AMATH 373 **Winter 2021**

Quantum Theory 1

Lecture Notes

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Preamble

After spending good part of the pre-requisite course on matrix formulation of Quantum Mechanics (QM), we shall place more emphasis in this course on Schrödinger's formulation involving wave functions and differential equations (DEs). Those two approaches my be considered as "Matrix Mechanics" and "Wave Mechanics" versions of QM, with the latter being "just" the so-called *position representation* of quantum mechanical states of various physical systems, as discussed in the textbook used for the pre-requisite course. The prominence of Wave Mechanics stems from many real-world applications involving the dynamics of particles in the external potential fields, which are typically defined in Classical Mechanics (CM) and Electromagnetic theory as functions of the position. Accordingly, the operators, which act on the QM state of particles are often conveniently expressed in the position representation as well. Moreover, "Wave Mechanics" is also the basis for many *ab initio* computational schemes that are currently used in modern Materials Science for predicting electronic and optical properties of nano-structures for their engineering applications. As for its educational value, "Wave Mechanics" belongs in a more traditional segment of Mathematical Physics, involving a mathematical "toolbox", which is universally shared by a diverse range of areas of Physics. For example, solving the problem of hydrogen atom in QM by means of the Schrödinger's equation in spherical coordinates involves techniques, which are also used in solving Maxwell's equations for plasmonic nano-particles of spherical shape. Of course, we shall not abandon "Matrix Mechanics", but shall rather use its formulation of QM when we disucss more fundamental and abstract concepts, e.g., when discussing algebraic properties of operators and their commutators. In that respect, Dirac's bra-ket notation, which was discussed in the pre-requisite course, provides an elegant way to switch between different representations of quantum states.

1 Introduction

1.1 Classical mechanics in Hamilton's form

A good point of departure in a course focusing on Wave Mechanics is to briefly review ideas of CM. Becasue many of our applications and examples will be concerned with a point particle of mass m, which moves in 1D along the x-axis under the action of some conservative force $F(x)$, let us begin by recalling that in CM the state of this system is fully defined by the position $x = x(t)$ and momentum $p = p(t)$. In a CM experiment, both these dynamical variables can be observed simultaneously at any time t. As you have seen in the pre-requisite course, and as we shall show later in this course on a very general level, in QM it is impossible to make accurate measurements of the position and momentum simultaneously because of the Heisenberg's uncertainty relation (HUR). In spite of this sharp contrast between the two views of the

same dynamical system, the formalism of Wave Mechanics is closely connected to the formalism of CM, in particular considering the central role of the Hamilton's function.

In CM, the position and the momentum constitute a dynamical system, with their time evolution governed by the pair of ordinary DEs (ODEs) called Hamilton's equations.

Definition 1.1. For a 1D system, Hamilton's function is defined as:

$$H(p,x) = \frac{p^2}{2m} + U(x)$$

where x is the position, $p = mv = m\frac{dx}{dt} = m\dot{x}$ is the momentum, $\frac{p^2}{2m}$ is the kinetic energy, and $U(x)$ is the potential function, such that $F(x) = -U'(x)$. Hamilton's equations of motion for $p(t)$ and $x(t)$ constitute a system of 1st order ODEs,

$$\begin{aligned} \dot{p} &= -\frac{\partial H}{\partial x} = -U'(x) = F(x), \\ \dot{x} &= \frac{\partial H}{\partial p} = \frac{p}{m} = v, \end{aligned}$$

which are subject to the initial conditions (ICs) at $t = 0$:

$$x(0) = x_0; \quad \text{and} \quad p(0) = p_0 = mv_0.$$

[Here, the dot indicates a derivative with respect to time, e.g., $\dot{p} = \frac{dp}{dt}$.]

The more familiar form of CM is based on Newton's 2nd law, expressed as a 2nd order ODE for $x(t)$, which follows from Hamilton's equations :

$$\frac{d^2x}{dt^2} = \ddot{x} = \frac{1}{m}F(x) \Rightarrow m\frac{d^2x}{dt^2} = F(x),$$

and is subject to the ICs at $t = 0$:

$$x(0) = x_0; \quad \text{and} \quad \dot{x}(0) = v_0 = p_0/m.$$

Example 1.1.1. Simple Harmonic Oscillator

$$U(x) = k\frac{x^2}{2}, \quad F(x) = -kx \quad \Rightarrow \quad \frac{d^2x}{dt^2} + \omega^2 x = 0, \quad \omega = \sqrt{\frac{k}{m}}.$$

Using Hamilton's equations, we can easily determine the time evolution of an arbitrary dynamical variable. Consider any differentiable function $f(x,p,t)$, with x, p and t treated as independent variables.

Then, with the help of Hamilton's equations, the Chain Rule gives:

$$\frac{df}{dt} = \frac{\partial f}{\partial x}\frac{dx}{dt} + \frac{\partial f}{\partial p}\frac{dp}{dt} + \frac{\partial f}{\partial t} = \frac{\partial H}{\partial p}\frac{\partial f}{\partial x} - \frac{\partial H}{\partial x}\frac{\partial f}{\partial p} + \frac{\partial f}{\partial t}$$

where $\frac{\partial H}{\partial p}\frac{\partial f}{\partial x} - \frac{\partial H}{\partial x}\frac{\partial f}{\partial p}$ can be written as $\{H, f\}$, referred to as the Poisson bracket of functions H and f. As simple applications of the Poisson bracket, notice that defining $f = p$, recovers the first of Hamilton's equations, while letting $f = x$, recovers the second of those equations.

Moreover, we can prove the conservation of total energy in CM for a particle moving in a conservative force field by defining $f = H(p, x)$ [recall that $H(p, x)$ does not depend explicitly on time, by assumption]. Substituting the solutions of the Hamilton's equations,

$$p = p(t; x_0, p_0), \quad x = x(t; x_0, p_0),$$

back into the Hamilton's function, which then becomes a composite function of time, we find its total rate of change is $\frac{dH}{dt} = \{H, H\} = 0$ because the function $H(p, x)$ "commutes" with itself within a Poisson's bracket, thereby giving the conservation of energy in the familiar form,

$$H(p, x) = \frac{p^2}{2m} + U(x) = Const = E.$$

1.2 Early QM ideas

The early history of QM, spanning the first decades of the 20th century, has shaped some of the key concepts in modern QM theory. In few words, it is the story of how scientists perceived light and matter, starting from Newton's corpuscular theory of light in late 1600s. That theory was fundamentally revised by Maxwell some 200 years later, when he formulated a mathematical framework describing the light as a wave process involving oscillating Electric and Magnetic (EM) fields.

Maxwell's theory describes a monochromatic light with the wavelength λ as an EM plane wave that propagates through free space at the speed c with the frequency of oscillation of those fields given at any point of space by $\nu = c/\lambda$. Therefore, the **dispersion relation** between the angular frequency $\omega = 2\pi\nu$ and the wavenumber $k = 2\pi/\lambda$ for light is **linear**:

$$\omega = ck.$$

With the classical theory of waves, it was then easy to explain all the well-known interference phenomena observed with light, such as, e.g., diffraction on a periodic grating with its period being of the size comparable to the wavelength of the light. Everything seemed to work well with the light phenomena in

Physics within Maxwell's theory, except for the phenomenon of photoelectric effect, i.e., the emission of electrons from metal illuminated by the light of certain wavelength, which was observed in experiments by Hertz and others towards the end of the 1900s. [By the way, photoelectric effect is the basis of the modern technique for probing materials known as Photoemission spectroscopy.]

It was Einstein who explained the photoelectric effect in his miraculous year by borrowing the idea of the "light quanta" from Max Planck, a (reluctant) father of QM. Namely, around the turn of the century (~ 1900), Planck made a ground breaking assumption about light in his desperate attempts to explain the "ultraviolet catastrophe" in the phenomenon of blackbody radiation by asserting that the EM radiation cannot deliver (or take up) energy to/from matter in infinitesimally small amounts. Einstein's explanation of the photoelectric effect using Planck's work on the black-body radiation gave rise to a notion that the light of frequency ν may be thought of as "shower of packets of energy" called photons, each carrying the amount of energy $E = h\nu = \hbar\omega$, where $\hbar = \frac{h}{2\pi}$ is Planck's constant. Of course, that did not mean that physicists had to return to Newton's corpuscular theory of light. It "simply" meant that light possesses inherent duality: it exhibits properties of both the waves and particles, depending on the type of experiment performed with light.

On the other hand, matter was deemed to naturally exhibit corpuscular properties until the experiment by Davisson and Germer in the 1920s. They observed that a mono-energetic, collimated beam of electrons undergoes diffraction on the surface of a nickel plate in a similar manner as the light does. This give rise to idea that there exists symmetry between light and matter because the Davisson - Germer experiment showed the massive particles also exhibit particle-wave duality, depending on the type of experiment. It turned out that, in fact, the Davisson - Germer experiment could be explained by using Bragg's theory of diffraction of light by assigning to each electron wave-like character, while the crystal lattice of nickel provided the periodic grating of an unprecedentedly small size. The only thing that was required to fit the experiment with Bragg's theory was a quantitative expression for the wavelength of a wave associated with electrons, which was soon provided by the DeBroglie's hypothesis. Namely, DeBroglie asserted that a free particle moving with the mechanical momentum p can be thought of as a wave with the wavelength given by $\lambda = \frac{h}{p}$, so that $p = \frac{h}{\lambda} = \hbar k$, with h being exactly the constant introduced by Planck.

And so, the circle was closed: now the matter was also perceived to possess an inherent particle-wave duality, like light. However, there is one important difference between the light particle-waves and the matter particle-waves. While the free propagating EM plane wave is characterized by linear dispersion relation between its frequency and wavenumber, $\omega = ck$, the situation is different for the material particle-waves. Considering the classical-mechanical energy-momentum relation for a non-relativistic free particle of mass m, $E = \frac{p^2}{2m}$, we can express the energy on the left-hand side via the Planck's formula as $E = \hbar\omega$ and the momentum on the right-hand side via the DeBroglie's relation $p = \hbar k$ to deduce that the dispersion

relation between the frequency and wavenumber of a free particle in QM is **quadratic**:

$$\omega = \frac{\hbar k^2}{2m}$$

1.3 Classical EM waves

We now want to develop a mathematical description of the particle-wave duality that would work for both the light phenomena and massive particles. Pretending that we never heard of Schrödinger's equation, we may invoke some properties of the solutions of classical wave equations on an infinite domain, to build a QM description of a massive free particle "from scratch".

Consider a classical, monochromatic EM wave of wavelength λ, which propagates freely along the x axis. From Maxwell's equations, it follows that any component of the associated E or M fields, which we denote generically by $\Psi(x,t)$, is a solution of the classical wave equation on an infinite domain $x \in \mathbb{R}$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \Psi}{\partial t^2}$$

that may be expressed in the form of plane waves

$$\Psi(x,t) = Ce^{i(kx-\omega t)} \quad \text{or} \quad \Psi(x,t) = Ce^{i(kx+\omega t)}$$

where $k = 2\pi/\lambda$ is the wave number and $\omega = ck$ the corresponding (angular) frequency.

In the experiments with classical EM waves one can generally measure both the field intensity Ψ and the energy density of the EM radiation, $I \propto |\Psi|^2$. As a consequence of this quadratic relation, one often observes various interference patterns in the energy density I, such as diffraction of light on a grating. Those observations can be described by using a linear superposition of plane waves of different wavelengths, $\lambda_1, \lambda_2, \ldots$, which is also a solution of the classical wave equation, thanks to its linearity,

$$\Psi(x,t) = C_1 e^{i(k_1 x-\omega_1 t)} + C_2 e^{i(k_2 x-\omega_2 t)} + \cdots \to \int_{-\infty}^{\infty} dk\, C(k)\, e^{i[kx-\omega(k)t]}$$

Notice that in the last expression, we have allowed that k may take arbitrary values in $\mathbb{R}$, so that the resulting integral constitutes a Fourier transform (FT) involving some function $C(k)$, with x being its conjugate variable and time is just parameter. Physically, $C(k)$ describes a continuous "mixture" of plane waves with different wavelengths, giving rise to the above expression for $\Psi(x,t)$ that constitutes a wave-packet solution of the classical wave equation. [Recall from AMATH 231 and AMATH 353 that solving the classical wave equation on an infinite domain is trivially achieved by applying techniques of the FT.]

It is important to realize that the function $C(k)$ can be "designed" to yield a "packet" of EM waves,

which can be spatially well-localized along the x axis and also propagates in time. Hence, we have a mathematical description of light, which is capable of describing both its particle-like and wave-like properties. Notice that, because of the linearity of the dispersion relation for the EM waves, $\omega = ck$, the "wave packet" of light propagates without distortion,

$$\Psi(x,t) = \int_{-\infty}^{\infty} dk\, C(k)\, e^{ik(x-ct)} = f(x-ct).$$

In other words, the shape of the function $\Psi(x,t)$ does not change when we observe it along the "characteristics" $x - ct = const$. [Notice that there also exists an equally valid "counter-propagating" solution of the wave equation, having the form $f(x+ct)$, which propagates along the characteristics $x + ct = const$.]

