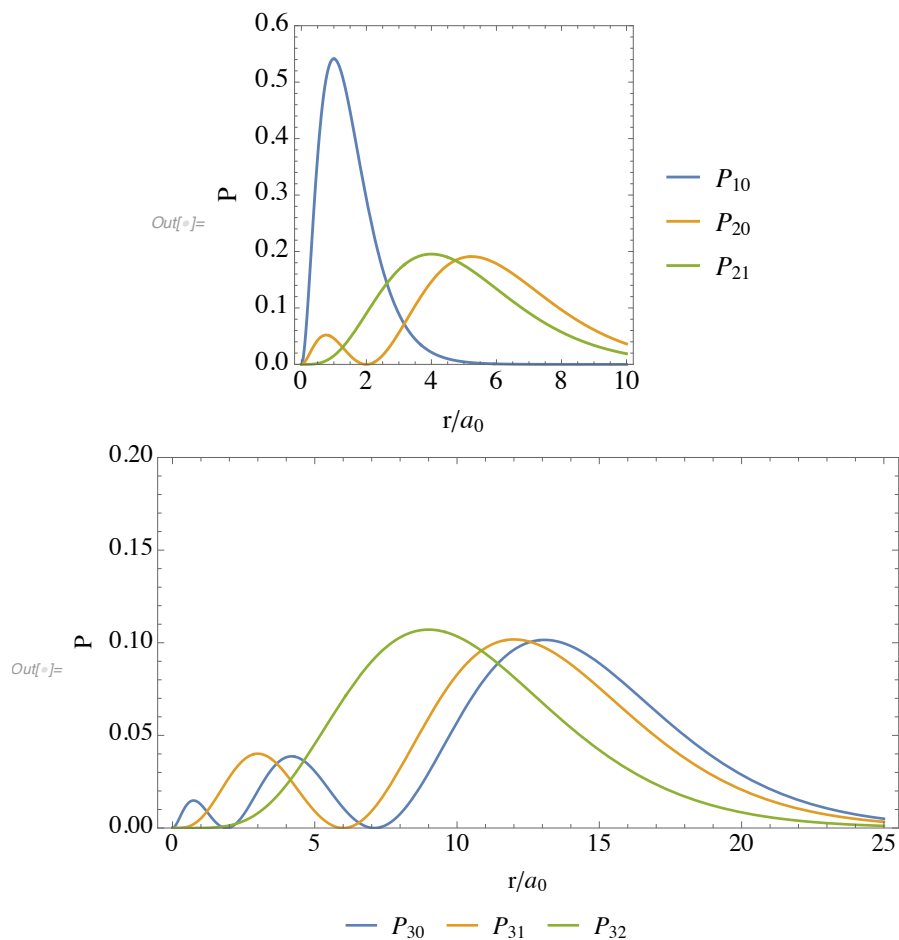
The above radial wavefunction satisfies the normalization condition

$$\int_0^\infty r^2 dr |R_{n\ell}(r)|^2 = 1 . \tag{80}$$

We define the probability density of finding the electron along the radial direction, as a function of r

$$P_{n\ell}(r) = r^2 dr |R_{n\ell}(r)|^2 = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta |\psi_{n\ell m}(\vec{r})|^2 . \tag{81}$$

The pictures below shows the shape of $P(r)$ for the lowest few states of hydrogen atom.



Clearly, all $P(r)$ vanishes at the origin $r = 0$ due to the r^2 factor in Eq. (81).

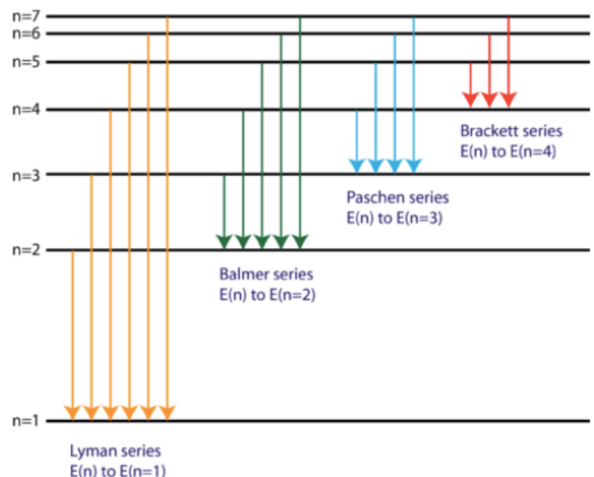
We can calculate the average of r under the ground state,

$$\begin{aligned}
 \langle 100|r|100\rangle &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 dr \psi_{n\ell m}^*(\vec{r}) r \psi_{n\ell m}(\vec{r}) \\
 &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta |Y_{00}(\theta, \phi)|^2 \int_0^\infty r^2 dr r R_{10}(r)^2 \\
 &= \int_0^\infty dr r P_{10}(r) \\
 &= \int_0^\infty dr r^3 e^{-2r/a} = \frac{3}{2}a .
 \end{aligned}
 \tag{82}$$

This exercise tells us that the size of the hydrogen atom in ground state is indeed characterized by the Bohr radius. However, unlike the Bohr model, there is no “orbit” at all for the electron moving around the proton. It is more appropriate to understand the electron distribution as a standing wave around the proton. The fundamental nature of the wave is encoded in $|n\ell m\rangle$, which is the solution to the Schrödinger equation. This is how hydrogen atom is described in quantum mechanics.

5.7. Selection Rules for Atomic Transitions

So far, by solving the Schrödinger equation for hydrogen atom, we manage to derive the energy levels and the corresponding wavefunctions of hydrogen atom states. However, we still cannot explain how an electron, in an excited state, turns into lower state leading to atomic transition lines. From the energy level difference, we could tell the frequency/wavelength of the radiated photon due to the transition (see the picture below). What we cannot tell is the rate for such a reaction to occur.



This is because the Hamiltonian we started with, $\hat{H} = \hat{p}^2/(2\mu) + V$ (see Eq. (51)), only includes the static electric potential. It does not contain the piece of electromagnetic radiation fields \vec{E} and \vec{B} . We need additional interaction terms in the Hamiltonian to account for the dynamics of atomic transitions.

The inclusion of electromagnetic radiation field is dictated by the minimal coupling rule, which promotes the momentum operator into the canonical momentum operator. For the case of electron, we make the replacement

$$\hat{p} \rightarrow \hat{p} - e\vec{A}, \quad (83)$$

where \vec{A} is the vector potential. It is related to the \vec{E} and \vec{B} fields via

$$\vec{E} = \frac{\partial \vec{A}}{\partial t} - \vec{\nabla}V, \quad \vec{B} = \vec{\nabla} \times \vec{A}. \quad (84)$$

With this replacement, the Hamiltonian becomes

$$\begin{aligned} \hat{H} &= \frac{(\hat{p} - e\vec{A}(\vec{r}))^2}{2\mu} + V(r) = \frac{(-i\hbar\vec{\nabla} - e\vec{A}(\vec{r}))^2}{2\mu} + V(r) \\ &= -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{ie\hbar\vec{\nabla} \cdot \vec{A}}{2\mu} + \frac{e^2\vec{A}^2}{2\mu} + V(r). \end{aligned} \quad (85)$$

The second term is relevant for atomic transition with a single photon emission.

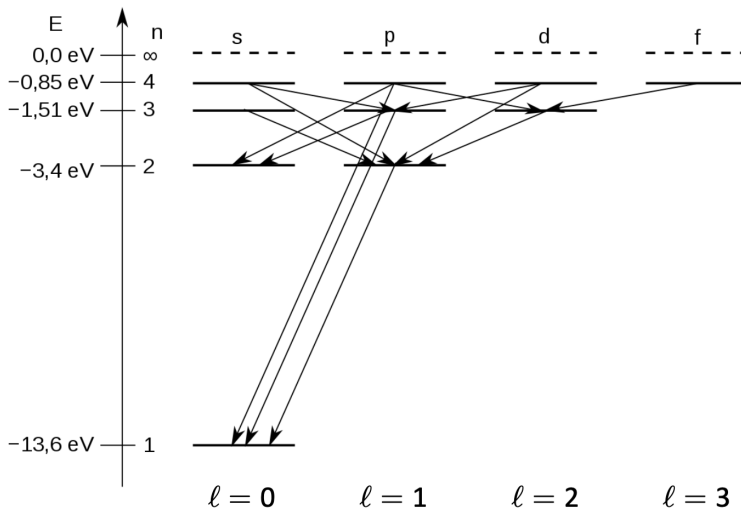
Deriving the atomic transition rate is beyond the scope of this course. It requires the time-dependent perturbation method. If you are interested in how the calculation is done, please see Chapter 18.5 of the textbook *Principles of Quantum Mechanics* by R. Shankar. In a nutshell,

$$\text{Decay rate} \propto \left\langle \left\langle n_f \ell_f m_f \left| \frac{\hat{p} \cdot \vec{A}}{\mu} \right| n_i \ell_i m_i \right\rangle \right\rangle^2 \quad (86)$$

Here, we simply present the selection rules for atomic transitions. Denoting the initial and final state of the transition by lower index “ i ” and “ f ”, we have

- Electron can de-excite from a higher energy level to a lower level, $n_i > n_f$.
- The orbital quantum number must change, $\ell_f - \ell_i = \pm 1$.
- The magnetic quantum number could change by ± 1 or stay unchanged, $m_f - m_i = 0, \pm 1$.
- The magnetic quantum number for spin remain unchanged, $(m_s)_f - (m_s)_i = 0$. This will be addressed in the next chapter.

These selection rules are illustrated by the following picture. As a concrete example, the $|n\ell m\rangle = |200\rangle$ state is forbidden to de-excite to the ground state $|100\rangle$, because the $\ell_f - \ell_i = \pm 1$ rule cannot be fulfilled.



5.8. The Paschen-Back Effect

The interacting Hamiltonian Eq. (85) not only leads to atomic transitions, but also observable effects when electron is exposed to external electromagnetic fields. At the end of this section, we consider the impact of an external magnetic field on the hydrogen atom. This leads to the Paschen-Back Effect discovered in 1921.

Consider a homogeneous magnetic field along the \hat{z} -axis direction, $\vec{B} = B\hat{z}$. In order to include its effect in the Schrödinger equation, we resort to Eq. (85). We choose the form of vector field to be¹

$$\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}, \quad (87)$$

which is consistent with $B = \vec{\nabla} \times \vec{A}$. It is straightforward to verify this relation

$$\begin{aligned} \vec{B} &= \vec{\nabla} \times \left(\frac{1}{2}\vec{B} \times \vec{r} \right) = \frac{1}{2} \left(\vec{B}(\vec{\nabla} \cdot \vec{r}) - (\vec{B} \cdot \vec{\nabla})\vec{r} \right) \\ &= \frac{3}{2}\vec{B} - \frac{1}{2}B_i \nabla_i \vec{r} = \frac{3}{2}\vec{B} - \frac{1}{2}\vec{B} = \vec{B}. \end{aligned} \quad (88)$$

With $\vec{B} = B\hat{z}$, Eq. (87) implies

$$A_x = -\frac{1}{2}By, \quad A_y = \frac{1}{2}Bx, \quad A_z = 0. \quad (89)$$

¹This choice is not unique though.