2 Free particle wave packets in QM

We want to use the above idea of a wave packet of light, which is well-localized in space, to describe particle-wave duality of a massive particle in QM, which can "mimic" the classical size of that particle, but is also able to describe the interference phenomena (like the Davisson-Germer experiment or the famous double-slit experiment), which are manifestations of particle's wave-lake character.

Assume that the state of a particle of mass m, which moves freely over the entire x axis (that is, with the potential is $U(x) = 0$), may be somehow described by a function $\Psi(x,t)$, called wave function, analogous to the wave packet developed above for the classical EM wave. However, we must replace the dispersion relation of the EM wave, $\omega = ck$, with the Planck-DeBroglie dispersion relation for particles, $\omega = \frac{\hbar k^2}{2m}$, giving

$$\Psi(x,t) = \int_{-\infty}^{\infty} dk\, C(k)\, e^{i[kx-\omega(k)t]} = \int_{-\infty}^{\infty} dk\, C(k) e^{ik(x-\frac{\hbar k}{2m}t)}$$

Notice that, we still do not know what equation can have such wave function $\Psi(x,t)$ as its solution, but it certainly cannot be the classical wave equation. One thing that we do know is that, because of the non-linear (i.e., quadratic) dispersion relation for free particle, $\omega = \frac{\hbar k^2}{2m}$, the associated wave packet $\Psi(x,t)$ propagates with distortion, which is a well-known phenomenon of the spreading of the wave packets in QM.

2.1 Probabilistic interpretation of wave function

Unlike the solutions of classical wave equations, the wave function in QM cannot be directly observed in an experiment, if for no better reason then because $\Psi(x,t)$ is generally a complex-valued function. An important question of how the state of a particle can be described by $\Psi(x,t)$ in QM is answered by Born's probabilistic interpretation of the wave function, where $\rho(x,t) = |\Psi(x,t)|^2$ provides the probability density for observing the particle's position. Specifically, for a sufficiently small interval dx,

$$|\Psi(x,t)|^2\, dx = \text{probability for observing the particle in the interval } (x, x+dx) \text{ at time } t.$$

Obviously, there is a lot to learn about free-particle wave packets in QM from the theory of FT. We may recall from AMATH 231 that the mean square convergence of the FT of some function is guaranteed by the square integrability of that function on $x \in \mathbb{R}$. This requirement goes hand-in-hand with Born's interpretation, because every probability density needs to be normalized according to $\int_{-\infty}^{\infty} \rho(x,t)\, dx = 1$ for all t. From the normalization condition we obtain the boundary conditions (BCs), to be imposed on

solutions of the yet to be determined wave equation in QM when $x \to \pm\infty$,

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\, dx = 1 \Rightarrow \lim_{x\to\pm\infty} \Psi(x,t) = 0, \quad \forall t.$$

To further establish a role for the FT of the wave function describing the unbounded motion of a free particle, let $C(k) \equiv \phi(k)/\sqrt{2\pi}$, and re-write the corresponding wave packet as

$$\begin{aligned} \Psi(x,t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \left\{ \phi(k)\, e^{-i\frac{\hbar k^2}{2m}t} \right\} e^{ikx} \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \Phi(k,t)\, e^{ikx}. \end{aligned}$$

Here, we have defined $\Phi(k,t) \equiv \phi(k)\, e^{-i\frac{\hbar k^2}{2m}t}$, so that $\Psi(x,t)$ and $\Phi(k,t)$ constitute a FT pair, with t being just a parameter describing their propagation in time. Thus, we may write an inverse FT as

$$\Phi(k,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, \Psi(x,t)\, e^{-ikx}$$

We may wonder whether the function $\Phi(k,t)$ contains some physical information about the particle. Staying in the domain of probabilistic interpretation, we recall Parseval's formula from AMATH 231,

$$\int_{-\infty}^{\infty} dk\, |\Phi(k,t)|^2 = \int_{-\infty}^{\infty} dx\, |\Psi(x,t)|^2.$$

Noting that the integral on the right-hand side = 1 because of the normalization of $\rho(x,t) = |\Psi(x,t)|^2$, it is then plausible to also assign to $|\Phi(k,t)|^2$ the meaning of a probability density, which is automatically normalized by the Parseval's formula, that is $\int_{-\infty}^{\infty} dk\, |\Phi(k,t)|^2 = 1$ for all t. Accordingly, $|\Phi(k,t)|^2\, dk$ is then the probability for observing the wavenumber in the interval $(k, k+dk)$. Notice that, for a free QM particle, this probability does not depend on time because $|\Phi(k,t)|^2 = |\phi(k)|^2 |e^{-i\frac{\hbar k^2}{2m}t}|^2 = |\phi(k)|^2$. [We'll see later that this is because $\Phi(k,t)$ is the so-called stationary state of the free particle Hamiltonian.] This then also implies that the function $\phi(k)$ contains the information about the intial state of the particle, say, at $t = 0$.

To make a closer contact with CM, recall the DeBroglie's relation $k = \frac{p}{\hbar}$, which allows us to write the probability for observing the particle's mechanical momentum in the interval $(p, p+dp)$ as

$$D(p)dp = |\phi(k)|^2 dk \Rightarrow D(p) = \left|\phi\Big(\frac{p}{\hbar}\Big)\right|^2 \frac{dk}{dp} = \frac{1}{\hbar}\left|\phi\Big(\frac{p}{\hbar}\Big)\right|^2 \Rightarrow \int_{-\infty}^{\infty} dp D(p) = 1.$$

Here, we have defined the probability density $D(p)$ for the momentum, which can be used to evaluate

various moments of p considered a random variable. Notice that the independence on time of $D(p)$ implies that the distribution of the mechanical momentum is conserved, which makes physical sense for a free particle, in the context of Newton's 1st law.

Recall that, in CM, Hamilton's equations provide deterministic information on the position and momentum, x and p, which are the two dynamic variables that completely define the state of the particle at time $t \geq 0$. On the other hand, in Wave Mechanics, the information on x and $p = \hbar k$ may only be obtained from the corresponding functions, $\Psi(x,t)$ and $\Phi(k,t)$, by using methods of classical probability theory. Notice that x and p (or x and k) are the two conjugate variables that appear in the FT pair describing a free particle wave packet. In other words, $\Psi(x,t)$ and $\Phi(k,t)$ are just two representations of one and the same quantum state of that particle, which use the position and momentum as variables. [We'll see later that x and p constitute the continuous eigen-spectra of the position and momentum operators in QM, respectively.]

Before studying some examples, in the next two sections we review some "aside" topics of technical relevance for the main course material.

2.2 ASIDE: Proof of Parseval's formula for Fourier transform

Even though Parseval's theorem was discussed in some detail in AMATH 231 for both Fourier series and FT, let us review its proof in the context of Wave Mechanics. For simplicity, consider the situation at time $= 0$, i.e., let $\phi(k) \equiv \Phi(k,0)$ and $\psi(x) \equiv \Psi(x,0)$, which constitute a FT pair at $t = 0$. Then,

$$\begin{aligned}
\int_{-\infty}^{\infty} dk\, |\phi(k)|^2 &= \int_{-\infty}^{\infty} dk\, \phi^*(k)\phi(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx'\, \psi^*(x') e^{ikx'} \int_{-\infty}^{\infty} dx\, \psi(x) e^{-ikx} \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, \psi(x) \int_{-\infty}^{\infty} dx'\, \psi^*(x') \int_{-\infty}^{\infty} dk\, e^{ik(x'-x)} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, \psi(x) \int_{-\infty}^{\infty} dx'\, \psi^*(x') 2\pi\delta(x'-x) \\
&= \int_{-\infty}^{\infty} dx\, \psi(x)\psi^*(x) = \int_{-\infty}^{\infty} dx\, |\psi(x)|^2.
\end{aligned}$$

In the first step, it was permissible to interchange the order of integration assuming that all the integrals exist, which is guaranteed by an assumption that the wave function $\psi(x)$ is square integrable. In the last step, we used the "sifting" property (see below) of Dirac's delta "function" $\delta(x'-x)$ in the integral over x'. This proof works for $t > 0$ as well.

2.3 ASIDE: Dirac's delta "function"

We have encountered the object called Dirac's delta function in several previous courses. As it plays an important role in Wave Mechanics, we again review some of its properties using the concept of a sampling

functional, an integral that samples the value of a function $f(x)$ at some point $x = x_0$. Then, the Dirac's delta function can be defined an the following way.

Definition 2.1. Let $f(x)$ be some "nice" function (differentiable and integrable as we please), and define the sampling functional

$$S[f, x_0] = \int_{-\infty}^{\infty} f(x)\delta(x - x_0)\, dx = \begin{cases} f(x_0), & x_0 \in D(f) \\ 0, & \text{otherwise,} \end{cases}$$

where $D(f)$ is the domain of definition of the function f.

Consider a sequence of functions $\{\delta_n(x)\}$, which can be considered as suitable representation of the Dirac's delta function $\delta(x)$, such that the following limit exists

$$\lim_{n\to\infty} S_n[f, x_0] = \lim_{n\to\infty} \int_{-\infty}^{\infty} f(x)\, \delta_n(x - x_0)\, dx = S[f, x_0]$$

Here is a list of some representations of the Dirac's delta function centered at $x_0 = 0$,

$$\begin{aligned} \delta_n(x) &= \begin{cases} n & |x| \le \frac{1}{2n} \\ 0 & \text{otherwise} \end{cases} \\ \delta_n(x) &= \frac{n}{\sqrt{\pi}} e^{-n^2x^2} \\ \delta_n(x) &= \frac{n}{\pi} \frac{1}{1 + n^2x^2} \\ \delta_n(x) &= \frac{\sin(nx)}{\pi x} = \frac{1}{2\pi} \int_{-n}^{n} e^{ikx} dk \end{aligned}$$

which shall all yield, in the limit $n \to \infty$,

$$\int_{-\infty}^{\infty} f(x)\delta_n(x)\, dx \approx \int_{-\infty}^{\infty} f(0)\delta_n(x)dx = f(0) \int_{-\infty}^{\infty} \delta_n(x)dx = f(0)$$

There exists a less formal definition of the Dirac's delta function, which captures the essence of its behaviour inside an integral.

Definition 2.2. $\delta(x) = \begin{cases} 0, & x \neq 0, \\ \text{undefined}, & x = 0, \end{cases}$ such that $\int_{-\infty}^{\infty} \delta(x)dx = \int_{0^-}^{0^+} \delta(x)dx = 1$

Various properties of Dirac's delta function

Sifting property

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0)dx = \int_{x_0^-}^{x_0^+} f(x_0)\delta(x - x_0)dx = f(x_0)$$

Integration by parts

$$\int_{-\infty}^{\infty} f(x)\delta'(x-x_0)dx = -f'(x_0)$$

Delta function is an even function: $\delta(-x) = \delta(x)$, so that, e.g.,

$$\int_{0}^{\infty} f(x)\delta(x)dx = \frac{1}{2}f(0)$$

Scaling

$$\delta(kx) = \frac{1}{|k|}\delta(x)$$

Composition with a differentiable function $g(x)$ having simple zeros at x_i

$$\delta(g(x)) = \sum_i \frac{\delta(x-x_i)}{|g'(x_i)|}$$

Example 2.2.1. We may want to review an example of the FT of the so-called "window function" from AMATH 231 in the context of a QM wave packets. A particle that is in initially (i.e., at $t = 0$) localized, and uniformly distributed in the interval $-\frac{L}{2} < x < \frac{L}{2}$ may be represented by the wave function given by

$$\psi(x) = A\, e^{i\alpha} \times \begin{cases} 1, & |x| \le \frac{L}{2} \\ 0, & \text{otherwise} \end{cases}$$

where $A = 1/\sqrt{L}$ to make $\rho(x) = |\psi(x)|^2$ normalized, and $\alpha \in \mathbb{R}$ being an arbitrary (possibly x-dependent) phase, which does not appear in the probability density $\rho(x) = 1/L$ for $|x| \le \frac{L}{2}$ and $\rho(x) = 0$ otherwise. One can easily find the moments of the position x by using standard definitions from the Probability theory:

$$\begin{aligned} E\{x\} = \bar{x} = \langle x \rangle &= \int_{-\infty}^{\infty} dx\, x\, \rho(x) = 0 \\ \langle x^2 \rangle &= \int_{-\infty}^{\infty} dx\, x^2 \rho(x) = \frac{L^2}{12} \\ \text{Variance} = \left\langle (x - \langle x \rangle)^2 \right\rangle &= \left\langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \right\rangle = \left\langle x^2 \right\rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2 = \left\langle x^2 \right\rangle - \langle x \rangle^2 \end{aligned}$$

We shall define the QM uncertainty in the position as standard deviation $\mathrm{St}\{x\} \equiv \Delta x$, giving

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{L}{\sqrt{12}}.$$

To find the probability density $D(p)$ for the momentum, let us set $\alpha = 0$ in $\psi(x)$ and perform its FT to

find:

$$\begin{aligned}\phi(k) &= \frac{1}{\sqrt{2\pi L}}\int_{-L/2}^{L/2} dx e^{-ikx} = \frac{1}{\sqrt{2\pi L}}\frac{2}{k}\sin\left(\frac{kL}{2}\right) \equiv \frac{\sqrt{L}}{\sqrt{2\pi}}\,\mathrm{sinc}\left(\frac{kL}{2}\right)\\ \Rightarrow D(p) &= \frac{1}{\hbar}\left|\phi\left(\frac{p}{\hbar}\right)\right|^2 = \frac{L}{2\pi\hbar}\,\mathrm{sinc}^2\left(\frac{pL}{2\hbar}\right).\end{aligned}$$

Example 2.2.2. Let us obtain probabilistic information on the position and momentum, x and p, for a Gaussian wave packet, which is defined at $t = 0$ by $\Psi(x, 0) = \psi(x) = Ae^{-\frac{x^2}{2d^2}}$. To find the normalization constant A, consider

$$\begin{aligned}\rho(x) &= A^2 e^{-\frac{x^2}{d^2}}, \quad \text{where normalization gives} \quad A:\\ \int_{-\infty}^{\infty} dx\rho(x) &= A^2\int_{-\infty}^{\infty} dx e^{-\frac{x^2}{d^2}} = A^2\, d\sqrt{\pi} = 1 \Rightarrow A = \frac{1}{\pi^{1/4}\sqrt{d}}\end{aligned}$$

The moments of the position x are obtained as:

$$\begin{aligned}\langle x\rangle &= \int_{-\infty}^{\infty} dx\, x\,\rho(x) = 0\\ \langle x^2\rangle &= \int_{-\infty}^{\infty} dx\, x^2\rho(x) = \frac{1}{2}d^2\\ \Rightarrow \Delta x &= \sqrt{\langle x^2\rangle - \langle x\rangle^2} = \frac{d}{\sqrt{2}}\end{aligned}$$

To find the moments of the momentum $p = \hbar k$, we first perform FT of $\psi(x)$ to find $D(p)$ and then use the standard definitions:

$$\begin{aligned}\phi(k) &= \frac{A}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dx e^{-\frac{x^2}{2d^2}-ikx} = \frac{\sqrt{d}}{\pi^{1/4}}e^{-\frac{1}{2}k^2d^2}\\ \Rightarrow \langle p\rangle &= \int_{-\infty}^{\infty} dp\, p\, D(p) = \hbar\int_{-\infty}^{\infty} dk k|\phi(k)|^2 = 0\\ \langle p^2\rangle &= \int_{-\infty}^{\infty} dp p^2 D(p) = \hbar^2\int_{-\infty}^{\infty} dk k^2|\phi(k)|^2 = \frac{\hbar^2}{2d^2}\\ \Rightarrow \Delta p &= \sqrt{\langle p^2\rangle - \langle p\rangle^2} = \frac{\hbar}{\sqrt{2}d}\end{aligned}$$

Forming the product of the uncertainties in the position and momentum for Gaussian wave packet for free particle, we recover the lower bound of the Heisenberg's Uncertainty Relation (HUR) for those two variables,

$$\Delta x\Delta p = \frac{\hbar}{2}$$

It should be remarked that such a "reciprocal" relation between the widths of a "signal" $\psi(x)$ and its Fourier "spectrum" $\phi(k)$ is a well-established duality property of the FT, often encountered in Engineering signal analysis.

2.4 An expression for the momentum operator

Working with free particles undergoing unbounded motion along the x axis, we can deduce an expression for the operator using manipulations of the FT and inverse FT. This operator can be used to extract probabilistic information about the momentum directly from the wave function $\Psi(x,t)$ in the position representation, without having to perform its FT to find $\Phi(k,t)$, which represents the same state in the momentum representation

For simplicity, consider $\phi(k) \equiv \Phi(k,0)$ and $\psi(x) \equiv \Psi(x,0)$, which constitute a FT pair at $t = 0$. How to find $\langle p \rangle$ directly from $\psi(x)$ without having to evaluate $\phi(k)$?

$$\begin{aligned}\langle p \rangle &= \int_{-\infty}^{\infty} dp\, pD(p) = \int_{-\infty}^{\infty} dp\, p \left|\phi\left(\frac{p}{\hbar}\right)\right|^2 \frac{1}{\hbar} = \hbar \int_{-\infty}^{\infty} dk k \phi^*(k)\phi(k) \\ &= \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} dk k \int_{-\infty}^{\infty} dx' e^{ikx'} \psi^*(x') \int_{-\infty}^{\infty} dx e^{-ikx} \psi(x).\end{aligned}$$

Using the identity $ke^{-ikx} \equiv i\frac{\partial}{\partial x} e^{-ikx}$, we may write

$$\langle p \rangle = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx'\, \psi^*(x') e^{ikx'} \int_{-\infty}^{\infty} dx\, \psi(x) \frac{\partial}{\partial x} e^{-ikx}$$

and perform integration by parts in the last factor, giving

$$\int_{-\infty}^{\infty} dx\, \psi(x) \frac{\partial}{\partial x} e^{-ikx} = \psi(x) e^{-ikx}\Big|_{-\infty}^{x=\infty} - \int_{-\infty}^{\infty} dx\, e^{-ikx} \frac{\partial \psi(x)}{\partial x}$$

where the first term vanishes because of the property $\psi(x) \to 0$ as $x \to \pm\infty$ that follows from the normalization of $\psi(x)$. Therefore, the mean (or expectation) value of p is given by

$$\begin{aligned}\langle p \rangle &= -\frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} dx\, \frac{\partial \psi(x)}{\partial x} \int_{-\infty}^{\infty} dx'\, \psi^*(x') \lim_{n\to\infty} \int_{-n}^{n} dk\, e^{ik(x'-x)} \\ &= \frac{\hbar}{i} \int_{-\infty}^{\infty} dx\, \frac{\partial \psi(x)}{\partial x} \int_{-\infty}^{\infty} dx'\, \psi^*(x')\, \delta(x'-x) \\ &= \int_{-\infty}^{\infty} dx\, \psi^*(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x)\end{aligned}$$

Invoking the Dirac's bra-ket notation, we may write this result compactly as

$$\langle p\rangle \equiv \langle\psi|\hat{p}|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi^*(x)\, \hat{p}\, \psi(x)$$

with the momentum operator defined in the position representation by $\hat{p} = \dfrac{\hbar}{i}\dfrac{\partial}{\partial x}$.

2.5 Time evolution of a wave packet

The time evolution of wave packets is an important concept in many areas of theoretical and applied Physics, which often helps shed light on the underlying interactions of waves with the propagating medium. It is equally important in Fluid mechanics, Electromagnetic theory, and QM of quasi-free particles. We have already seen that, for a general wave packet

$$\Psi(x,t) = \int_{-\infty}^{\infty} dk\, C(k)\, e^{i[kx-\omega(k)t]} \qquad (*)$$

when the dispersion relation $\omega = \omega(k)$ is defined by a non-linear function $\omega(k)$, one may expect that the shape of the probability density $\rho(x,t) = |\Psi(x,t)|^2$ evolves in time with distortion. In that context, there are two important quantities, the so-called phase velocity of the wave packet, defined as $v_{ph} = \frac{\omega(k)}{k}$, and its group velocity, defined as $v_{gr} = \frac{d\omega(k)}{dk}$, which are generally both functions of k.

Example 2.2.3. For a light wave with the dispersion $\omega = ck$, we find that $v_{ph} = v_{gr} = c$, whereas for a free particle wave with the dispersion $\omega = \frac{\hbar k^2}{2m}$, we find $v_{ph} = \frac{\hbar k}{2m} = \frac{p}{2m} = \frac{v}{2}$, which is only one half of the CM velocity of the particle. On the other hand, it is the group velocity of the free particle wave, $v_{gr} = \frac{\hbar k}{m} = \frac{p}{m} = v$, which reproduces the expected classical limit.

If the wave packet in $(*)$ is initially (at $t = 0$) well-localized by the function $C(k)$ being strongly peaked at some $k = k_0$, then one can linearize the dispersion function in the exponent according to $\omega(k) \approx \omega(k_0) + v_{gr}(k_0)(k - k_0)$, giving

$$\Psi(x,t) \approx e^{-i[\omega(k_0)-v_{gr}(k_0)k_0]t} \int_{-\infty}^{\infty} dk\, C(k)\, e^{ik[x-v_{gr}(k_0)t]}.$$

Thus, we can write $\rho(x,t) \approx \rho(x - v_{gr}(k_0)t, 0)$, showing that, for not too long times, the wave packet propagates approximately without distortion, with its "center of gravity" moving with the group speed $v_{gr}(k_0)$. This is certainly a desirable feature for a free-particle wave packet because v_{gr} relates to the CM velocity, as shown in the above example. Of course, for longer times, there will be a distortion in shape of the wave packet, giving rise to the well-known wave-packet spreading in QM.

We are going to illustrate this spreading by studying an example of a time dependent Gaussian wave packet, which is initially "prepared" in such a state that it moves with some speed v_0.

Example 2.2.4. Gaussian wave packet with initial velocity v_0

Find the probability density $D(p)$ for a Gaussian wave packet that moves at the velocity v_0 at $t = 0$.

$$\begin{aligned}
\psi(x) &= \Psi(x,0) = \frac{1}{\pi^{1/4}\sqrt{d}} e^{-\frac{x^2}{2d^2}}\, e^{i\frac{m}{\hbar}v_0 x}, \quad \rho(x,0) = \frac{e^{-\frac{x^2}{d^2}}}{d\sqrt{\pi}} \\
\phi(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \psi(x) e^{-ikx} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \frac{e^{x^2} 2d^2}{\pi^{1/4}\sqrt{d}} e^{-i\left(k - \frac{mv_0}{\hbar}\right)x} \\
&= \frac{\sqrt{d}}{\pi^{1/4}} e^{-\frac{1}{2}\left(k-\frac{mv_0}{\hbar}\right)^2 d^2} \qquad (**)
\end{aligned}$$

where the last step follows from the famous Shift formula for FT, AMATH 231. Therefore,

$$D(p) = \frac{1}{\hbar}\left|\phi\left(\frac{p}{\hbar}\right)\right|^2 = \frac{d}{\hbar\sqrt{\pi}} e^{\frac{-(p-mv_0)^2}{\hbar^2} d^2},$$

showing that the factor $e^{i\frac{m}{\hbar}v_0 x}$ in $\psi(x)$ gives rise to a shift in the probability density for the momentum according to $D(p) \mapsto D(p - mv_0)$. Clearly, it is easy to show then that $\langle p \rangle = mv_0$ for all $t \geq 0$.

Example 2.2.5. Time dependence of a Gaussian wave packet

Knowing $\phi(k) \equiv \Phi(k,0)$, given in $(**)$, we can obtain an expression for $\Psi(x,t)$ for $t > 0$ starting from

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \Phi(k,t)\, e^{ikx}, \quad \text{where} \quad \Phi(k,t) = \phi(k)\, e^{-i\omega(k)t}, \quad \text{with} \quad \omega(k) = \frac{\hbar k^2}{2m}.$$

Working out the details of integration in an upcoming assignment problem, you'll be able to show that the uncertainty in the position of the wave packet is a function of time, given by $\Delta x(t) = \frac{d}{\sqrt{2}}\sqrt{1 + \left(\frac{\hbar t}{md^2}\right)^2}$. It is clear from this result that the Gaussian wave packet describing free particle is spreading on a time scale given by $\tau = md^2/\hbar$, where d is a measure of the initial width of the wave packet. Obviously, for large, massive particles, this time scale becomes large so that their spreading is not observable at times $t \ll \tau$. On the other hand, for atomic and subatomic particles, the condition $t \gg \tau$ is quickly reached, so that the wave packets associated with such particles are very broadly spread out.

3 Time-dependent Schrödinger equation

An axiom of QM states that the time evolution of a wave function is governed by the time-dependent Schrödinger equation (TDSE), given by

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t)$$

where $\hat{H}$ is the Hamilton's operator, or Hamiltonian in the position representation, which his obtained from the CM Hamilton's function $H(p,x) = \dfrac{p^2}{2m} + U(x)$ by replacing $p \to \dfrac{\hbar}{i}\dfrac{\partial}{\partial x} \equiv \hat{p}$, so that

$$\hat{p}^2 = \hat{p}\hat{p} = -\hbar^2\frac{\partial^2}{\partial x^2} \Rightarrow \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$$

giving the TDSE is a 2nd order linear homogeneous partial DE (PDE):

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

The solutions of the TDSE are subject to:

- **Initial condition** (IC) at $t = 0$: $\Psi(x,0) = f(x)$, where $f(x)$ is a known function, which is assumed to be normalized according to: $\int_{-\infty}^{\infty}|f(x)|^2\,dx = 1$.
- **Boundary conditions** (BCs) at $x \to \pm\infty$: $\Psi(\pm\infty,t) = 0$ for all $t \geq 0$, which may arise for both bounded and unbounded motion. In the latter case, there exist other types of BCs, which will be discussed later.