Plugging Eq. (87) into Eq. (85), we get

$$\begin{aligned}\hat{H} &= \frac{1}{2\mu} \left((\hat{p}_x - eBy/2)^2 + (\hat{p}_y + eBx/2)^2 + \hat{p}_z^2 \right) + V(r) \\ &= \frac{1}{2\mu} \left(\hat{p}^2 + eB\hat{L}_z + \frac{1}{4}e^2B^2(x^2 + y^2) \right) + V(r) .\end{aligned}\quad (90)$$

To proceed, we notice that the term proportional to B^2 in the above Lagrangian is subdominant to the term proportional to B . Indeed, even in today's laboratories, the largest magnetic field we could create is less than 10 Tesla. We take the average of the B^2 and B terms under a generic hydrogen wavefunction, using the approximations $\langle \hat{L}_z \rangle \sim \hbar$ and $\langle x^2 + y^2 \rangle \sim a^2$. The ratio of the two averages is

$$\frac{\langle B^2\text{-term} \rangle}{\langle B\text{-term} \rangle} \sim \frac{eBa^2}{\hbar} \lesssim \frac{e \text{ 10 Tesla } (1 \text{ \AA})^2}{\hbar} . \quad (91)$$

Using the unit conversions $1 \text{ \AA} = 10^{-10} \text{ m}$, and $1 \text{ Tesla} = 5.8 \times 10^{-11} \text{ MeV} \frac{2m}{e\hbar}$ where $m = 0.511 \text{ MeV}/c^2$ is the electron mass, we find

$$\frac{\langle B^2\text{-term} \rangle}{\langle B\text{-term} \rangle} \lesssim \frac{5.9 \times 10^{-30} \text{ m}^2 \text{ MeV}^2}{\hbar^2 c^2} . \quad (92)$$

Finally, using $\hbar c = 1.97 \times 10^{-13} \text{ MeV m}$, we find

$$\frac{\langle B^2\text{-term} \rangle}{\langle B\text{-term} \rangle} \lesssim 1.5 \times 10^{-4} \ll 1 . \quad (93)$$

This comparison shows that the B^2 term in Eq. (90) is indeed negligible for the case of hydrogen atom. This means the magnetic field is weak, thus we can only keep its leading effect, which is linear in B . Under this approximation, the Hamiltonian becomes

$$\hat{H} = \left(\frac{\hat{p}^2}{2\mu} + V(r) \right) + \frac{eB}{2\mu} \hat{L}_z . \quad (94)$$

The bracket is the Hamiltonian we used to solve for the hydrogen atom earlier this chapter. The last term is a (small) correction to the it.

We further assume that the hydrogen atom wavefunctions remain the same as derived in chapter 5.6. This is an approximation. The wavefunctions do change, and the change is proportional to B in the weak field limit. The corresponding effect on the energy level occurs at higher order.

With the same $|n\ell m\rangle$ states, we consider the impact of the last term in Eq. (94) on the hydrogen energy levels. The time-independent Schrödinger equation now reads

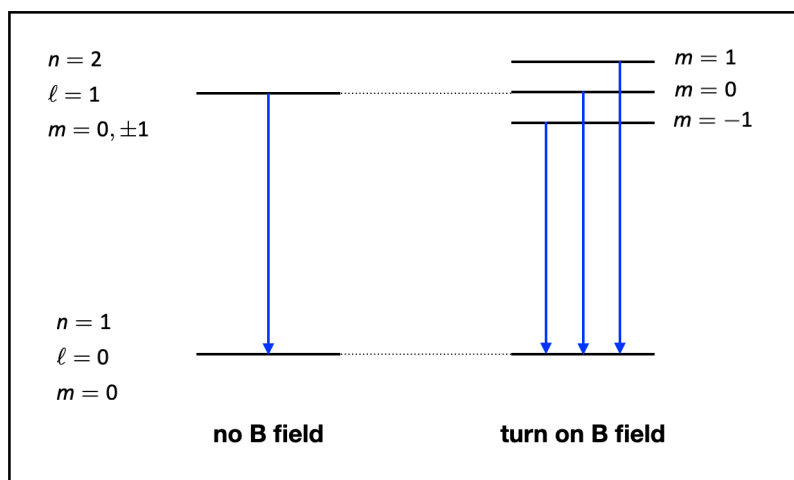
$$\left\{ \left(\frac{\hat{p}^2}{2\mu} + V(r) \right) + \frac{eB}{2\mu} \hat{L}_z \right\} |n\ell m\rangle = E_{n\ell m} |n\ell m\rangle . \quad (95)$$

It is straightforward to obtain

$$E_{n\ell m} = E_n + \frac{meB\hbar}{2\mu}, \tag{96}$$

where E_n is the energy eigenstate of $|n\ell m\rangle$ in the absence of the magnetic field, given by Eq. (67).

Clearly, the presence of an external magnetic field breaks the degeneracy for different magnetic quantum numbers (that is why m is called the magnetic quantum number). We expect the energy level splitting as illustrated by the picture below. The amount of splitting is proportional to the strength of the magnetic field. This is indeed what has been observed experimentally.



5.9. Added Note: Algebraic Method for Hydrogen

The discussion here is somewhat beyond the scope of this course. Skip it if you do not have time.

I am still presenting such a discussion because it is very elegant. It is a generalization of the algebraic method solution to the 1D harmonic oscillator discussed in the previous chapter. Here we present an algebraic method for solving the hydrogen atom.

The starting point is Eq. (58) for the radial wavefunction, which can be rewritten in the form of a 1D Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \chi(r) - \frac{e^2}{4\pi\epsilon_0 r} \chi(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \chi(r) = E\chi(r). \tag{97}$$

The Hamiltonian can be rewritten in terms of the Bohr radius $a = 4\pi\epsilon_0\hbar^2/(\mu e^2)$,

$$\hat{H}_\ell = \frac{\hat{p}^2}{2\mu} - \frac{\hbar^2}{\mu a r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} . \quad (98)$$

where $\hat{p} = -i\hbar d/dr$.

In analogy to the harmonic oscillator, we introduce raising and lowering operators of the following forms

$$\hat{a}_\pm(\ell) = \frac{\hbar a}{\sqrt{2}\hbar} \left(\mp \frac{d}{dr} + \frac{\ell+1}{r} - \frac{1}{(\ell+1)a} \right) . \quad (99)$$

It is straightforward to show that

$$\begin{aligned} \hat{a}_-(\ell)\hat{a}_+(\ell) &= \frac{a^2}{2\hbar^2} \left(\hat{p}^2 + \hbar^2 \left(\frac{\ell+1}{r} - \frac{1}{(\ell+1)a} \right)^2 + \hbar^2 \frac{d}{dr} \left(\frac{\ell+1}{r} - \frac{1}{(\ell+1)a} \right) \right) \\ &= \frac{\mu a^2}{\hbar^2} \left(\frac{\hat{p}^2}{2\mu} - \frac{\hbar^2}{\mu a r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right) + \frac{1}{2(\ell+1)^2} , \end{aligned} \quad (100)$$

and

$$\hat{a}_+(\ell)\hat{a}_-(\ell) = \frac{\mu a^2}{\hbar^2} \left(\frac{\hat{p}^2}{2\mu} - \frac{\hbar^2}{\mu a r} + \frac{(\ell+1)(\ell+2)\hbar^2}{2\mu r^2} \right) + \frac{1}{2(\ell+1)^2} . \quad (101)$$

Comparing these with the Hamiltonian in Eq. (98), we find the following relationships

$$\hat{H}_\ell = \frac{\hbar^2}{\mu a^2} \left(\hat{a}_-(\ell)\hat{a}_+(\ell) - \frac{1}{2(\ell+1)^2} \right) , \quad \hat{H}_{\ell+1} = \frac{\hbar^2}{\mu a^2} \left(\hat{a}_+(\ell)\hat{a}_-(\ell) - \frac{1}{2(\ell+1)^2} \right) . \quad (102)$$

It is clear that

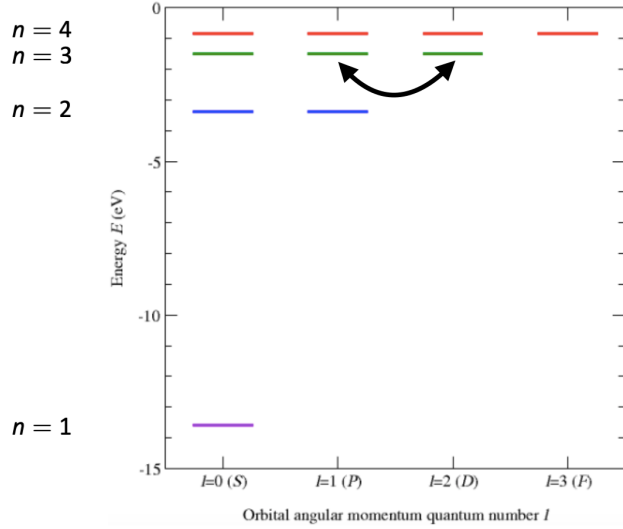
$$\hat{H}_\ell \hat{a}_-(\ell) = \hat{a}_-(\ell) \hat{H}_{\ell+1} , \quad \hat{a}_+(\ell) \hat{H}_\ell = \hat{H}_{\ell+1} \hat{a}_+(\ell) . \quad (103)$$

They imply that if $|\psi\rangle$ is an eigenstate of the Hamiltonian $\hat{H}_{\ell+1}$ with energy E , then $\hat{a}_-(\ell)|\psi\rangle$ is the eigenstate of \hat{H}_ℓ with the same energy. Similarly, if $|\psi\rangle$ is an eigenstate of the Hamiltonian \hat{H}_ℓ with energy E , then $\hat{a}_+(\ell)|\psi\rangle$ is the eigenstate of $\hat{H}_{\ell+1}$ with the same energy.

This implies that the operators $\hat{a}_\pm(\ell)$ play the role of raising and lowering operators with respect to the orbital quantum number ℓ ,

$$\hat{a}_-(\ell) |E, \ell+1\rangle \propto |E, \ell\rangle , \quad \hat{a}_+(\ell) |E, \ell\rangle \propto |E, \ell+1\rangle \quad (104)$$

$\hat{a}_-(\ell)$ is the lowering operators of the orbital quantum number but does not change principle quantum number. The action of $\hat{a}_+(\ell)$ also illustrated by the picture below (see the black arrows).



One physical input to make further progress is to assume that at each energy level, there exist a state with the highest (and finite) orbital quantum number ℓ_{\max} , such that a raising operator acting on this state gives zero

$$\hat{a}_+(\ell_{\max}) \left| E, \ell_{\max} \right\rangle = 0 . \tag{105}$$

In other words, no state with $\ell_{\max} + 1$ exists.

Together with the first equation of Eq. (102), we can obtain the eigenvalue equation for this state

$$\begin{aligned} E \left| E, \ell_{\max} \right\rangle &= \hat{H}_{\ell_{\max}} \left| E, \ell_{\max} \right\rangle = \frac{\hbar^2}{\mu a^2} \left(\hat{a}_-(\ell_{\max}) \hat{a}_+(\ell_{\max}) - \frac{1}{2(\ell_{\max} + 1)^2} \right) \left| E, \ell_{\max} \right\rangle \\ &= -\frac{\hbar^2}{2\mu(\ell_{\max} + 1)^2 a^2} \left| E, \ell_{\max} \right\rangle . \end{aligned} \tag{106}$$

This helps to find the energy eigenvalue

$$E_n = -\frac{\hbar^2}{2n^2\mu a^2} , \tag{107}$$

where we introduce the principle quantum number $n = \ell_{\max} + 1$. This result is consistent with Eq. (71).

This is how W. Pauli managed to derive the energy levels of hydrogen and explain the atomic lines, without the knowledge of the Schrödinger equation!

■ The end.

Chapter 6. Spin

So far in this lecture, we have described the electron as a particle/wave which carries an intrinsic electric charge $q = -e$. In the case of hydrogen atom, this charge dictates the static Colomb potential sourced by the proton, which is used in the Schrödinger equation. All the results derived there, including the hydrogen energy levels, wavefunctions, and even the energy shift in the external magnetic field, are based on the presence of this electric charge, and no others.

In fact, there is more than just the electric charge. The electron also carries another intrinsic quantity, which is the spin (Pauli, 1924; Uhlenbeck and Goudsmit, 1925). Spin is a kind of angular momentum, similar to the orbital angular momentum \vec{L} discussed earlier.¹ Thus it is a vector and has three components. We denote the spin angular momentum operator as $\vec{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ hereafter. When we say an electron has spin, what we mean is that the electron is in an eigenstate state of spin operator(s) (for details see below).

However, there is a fundamental difference between the orbital and spin angular momenta. The orbital angular momentum operator \vec{L} was introduced when we talk about the electron in the hydrogen atom, when it “orbits” around the proton. The corresponding orbital angular momentum eigenstate $|\ell m\rangle$ is determined by the spatial distribution of the electron. In contrast, the existence of electron’s spin has nothing to do with its spatial distribution and does not require the electron to be inside an atom or any potential. Under any circumstances (even if the electron is free, at rest, or moving as a plane wave), where there is no need to introduce \vec{L} , we still need to introduce the concept of spin (in addition to the electric charge), in order to fully describe the electron.

As mentioned above, the spin operator \vec{S} is a three-vector. It satisfies all the general properties of angular momentum operators,

$$\begin{aligned} [\hat{S}_a, \hat{S}_b] &= i\hbar\varepsilon_{abc}\hat{S}_c, \\ [\vec{S}^2, \hat{S}_a] &= 0, \end{aligned} \tag{1}$$

where the indices $a, b, c = x, y, z$. (When the same index appear twice, it is summed over x, y, z implicitly.) Moreover, because spin does not depend on the spatial distribution of the electron, \vec{S} commutates with the \vec{r} , \vec{p} , \vec{L} operators and does not act on the part of wavefunction that is a function of position, $\psi(\vec{r})$.

Due to the above commutation relations, there exist common eigenstates of

¹It is worth emphasizing that the electron spin is not a classical concept and has no correspondance in the classical limit. You are not supposed to naively think of spin as the electron spinning around some axis. It is interesting to read about some history here: <http://lorentz.leidenuniv.nl/history/spin/spin.html>

the \vec{S}^2 and \hat{S}_z operators, which we will call the spin states. They are labeled by quantum numbers s and m_s , respectively. When the \vec{S}^2 and \hat{S}_z operators acting on a $|s m_s\rangle$ state, we can get their eigenvalues

$$\begin{aligned}\vec{S}^2 |s m_s\rangle &= s(s+1)\hbar^2 |s m_s\rangle, \\ \hat{S}_z |s m_s\rangle &= m_s\hbar |s m_s\rangle.\end{aligned}\tag{2}$$

Because \hat{S}_x and \hat{S}_y do not commute with \hat{S}_z , the above spin state $|s m_s\rangle$ is not an eigenstate of them. The spin state satisfies the normalization condition, which under Dirac's bra and ket notation, take the simple form

$$\langle s' m'_s | s m_s \rangle = \delta_{ss'} \delta_{m_s m'_s}\tag{3}$$

Our experience with the orbital angular momentum told us that $\ell = 0, 1, 2, \dots$ must be integers. However, the possible values of s quantum number is broader than those, it can be either an integer or a half-integer (non-negative), $s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$. For given s , the possible values of m_s are $-s, -(s-1), \dots, (s-1), s$. In nature, we have discovered particles with various values of spin s .

- Spin-0: Higgs boson, pions in strong interactions ...
- Spin- $\frac{1}{2}$: electron, proton, neutron ...
- Spin-1: photon ...
- Spin-2: graviton ...

In particular, we will continue to talk about the electron, where $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$ (often called spin-up and spin-down states). The common eigenstates of \vec{S}^2 and \hat{S}_z are denoted by $|\frac{1}{2} m_s\rangle$ with $m_s = \pm\frac{1}{2}$, and they satisfy

$$\begin{aligned}\vec{S}^2 \left| \frac{1}{2} \pm \frac{1}{2} \right\rangle &= \frac{3\hbar^2}{4} \left| \frac{1}{2} \pm \frac{1}{2} \right\rangle, \\ \hat{S}_z \left| \frac{1}{2} \pm \frac{1}{2} \right\rangle &= \pm \frac{\hbar}{2} \left| \frac{1}{2} \pm \frac{1}{2} \right\rangle.\end{aligned}\tag{4}$$

(Some people also denote $|\frac{1}{2} \pm \frac{1}{2}\rangle$ as $|\uparrow\rangle, |\downarrow\rangle$, for simplicity.)

A general spin state (wavefunction) can be written as a linear combination of $|\frac{1}{2} \pm \frac{1}{2}\rangle$, as

$$|\psi_s\rangle = \alpha \left| \frac{1}{2} \frac{1}{2} \right\rangle + \beta \left| \frac{1}{2} - \frac{1}{2} \right\rangle.\tag{5}$$

where α, β are complex numbers in general. If α, β satisfy $\sqrt{|\alpha|^2 + |\beta|^2} = 1$, this state is properly normalized, *i.e.*, $\langle \psi_s | \psi_s \rangle = 1$. The statistical interpretation of wavefunction in quantum mechanics tells that the probability of finding the electron in the spin up (or down) state is $|\alpha|^2$ (or $|\beta|^2$).

6.1. The matrix representation

Here we introduce a useful way of doing calculations involving spin states and operators. Introduce the Pauli matrices $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (6)$$

These 2×2 matrices satisfy the commutation relations

$$\begin{aligned} [\sigma_a, \sigma_b] &= 2i\varepsilon_{abc}\sigma_c, \\ [\vec{\sigma}^2, \sigma_a] &= 0, \end{aligned} \quad (7)$$

with indices $a, b, c = x, y, z$, as well as a couple of simple properties,

$$\vec{\sigma}^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3\mathbb{1}, \quad \sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \mathbb{1}, \quad (8)$$

where $\mathbb{1}$ denotes the 2×2 unit matrix. The above commutation relations are very similar to those of the spin operators, Eq. (1), up to a factor of 2. This comparison suggests the existence of the following matrix representation of operator \vec{S} ,

$$\vec{S} = \frac{\hbar}{2} \vec{\sigma}. \quad (9)$$

At the same time, the spin states also have the column matrix representation

$$\left| \frac{1}{2} \frac{1}{2} \right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \left| \frac{1}{2} -\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (10)$$

The representation of the corresponding bra are row matrices

$$\left\langle \frac{1}{2} \frac{1}{2} \right| = (1 \ 0), \quad \left\langle \frac{1}{2} -\frac{1}{2} \right| = (0 \ 1). \quad (11)$$

These definitions are consistent with the eigenvalue equations Eq. (4) and the normalization condition Eq. (3).

A general spin state (wavefunction) in Eq. (5) can now be written as

$$|\psi_S\rangle = \alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \quad (12)$$

With the matrix definitions of \hat{S}_x and \hat{S}_y , we are able to explicitly work out how they act on a given spin state (also a matrix). For example, we can calculate the average of \hat{S}_x , \hat{S}_y under the state $|\psi_S\rangle$ as

$$\begin{aligned} \langle \psi_S | \hat{S}_x | \psi_S \rangle &= (\alpha^* \ \beta^*) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\hbar}{2} (\alpha^* \beta + \beta^* \alpha) = \hbar \operatorname{Re}(\alpha \beta^*), \\ \langle \psi_S | \hat{S}_y | \psi_S \rangle &= (\alpha^* \ \beta^*) \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = i \frac{\hbar}{2} (-\alpha^* \beta + \beta^* \alpha) = \hbar \operatorname{Im}(\alpha \beta^*). \end{aligned} \quad (13)$$

Both averages are real numbers of course, since \hat{S}_x and \hat{S}_y are hermitian operators. Here one should note, the principle the quantum mechanics dictates that, each time we make a measurement of an hermitian operator under any state, the result we get must be one of its eigenvalues, which in the case of \hat{S}_x or \hat{S}_y is $\pm\hbar/2$. Therefore, the above average value we derive should be interpreted as the average value after making many measurements of the operator under that state $|\psi_S\rangle$.

Another useful exercise is to find out values for α and β such that $|\psi_S\rangle$ is an eigenstate of \hat{S}_x (or \hat{S}_y). Let's focus on the \hat{S}_x operator. Clearly

$$\hat{S}_x|\psi_S\rangle = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \beta \\ \alpha \end{pmatrix} . \quad (14)$$

Noting that $\begin{pmatrix} \beta \\ \alpha \end{pmatrix} = \pm \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ when $\alpha = \pm\beta$. The normalization condition $\sqrt{|\alpha|^2 + |\beta|^2} = 1$ further implies $\alpha = \pm\beta = \sqrt{1/2}$, up to an unphysical common phase factor $e^{i\theta}$ which is set to be 1. Thus we derive

$$\hat{S}_x \begin{pmatrix} \sqrt{1/2} \\ \sqrt{1/2} \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \sqrt{1/2} \\ \sqrt{1/2} \end{pmatrix}, \quad \hat{S}_x \begin{pmatrix} \sqrt{1/2} \\ -\sqrt{1/2} \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} \sqrt{1/2} \\ -\sqrt{1/2} \end{pmatrix} . \quad (15)$$

The two eigenvalues of \hat{S}_x are $\pm\hbar/2$, the same as those of \hat{S}_z . You are encouraged to work out the eigenstates and eigenvalues of \hat{S}_y operator as an exercise.

6.2. A few properties of the Pauli matrices

Below the indices $a, b, c = x, y, z$. When the same index appear twice, it is summed over x, y, z implicitly.

$$\begin{aligned} \sigma_a^2 &= \mathbb{1} , \\ \text{Tr}(\sigma_a) &= 0 , \\ \text{Det}(\sigma_a) &= -1 , \\ \sigma_x \sigma_y \sigma_z &= i \mathbb{1} , \\ [\sigma_a, \sigma_b] &\equiv \sigma_a \sigma_b - \sigma_b \sigma_a = 2i \varepsilon_{abc} \sigma_c , \\ \{\sigma_a, \sigma_b\} &\equiv \sigma_a \sigma_b + \sigma_b \sigma_a = 2\delta_{ij} \mathbb{1} , \\ \sigma_a \sigma_b &= \delta_{ij} \mathbb{1} + i \varepsilon_{abc} \sigma_c , \\ (\vec{\sigma} \cdot \vec{A})(\vec{\sigma} \cdot \vec{B}) &= \vec{A} \cdot \vec{B} + i \vec{\sigma} \cdot (\vec{A} \times \vec{B}) , \\ e^{i\vec{\sigma} \cdot \vec{A}} &= \cos |\vec{A}| + i \frac{\vec{\sigma} \cdot \vec{A}}{|\vec{A}|} \sin |\vec{A}| , \\ e^{i\sigma_z \theta} &= \cos \theta + i \sigma_z \sin \theta . \end{aligned} \quad (16)$$

Define ladder operators

$$\hat{S}_{\pm} \equiv \hat{S}_x \pm i\hat{S}_y = \frac{1}{2}(\sigma_x \pm i\sigma_y) . \quad (17)$$

It is straightforward to verify

$$\hat{S}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \hat{S}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad (18)$$

thus

$$\begin{aligned} \hat{S}_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 \\ 0 \end{pmatrix} = 0, & \hat{S}_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \\ \hat{S}_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 \\ 1 \end{pmatrix}, & \hat{S}_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= \begin{pmatrix} 0 \\ 0 \end{pmatrix} = 0. \end{aligned} \quad (19)$$

6.3. Adding the spin wavefunction to hydrogen

Now that we know electron has spin and is also described by a spin wavefunction. Let us consider the hydrogen atom again. The question here is how to write down a complete wavefunction of the electron that contains both information about its spatial distribution (described by $\psi_{m\ell m}(\vec{r})$ or the ket $|n\ell m\rangle$) and the information about its spin (described by $|\frac{1}{2} m_s\rangle$). Consider the same Hamiltonian as before,

$$\hat{H}_0 = \frac{\vec{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r}. \quad (20)$$

Although we introduced the electron spin, it does not modify the Hamiltonian (at this leading order[†]).

The key here is to notice that the spin operators \vec{S}^2 , \vec{S}_z commutes with \hat{H} , \vec{L}^2 and \hat{L}_z operators. Therefore, if we multiply $|\frac{1}{2} m_s\rangle$ which is the common eigenstate of \vec{S}^2 , \vec{S}_z , with $|n\ell m\rangle$, which is the common eigenstate of \hat{H} , \vec{L}^2 and \hat{L}_z , the product state

$$|n\ell m m_s\rangle \equiv |n\ell m\rangle \left| \frac{1}{2} m_s \right\rangle, \quad (21)$$

will be a common eigenstate of all these operators. It is properly normalized,

$$\langle n'\ell' m' m'_s | n\ell m m_s \rangle = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'} \delta_{m_s m'_s}. \quad (22)$$

Eq. (21) can be written in the matrix form

$$\left| n\ell m \frac{1}{2} \right\rangle = \begin{pmatrix} |n\ell m\rangle \\ 0 \end{pmatrix}, \quad \left| n\ell m -\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ |n\ell m\rangle \end{pmatrix}. \quad (23)$$

Clearly, introducing the spin wavefunction does not affect the spatial distribution of the electron. With the above Hamiltonian operator, it is obvious that the energy levels of the hydrogen atom do not change, *i.e.*,

$$\hat{H}_0 |n\ell m m_s\rangle = E_n |n\ell m m_s\rangle, \quad (24)$$

where $E_n = -\mu e^4 / (32\pi^2 \epsilon_0^2 \hbar^2 n^2)$ remains the same as before. As a result, the atomic lines, or the photon energies due to spontaneous de-excitation, remain the same.