Example 3.0.1. Verify that the free-particle wave-packet, which was devised earlier by combining the solution of a classical wave equation in the form of a Fourier transform with the Planck-DeBroglie dispersion relation $\omega(k) = \frac{\hbar k^2}{2m}$ satisfies the TDSE with $U(x) = 0$

$$\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \\
\Rightarrow \left(i\hbar\frac{\partial}{\partial t} - \hat{H}\right)\Psi(x,t) &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\,\phi(k)\left(i\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)e^{ikx-i\omega(k)t} \\
&= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\phi(k)\left(\hbar\omega(k) - \frac{\hbar^2k^2}{2m}\right)e^{ikx-i\omega(k)t} \equiv 0
\end{aligned}$$

However, solving the TDSE with a general potential $U(x)$ is highly non-trivial. We outline the solution procedure in three steps.

In the **first step**, we perform *separation of variables* in TDSE assuming $\Psi(x,t) = \psi(x)\theta(t)$:

$$\begin{aligned} i\hbar\frac{\partial\Psi(x,t)}{\partial t} &= \hat{H}\Psi(x,t) \Rightarrow i\hbar\psi(x)\frac{d\theta(t)}{dt} = \theta(t)\hat{H}\psi(x) \\ \Rightarrow i\hbar\frac{\theta'(t)}{\theta(t)} &= \frac{\hat{H}\psi(x)}{\psi(x)} = \text{"separation constant"} = E \\ \Rightarrow & \begin{cases} \theta'(t) = -\frac{i}{\hbar}E\theta(t) \Rightarrow \theta(t) = c\, e^{-\frac{i}{\hbar}Et}, \\ \hat{H}\psi(x) = E\psi(x). \end{cases} \end{aligned}$$

While the time dependent part $\theta(t)$ is obtained trivially, we find that the x-dependent part of the solution, $\psi(x)$, must satisfy the so-called time independent Schrödinger equation (TISE), $\hat{H}\psi(x) = E\psi(x)$, given explicitly by:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x) \quad \text{or} \quad \psi''(x) + \frac{2m}{\hbar^2}[E - U(x)]\psi(x) = 0$$

which is a 2nd order ODE (for 1D motion) with unknown "separation constant" E.

We now proceed by first considering **bounded motion** in 1D, such that $U(x) \to \infty$ as $x \to \pm\infty$, which imposes the BCs on the solution of TISE that require $\psi(x) \to 0$ as $x \to \pm\infty$. In other words, the TISE constitutes the so-called Boundary-value problem (BVP), which may be expressed in Dirac's notation as $\hat{H}|\psi\rangle = E|\psi\rangle$, and hence may be considered an Eigen-value problem (EVP), with the wave function $\psi(x)$ called eigenfunction (equivalently $|\psi\rangle$ is called eigenvector) and E called eigenvalue. Recognizing that the "allowed" values of E relate to the "Hamilton's function–turned–Hamilton's operator", expressing in some way the conservation of energy at the QM level, we shall also call each such vale of E the eigenenergy. The collection of those values of E will be then called eigenenergy spectrum for the specific Hamiltonian $\hat{H}$.

In the realm of DEs there exists a theory, which parallels the theory of EVPs in Linear algebra, but is implemented to solving BVPs, and is therefore directly applicable to the TISE in the position representation. It can be briefly summarized in the following "theorem":

Theorem 3.1. Sturm-Liouville Theory (SLT) tells us that, if $\hat{H}$ is Hermitian, then solutions of the BVP are such that:

1. eigenvalues are real and they form an ordered sequence of discrete values, bounded below,

$$E_1 < E_2 < E_3 < \cdots$$

2. to each E_n there corresponds one or more eigenfunctions $\psi_n(x)$, with $n = 1, 2, 3, \cdots$, having the properties:

a) orthogonality

b) normalization

c) completeness

The indices n, which arise in the solution of the BVP, $\hat{H}\psi_n = E_n\psi_n$, are called quantum numbers, and they label different possible states of the system. For any fixed n, the solution of TDSE is called the n-th *stationary state*, given by

$$\Psi_n(x,t) = \psi_n(x)\, e^{-\frac{i}{\hbar}E_n t}$$

Notice that the probability density in the n-th stationary state is independent of time,

$$|\Psi_n(x,t)|^2 = |\psi_n(x)|^2 \equiv \rho_n(x)$$

In the **second step** of solving the TDSE, we seek its general solution in the form of *linear superposition* of stationary states,

$$\Psi(x,t) = \sum_{n=1}^{\infty} C_n\, \Psi_n(x,t) = \sum_{n=1}^{\infty} C_n\, \psi_n(x)\, e^{-\frac{i}{\hbar}E_n t}$$

which is a generalized Fourier series with $t \geq 0$ being just a parameter describing its time evolution. Theoretical issues regrading the convergence of such series were discussed in AMATH 231.

For the **unbounded motion** in 1D with, say, $U(x) \to 0$ as $x \to \pm\infty$, there exists a part of the eigenenergy spectrum taking continuous values $E > 0$, for which we can generalize our wave-packet formalism developed in the previous chapter for free particles with $U(x) = 0$. Namely, using linear superposition for the continuous part of the TDSE eigenenergy spectrum gives rise to a generalized Fourier transform,

$$\Psi(x,t) = \int_{-\infty}^{\infty} dk\, C(k)\, e^{ikx} e^{-i\omega(k)t}$$

where the integral over $k \in \mathbb{R}$ replaces the summation over n in the generalized Fourier series, the function $C(k)$ plays the role of the Fourier coefficients C_n, the (un-normalized) free-particle plane wave e^{ikx} plays the role of the bound-state eigenfunction $\psi_n(x)$, and the Planck-DeBroglie energy $E \equiv \hbar\omega(k) = \frac{\hbar^2 k^2}{2m}$ plays the role of the bound-state eigenenergy E_n.

Before we get to a discussion of a more general case of the mixed spectra of eigenenergies, we need to define one the most important algebraic "devices", the inner product, which is needed for the third step of the solution procedure.

Definition 3.1. The inner product of any two functions that are square integrable is

$$\langle f|g\rangle = \int_{-\infty}^{\infty} f^*(x) g(x) dx.$$

The norm $\|f\|$ of a function $f(x)$ is defined with its square given by

$$\|f\|^2 = \langle f|f\rangle = \int_{-\infty}^{\infty} |f(x)|^2 dx.$$

Then, the *orthonormality* of a discrete set $\{\psi_n(x)\}$ of the solutions of a TISE for bounded motion is expressed in terms of their inner product and the Kronecker delta as

$$\langle \psi_n|\psi_m\rangle = \delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}$$

This relation is then used in the **third step** of solving the TDSE for bounded motion to find the Fourier coefficients C_n from the IC. This is achieved by setting $t = 0$ in the general solution,

$$\Psi(x, 0) = f(x) = \sum_{n=1}^{\infty} C_n \psi_n(x),$$

multiplying this equation with $\psi_m^*(x)$ for an arbitrarily chosen fixed m, and integrating over x. As a result, we obtain

$$\langle \psi_m|f\rangle = \sum_{n=1}^{\infty} C_n \langle \psi_m|\psi_n\rangle = \sum_{n=1}^{\infty} C_n \, \delta_{mn} = C_m$$

where the last equality follows from the sifting property of the Kronecker delta δ_{mn}, so that finally we have

$$C_n = \langle \psi_n|f\rangle = \int_{-\infty}^{\infty} \psi_n^*(x) f(x) dx.$$

An expression for the *completeness* of the set of orthonormal solutions of the TISE for bounded motion, $\{\psi_n(x)\}$, which could be used as a basis in the space of all square-integrable functions, may be obtained in terms of the Dirac's delta function by recognizing

$$f(x) = \sum_{n=1}^{\infty} \psi_n(x) C_n = \sum_{n=1}^{\infty} \psi_n(x) \int_{-\infty}^{\infty} \psi_n^*(x') f(x') dx' = \int_{-\infty}^{\infty} f(x') \left[\sum_{n=1}^{\infty} \psi_n^*(x') \psi_n(x) \right] dx'.$$

By comparing the first and the last expressions in the above string of equalities, and invoking the sifting property of Dirac's delta function, we may claim that

$$\sum_{n=1}^{\infty} \psi_n^*(x') \psi_n(x) = \delta(x' - x).$$

ASIDE: Dirac's bra-ket notation

The completeness relation may also be expressed in an operator form as

$$\sum_{n=1}^{\infty} |\psi_n\rangle\langle\psi_n| = \hat{1},$$

which is sometimes called "resolution of the identity operator $\hat{1}$". The terms in the above summation may be considered to be the "outer" products of two vectors, $|\psi_n\rangle$ and its dual (or transpose) vector $\langle\psi_n|$, as seen in Linear algebra, which form the projection operator $|\psi_n\rangle\langle\psi_n|$ for the nth quantum state. Moreover, we regard the eigenfunction $\psi_n(x)$, obtained in the process of solving TISE for bounded motion as the position representation of the nth quantum state, i.e.,

$$\langle x|n\rangle \equiv \langle x|\psi_n\rangle = \psi_n(x), \qquad \langle n|x\rangle \equiv \langle\psi_n|x\rangle = \psi_n^*(x).$$

Here, $|x\rangle$ is an eigenstate of the position operator, $\hat{x}|x\rangle = x|x\rangle$, and x is its eigenvalue $\in \mathbb{R}$. Since the EVP for the position operator $\hat{x}$ has continuous spectrum, we express its orthogonality in terms of Dirac's delta function, $\langle x|x'\rangle = \delta(x'-x)$, rather than Kronecker delta. This relation may also be interpreted as the position eigenvector $|x'\rangle$ expressed in its own eigenbasis. To demonstrate how the above resolution of the identity operator works in Dirac's notation, we "insert" $\hat{1}$ in the inner product $\langle x|x'\rangle$ and obtain

$$\langle x|x'\rangle = \langle x|\hat{1}|x'\rangle = \langle x|\left(\sum_{n=1}^{\infty}|\psi_n\rangle\langle\psi_n|\right)|x'\rangle = \sum_{n=1}^{\infty}\langle x|\psi_n\rangle\langle\psi_n|x'\rangle = \sum_{n=1}^{\infty}\psi_n^*(x')\psi_n(x) = \delta(x'-x).$$

3.1 Types of energy spectra

Consider TDSE, $i\hbar\dfrac{\partial\Psi}{\partial t} = \hat{H}\Psi$ and corresponding TISE: $\hat{H}\psi(x) = E\psi(x)$ for a potential satisfying $\lim_{x\to\pm\infty} U(x) \equiv U_{L,R} < \infty$ (see figure).

If $\min\{U(x)\} < E < \min\{U_L, U_R\}$, we get quantization of energy, $E_1 < E_2 < \cdots < E_{n_{max}}$, which constitutes discrete part of the energy spectrum corresponding to bounded motion.

If $E >$min $\{U_L, U_R\} \equiv E_{min} \geq E_{n_{max}}$, no quantization of energy occurs, and E is real number $\geq E_{min}$ corresponding to unbounded motion, which constitutes continuous part of the energy spectrum.

Therefore, general solution of TDSE may be written as

$$\Psi(x,t) = \sum_{n=1}^{n_{max}} a_n\psi_n(x)e^{-\frac{i}{\hbar}E_n t} + \int_{E_{min}}^{\infty} dE\, a(E)\psi_E(x)e^{-\frac{i}{\hbar}Et}.$$

The coefficients a_n and the function $a(E)$ can be, in principle, found from the initial condition $\Psi(x,0) =$

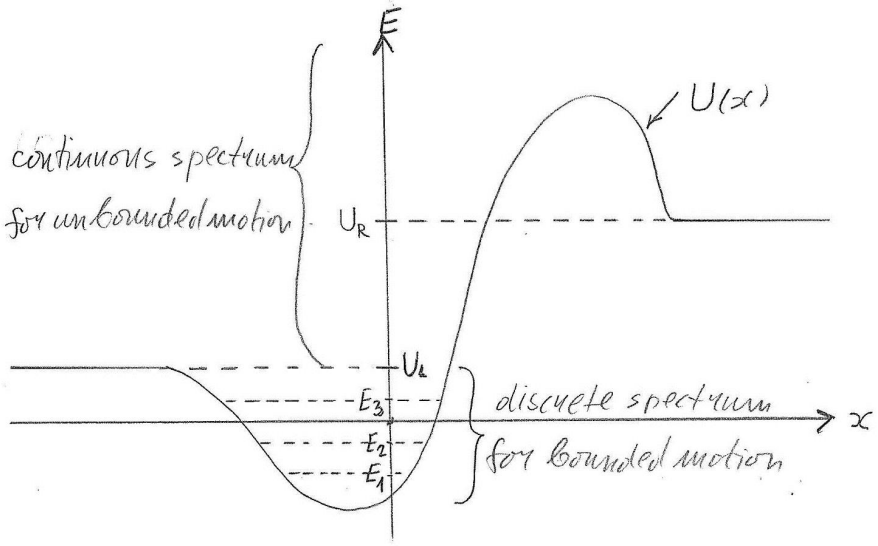


Figure 1: Mixed energy spectrum

$f(x)$, but we need to first carefully consider the orthogonality of the eigenfunctions $\psi_E(x)$ in the continuous spectrum .