Because the operator in charge of atomic transition, $e\vec{A}(\vec{r}) \cdot \vec{p} / \mu$, also commutes with \vec{S}^2 , \vec{S}_z , the atomic transitions cannot affect the spin wavefunction. This observation leads to another important “selection rule” for atomic transitions

$$\Delta m_s = 0 . \quad (25)$$

In other words, before and after each atomic transition, the m_s quantum number of the electron state must be the same.

6.4. Pauli exclusion principle

The Pauli exclusion principle (suggested in 1925) states that in a system with more than one electrons, each electron must occupy a different state, and no two electrons can be in the state. The main motivation for Pauli to propose this principle is to understand atoms ($Z > 1$) containing more than one electron.

In the real world, for multi-electron atoms, it was never observed that all the electrons sit in the ground state. Instead, they fill up various energy levels, leading to different elements and the periodic table. This is the origin of chemistry. Physically, it is quite puzzling why an electron would not radiate photon and lower its energy all the way to the ground state.

Pauli conjectured that in addition to the hydrogen quantum numbers n, ℓ, m , there should be a fourth degree of freedom with a new quantum number. This leads to two possibilities for the electron for fixed n, ℓ, m . Now that we know the new quantum number is spin, and electron has spin 1/2, the two possible states corresponds to $m_s = \pm 1/2$. As a result, if you think of the atom states as seats in a theatre. In the ground state $(n, \ell, m) = (1, 0, 0)$, there are two seats for $m_s = \pm 1/2$. For the first excitation $n = 2$, the possible values of ℓ, m allow for four seats, but with the spin quantum number, the number of seats double to eight. One could enumerate further. The Pauli exclusion principle demands that if we fill these seats with electrons, we must follow the rule that at most one electron per seat. Therefore, electrons cannot all sit in the ground state seats with lowest energy. They have to be packed up. Filling the seats up from bottom up leads to the famous periodic table of elements.

As a mathematical formulation of the above description, the total wavefunction of many electron system must be odd (changes its overall sign) under the interchange of any two electrons. We are not elaborating on this further.

The Pauli exclusion principle can be further generalized to the spin-statistics theorem for identical fermions of any type, which leads to the famous Fermi-Dirac

distribution in statistical physics. These have important applications in many branches of modern physics.

6.5. The Paschen-Back effect (again)

The real world is less simple (and more fun) than the conclusion of chapter 6.3. Once we introduce the spin, it does also introduce other ways for electron to interact. There are new terms involving the electron spin that need to be added to the leading order Hamiltonian \hat{H}_0 . The presence of these terms will eventually modify the energy levels and atomic lines. The magnitude of these modifications is typically small and they act as small corrections to the leading order results derived based on \hat{H}_0 . In other words, the basic structure of the hydrogen atom solutions still remain the same, up to these corrections. In the next sections, we will discuss such corrections, in a more intuitive but less rigorous way. There is the approach of systematically evaluating these corrections by using the perturbation theory, that will be detailed in later courses PHYS 4047 and 4708.

Let us revisit the Paschen-Back effect (1921) discussed in previous chapter, where we consider the hydrogen atom in an external homogeneous magnetic field, $\vec{B} = B\hat{z}$, and we have introduced a new interacting Hamiltonian

$$\Delta\hat{H} = \frac{eB}{2\mu}\hat{L}_z = \frac{e}{2\mu}\vec{B} \cdot \vec{L} . \quad (26)$$

Now that we introduced the spin, there will be another similar term, with \vec{L} replaced by \vec{S} ,

$$\Delta\hat{H} = \frac{eB}{\mu}\hat{S}_z = \frac{e}{\mu}\vec{B} \cdot \vec{S} . \quad (27)$$

Note a factor of 2 difference in the denominator.

You may ask why. These terms are not just added by hand. Indeed, they can be derived from relativistic quantum mechanics, where the electron obeys a more fundamental Dirac equation which was invented to include its spin degree of freedom. The Schrödinger equation with \hat{H}_0 plus these correction terms are the low energy limit of the Dirac equation. We will not elaborate on this further.

The total Hamiltonian, after including Eqs. (26) and (27), takes the form

$$\hat{H} = \hat{H}_0 + \frac{eB}{2\mu} \left(\hat{L}_z + 2\hat{S}_z \right) . \quad (28)$$

The extra terms proportional to B will cause a shift to the hydrogen energy levels. To evaluate the shift, we make the approximation that the hydrogen atom wavefunctions are assumed unaffected by the magnetic field at leading order (see

remarks on page 6) and they still takes the form Eq. (21),

$$|n\ell m m_s\rangle = |n\ell m\rangle \left| \frac{1}{2} m_s \right\rangle . \quad (29)$$

It is important to note that after adding the new term $\Delta\hat{H}$, the total Hamiltonian operator still commutes with \vec{L} and \vec{S} . As a result, the $|n\ell m m_s\rangle$ states are still the common eigenstate of the operators, \hat{H} , \vec{L}^2 , \hat{L}_z , \vec{S}^2 and \hat{S}_z .

It is straightforward to write down the time-independent Schrödinger equation,

$$\hat{H} |n\ell m m_s\rangle = \left(E_n + \frac{eB}{2\mu} (m + 2m_s) \right) |n\ell m m_s\rangle . \quad (30)$$

The shift in energy caused by the magnetic field is

$$\Delta E_{n\ell m m_s} = \frac{e\hbar B}{2\mu} (m + 2m_s) , \quad (31)$$

which are dictated by the corresponding magnetic quantum numbers. Like m , m_s is also a magnetic quantum number because it contributes to the energy shift in the presence of an external magnetic field.

Because electron has spin $\frac{1}{2}$, depending the value of $m_s = \pm\frac{1}{2}$, the picture of energy level splitting for atomic transition ($2P \rightarrow 1S$) becomes the following. The energy shift to each level is

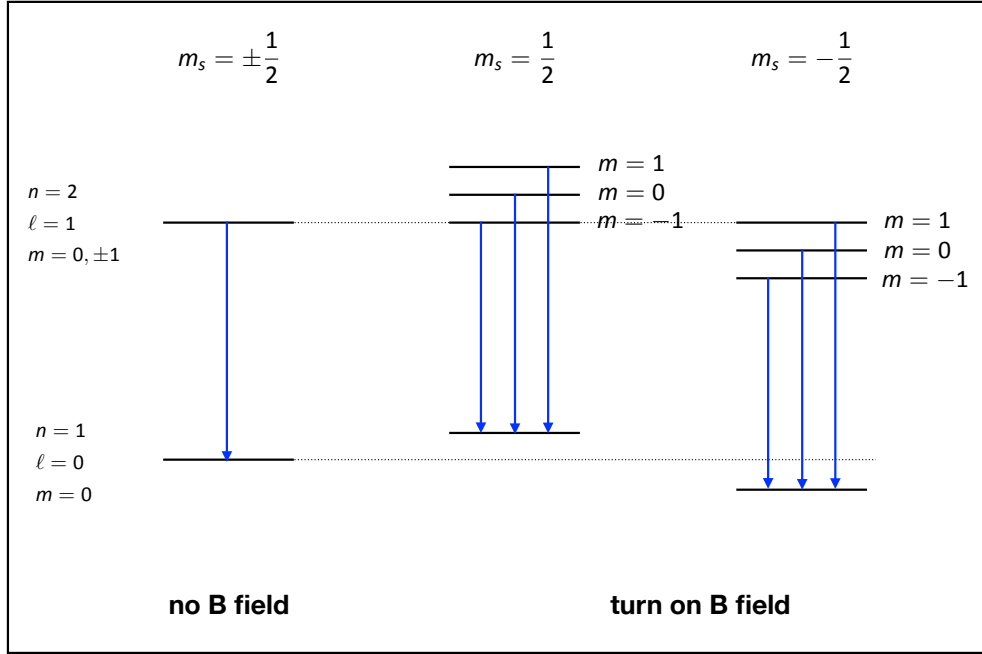
$$\begin{aligned} \Delta E_{100 \pm \frac{1}{2}} &= \pm \frac{e\hbar B}{2\mu} , \\ \Delta E_{211 \frac{1}{2}} &= \frac{e\hbar B}{\mu} , & \Delta E_{210 \frac{1}{2}} &= \frac{e\hbar B}{2\mu} , & \Delta E_{21-1 \frac{1}{2}} &= 0 , \\ \Delta E_{211 -\frac{1}{2}} &= 0 , & \Delta E_{210 -\frac{1}{2}} &= -\frac{e\hbar B}{2\mu} , & \Delta E_{21-1 -\frac{1}{2}} &= -\frac{e\hbar B}{\mu} . \end{aligned} \quad (32)$$

Because of the $\Delta m_s = 0$ selection rule, the three atomic lines remain the same as the previous result (Chapter 5) without including the spin effects. (But the description is more realistic here, of course.)

Quantitatively, the above energy shifts are of order $e\hbar B/\mu$, which for $B = 10$ Tesla and $\mu \simeq m_e = 0.511 \text{ MeV}/c^2$, is

$$\Delta E \sim e\hbar B/m_e \simeq 1.2 \times 10^{-3} \text{ eV} , \quad (33)$$

which is indeed much smaller than the $2P-1S$ binding energy difference ($\sim 10 \text{ eV}$).



Before closing this section, I want to introduce another concept (terminology) based on the interacting Hamiltonian Eq. (27), which is the magnetic dipole moment of the electron. It is a three-vector,

$$\vec{\mu} = -g \frac{e}{2m_e} \vec{S}, \quad (34)$$

where we introduce the g -factor, $g = 2$. The interacting Hamiltonian Eq. (27) can also be written as (with \vec{B} is along the z -direction, and the reduced mass $\mu \simeq m_e$)

$$\Delta \hat{H} \simeq -\vec{B} \cdot \vec{\mu} = -B \hat{\mu}_z. \quad (35)$$

Because the eigenvalues of \hat{S}_z are $m_s \hbar = \pm \frac{1}{2} \hbar$. It is also useful to define the Bohr magneton

$$\mu_B = \frac{e \hbar}{2m_e} \simeq 5.8 \times 10^{-11} \text{ MeV/Tesla}. \quad (36)$$

Thus we can also write $\Delta \hat{H} = \pm g \mu_B B$.

One more word about the g -factor at the modern research frontier. At the level of discussion above, $g = 2$. At more fundamental level, the value of g receives radiative corrections, which makes it slightly larger than 2 (at $\sim 10^{-3}$ level). Nowadays, theorists have calculated the g -factor up to very high precision. Meanwhile, experimentalists are also clever enough to measure g to very high precision. The theory and experiment agree well with each other, at the impressive level of

$$g^{\text{SM}} - g^{\text{EXP}} \sim 10^{-12}. \quad (37)$$

It serves as one of the important precision tests of the fundamental theories in particle physics.

6.6. Spin precession

Another interesting quantum mechanical effect of electron spin is the precession in external magnetic field. We consider an unbounded electron in this case, not in an atom. With a homogeneous magnetic field in the z -direction, the Hamiltonian can be written as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{H}_{\text{int}} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{geB}{2m_e}\hat{S}_z, \quad (38)$$

where $g = 2$. Let's consider the electron is at rest and we are only interested in its spin state, which takes the following form at time $t = 0$

$$|\psi_S(0)\rangle = \begin{pmatrix} \cos \theta \\ \sin \theta \end{pmatrix}. \quad (39)$$

Because of the above interaction term, such a state is no longer a stationary state. We can find how it evolves with time by solving the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi_S(t)\rangle = \hat{H}_{\text{int}}|\psi_S(t)\rangle, \quad (40)$$

or

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_+(t) \\ c_-(t) \end{pmatrix} = \Omega\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} c_+(t) \\ c_-(t) \end{pmatrix}, \quad (41)$$

where $\Omega = geB/(2m_e)$.

With the initial conditions in Eq. (39), we can derive

$$c_+(t) = \cos \theta e^{-i\Omega t/2}, \quad c_-(t) = \sin \theta e^{i\Omega t/2}, \quad (42)$$

or

$$|\psi_S(t)\rangle = \begin{pmatrix} \cos \theta e^{-i\Omega t/2} \\ \sin \theta e^{i\Omega t/2} \end{pmatrix}. \quad (43)$$

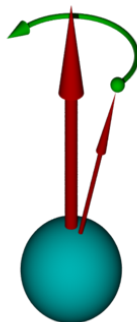
The spin up and down states develops opposite exponential phase factors.

We can calculate the average of the total spin operator \vec{S} under this periodi-

cally evolving state, which gives

$$\begin{aligned}
 \langle \psi_S(t) | \hat{S}_z | \psi_S(t) \rangle &= \begin{pmatrix} \cos \theta e^{-i\Omega t/2} & \sin \theta e^{i\Omega t/2} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \cos \theta e^{-i\Omega t/2} \\ \sin \theta e^{i\Omega t/2} \end{pmatrix} \\
 &= \frac{\hbar}{2} \cos 2\theta , \\
 \langle \psi_S(t) | \hat{S}_x | \psi_S(t) \rangle &= \begin{pmatrix} \cos \theta e^{-i\Omega t/2} & \sin \theta e^{i\Omega t/2} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos \theta e^{-i\Omega t/2} \\ \sin \theta e^{i\Omega t/2} \end{pmatrix} \\
 &= \frac{\hbar}{2} \sin 2\theta \cos \Omega t , \\
 \langle \psi_S(t) | \hat{S}_y | \psi_S(t) \rangle &= \begin{pmatrix} \cos \theta e^{-i\Omega t/2} & \sin \theta e^{i\Omega t/2} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \cos \theta e^{-i\Omega t/2} \\ \sin \theta e^{i\Omega t/2} \end{pmatrix} \\
 &= \frac{\hbar}{2} \sin 2\theta \sin \Omega t ,
 \end{aligned} \tag{44}$$

Therefore, we can think of the spin vector of this state is precessing around the z -axis with a frequency Ω (see picture below). However, one could keep in mind the statistical interpretation of wavefunction in quantum mechanics. Each time when we make a measurement of spin in the x , y or z direction, we will get either $+\hbar/2$ or $-\hbar/2$, *i.e.*, one of its eigenvalues. The above results are interpreted as the average value of the corresponding operator after we make many measurements at a given time t . The time dependence of an average value $\langle \hat{S}_a \rangle$ means the distribution of $\pm\hbar/2$ from the many measurements varies with time.



It is worth looking at the spin precession frequency again,

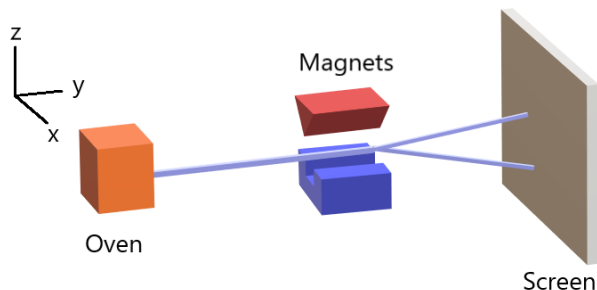
$$\Omega = \frac{geB}{2m_e} . \tag{45}$$

In classical physics, a magnetic dipole $\vec{\mu}_c$ can be created due to a circular current, *e.g.*, if you really think of the electron as a rotating charged ball. This leads to a classical angular momentum \vec{L}_c . When we put this classical dipole in an external magnetic field \vec{B} , it precesses because of a torque $\vec{\tau} = \vec{r} \times \vec{F} = d\vec{L}_c/dt = \vec{\mu}_c \times \vec{B}$. For

a point charge orbiting on a circle with radius r , the magnetic dipole is equal to the current times area, $\mu_c = (\pi r^2)I = (\pi r^2)(dQ/dt) = (\pi r^2)ev/(2\pi r) = evr/2$. The magnitude of angular momentum is equal to mvr , thus $\vec{\mu}_c = \frac{e}{2m}\vec{L}$. This leads to $d\vec{L}_c/dt = (e/2m)\vec{L} \times \vec{B}$, and a precession frequency equal to $eB/(2m)$. Compared to Eq. (45), there is a factor of 2 difference (because $g = 2$)! Or we could say that, the magnetic moment of an electron is approximately twice what it should be in classical mechanics.

6.7. The Stern-Gerlach experiment

The Stern-Gerlach experiment (1922) provides a strong experimental support for the existence of the electron spin (or in turn its magnetic dipole moment). The experimental setup is shown in the picture below.



In this picture, the electrons are freed by the heat in an oven (the red block) and focused to travel through a magnetic field (between the red and blue magnets) and finally reach the screen to be recorded. The magnetic field is instrumented to be inhomogeneous, of the form

$$\vec{B} = (B_0 + \gamma z)\hat{z} - \gamma x\hat{x} . \quad (46)$$

where B_0, γ are constants. The component of \vec{B} in the x -direction has to there because the Maxwell's equations state that $\nabla \cdot \vec{B} = 0$, although it does not play an essential role in the physics result discussed below.

Here we are most interested in the quantum effect due to the electron spin, rather than its spatial distribution (the wave behavior). Therefore, the electrons are made with high enough momenta such that its de Broglie wavelength is much smaller than the length scale between the magnets. As a result the interference/diffraction effect from the wave nature (c.f. the double-slit experiment) do not manifest. In other words, we are able to see the trajectory of the electron like a classical moving particle in this case.

The quantum effect is due to the electron spin. Including the spin- \vec{B} -field interaction, the total Hamiltonian takes the form (note there is no orbital angular

momentum here because electrons are not in atoms)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + \frac{e}{m_e}\vec{B} \cdot \vec{S} = -\frac{\hbar^2}{2m_e}\nabla^2 + \frac{e}{m_e} \left((B_0 + \gamma z)\hat{S}_z - \gamma x\hat{S}_x \right) . \quad (47)$$

Effectively, we can consider the second term as a potential energy term $V(\vec{r})$.

Apply the Ehrenfest theorem,

$$\frac{d\langle \vec{p} \rangle}{dt} = -\langle \nabla V(\vec{r}) \rangle , \quad (48)$$

and focus on the z -direction,

$$\frac{d\langle \hat{p}_z \rangle}{dt} = -\left\langle \frac{d}{dz} V(\vec{r}) \right\rangle = -\frac{e}{m_e} \gamma \langle \hat{S}_z \rangle . \quad (49)$$

As mentioned above, we work in the limit where the electron travels like a classical particle, hence, Eq. (49) can be understood as a “force” exerted on the electron in the z -direction (Newton’s law tells $F = ma = dp/dt$).

For each electron passing through the experiment, the measurement of \hat{S}_z returns one of its eigenvalues $m_s \hbar = \pm \frac{\hbar}{2}$. Depending on the sign of the m_s quantum number, the force acting on this electron points to either $+z$ or $-z$ direction. As a result, the electron’s trajectory will bend either upward or downward in the z -direction. On the screen, we will see the electron to arrive at locations either above or below the horizontal x - y plane. When we inject many electrons through the Stern-Gerlach experiment, the electron hits on the screen will distribute discretely in two regions (note NOT continuous). This is indeed what is observed experimentally!

Looking back, if we had not introduced the electron spin and its interaction with the magnetic field, we would have concluded that the electrons just travel in straight lines and do not bend away from the x - y plane. The striking signals observed in the Stern-Gerlach experiment offers a strong evidence supporting the existence of the electron spin.

6.8. Spin-orbit coupling and hydrogen fine structure

We have discussed a few new terms in the Hamiltonian when we go beyond the leading order, for the electron spin to interact with external magnetic field. In addition to those, even in the absence of any external field, there still exists an interaction term for electron inside the atom. It is the coupling between the spin and orbital angular momentum,

$$\Delta \hat{H} = \frac{1}{2\mu^2 c^2} \frac{e^2}{4\pi\epsilon_0 r^3} \vec{S} \cdot \vec{L} , \quad (50)$$

where c is the speed of light. This is called the spin-orbit coupling term which could also be derived from the Dirac equation. It contributes to the fine-structure splittings of hydrogen energy levels that has been measured experimentally.

The total Hamiltonian is now

$$\hat{H} = \hat{H}_0 + \Delta\hat{H}, \quad \hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}. \quad (51)$$

Unlike the spin- B -field interaction discussed earlier, Here, the presence of spin-orbit coupling has a more dramatic impact on the structure of hydrogen atom solutions, *i.e.*, the organization of energy eigenstates and eigenvalues. The key point is that with the $\vec{S} \cdot \vec{L}$ term, the total Hamiltonian operator \hat{H} no longer commutates with \vec{L} or \vec{S} ,

$$[\hat{H}, \vec{S}] \neq 0, \quad [\hat{H}, \vec{L}] \neq 0. \quad (52)$$

This means the average of \vec{S} or \vec{L} operators are not conserved quantities. Before, we found common eigenstates of \hat{H} , \vec{L}^2 , \hat{L}_z , \vec{S}^2 and \hat{S}_z . operators. We cannot do the same any more. The $|nlmm_s\rangle$ state derived in the absence of spin-orbit coupling are no longer valid stationary states. More explicitly, if we insist acting the \hat{H} on the $|nlmm_s\rangle$

$$\hat{H} |nlmm_s\rangle = E_n |nlmm_s\rangle + |\text{other states}\rangle, \quad (53)$$

the righthand side includes the leading order result $E_n |nlmm_s\rangle$ when $\hat{H} = \hat{H}_0$, plus a linear combination of several states with quantum numbers other than n, ℓ, m, m_s . The latter are caused by the spin-orbit coupling $\Delta\hat{H}$. This is not an eigenvalue equation of \hat{H} for us to find its energy eigenvalues, because we are using the wrong states, *i.e.*, $|nlmm_s\rangle$ is not the correct energy eigenstate of the total Hamiltonian. We need a new pathway forward.

To proceed, we notice that although neither \vec{S} nor \vec{L} commutates with \hat{H} , their sum do. Let us define the total angular momentum operator

$$\vec{J} \equiv \vec{S} + \vec{L}. \quad (54)$$

Here \vec{J} satisfies all the basic properties of angular momentum, *i.e.*, $[J_a, J_b] = i\hbar\epsilon_{abc}J_c$, and $[\vec{J}^2, \hat{J}_a] = 0$. Hereafter, we denote the total angular momentum quantum numbers as j and m_j .

It is straightforward to verify that

$$[\hat{H}, \vec{J}] = 0. \quad (55)$$

This suggests that we could find common eigenstates of \hat{H} , \vec{J}^2 , \hat{J}_z . In addition, we can also verify that the \vec{L}^2 operator still commutates with all these operators (although \vec{L} does not). Therefore, common eigenstates should exist for the following set of operators

$$\hat{H}, \quad \vec{J}^2, \quad \hat{J}_z, \quad \vec{L}^2. \quad (56)$$

It is our following task to derive the form of such common eigenstates.

We will use the Pauli matrix representation of spin operator $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$. The total angular momentum operator can be written as $\vec{J} = \frac{\hbar}{2}\vec{\sigma} + \vec{L}\mathbb{1}$. In this case, the common eigenstate takes the column matrix form

$$|\psi\rangle = \begin{pmatrix} a|\ell m\rangle \\ b|\ell' m'\rangle \end{pmatrix}, \quad (57)$$

where the coefficients a, b are to be determined. Each component of the column matrix is proportional to a spherical harmonic function. Note that we have left out the quantum number n which has to do with the radial coordinate r dependence. At the moment, we can think of the r dependence are carried by a, b implicitly. This state is properly normalized if

$$\int_0^\infty r^2 dr \sqrt{a(r)^2 + b(r)^2} = 1. \quad (58)$$

In such a state, the spin information is encoded in the two components of the column matrix, whereas the spatial (angular) distribution information is encoded in the orbital angular momentum eigenstates $|\ell m\rangle$ and $|\ell' m'\rangle$.