Obviously, we have to abandon the BCs $\psi_E(\pm\infty) = 0$ for the continuous spectrum and invoke the so-called periodic BCs for unbounded motion. In addition, we would need two kinds of eigenfunctions, say $\psi_E^{(\pm)}(x)$, describing motion to the right and to the left, respectively, at a given energy $E \geq E_{min}$.

3.2 Free particle revisited

For a free particle, $U(x) = 0$, instead of solving TISE $\hat{H}\psi_E(x) = E\psi_E(x)$, we solve the eigenvalue problem for the momentum operator $\hat{p}$ in the position representation,

$$\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}, \quad \hat{p}\psi_p(x) = p\psi_p(x)$$

Notice that $\psi_p(x)$ is also an eigenfunction of $\hat{H}$ because

$$\hat{H}\psi_p(x) = \frac{\hat{p}^2}{2m}\psi_p(x) = \frac{1}{2m}\hat{p}\left(\hat{p}\psi_p(x)\right) = \frac{1}{2m}\hat{p}\left(p\psi_p(x)\right) = \frac{p}{2m}\hat{p}\psi_p(x) = \frac{p^2}{2m}\psi_p(x) = E_p\psi_p(x)$$

so the solution of TISE for free particle, $\hat{H}\psi_p(x) = E_p\psi_p(x)$, has eigenstates labeled by p and eigenenergies given by $E_p = \frac{p^2}{2m} > 0$. Here, $\psi_p(x)$ is a solution of the momentum EVP with $p \in \mathbb{R}$, given by

$$\hat{p}\psi_p(x) = p\psi_p(x) \Rightarrow \psi_p'(x) = \frac{i}{\hbar}p\psi_p(x) \Rightarrow \psi_p(x) = Ce^{i\frac{p}{\hbar}x}.$$

An advantage of using the eigenfunctions of $\hat{p}$ to construct a general solution of TDSE for free particle,

$$\Psi(x,t) = \int_0^\infty dE\ a(E)\psi_E(x)e^{-\frac{i}{\hbar}Et} \to \int_{-\infty}^\infty dp\ b(p)\psi_p(x)e^{-i\frac{E_p}{\hbar}t}$$

where the sign of p gives a resolution of the direction of motion: $p > 0 \Rightarrow$ motion to the right, $p < 0 \Rightarrow$ motion to the left (more about it later).

Question: How can we express the orthonormality of the momentum eignefunctions $\psi_p(x) = C\, e^{i\frac{p}{\hbar}x}$, i.e., what should be C?

Recall, for bounded motion: $\langle\psi_{n'}|\psi_n\rangle = \delta_{n'n}$ = Kronecker delta in discrete spectrum. Now, we want $\langle\psi_{p'}|\psi_p\rangle = \delta(p'-p)$ = Dirac delta (function), so that

$$\langle\psi_{p'}|\psi_p\rangle = \int_{-\infty}^\infty \psi^*_{p'}(x)\psi_p(x)dx = |C|^2\int_{-\infty}^\infty dx e^{\frac{i}{\hbar}(p-p')x} = |C|^2 2\pi\hbar\,\delta(p'-p) \Rightarrow C = \frac{1}{\sqrt{2\pi\hbar}}$$

and hence the delta-function normalized eigenfunction of the momentum operator in the position representation is

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{i\frac{p}{\hbar}x}$$

This result for C may also be obtained by considering the solution $\psi_p(x) = Ce^{i\frac{p}{\hbar}x}$ on finite interval $|x| \le \frac{L}{2}$, imposing the periodic BC: $\psi_p\left(-\frac{L}{2}\right) = \psi_p\left(\frac{L}{2}\right)$, and letting $L \to \infty$. As a result, one would ensure $\langle\psi_{p'}|\psi_p\rangle \to \delta(p'-p)$ by letting $C = 1/\sqrt{2\pi\hbar}$.

So, we have recovered the free-particle wave packet, written in terms of the momentum eigenfunctions $\psi_p(x)$ as

$$\Psi(x,t) = \int_{-\infty}^\infty dp\, b(p)\, \psi_p(x)\, e^{-\frac{i}{\hbar}E_p t} = \int_{-\infty}^\infty dp\, b(p)\, \frac{e^{i\frac{p}{\hbar}x}}{\sqrt{2\pi\hbar}}\, e^{-i\frac{p^2}{2m\hbar}t}$$

To find $b(p)$ from the IC: $\Psi(x,0) = f(x)$ (with $\|f\| = 1$), we use the delta-function orthonormality of $\psi_p(x)$,

$$\begin{aligned}
f(x) &= \int_{-\infty}^\infty dp\ b(p)\,\psi_p(x) \\
\langle\psi_{p'}|f\rangle &= \int_{-\infty}^\infty dp\, b(p)\langle\psi_{p'}|\psi_p\rangle = \int_{-\infty}^\infty dp\, b(p)\delta(p-p') = b(p') \\
\Rightarrow b(p) &= \langle\psi_p|f\rangle = \int_{-\infty}^\infty dx\,\psi^*_p(x)f(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^\infty dx\, e^{-i\frac{p}{\hbar}x}f(x) = \frac{1}{\sqrt{\hbar}}\phi\left(\frac{p}{\hbar}\right).
\end{aligned}$$

Notice that $b(p) = \frac{1}{\sqrt{\hbar}}\phi(k)$ with $k = p/\hbar$, where $\phi(k)$ was introduced earlier for free particle wave packets.

At this point, we may invoke a QM axiom, which assigns the probabilistic interpretation to $|\langle\psi_p|f\rangle|^2$,

and recognize that, for the continuous energy spectrum,

$$|b(p)|^2 = |\langle \psi_p | f \rangle|^2 = \frac{1}{\hbar} \left| \phi\left(\frac{p}{\hbar}\right) \right|^2 = D(p)$$

is the familiar probability density for the momentum, obtained earlier from Parseval formula for a free-particle wave packet in 1D.

ASIDE: Dirac's bra-ket notation

We see that the eigenfunction $\psi_p(x)$ is the position representation of the eigenstate $|p\rangle$ of the momentum EVP $\hat{p}|p\rangle = p|p\rangle$,

$$\langle x|p\rangle \equiv \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{p}{\hbar}x},$$

while its complex conjugate,

$$\langle p|x\rangle \equiv \psi_p^*(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{-i\frac{p}{\hbar}x},$$

may be considered to be the momentum representation of the position eigenstate $|x\rangle$. Together, they constitute the kernels in the dual integrals defining the Fourier transform pair $f(x)$ and $b(p)$.

The orthonormality of the eigenstates $|p\rangle$,

$$\langle p'|p\rangle \equiv \langle \psi_{p'}|\psi_p\rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dx\, e^{\frac{i}{\hbar}(p-p')x} = \delta(p-p') = \int_{-\infty}^{\infty} dx\, \langle p'|x\rangle\langle x|p\rangle$$

is consistent with the completeness of the position eigenbasis,

$$\int_{-\infty}^{\infty} dx\, |x\rangle\langle x| = \hat{1}.$$

Similarly, the completeness of the momentum eigenbasis in the position representation may be expressed in terms of delta function,

$$\int_{-\infty}^{\infty} dp\, \psi_p^*(x')\psi_p(x) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp\, e^{\frac{i}{\hbar}(x-x')p} = \delta(x-x')$$

or as a "resolution of the identity operator" in the Dirac's bra-ket notation,

$$\int_{-\infty}^{\infty} |p\rangle\langle p|\, dp = \hat{1},$$

which is consistent with the delta-function normalization of the position eigenstates,

$$\langle x'|x\rangle = \int_{-\infty}^{\infty} dp\, \langle x|p\rangle\langle p|x'\rangle = \delta(x-x').$$

3.3 Examples of bounded motion in 1D

The form of $U(x)$ sometimes requires careful consideration of BCs for solutions of TISE

Example 3.1.1.

$$U(x) = U_0\left(x + \frac{1}{x}\right), \quad x > 0$$

requires that $\psi(x) = 0$ for $x \leq 0$ and $\lim_{x\to\infty} \psi(x) = 0$

Example 3.1.2. Piecewise continuous potential

$$U(x) = \begin{cases} \infty & x \leq a \\ U_1 & a < x \leq b \\ U_2 & b < x \leq c \\ \infty & x \geq c \end{cases}$$

which has infinite jumps at $x = a$, c and finite jump at $x = b$, implies a solution of TISE in piecewise form:

$$\psi(x) = \begin{cases} 0 & x \leq a \\ \cdots & a < x \leq b \\ \cdots & b < x \leq c \\ 0 & x \geq c \end{cases}$$

Note that we must impose matching conditions for the solution at points where $U(x)$ has jumps:

$$\left.\begin{array}{l} \psi(a^+) = \psi(a^-) \equiv 0 \\ \psi(c^-) = \psi(c^+) \equiv 0 \end{array}\right\} \psi(x) \text{ is continuous when } U(x) \text{ has infinite jumps}$$

$$\left.\begin{array}{l} \psi(b^-) = \psi(b^+) \\ \psi'(b^-) = \psi'(b^+) \end{array}\right\} \psi(x) \text{ is } C^1 \text{ when } U(x) \text{ has finite jump}$$

Example 3.1.3. Solve TISE for a particle in box (PIB), defined by $U(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{elsewhere} \end{cases}$

We have $\psi(x) = 0$ for $x \leq 0$ and $x \geq L$, whereas the TISE for $0 \leq x \leq L$ reads

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x)$$

Assume $E \geq 0$, define $k = \frac{\sqrt{2mE}}{\hbar} \geq 0$, and solve $\psi''(x) + k^2\psi(x) = 0$, subject to: $\psi(0) = 0, \psi(L) = 0$:

$$\psi = Ae^{ikx} + Be^{-ikx} = C_1\cos(kx) + C_2\sin(kx) \Rightarrow \psi(0) = C_1 = 0;\ \psi(L) = C_2\sin(kL) = 0 \Rightarrow kL = n\pi \Rightarrow k_n = n\frac{\pi}{L}$$

Hence we get

$$\begin{aligned} E_n &= \frac{\hbar^2}{2m}\left(n\frac{\pi}{L}\right)^2, n = 1, 2, 3, \cdots \\ \psi_n(x) &= C\,\sin\left(n\frac{\pi}{L}x\right) \end{aligned}$$

Find C from normalization:

$$\begin{aligned} \int_{-\infty}^{\infty}|\psi_n|^2 dx &= C^2\int_0^L \sin^2\left(n\frac{\pi}{L}x\right)dx = C^2\frac{L}{2} = 1 \Rightarrow C = \sqrt{\frac{2}{L}} \\ \Rightarrow \psi_n(x) &= \sqrt{\frac{2}{L}}\sin\left(n\frac{\pi}{L}x\right) \end{aligned}$$

Notice that $\{\psi_n(x)\}$ is orthonormal set:

$$\langle\psi_{n'}|\psi_n\rangle = \int_{-\infty}^{\infty}\psi^*_{n'}(x)\psi_n(x)\,dx = \frac{2}{L}\int_0^L \sin\left(n'\frac{\pi}{L}x\right)\sin\left(n\frac{\pi}{L}x\right)\,dx = \delta_{n'n}$$

Solve TDSE $i\hbar\dfrac{\partial\Psi}{\partial t} = \hat{H}\Psi$, subject to the IC: $\Psi(x,0) = f(x)$, such that $\displaystyle\int_0^L |f(x)|^2 dx = 1$.

Principle of linear superposition gives:

$$\Psi(x,t) = \sum_{n=1}^{\infty} C_n\psi_n(x)e^{-\frac{i}{\hbar}E_n t}$$

Determine C_n's from the IC:

$$C_n = \langle\psi_n|f\rangle = \int_{-\infty}^{\infty}\psi^*_n(x)f(x)dx = \sqrt{\frac{2}{L}}\int_0^L \sin\left(n\frac{\pi}{L}x\right)\,f(x)\,dx$$

3.4 Probabilistic interpretation of solutions for bounded motion

Consider the general solution of TDSE for bounded motion

$$\Psi(x,t) = \sum_{n=1}^{\infty} C_n\psi_n(x)e^{-\frac{i}{\hbar}E_n t}$$

and the corresponding generalized Fourier series

$$f(x) = \sum_{n=1}^{\infty} C_n\psi_n(x),$$

which is used to determine the coefficients that will accommodate the IC $\Psi(x,0) = f(x)$ for (almost) any normalized initial wave function $f(x)$.