- First, we require $|\psi\rangle$ to be the eigenstate of the operator \vec{L}^2 . This could be fulfilled if $\ell = \ell'$, so that

$$\vec{L}^2|\psi\rangle = \begin{pmatrix} a\vec{L}^2|\ell m\rangle \\ b\vec{L}^2|\ell m'\rangle \end{pmatrix} = \begin{pmatrix} a\ell(\ell+1)\hbar^2|\ell m\rangle \\ b\ell(\ell+1)\hbar^2|\ell m'\rangle \end{pmatrix} = \ell(\ell+1)\hbar^2|\psi\rangle, \quad (59)$$

- Second we require $|\psi\rangle$ to be eigenstate of $\hat{J}_z = \frac{\hbar}{2}\sigma_z + \hat{L}_z\mathbb{1}$. Acting \hat{J}_z on $|\psi\rangle$ leads to

$$\begin{aligned} \hat{J}_z|\psi\rangle &= \begin{pmatrix} \hat{L}_z + \hbar/2 & 0 \\ 0 & \hat{L}_z - \hbar/2 \end{pmatrix} \begin{pmatrix} a|\ell m\rangle \\ b|\ell m'\rangle \end{pmatrix} \\ &= \begin{pmatrix} a(\hat{L}_z + \hbar/2)|\ell m\rangle \\ b(\hat{L}_z - \hbar/2)|\ell m'\rangle \end{pmatrix} \\ &= \begin{pmatrix} a(m+1/2)\hbar|\ell m\rangle \\ b(m'-1/2)\hbar|\ell m'\rangle \end{pmatrix}. \end{aligned} \quad (60)$$

Clearly, if $m' = m + 1$, then $|\psi\rangle$ is an eigenstate of \hat{J}_z ,

$$\hat{J}_z|\psi\rangle = \begin{pmatrix} a(m+1/2)\hbar|\ell m\rangle \\ b(m+1/2)\hbar|\ell m+1\rangle \end{pmatrix} = (m+1/2)\hbar|\psi\rangle. \quad (61)$$

This determines the magnetic quantum number of total angular momentum

$$m_j\hbar = (m+1/2)\hbar = (m'-1/2)\hbar. \quad (62)$$

- Next, require $|\psi\rangle$ to be eigenstate of \vec{J}^2 . This operator takes the following matrix form

$$\begin{aligned}\vec{J}^2 &= (\vec{L} + \vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{S} \cdot \vec{L} \\ &= (\vec{L}^2 + 3\hbar^2/4)\mathbb{1} + \hbar(\sigma_x \hat{L}_x + \sigma_y \hat{L}_y + \sigma_z \hat{L}_z) \\ &= \begin{pmatrix} \vec{L}^2 + 3\hbar^2/4 + \hbar \hat{L}_z & \hbar \hat{L}_- \\ \hbar \hat{L}_+ & \vec{L}^2 + 3\hbar^2/4 - \hbar \hat{L}_z \end{pmatrix},\end{aligned}\quad (63)$$

where $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$. Requiring $\vec{J}^2|\psi\rangle = \lambda\hbar^2|\psi\rangle$ amounts to

$$\begin{pmatrix} \vec{L}^2 + 3\hbar^2/4 + \hbar \hat{L}_z & \hbar \hat{L}_- \\ \hbar \hat{L}_+ & \vec{L}^2 + 3\hbar^2/4 - \hbar \hat{L}_z \end{pmatrix} \begin{pmatrix} a|\ell m\rangle \\ b|\ell m + 1\rangle \end{pmatrix} = \lambda\hbar^2 \begin{pmatrix} a|\ell m\rangle \\ b|\ell m + 1\rangle \end{pmatrix}.\quad (64)$$

Using the relation

$$\hat{L}_\pm|\ell m\rangle = \hbar\sqrt{(\ell \mp m)(\ell \pm m + 1)}|\ell m \pm 1\rangle,\quad (65)$$

we get two coupled linear equations of a and b

$$\begin{cases} (\ell(\ell + 1) + \frac{3}{4} + m - \lambda) a + \sqrt{(\ell - m)(\ell + m + 1)}b = 0 \\ \sqrt{(\ell + m)(\ell - m + 1)}a + (\ell(\ell + 1) + \frac{3}{4} - (m + 1) - \lambda) b = 0 \end{cases}.\quad (66)$$

For these equations to have nontrivial solution $a, b \neq 0$, we need

$$\det \begin{pmatrix} (\ell(\ell + 1) + \frac{3}{4} + m - \lambda) & \sqrt{(\ell - m)(\ell + m + 1)} \\ \sqrt{(\ell + m)(\ell - m + 1)} & (\ell(\ell + 1) + \frac{3}{4} - (m + 1) - \lambda) \end{pmatrix} = 0,\quad (67)$$

which leads to two possible values of λ ,

$$\lambda = (\ell + 1/2)(\ell + 3/2), \quad \lambda = (\ell - 1/2)(\ell + 1/2).\quad (68)$$

If we define $\lambda = j(j + 1)$, then the j quantum number have two possible values

$$j = \ell \pm 1/2.\quad (69)$$

The eigenvalue of the \vec{J}^2 operator is $j(j + 1)\hbar^2$. Because the eigenvalues of \vec{J}^2 cannot be negative, the $j = \ell - 1/2$ solution is only possible if $\ell \geq 1$. The possible values of m_j are

$$m_j = -j, -(j - 1), \dots, (j - 1), j.\quad (70)$$

There are $2j + 1$ values.

With the above values of λ , we can use Eq. (66) to derive the ratio of a/b , which is

$$\begin{aligned} \frac{a}{b} &= \sqrt{\frac{\ell + m + 1}{\ell - m}}, & \text{for } j = \ell + 1/2 \\ \frac{a}{b} &= -\sqrt{\frac{\ell - m}{\ell + m + 1}}, & \text{for } j = \ell - 1/2 \end{aligned} \quad (71)$$

To summarize, the above list of exercises leads to the following form of $|\psi\rangle$ as common eigenstate of \vec{J}^2 , \hat{J}_z and \vec{L}^2 operators. For $j = \ell + 1/2$,

$$|\psi\rangle = \frac{R(r)}{\sqrt{2j}} \begin{pmatrix} \sqrt{j + m_j} |j - \frac{1}{2} \ m_j - \frac{1}{2}\rangle \\ \sqrt{j - m_j} |j - \frac{1}{2} \ m_j + \frac{1}{2}\rangle \end{pmatrix}. \quad (72)$$

For $j = \ell - 1/2$,

$$|\psi\rangle = \frac{R(r)}{\sqrt{2(j+1)}} \begin{pmatrix} -\sqrt{j - m_j + 1} |j + \frac{1}{2} \ m_j - \frac{1}{2}\rangle \\ \sqrt{j + m_j + 1} |j + \frac{1}{2} \ m_j + \frac{1}{2}\rangle \end{pmatrix}. \quad (73)$$

Here we factorize the r dependence in the function $R(r)$. These states are properly normalized if $\int r^2 dr |R(r)|^2 = 1$.

Finally, we are ready to determine $R(r)$ and the energy eigenvalue, by insert the above $|\psi\rangle$ solutions to the time-independent Schrödinger equation, $\hat{H}|\psi\rangle = E|\psi\rangle$. Let us be specific and consider the S -wave ($\ell = 0$) and P -wave ($\ell = 1$) states.

For $\ell = 0$, the only possible value of j is $1/2$. In this case the Schrödinger equation takes the form

$$\left(-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{e^2}{4\pi\epsilon_0 r} \right) R(r) = ER(r). \quad (74)$$

This is identical to the Schrödinger equation when we solved the hydrogen atom in Chapter 5 with $\ell = 0$. The spin-orbit coupling term does not show up because the operator $\vec{S} \cdot \vec{L}$ acting on the $\ell = 0$ state gives zero. As before, the solutions of $R(r)$ are the Laguerre polynomials. The energy eigenvalue of the ground state ($1S$ state) remains the same, $E_1 = -13.6 \text{ eV}$.

For $\ell = 1$, there are two possible value of $j = 1/2, 3/2$, and there are two Schrödinger equations, respectively,

$$\left(-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{\hbar^2}{\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r} \pm \frac{e^2 \hbar^2}{16\pi\epsilon_0 c^2 \mu^2 r^3} \right) R(r) = ER(r), \quad (75)$$

If the last term (due to spin-orbit coupling) in the bracket was zero, then we would be also back to the leading order Schrödinger equation in Chapter 5 with $\ell = 1$,

which would give identical wavefunction and energy eigenvalues. In particular for the first excited state with $\ell = 1$ ($2P$ state), the energy would be $E_2 = -3.4\text{ eV}$ with the spin-up and spin-down states degenerate. However, the presence of the spin-orbit coupling will split the $2P$ state into two levels, labelled by $j = 1/2$ and $3/2$. The two states are usually referred to as the $2P_{1/2}$ and $2P_{3/2}$ states.

Here we will not solve the equations (which requires perturbative methods, the task of PHYS 4707 and 4708), but give a rough estimate of the new term,

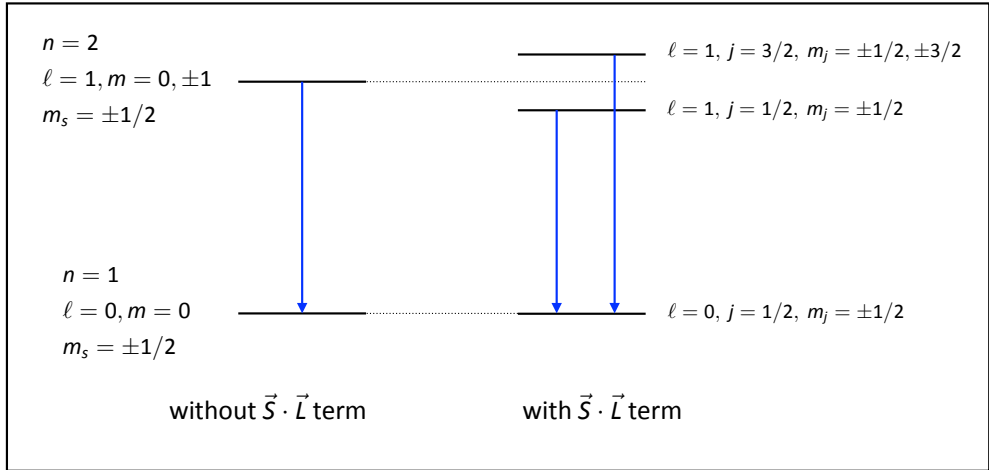
$$\Delta E \simeq \pm \frac{e^2 \hbar^2}{16\pi\epsilon_0 c^2 m_e^2 a^3} \simeq \pm \frac{\alpha \hbar^3}{4cm_e^2 a^3}, \tag{76}$$

where we have used twice of the Bohr radius $2a$ to replace the r in the denominator of the spin-orbit term. Using $m_e = 0.511\text{ MeV}/c^2$, and $\hbar c = 1.97 \times 10^{-13}\text{ MeV} \cdot \text{m}$, we get

$$\Delta E \simeq \pm 5 \times 10^{-5}\text{ eV}. \tag{77}$$

This is much lower than the leading order binding energy (of order eV).

This leads to the following picture of atomic lines for spontaneous de-excitation. The $2P \rightarrow 1S$ transition line splits into double lines. This is observed experimentally as technology progresses. In the history, the discovery of double line first motivated the concept of electron having spin. The agreement between theory calculation and experimental finding provide another strong evidence supporting this idea.

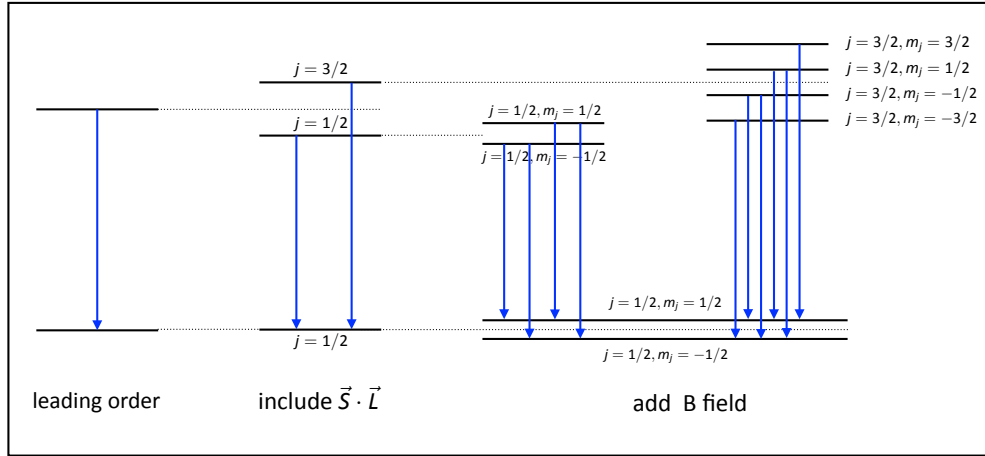


6.9. Anomalous Zeeman effect

It is more fun to turn on the external magnetic field, and taken into account of both the $\vec{S}-\vec{B}$, $\vec{L}-\vec{B}$ interactions and the spin-orbital coupling. If the strength of magnetic field is adjusted so that the energy shift calculated in Eq. (32) is comparable to that in Eq. (76), we see the rich atomic transition lines in the following

plot. We will not go to the details of it, but only comment that, intuitively, compared to the previous plot, adding the magnetic field will further split the states with different magnetic quantum number m_j .

Selection rules: $\Delta\ell = \pm 1$, $\Delta j = 0, \pm 1$, $\Delta m_j = 0, \pm 1$.



6.10. Clebsch-Gordan coefficients

In section 6.7, we introduced the total angular momentum operator \vec{J} and the corresponding eigenstates. This is especially useful in the presence of the spin-orbit coupling. In Eqs. (72) and (73), we have derived how to combine the orbital angular momentum eigenstates $|\ell m\rangle$ and the spin eigenstates $|1/2 \pm 1/2\rangle$ into the total angular momentum eigenstates $|j m_j\rangle$.

For $j = \ell + \frac{1}{2}$ case (let's leave out the radial coordinate r dependence which is an overall factor),

$$\begin{aligned}
 |j m_j\rangle &= \frac{1}{\sqrt{2j}} \left(\sqrt{j + m_j} \left| j - \frac{1}{2} m_j - \frac{1}{2} \right\rangle \right. \\
 &\quad \left. + \sqrt{j - m_j} \left| j - \frac{1}{2} m_j + \frac{1}{2} \right\rangle \right) \\
 &= \sqrt{\frac{j + m_j}{2j}} \left| j - \frac{1}{2} m_j - \frac{1}{2} \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{j - m_j}{2j}} \left| j - \frac{1}{2} m_j + \frac{1}{2} \right\rangle \left| \frac{1}{2} -\frac{1}{2} \right\rangle,
 \end{aligned} \tag{78}$$

whereas for $j = \ell - \frac{1}{2}$ case

$$\begin{aligned}
 |j m_j\rangle &= \frac{1}{\sqrt{2j+2}} \left(-\sqrt{j - m_j + 1} \left| j + \frac{1}{2} m_j - \frac{1}{2} \right\rangle \right. \\
 &\quad \left. + \sqrt{j + m_j + 1} \left| j + \frac{1}{2} m_j + \frac{1}{2} \right\rangle \right) \\
 &= -\sqrt{\frac{j - m_j + 1}{2j+2}} \left| j + \frac{1}{2} m_j - \frac{1}{2} \right\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{j + m_j + 1}{2j+2}} \left| j + \frac{1}{2} m_j + \frac{1}{2} \right\rangle \left| \frac{1}{2} -\frac{1}{2} \right\rangle.
 \end{aligned} \tag{79}$$

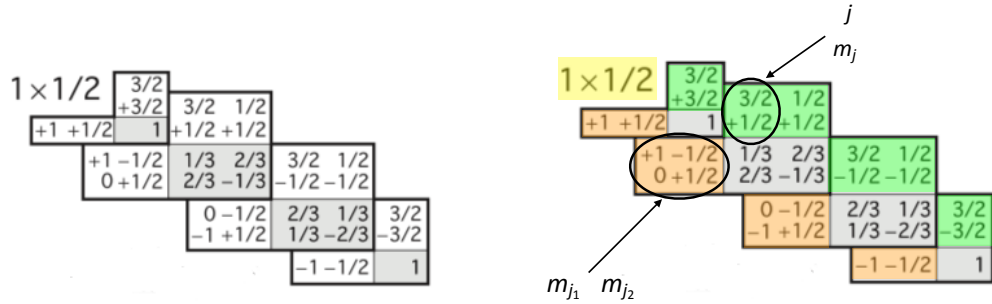
Clearly, for each case, the righthand side sums over all possible m and m_s combinations, with their sum $m + m_s = m_j$ held fixed.

The above examples can be generalized to the following rules for combining two generic angular momentum states with j_1 and j_2 quantum numbers. The total angular momentum quantum number j takes the value $|j_1 - j_2|, |j_1 - j_2| + 1, \dots, |j_1 + j_2|$. Any total angular momentum eigenstate can be decomposed as

$$\begin{aligned}
 |j \ m_j\rangle &= \sum_{m_{j_1}, m_{j_2}} CG_{m_{j_1}, m_{j_2}} |j_1 \ m_{j_1}\rangle |j_2 \ m_{j_2}\rangle \delta_{m_j, m_{j_1} + m_{j_2}} \\
 &= \sum_{m_{j_1}} CG_{m_{j_1}, m_j - m_{j_1}} |j_1 \ m_{j_1}\rangle |j_2 \ m_j - m_{j_1}\rangle,
 \end{aligned}
 \tag{80}$$

where $CG_{m_{j_1}, m_{j_2}}$ are called Clebsch-Gordan (CG) coefficients. They can be derived algebraically using the angular momentum operator properties. What we did in section 6.7 is an explicit example and one of the simplest. For convenience, people have invented the Clebsch-Gordan table to conveniently find these coefficients.

We give a simple example here on how to use the table. The picture in below (left) is part relevant for adding $j_1 = 1$ and $j_2 = 1/2$ states. To better explain it, we color and label it up in the right plot.



To start with, the values of j_1, j_2 are given by the two numbers in yellow shaded background. The possible values for total angular momentum j and m_j are in each column of green shaded regions. For example we can focus on a particular state $j = 3/2$ and $m_j = 1/2$ (in the higher circle), it could be decomposed in two ways, $j_1 = 1, m_{j_1} = 1, j_2 = 1/2, m_{j_2} = -1/2$ or $j_1 = 1, m_{j_1} = 0, j_2 = 1/2, m_{j_2} = 1/2$. The corresponding values of m_{j_1}, m_{j_2} are shown in each row of the orange shaded regions. In this case, they are inside the lower circle. The corresponding CG coefficients are in the gray regions along the same column and row (we need to add square root to each value²). Thus we can write

$$\left| \frac{3}{2} \ \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| 1 \ 1 \right\rangle \left| \frac{1}{2} \ -\frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1 \ 0 \right\rangle \left| \frac{1}{2} \ \frac{1}{2} \right\rangle,
 \tag{81}$$

²When there is a minus sign, take it out of the square root!

This agrees with Eq. (78) where we set $j = 3/2$.

The more complete version of the Clebsch-Gordan table is found at <http://pdg.lbl.gov/2019/reviews/rpp2018-rev-clebsch-gordan-coefs.pdf>. You are encouraged to practice with more examples in order to appreciate the rules of this table. As an exercise, the addition of two spin states ($j_1 = j_2 = 1/2$) could result in total spin $j = 0$ or 1 . Use Eq. (80) and the CG table to find the decomposition of the total spin states $|0\ 0\rangle$, $|1\ 0\rangle$, $|1\ \pm 1\rangle$ into the two electron spin states.

■ The end.

Chapter 7. Topics in 2D Case

In this chapter, we study the solutions to the Schrödinger equation with two space dimensions, and visit a couple of modern topics in quantum mechanics. We first write down the time-independent Schrödinger equation for fixed energy E in the Cartesian coordinate space

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + V(x, y) \right] \psi(x, y) = E\psi(x, y) . \quad (1)$$

How to proceed depends on the form the potential energy $V(x, y)$. Hereafter, we will focus on central potentials, $V = V(r)$, where $r = \sqrt{x^2 + y^2}$. In this case, it is convenient to go to the polar coordinates described by r and $\varphi = \arctan(y/x)$.

In the polar coordinates, the Schrödinger equation takes the form

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} \right) + V(r) \right] \psi(r, \varphi) = E\psi(r, \varphi) . \quad (2)$$

Because the φ dependence in the Hamiltonian only reside in the $\partial^2/\partial\varphi^2$ term, the wavefunction can be factorized into

$$\psi(r, \varphi) = R(r)f(\varphi) , \quad (3)$$

and the above Schrödinger equations can be rewritten as,

$$r^2 E - \frac{r^2}{R(r)} \left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) + V(r) \right] R(r) = -\frac{1}{f(\varphi)} \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \varphi^2} f(\varphi) . \quad (4)$$

Clearly, the lefthand side of the equation only depends on r , whereas the righthand side only depends on φ . And the equation always hold for arbitrary values of r and φ . Thus, both sides must be equal to a constant, C , which is independent of r or φ . This leads to two differential equations, for r and φ , separately.

The equation for φ is easy to solve. It takes the form

$$\frac{\partial^2}{\partial \varphi^2} f(\varphi) + \frac{2\mu C}{\hbar^2} f(\varphi) = 0 . \quad (5)$$

Its general solution is

$$f(\varphi) = A \exp \left(i \sqrt{\frac{2\mu C}{\hbar^2}} \varphi \right) . \quad (6)$$

The function $f(\varphi)$ must satisfy the periodic condition, $f(\varphi) = f(\varphi + 2\pi)$, and the normalization condition $\int_0^{2\pi} f(\varphi) d\varphi = 1$. They fix the form of $f(\varphi)$,

$$f(\varphi) = \sqrt{\frac{1}{2\pi}} e^{im\varphi} , \quad (7)$$

where $m = 0, \pm 1, \pm 2, \dots$, must be integers. In turn, we get

$$C = \frac{m^2 \hbar^2}{2\mu} . \quad (8)$$

With the above value of C , the differential equation for the radial part of the wavefunction $R(r)$ can be written as

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) + \frac{m^2 \hbar^2}{2\mu r^2} + V(r) \right] R(r) = ER(r) . \quad (9)$$

Once the explicit form of $V(r)$ is known, one could proceed solving the equation and derive the energy eigenvalue E and the corresponding eigenfunction $R(r)$.