According to an axiom of QM, $p_n = |C_n|^2 \equiv |\langle \psi_n | f \rangle|^2$ gives the probability that the system is initially found in the n-th eigenstate of the associated TISE, and hence has the energy E_n. Assuming that the IC for TDSE is a normalized function, $\|f\| = 1$, we invoke Parseval's formula for Fourier series studied in AMATH 231,

$$\sum_{n=1}^{\infty} |C_n|^2 = \int_{-\infty}^{\infty} |f(x)|^2 \, dx,$$

so that $\int_{-\infty}^{\infty} |f(x)|^2 \, dx = \|f\|^2 = 1$ implies the normalization

$$\sum_{n=1}^{\infty} p_n = 1.$$

Moreover, $|\langle \psi_n | \Psi(t) \rangle|^2$ gives the probability that the system is observed in the n-th eigenstate $|\psi_n\rangle$ at time $t \geq 0$. Notice that this probability does not depend on time:

$$\begin{aligned} |\langle \psi_n | \Psi(t) \rangle|^2 &= \left| \int_{-\infty}^{\infty} \psi_n^*(x) \Psi(x,t) dx \right|^2 = \left| \int_{-\infty}^{\infty} \psi_n^*(x) \left[\sum_{n'=1}^{\infty} C_{n'} \psi_{n'}(x) e^{-\frac{i}{\hbar} E_{n'} t} \right] dx \right|^2 \\ &= \left| \sum_{n'=1}^{\infty} C_{n'} e^{-\frac{i}{\hbar} E_{n'} t} \int_{-\infty}^{\infty} \psi_n^*(x) \psi_{n'}(x) dx \right|^2 = \left| \sum_{n'=1}^{\infty} C_{n'} e^{-\frac{i}{\hbar} E_{n'} t} \, \delta_{nn'} \right|^2 = \left| C_n e^{-\frac{i}{\hbar} E_n t} \right|^2 = |C_n|^2 \equiv p_n \end{aligned}$$

This should be compared with the probabilistic interpretation of the solutions of the TDSE for a free particle wave packet using the continuum of the momentum eigenstates $|\psi_p\rangle$, which gives the probability density independent of time,

$$|b(p)|^2 = |\langle \psi_p | f \rangle|^2 = D(p).$$

We are now equipped with the set of probabilities p_n and the corresponding eigenenergies E_n that can be taken by a particle undergoing bounded motion, which is initially "prepared" in a state described by the wavefunction $f(x)$. Thus, the total (expected) energy is given by $\overline{E} = \sum_{n=1}^{\infty} p_n \, E_n$, which is independent of time, expressing the conservation of energy at the probabilistic level. Moreover, we can apply rules of the classical probability theory to express the kth moment of energy as

$$\overline{E^k} = \sum_{n=1}^{\infty} p_n \, E_n^k,$$

enabling us to evaluate, e.g., the uncertainty in energy as $\Delta E = \sqrt{\overline{E^2} - \overline{E}^2}$, which is also independent of time.

3.5 Continuity equation and conservation of probability

Consider TDSE and its complex conjugate: $\frac{\partial}{\partial t}\Psi(x,t) = \frac{1}{i\hbar}\hat{H}\Psi(x,t)$ and $\frac{\partial}{\partial t}\Psi^*(x,t) = -\frac{1}{i\hbar}\hat{H}\Psi^*(x,t)$, where $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$. Then, the time rate of change of the probability density for the position is

$$\begin{aligned}
\frac{\partial}{\partial t}\rho(x,t) &= \frac{\partial}{\partial t}|\Psi(x,t)|^2 = \frac{\partial}{\partial t}\Psi^*\Psi = \Psi^*\frac{\partial \Psi}{\partial t} + \Psi\frac{\partial \Psi^*}{\partial t} \\
&= \frac{1}{i\hbar}[\Psi^*\hat{H}\Psi - \Psi\hat{H}\Psi^*] = -\frac{\hbar}{2mi}\left[\Psi^*\frac{\partial^2\Psi}{\partial x^2} - \Psi\frac{\partial^2\Psi^*}{\partial x^2}\right] \\
\Rightarrow \frac{\partial \rho}{\partial t} &= -\frac{\hbar}{2mi}\frac{\partial}{\partial x}\left[\Psi^*\frac{\partial \Psi}{\partial x} - \Psi\frac{\partial \Psi^*}{\partial x}\right] = -\frac{\hbar}{2mi}\frac{\partial}{\partial x}\left[2i\Im\left[\Psi^*\frac{\partial \Psi}{\partial x}\right]\right] \\
&= -\frac{\partial}{\partial x}j(x,t)
\end{aligned}$$

where we have defined the *probability flux density* as

$$j(x,t) = \frac{\hbar}{m}\Im\left[\Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t)\right] = \frac{1}{m}\Re\left[\Psi^*(x,t)\,\hat{p}\,\Psi(x,t)\right]$$

in such a way that we obtain a continuity equation relating ρ and j:

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0.$$

Example 3.1.4. Prove that, for bounded motion, $\|\Psi(t)\|^2 \equiv \int_{-\infty}^{\infty}\rho(x,t)\,dx = \text{constant} = 1$ for all $t \geq 0$:

$$\begin{aligned}
\frac{d}{dt}\int_{-\infty}^{\infty}\rho(x,t)dx &= \int_{-\infty}^{\infty}\frac{\partial \rho(x,t)}{\partial t}dx = -\lim_{\substack{a\to-\infty \\ b\to\infty}}\int_a^b \frac{\partial j(x,t)}{\partial x}dx \\
&= -\lim_{\substack{a\to-\infty \\ b\to\infty}} j(x,t)\Big|_a^b = \lim_{a\to-\infty} j(a,t) - \lim_{b\to\infty} j(b,t) = 0
\end{aligned}$$

where the last equality follows from the BCs at infinity, $\Psi(\pm\infty,t) = 0$, imposed on the TDSE for bounded motion, and the definition of the probability flux density $j(x,t)$. Hence, $\|\Psi(t)\| =$ constant and, since $\|\Psi(0)\| = \|f\| = 1$ at $t = 0$, we have $\|\Psi(t)\| = 1$ for all $t \geq 0$.

3.6 Expectation value and matrix elements of an operator

According to an axiom of QM, to each physical observable, there corresponds an operator $\hat{\Omega} = \Omega(\hat{p}, x) = \Omega(\hat{p}, \hat{x})$.

Measurements of $\hat{\Omega}$ in some state $\Psi(x,t)$ that describes bounded motion give its expectation value at time t as

$$\begin{aligned}\langle\hat{\Omega}\rangle_t &= \langle\Psi(t)|\hat{\Omega}|\Psi(t)\rangle = \int_{-\infty}^{\infty}\Psi^*(x,t)[\hat{\Omega}\Psi(x,t)]\,dx = \int_{-\infty}^{\infty}dx\sum_{n'=1}^{\infty}C^*_{n'}\psi^*_{n'}(x)e^{\frac{i}{\hbar}E_{n'}t}\sum_{n=1}^{\infty}C_n\,e^{-\frac{i}{\hbar}E_nt}\hat{\Omega}\psi_n(x)\\ &= \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}C^*_{n'}C_ne^{\frac{i}{\hbar}(E_{n'}-E_n)t}\left[\int_{-\infty}^{\infty}\psi^*_{n'}(x)\hat{\Omega}\psi_n(x)\,dx\right] = \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}C^*_{n'}C_ne^{\frac{i}{\hbar}(E_{n'}-E_n)t}\Omega_{n'n}\end{aligned}$$

where $\Omega_{n'n} \equiv \langle\psi_{n'}|\hat{\Omega}|\psi_n\rangle = \int_{-\infty}^{\infty}\psi^*_{n'}(x)\,\hat{\Omega}\,\psi_n(x)\,dx$ is a matrix element of $\hat{\Omega}$ in the basis $\{\psi_n(x)\}$.

Notice that, if $\hat{\Omega}$ is Hermitian operator, then $\Omega_{n'n} = \Omega^*_{nn'}$, and hence its expectation value $\langle\hat{\Omega}\rangle_t$ is real.

Example 3.1.5. Show that average energy $\overline{E} = \langle\hat{H}\rangle_t = $ constant:

$$\begin{aligned}H_{n'n} &= \langle\psi_{n'}|\hat{H}|\psi_n\rangle = \langle\psi_{n'}|\hat{H}\psi_n\rangle = \int\psi^*_{n'}(x)\hat{H}\psi_n(x)dx = E_n\langle\psi_{n'}|\psi_n\rangle = E_n\delta_{n'n}\\ \overline{E} &= \langle\hat{H}\rangle_t = \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}C^*_{n'}C_ne^{\frac{i}{\hbar}(E_{n'}-E_n)t}E_n\delta_{n'n} = \sum_{n=1}^{\infty}C^*_nC_ne^{\frac{i}{\hbar}(E_n-E_n)t}E_n = \sum_{n=1}^{\infty}|C_n|^2E_n = \sum_{n=1}^{\infty}p_nE_n = \text{const}\end{aligned}$$

Uncertainty in E, $\Delta E = \sqrt{\overline{E^2} - \overline{E}^2} = \sqrt{\langle\hat{H}^2\rangle_t - \langle\hat{H}\rangle_t^2} = $ constant because:

$$\begin{aligned}H^2_{n'n} &= \langle\psi_{n'}|\hat{H}^2|\psi_n\rangle = \langle\psi_{n'}|\hat{H}\hat{H}\psi_n\rangle = E_n\langle\psi_{n'}|\hat{H}\psi_n\rangle = E_n^2\langle\psi_{n'}|\psi_n\rangle = E_n^2\delta_{n'n}\\ \overline{E^2} &= \langle\hat{H}^2\rangle_t = \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}C^*_{n'}C_ne^{\frac{i}{\hbar}(E_{n'}-E_n)t}E_n^2\delta_{n'n} = \sum_{n=1}^{\infty}C^*_nC_ne^{\frac{i}{\hbar}(E_n-E_n)t}E_n^2 = \sum_{n=1}^{\infty}|C_n|^2E_n^2 = \sum_{n=1}^{\infty}p_nE_n^2 = \text{const}\end{aligned}$$

Note that, for a stationary state with fixed $n = n_0$, $\Psi_{n_0}(x,t) = \psi_{n_0}(x)e^{-\frac{i}{\hbar}E_{n_0}t}$, we have $p_n = \delta_{nn_0}$, so that

$$\overline{E} = E_{n_0}, \quad \overline{E^2} = E^2_{n_0} \Rightarrow \Delta E = \sqrt{\overline{E^2} - \overline{E}^2} = 0.$$

While this result is deduced for the uncertainty in the expectation value of the Hamiltonian in its eigenstate $|n_0\rangle$, it can be generalized to any operator $\hat{\Omega}$ in QM: the uncertainty in the expectation value of an operator, when taken in an eigenstate of that operator, will necessarily vanish.

Example 3.1.6. Evaluate matrix elements of position and momentum in the particle-in-box (PIB) system with

$$E_n = \frac{\hbar^2}{2m}\left(n\frac{\pi}{L}\right)^2, \quad \psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(n\frac{\pi}{L}x\right) \quad \text{for} \quad 0 \le x \le L$$

$$\begin{aligned} x_{n'n} &= x_{nn'} = \langle\psi_{n'}|x|\psi_n\rangle = \int \psi^*_{n'}(x)x\psi_n(x)\,dx = \begin{cases} \frac{L}{2} & n' = n \\ -\frac{8n'nL}{(n'^2-n^2)^2\pi^2} & n' \neq n \end{cases} \\ p_{n'n} &= p^*_{nn'} = \langle\psi_{n'}|\hat{p}|\psi_n\rangle = \int \psi^*_{n'}\frac{\hbar}{i}\frac{\partial}{\partial x}\psi_n(x)\,dx = \begin{cases} 0 & n' = n \\ -i\frac{\hbar}{L}\frac{4n'n}{n'^2-n^2} & n' \neq n \end{cases} \end{aligned}$$

Example 3.1.7. Verify HUR for the PIB system in the nth stationary state

$$\begin{aligned} x_{nn} &= \overline{x}_n = \frac{L}{2} \\ \overline{x^2}_n &= \int x^2|\psi_n(x)|^2\,dx = \frac{2}{L}\int_0^L x^2\sin^2\left(n\frac{\pi}{L}x\right)\,dx = L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) \\ \Delta x &= \sqrt{\overline{x^2}_n - \overline{x}_n^2} = L\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}} \\ p_{nn} &= \overline{p}_n = 0 \\ \overline{p^2}_n &= \langle\psi_n|\hat{p}^2|\psi_n\rangle = \int \psi^*_n(x)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2\psi_n(x)\,dx = -\hbar^2\int \psi^*_n(x)\psi''_n(x)\,dx = \cdots \end{aligned}$$

Notice that $\overline{p^2}_n$ can be found without any computation by using TISE $\hat{H}\psi_n = E_n\psi_n$ and recalling that $\hat{H} = \frac{\hat{p}^2}{2m}$ in the interval $0 \le x \le L$ where eigenfunctions are nonzero, so that

$$\begin{aligned} \overline{p^2}_n &= \langle\psi_n|2m\hat{H}|\psi_n\rangle = 2mE_n\|\psi_n\|^2 = \hbar^2\left(n\frac{\pi}{L}\right)^2 \\ \Rightarrow \Delta p_n &= \sqrt{\overline{p^2}_n} = n\frac{\pi}{L}\hbar \\ \Rightarrow \Delta p_n\Delta x_n &= \frac{\hbar}{2}\sqrt{n^2\frac{\pi^2}{3} - 2} > \frac{\hbar}{2} \quad \text{for} \quad n = 1, 2, 3, \ldots \end{aligned}$$

4 Examples of unbounded motion

4.1 Conservation of probability flux for unbounded motion

Consider unbounded motion of a particle of mass m in the general case of a potential such that $\lim_{x\to\mp\infty} U(x) = U_{L,R} < \infty$ (see Figure 1 on page 21 in section 3.1). Assume that the particle may be represented by a wave-packet of very large width d, so that we may neglect its spreading over times $\tau = \frac{m}{\hbar}d^2 \to \infty$. In addition, by HUR, $\Delta x \propto d \to \infty$ implies $\Delta p \to 0$, and hence $\Delta E \approx \frac{p}{m}\Delta p \to 0$, so that we may assume that the particle moves at a fixed (that is, statistically sharp) energy $E = \dfrac{p^2}{2m}$, which belongs to a continuous part of the energy spectrum at $E > \min(U_L, U_R)$.