6.1. Isotropic harmonic oscillator

Let us consider the first concrete problem, a two dimensional isotropic harmonic oscillator, where the potential energy takes form

$$V(r) = \frac{1}{2} \mu \omega^2 r^2 . \quad (10)$$

Plugging it into Eq. (9), we get

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) + \frac{m^2 \hbar^2}{2\mu r^2} + \frac{1}{2} \mu \omega^2 r^2 \right] R(r) = ER(r) . \quad (11)$$

Defining $k = \sqrt{2\mu E/\hbar^2}$ and $\lambda = \mu\omega/\hbar$, the above equation becomes

$$R''(r) + \frac{1}{r} R'(r) - \frac{m^2}{r^2} R(r) + (k^2 - \lambda^2 r^2) R(r) = 0 , \quad (12)$$

where the ' means derivative with respect to r . Further define

$$R(r) = r^{|m|} e^{-\lambda r^2/2} u(r) . \quad (13)$$

The differential equation for $u(r)$ is

$$u''(r) + \left(\frac{2|m|+1}{r} - 2\lambda r \right) u'(r) - \left(2\lambda(|m|+1) - k^2 \right) u(r) = 0 . \quad (14)$$

Next, make coordinate transformation $\xi = \lambda r^2$ and treat u as a function of ξ , we could get

$$\xi \frac{d^2 u}{d\xi^2} + (|m|+1-\xi) \frac{du}{d\xi} - \frac{1}{2} \left(|m|+1 - \frac{k^2}{2\lambda} \right) u = 0 . \quad (15)$$

This equation has the form of the general associated Laguerre differential equation. The standard way of solving it is to Taylor expand $u(\xi) = \sum_{n=0}^{\infty} c_n \xi^n$, plug it into the equation, and derive the iteration relations among c_n ,

$$c_{n+1} = \frac{n + \frac{1}{2}(|m| + 1 - k^2/2\lambda)}{(n+1)(n+|m|+1)} c_n . \quad (16)$$

The series expansion will be truncated into a polynomial if $\frac{1}{2}(|m| + 1 - k^2/2\lambda)$ is equal to $-n_r$, where $n_r = 0, 1, 2, \dots$ is a non-negative integer. Resorting the definition of k and λ , we find the energy eigenvalues are quantized

$$\begin{aligned} E &= \hbar\omega(2n_r + |m| + 1) , \\ m &= 0, \pm 1, \pm 2, \dots , \quad n_r = 0, 1, 2, \dots \end{aligned} \quad (17)$$

In the following table, we enumerate the lowest few energy levels and the corresponding quantum numbers and degrees of degeneracy

ground state	$E = \hbar\omega$	$n_r = m = 0$	1	(18)
first excited state	$E = 2\hbar\omega$	$n_r = 0, m = \pm 1$	2	
second excited state	$E = 3\hbar\omega$	$n_r = 1, m = 0$ or $n_r = 0, m = \pm 2$	3	
third excited state	$E = 4\hbar\omega$	$n_r = 1, m = \pm 1$ or $n_r = 0, m = \pm 3$	4	

There is no upper limit on the possible energy eigenvalues.

Given that the potential energy term for an isotropic harmonic oscillation has a very special form,

$$V(r) = \frac{1}{2} \mu \omega^2 r^2 = \frac{1}{2} \mu \omega^2 (x^2 + y^2) , \quad (19)$$

there is an alternative way of solving the problem just in Cartesian coordinates. Because the potential energy is simply the sum of those in the x and y directions, the wavefunction can be factorized into

$$\psi(x, y) = \psi_{n_x}(x) \psi_{n_y}(y) , \quad (20)$$

where $\psi_{n_x}(x)$ and $\psi_{n_x}(y)$ are the wavefunctions for two 1D harmonic oscillators, with corresponding energy eigenvalues

$$E_{n_x} = \hbar\omega \left(n_x + \frac{1}{2} \right) , \quad E_{n_y} = \hbar\omega \left(n_y + \frac{1}{2} \right) \quad (21)$$

respectively. The total energy eigenvalue in the 2D case is

$$E = \hbar\omega(n_x + n_y + 1) , \quad (22)$$

where $n_{x,y} = 0, 1, 2, \dots$. It is straightforward to verify that the possible values of E and the corresponding degeneracy is the same as those listed in Table. [18](#)

Comparing the two approaches offers a nice way of understanding how the solutions to 2D isotropic harmonic oscillator are organized.

Exercise: work out 3D harmonic oscillator in both Cartesian and spherical coordinates and compare results like above. Pay special attention to the degrees of degeneracy.

More generally, there are many 2D problems with a central potential that cannot be written as the sum of potential in each Cartesian direction, unlike the isotropic harmonic oscillator. In those cases, we have to solve the Schrödinger equation using the polar coordinates, in the same fashion as we did from Eqs. (10) to (17).

6.2. Electron moving on a ring

As the second problem, consider a special case where the electron is confined to a ring with fixed radius R . At the moment, we assume there is no external potential, thus $V = 0$. Starting from Eq. (2) and assume that ψ is only a function of φ and replace r by R in the equation, leads to

$$-\frac{\hbar^2}{2\mu R^2} \frac{\partial^2}{\partial \varphi^2} \psi(\varphi) = E\psi(\varphi) . \quad (23)$$

We have encountered and solved an equation like this before, Eq. (5), and found

$$\psi(\varphi) = \sqrt{\frac{1}{2\pi}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \dots . \quad (24)$$

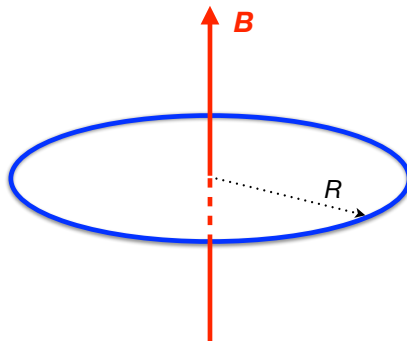
The corresponding energy eigenvalue is

$$E = \frac{m^2 \hbar^2}{2\mu R^2} . \quad (25)$$

For $m > 0$, each energy level has a two-fold degeneracy, i.e., the $\pm m$ states are degenerate with each other.

6.3. Ring plus solenoid

Next, let's consider adding an infinitely long solenoid passing through the center of the ring and perpendicular to the plane in which the ring resides (assumed to be the x - y plane). Running an electric current the solenoid could create a constant magnetic field inside it. We assume the magnetic field strength points along the z -axis direction, $\vec{B} = B\hat{z}$. A picture of this setup is shown below.



Clearly, if the solenoid is infinitely long, no B field will leak out of it, thus the magnetic field strength is zero at the ring location (in blue). Hence we do not need to worry about the electron spin interactions. However, the presence of the solenoid and magnetic field still have an impact on the energy levels of the electron in the ring.

For electron to interact with the external electromagnetic field, we need to consider the vector potential \vec{A} , which is nonzero outside the solenoid. The magnetic field strength \vec{B} is related to \vec{A} as

$$\vec{B} = \nabla \times \vec{A}. \quad (26)$$

Using the Stokes theorem, the total flux of magnetic field strength can be calculated as

$$\Phi = \int_S d\vec{S} \cdot \vec{B} = \int_S d\vec{S} \cdot (\nabla \times \vec{A}) = \oint_C d\vec{l} \cdot \vec{A}, \quad (27)$$

where S is the area where \vec{B} passes through (inside the solenoid), and C is any closed path around it. For our ring problem, we can consider C to be the along ring, and choose

$$\vec{A} = A_\varphi \hat{\varphi}. \quad (28)$$

In this case, the righthand side of Eq. (27) can be calculated, and yields $\Phi = 2\pi R A_\varphi$. Therefore, we derive the vector potential

$$\vec{A} = \frac{\Phi}{2\pi R} \hat{\varphi}. \quad (29)$$

Following the minimal coupling principle, the momentum operator in the Hamiltonian make a shift, $\vec{p} \rightarrow \vec{p} + e\vec{A}$, and the Schrödinger equation becomes,

$$-\frac{\hbar^2}{2\mu R^2} \left(\frac{\partial}{\partial \varphi} + \frac{ie\Phi}{2\pi\hbar} \right)^2 \psi(\varphi) = E\psi(\varphi). \quad (30)$$

The solution to this equation is identical to Eq. (24),

$$\psi(\varphi) = \sqrt{\frac{1}{2\pi}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \dots, \quad (31)$$

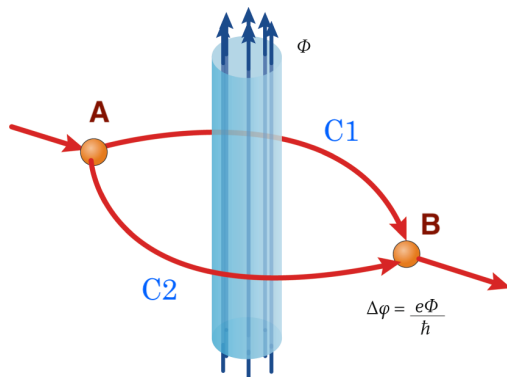
but the energy eigenvalues become

$$E = \frac{\hbar^2}{2\mu R^2} \left(m + \frac{e\Phi}{2\pi\hbar} \right)^2 . \quad (32)$$

For generic values of flux Φ , the energy levels shift and the original $\pm m$ degeneracy is broken. Such an energy shift is a pure quantum mechanical effect.

6.4. The Aharonov-Bohm effect

Here we consider an experiment which is topologically similar to the ring problem, where we send an electron to travel around a solenoid with magnetic flux. Because electron is not a bounded to a ring, its energy can be adjusted as an input parameter and does not have to follow the result in Eq. (32). A picture of this setup is shown below.



An electron is released at point A and detected at point B. We make sure that the solenoid is well shielded such that electron could only pass on the side of it (no penetration through). Because there are two topologically different paths C_1 and C_2 , interference effect could occur if the wavefunction of electron evolves differently on the two paths.

To further quantify, we consider the time-dependent Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \left(\nabla + \frac{ie\vec{A}(\vec{r})}{\hbar} \right)^2 \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) . \quad (33)$$

where we set $V = 0$. Here we want to keep the discussion general and keep the form of \vec{A} implicit. It is useful to define

$$\Psi(\vec{r}, t) = \Psi_0(\vec{r}, t) \exp \left(-\frac{ie}{\hbar} \int_{\vec{r}_A}^{\vec{r}} d\vec{r}' \cdot \vec{A}(\vec{r}') \right) , \quad (34)$$

where the line integral is along certain path starting from point A, and Ψ_0 satisfies the Schrödinger equation without \vec{A} ,

$$-\frac{\hbar^2}{2\mu} \nabla^2 \Psi_0(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi_0(\vec{r}, t) . \quad (35)$$

This way, we have completely factorized the \vec{A} field and path dependence into the exponential. For any path C ,

$$\exp\left(-\frac{ie}{\hbar} \int_C d\vec{r}' \cdot \vec{A}(\vec{r}')\right), \quad (36)$$

As a result, the wavefunction of electron completing the paths C_1 and C_2 will develop a phase difference factor. The interference term between the two is proportional to

$$\Psi_{C_1} \Psi_{C_2}^* \propto \exp\left(-\frac{ie}{\hbar} \int_{C_1} d\vec{r}' \cdot \vec{A}(\vec{r}') + \frac{ie}{\hbar} \int_{C_2} d\vec{r}' \cdot \vec{A}(\vec{r}')\right), \quad (37)$$

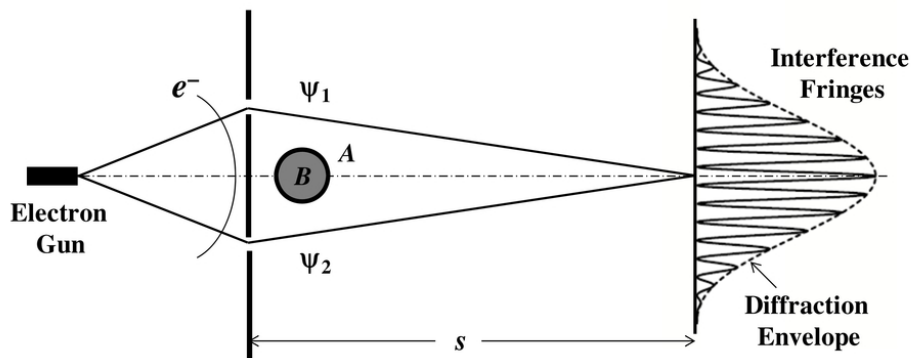
Because the two paths C_1, C_2 form a closed path C_{12} around the solenoid, we can rewrite the interference term as

$$\Psi_{C_1} \Psi_{C_2}^* \propto \exp\left(-\frac{ie}{\hbar} \oint_{C_{12}} d\vec{r}' \cdot \vec{A}(\vec{r}')\right) = \exp\left(-\frac{ie}{\hbar} \int_S d\vec{S} \cdot \vec{B}\right) = e^{-ie\Phi/\hbar}. \quad (38)$$

Notable, this result only depends on the total magnetic flux but not on any particular form of the paths C_1, C_2 . We are allowed to deform them freely as long as C_{12} still encloses the solenoid. This implies that the result has a topological nature. The corresponding topological phase is

$$\frac{e\Phi}{\hbar}. \quad (39)$$

Such a phase is physical and can be measured experimentally. For example, if we insert a solenoid to the electron double-slit experiment (see the picture below), it will cause a vertical shift to the interference patterns on the screen. The magnitude of the shift depends on the magnetic flux Φ . (If the Φ is made time dependent, the patterns will be dancing on the screen;)



■ The end.