Thus, the solution of the TDSE is simply given by a stationary state wave function

$$\Psi(x,t) = \psi(x)e^{-\frac{i}{\hbar}Et}$$

so that the probability density $\rho(x) = |\Psi(x,t)|^2 =$ independent of t.

Also the probability flux is independent of t:

$$j(x) = \frac{\hbar}{2mi}\left[\Psi^*\frac{\partial}{\partial x}\Psi - \Psi\frac{\partial}{\partial x}\Psi^*\right] = \frac{1}{m}\Re\left[\Psi^*(x,t)\,\hat{p}\,\Psi(x,t)\right] = \frac{1}{m}\Re[\psi(x)^*\,\hat{p}\,\psi(x)]$$

Notice that, because the BCs $\psi(\pm\infty) = 0$ do not necessarily apply for unbounded motion, the flux does not have to vanish as $x \to \mp\infty$.

Consider potential $U(x)$, such that $U(x) = U_L$=constant for $x < x_L < 0$ and $U(x) = U_R$=constant for $x > x_R > 0$, with both $|x_L|$ and x_R being very large but still $\ll d$, whereas $U(x)$ is arbitrary for $x_L \le x \le x_R$. Define the probability that the particle can be found in the interval $[x_L, x_R]$,

$$P_{[x_L,x_R]} = \int_{x_L}^{x_R} \rho(x)dx$$

and integrate the continuity equation $\frac{\partial\rho}{\partial t} + \frac{\partial j}{\partial x} = 0$ over $[x_R, x_R]$,

$$\int_{x_L}^{x_R}\left(\frac{\partial\rho}{\partial t} + \frac{\partial j}{\partial x}\right)dx = 0$$

Because ρ is independent of time, we have $\frac{d}{dt}P_{[x_L,x_R]} \equiv \int_{x_L}^{x_R}\frac{\partial\rho}{\partial t}\,dx = 0$, so that

$$0 = \int_{x_L}^{x_R}\frac{\partial j}{\partial x}dx = j(x_R) - j(x_L).$$

So, on defining $j_{L,R} \equiv j(x_{L,R})$ and letting $x_{L,R} \to \mp\infty$, we have a statement of the conservation of flux for unbounded motion in 1D, written as

$$j_L = j_R$$

4.2 Transmission and reflection probabilities

For the unbounded motion in the potential, which levels off at U_L=constant for $x < x_L$ and at U_R=constant for $x > x_R$, assume the energy $E > \max(U_L, U_R)$, and solve TISE in the piece-wise manner. In the regions $x < x_L$ and $x > x_R$ where the potential is constant, we have

$$-\frac{\hbar^2}{2m}\psi''(x) + U(x)\psi(x) = E\psi(x) \quad \to \quad \psi''(x) + k_{L,R}^2\,\psi(x) = 0, \quad k_{L,R} \equiv \frac{\sqrt{2m(E-U_{L,R})}}{\hbar}$$

giving the full solution of the TISE as

$$\psi(x) = \begin{cases} \psi_L(x) \equiv Ae^{ik_L x} + Be^{-ik_L x}, & x < x_L \\ \text{something}, & x_L < x < x_R \\ \psi_R(x) \equiv Ce^{ik_R x} + De^{-ik_R x}, & x > x_R \end{cases}$$

We can now easily calculate the fluxes in the far regions. For $x < x_L$ we obtain

$$\begin{aligned} j_L &= \frac{1}{m}\Re\left[\psi_L^*(x)\frac{\hbar}{i}\frac{\partial}{\partial x}\psi_L(x)\right] = \frac{1}{m}\Re\left\{\left[A^*e^{-ik_L x} + B^*e^{ik_L x}\right]\hbar k_L\left[Ae^{ik_L x} - Be^{-ik_L x}\right]\right\} \\ &= \frac{\hbar k_L}{m}\Re\left[|A|^2 - |B|^2 + AB^*e^{2ik_L x} - A^*Be^{-2ik_L x}\right] = \frac{\hbar k_L}{m}Re\left[|A|^2 - |B|^2 + 2i\Im\left(AB^*e^{2ik_L x}\right)\right] \\ &= v_L\left(|A|^2 - |B|^2\right) = v_L|A|^2 - v_L|B|^2 \equiv j_L^{in} - j_L^{out} \end{aligned}$$

where we defined the particle speed far to the left by $v_L = \dfrac{\hbar k_L}{m}$, and the incoming and outgoing fluxes far to the left by $j_L^{in} = v_L|A|^2$ and $j_L^{out} = v_L|B|^2$, respectively. Similarly, we define the speed $v_R = \dfrac{\hbar k_R}{m}$ far to the right and find the flux for $x > x_R$ to be

$$j_R = v_R\left(|C|^2 - |D|^2\right) = v_R|C|^2 - v_R|D|^2 \equiv j_R^{out} - j_R^{in}$$

Therefore, the conservation of flux $j_L = j_R$ can be rewritten as

$$j_L^{in} + j_R^{in} = j_L^{out} + j_R^{out}$$

indicating that the total current that is incoming onto the interval $[x_L, x_R]$ from the regions far to the left and far to the right, equals the total current outgoing to the regions far to the left and far to the right.

In typical experimental situations, one sends a beam of particle as a plane wave incoming from either far left or far right regions, and measures the fractions of the the beam, which is reflected and transmitted by the potential in the interval $[x_L, x_R]$. To be specific, let $D = 0$, so that $j_R^{inc} = 0$, and define the transmission and reflection probabilities for particles incoming from the left and being either transmitted to the right or reflected back to the left:

$$T_{LR} = \frac{j_R^{out}}{j_L^{inc}} = \frac{v_R|C|^2}{v_L|A|^2} = \frac{v_R}{v_L}\left|\frac{C}{A}\right|^2; \quad R_{LL} = \frac{j_L^{out}}{j_L^{in}} = \frac{v_L|B|^2}{v_L|A|^2} = \frac{|B|^2}{|A|^2} = \left|\frac{B}{A}\right|^2$$

So, due to conservation of flux, we have the normalization of probabilities (or unitarity relation):

$$T_{LR} + R_{LL} = \frac{j_R^{out} + j_L^{out}}{j_L^{in}} = 1$$

Notice that, since we only need to find ratios of the coefficients, $\frac{C}{A}$ and $\frac{B}{A}$, we may as well set $A = 1$.

Similar relations may be obtained for particles incoming from the right by setting $A = 0$ and $D = 1$.

4.3 Transmission over potential step

We have the potential

$$U(x) = \begin{cases} V_0 > 0, & x \geq 0, \\ 0, & x < 0 \end{cases}$$

Solving TISE for $E > V_0 > 0$:

$$x < 0: \quad \psi''(x) + k^2\psi(x) = 0, \quad k = \frac{\sqrt{2mE}}{\hbar} \Rightarrow \psi(x) = Ae^{ikx} + Be^{-ikx} \equiv \psi_L(x)$$
$$x > 0: \quad \psi''(x) + k'^2\psi(x) = 0, \quad k' = \frac{\sqrt{2m(E-V_0)}}{\hbar} \Rightarrow \psi(x) = Ce^{ik'x} + De^{-ik'x} \equiv \psi_R(x)$$

Let $D = 0, A = 1$. Since $U(x)$ has finite jump at $x = 0$, $\psi(x)$ must be C^1, so that

$$\begin{aligned} \psi_L(0) &= \psi_R(0) \Rightarrow A + B = C + D \Rightarrow 1 + B = C \\ \psi'_L(0) &= \psi'_R(0) = ik(A - B) = ik'(C - D) \Rightarrow k(1 - B) = k'C \end{aligned}$$

Hence $C - B = 1$ and $k'C + kB = k$ so that

$$C = \frac{2k}{k + k'}, \; B = \frac{k - k'}{k + k'} \Rightarrow T_{LR} = \frac{k'}{k}|C|^2 = \frac{4k'k}{(k' + k)^2}, \; R_{LL} = |B|^2 = \frac{(k - k')^2}{(k + k')^2}$$

Comment: what happens for $V_0 > E > 0$? We have then $k' \to i\kappa$, where $\kappa = \frac{\sqrt{2m(V_0-E)}}{\hbar} > 0$, so

$$B \to \frac{k-i\kappa}{k+i\kappa}, \quad R_{LL} \to \left|\frac{k-i\kappa}{k+i\kappa}\right|^2 = \frac{k^2+\kappa^2}{k^2+\kappa^2} = 1.$$

We have a 100 % reflection, with the solution in the region $x < 0$ being a standing wave. We also must have $T_{LR} = 0$, which follows from the solution $\psi_R(x) = Ce^{-\kappa x}$ in the region $x > 0$, giving

$$j_R^{out} = \frac{1}{m}\Re\left\{\psi_R^*(x)\frac{\hbar}{i}\frac{\partial}{\partial x}\psi_R(x)\right\} = 0.$$

4.4 Tunneling through rectangular potential barrier

$$U(x) = \begin{cases} 0, & x < 0 \\ U_0 > 0, & 0 \le x \le L \\ U_s > 0, & x > L \end{cases}$$

For $0 < U_s < E < U_0$, the piece-wise solution of TISE may be written as

$$\psi''(x) + \frac{2m}{\hbar^2}[E - U(x)]\psi(x) = 0 \Rightarrow \psi(x) = \begin{cases} \psi_1(x), & x < 0, & k = \sqrt{2mE}/\hbar > 0 \\ \psi_2(x), & 0 \le x \le L, & \kappa = \sqrt{2m(U_0-E)}/\hbar > 0 \\ \psi_3(x), & x > L, & k' = \sqrt{2m(E-U_s)}/\hbar \end{cases}$$

where

$$\psi_1'' + k^2\psi_1 = 0 \quad \Rightarrow \quad \psi_1(x) = Ae^{ikx} + Be^{-ikx} \tag{1}$$
$$\psi_2'' - \kappa^2\psi_2 = 0 \quad \Rightarrow \quad \psi_2(x) = Ce^{-\kappa x} + De^{\kappa x} \tag{2}$$
$$\psi_3'' + k'^2\psi_3 = 0 \quad \Rightarrow \quad \psi_3(x) = Fe^{ik'x} + Ge^{-ik'x}. \tag{3}$$

Because $U(x)$ has finite jumps at $x = 0$ and $x = L$, the solution of the TISE must be C^1 giving **four** boundary/matching conditions:

$$\psi_1(0) = \psi_2(0), \quad \psi_1'(0) = \psi_2'(0), \quad \psi_2(L) = \psi_3(L), \quad \psi_2'(L) = \psi_3'(L)$$

To find T_{LR} and R_{LL}, declare $G = 0$ and define

$$T_{LR} = \frac{k'}{k}\left|\frac{F}{A}\right|^2, R_{LL} = \left|\frac{B}{A}\right|^2, \quad \text{where we may let} \quad A = 1$$

So, we have 4 unknowns (B, C, D, F) and 4 conditions, which can be written as a **non-homogeneous**

system of 4 equations, $M_{4\times4}\begin{pmatrix} B \\ C \\ D \\ F \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$, where $M_{4\times4}$ is a nonsingular 4×4 matrix whose coefficients depend on the parameters that define the potential and on the particle energy E, which can take arbitrary value in the continuous art of the energy spectrum.

For the special case of a barrier with $U_s = 0$ and $0 < E < U_0$, we obtain after some algebra

$$F = \frac{e^{-ikL}}{\cosh(\kappa L) + i\frac{\kappa^2-k^2}{2\kappa k}\sinh(\kappa L)}.$$

Thus, the transmission probability may be written as $T_{LR} \equiv T = |F|^2 = 1 - R_{LL}$, where

$$R_{LL} \equiv R = \frac{(k^2+\kappa^2)^2\sinh^2(\kappa L)}{(k^2+\kappa^2)^2\sinh^2(\kappa L) + 4k^2\kappa^2} = \left[1 + \frac{4k^2\kappa^2}{(k^2+\kappa^2)^2\sinh^2(\kappa L)}\right]^{-1}.$$

Comment 1: If L is large and/or U_0 is large, then we obtain approximately $T \approx e^{-2\kappa L} = e^{-2\frac{L}{\hbar}\sqrt{2m(U_0-E)}}$. This is a typical QM behaviour of the transmission probability for opaque potential barriers.

Comment 2: If $E > U_0 > 0$, then we have $\sinh\left(iL\frac{\sqrt{2m(E-U_0)}}{\hbar}\right) = i\sin\left(L\frac{\sqrt{2m(E-U_0)}}{\hbar}\right)$ so

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

showing that $R = 0$ when $\frac{L}{\hbar}\sqrt{2m(E-U_0)} = n\pi$, which occurs at energies $E_n = U_0 + \left(n\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}$, with $n = 1, 2, 3, \ldots$. Notice that this 100% transmission occurs when the deBroglie's wavelengths, associated with the kinetic energy of the particle $E_n - U_0 = \frac{\hbar^2k_n^2}{2m}$ moving in the interval $0 < x < L$, are commensurate with the width of that interval, $\lambda_n \equiv 2\pi/k_n = 2L/n$.

Comment 3: The above expression for R also works when $E > 0 > U_0 \equiv -W_0$, describing transmission and refection of a particle moving "above" a potential well of the depth $W_0 > 0$ with the kinetic energy E in the continuous part of the spectrum of that well. Then, $R \to 1$ as $E \to 0$ unless $2mW_0L^2 = (n\pi\hbar)^2$. This may serve as a qualitative model for the Ramsauer-Townsend effect.

Comment 4: The tunneling potential with $U_0 > 0$ and $U_s = 0$ behaves like a delta-function potential when we let $U_0 \to \infty$ and $L \to 0$ in such a manner that their product remains constant, $U_0L = \alpha > 0$. Taking this limit, one can show that $F \to 1/(1+i\beta)$, where $\beta = m\alpha/(\hbar^2k)$. A delta-function potential is suitable for modelling the transmission phenomena in layered heterostructures involving 2D materials.

4.5 Tunneling through a delta potential barrier

Consider a TISE in 1D with the potential $U(x) = \alpha\,\delta(x)$, with α being parameter that defines the "strength" of the delta-function potential. So, we have

$$\psi''(x) - \frac{2m\alpha}{\hbar^2}\delta(x)\psi(x) + k^2\psi(x) = 0$$

where $k = \frac{\sqrt{2mE}}{\hbar}$, with a solution given in the piece-wise form by

$$\psi(x) = \begin{cases} \psi_L(x) = Ae^{ikx} + Be^{-ikx}, & x < 0 \\ \psi_R(x) = Fe^{ikx} + Ge^{-ikx}, & x > 0 \end{cases}$$

[notice that we did not include point $x = 0$ in the solution].

As before, to find the T and R probabilities let $G = 0$ and $A = 1$. Since $U(x)$ has an **infinite** jump at $x = 0$, the solution is just continuous at $x = 0$, implying

$$\psi_L(0) = \psi_R(0) \Rightarrow 1 + B = F. \qquad (*)$$

However, the derivative $\psi'(x)$ has a finite jump at $x = 0$, the size of which can be determined by integrating the TISE, term by term, from $x = 0^-$ to $x = 0^+$,

$$\int_{0^-}^{0^+} \psi''(x)\,dx - \frac{2m\alpha}{\hbar^2}\int_{0^-}^{0^+} \delta(x)\psi(x)\,dx + k^2\int_{0^-}^{0^+} \psi(x)\,dx = 0.$$

Notice that the first term gives the jump in $\psi'(x)$ at $x = 0$, the integral in the second term is evaluated using the sifting property of the delta function, whereas te third term gives zero (WHY?). Thus, we get the jump condition at $x = 0$ as

$$\psi'_R(0) - \psi'_L(0) = \frac{2m\alpha}{\hbar^2}\psi(0) \Rightarrow ikF - ik(1 - B) = \frac{2m\alpha}{\hbar^2}F, \qquad (**)$$

where on the right hand side we could use either $\psi_L(0)$ or $\psi_R(0)$ in place of $\psi(0)$ because $\psi(x)$ is continuous.

Solving the system (*) and (**) for B and F, we finally obtain

$$\begin{cases} B = \frac{-i\beta}{1+i\beta} & \rightarrow \quad R = |B|^2 = \frac{\beta^2}{1+\beta^2} \\ F = \frac{1}{1+i\beta} & \rightarrow \quad T = |F|^2 = \frac{1}{1+\beta^2} \end{cases} \qquad \text{where} \qquad \beta \equiv \frac{m\alpha}{\hbar^2 k}.$$

Notice that we never specified the sign of the parameter α, so the above formulas apply equally to tunneling through a delta-potential barrier or transmission above a delta-potential well.

4.6 Transfer matrix method for transmission through periodic potential

Consider unbounded motion of a particle with mass m at energy $E > 0$ in the presence of a potential $U(x)$, which is non-zero in $x \in [0, L]$ and zero outside that interval.

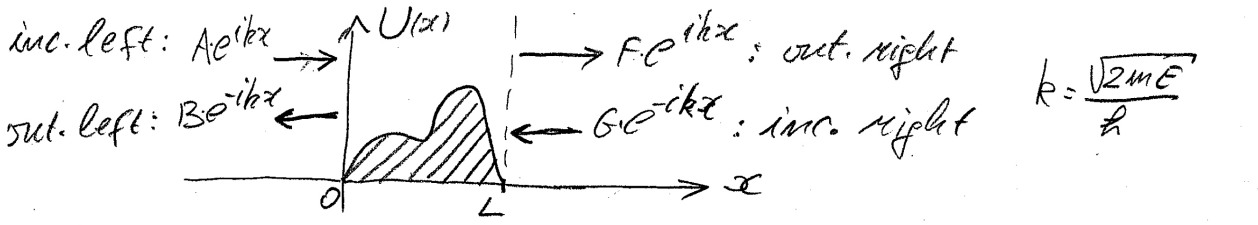


Figure 2: Localized potential in $[0, L]$ with incoming and outgoing plane waves on the left of that interval: Ae^{ikx} and Be^{-ikx}, and outgoing and incoming plane waves on the right of that interval: Fe^{ikx} and Ge^{-ikx}.

If $f(x)$ and $g(x)$ are two linearly independent solutions of TISE with the potential $U(x)$ on $x \in [0, L]$, whereas outside that interval the particle moves freely, we can write the full solution of TISE in piecewise manner as

$$\psi(x) = \begin{cases} A\, e^{ikx} + B\, e^{-ikx}, & x < 0 \\ C\, f(x) + D\, g(x), & 0 \le x \le L \\ F\, e^{ikx} + G\, e^{-ikx}, & x > L \end{cases} \qquad (1)$$

where $k = \sqrt{2mE}/\hbar$. From the requirement that the solution is C^1 at $x = 0$ and $x = L$, the four resulting equations can be used to eliminate the coefficients C and D, giving rise to two relations among the coefficients A, B, F and G, which can written in matrix form in two ways, thereby defining the scattering matrix $\underline{S}$ and the transfer matrix $\underline{M}$ according to

$$\underline{S} = \text{ scattering matrix } : \quad \begin{pmatrix} B \\ F \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A \\ G \end{pmatrix}, \qquad (2)$$

$$\underline{M} = \text{ transfer matrix } : \quad \begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}. \qquad (3)$$

4.6.1 Properties of the scattering and transfer matrices

1. From the conservation of the probability flux, written for the regions $x < 0$ and $x > L$ as

$$j_L \equiv v(|A|^2 - |B|^2) = v(|F|^2 - |G|^2) \equiv j_R,$$

where $v = \hbar k/m$, we obtain $|B|^2 + |F|^2 = |A|^2 + |G|^2$. This relation can be written in matrix form as

$$(B^* F^*) \begin{pmatrix} B \\ F \end{pmatrix} = \underbrace{(A^* G^*) \underline{\widetilde{S}}^*}_{\text{from Eq.(2)}} \underline{S} \begin{pmatrix} A \\ G \end{pmatrix} = (A^* G^*) \underbrace{\underline{\widetilde{S}}^* \underline{S}}_{\underline{1}} \begin{pmatrix} A \\ G \end{pmatrix} = (A^* G^*) \begin{pmatrix} A \\ G \end{pmatrix},$$

where in the first equality we used the complex conjugate of the transposed Eq. (2). The last equality shows that $\underline{S}$ must be *unitary matrix*, $\underline{S}^\dagger = \underline{S}^{-1}$, where the Hermitian conjugate is $\underline{S}^\dagger = \underline{\widetilde{S}}^*$, with $\sim$ for the transpose matrix and $*$ for complex conjugate.

2. The time reversal invariance is established by applying the change of sign of time, $t \to -t$, in the complex conjugate of the TDSE, $-i\hbar \dfrac{\partial \Psi^*(x,t)}{\partial t} = \hat{H} \Psi^*(x,t)$. Its solution, $\Psi^*(x,t) = \psi^*(x)\, e^{-\frac{i}{\hbar}(-t)E}$, shows that $\psi^*(x)$ is also a solution of the TISE with the same energy $E > 0$,

$$\psi^*(x) = \begin{cases} B^*\, e^{ikx} + A^*\, e^{-ikx}, & x < 0 \\ C^*\, f^*(x) + D^*\, g^*(x), & 0 \le x \le L \\ G^*\, e^{ikx} + F^*\, e^{-ikx}, & x > L \end{cases}$$

By comparison with the solution in Eq. (1), we conclude that taking complex conjugate of various coefficients changes their incoming character into an outgoing type and vice versa, namely, $A \leftrightarrow B^*$, $B \leftrightarrow A^*$, $F \leftrightarrow G^*$, $G \leftrightarrow F^*$. Therefore, Eq. (2) can also be written in the following form

$$\begin{pmatrix} A^* \\ G^* \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} B^* \\ F^* \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} S_{11}^* & S_{12}^* \\ S_{21}^* & S_{22}^* \end{pmatrix} \begin{pmatrix} A^* \\ G^* \end{pmatrix},$$

where in the second equality we used the complex conjugate of Eq. (2). Thus, $\underline{S}\underline{S}^* = \underline{1}$, which when combined with $\underline{\widetilde{S}}^* \underline{S} = \underline{1}$ shows that $\underline{S}$ is also a *symmetric matrix*.

3. Similarly, the statement of the conservation of flux, $|F|^2 - |G|^2 = |A|^2 - |B|^2$, can be rewritten as

$$(F^* G^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix} = \underbrace{(A^* B^*) \underline{\widetilde{M}}^*}_{\text{from Eq.(3)}} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \underline{M} \begin{pmatrix} A \\ B \end{pmatrix} = (A^* B^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix},$$

where in the first equality we used the complex conjugate of the transposed Eq. (3). So, we must have

$$\begin{pmatrix} M_{11}^* & M_{21}^* \\ M_{12}^* & M_{22}^* \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

giving four relations among the elements of the transfer matrix

$$|M_{11}|^2 - |M_{21}|^2 = 1, \quad |M_{22}|^2 - |M_{12}|^2 = 1, \quad M_{11}^* M_{12} = M_{21}^* M_{22}, \quad M_{12}^* M_{11} = M_{22}^* M_{21}. \tag{4}$$

4. By the time reversal invariance, Eq. (3) can also be written as

$$\begin{pmatrix} G^* \\ F^* \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} B^* \\ A^* \end{pmatrix} \quad \Longrightarrow \quad \begin{pmatrix} G \\ F \end{pmatrix} = \begin{pmatrix} M_{11}^* & M_{12}^* \\ M_{21}^* & M_{22}^* \end{pmatrix} \begin{pmatrix} B \\ A \end{pmatrix} \quad \Longrightarrow$$

$$\Longrightarrow \quad \begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} M_{22}^* & M_{21}^* \\ M_{12}^* & M_{11}^* \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix},$$

where in the second line we invoked the original form of Eq. (3). By comparison of the matrix elements on both sides of the last equality, we conclude that $M_{11} = M_{22}^*$ and $M_{12} = M_{21}^*$. When combined with the first relation in Eq. (4), these conclusions imply that $\underline{M}$ has a unit determinant,

$$\det(\underline{M}) = M_{11}M_{22} - M_{12}M_{21} = |M_{11}|^2 - |M_{21}|^2 = 1. \tag{5}$$

Moreover, the trace of $\underline{M}$ can be written as

$$\mathrm{Tr}(\underline{M}) = M_{11} + M_{22} = M_{11} + M_{11}^* \equiv 2\,\mathrm{Re}\{M_{11}\}. \tag{6}$$

Comment: If we want to find transmission and reflection coefficients for a wave incoming from the left, we set $A = 1, G = 0$ in Eq. (2). So, $B = S_{11}$ and $F = S_{21}$, giving $T_{LR} = |S_{21}|^2$ and $R_{LL} = |S_{11}|^2$.

Example 4.0.1. For a delta-potential $U(x) = \alpha\,\delta(x-a)$ where we let $a \to 0^+$, we find

$$\underline{M} = \begin{pmatrix} 1 - i\beta & -i\beta \\ i\beta & 1 + i\beta \end{pmatrix} \quad , \quad \underline{S} = \begin{pmatrix} -\dfrac{i\beta}{1+i\beta} & \dfrac{1}{1+i\beta} \\ \dfrac{1}{1+i\beta} & -\dfrac{i\beta}{1+i\beta} \end{pmatrix} \qquad \text{where} \qquad \beta = \frac{m\,\alpha}{\hbar^2 k}.$$

4.6.2 Transmission through periodic structure

Let a periodic potential with period L be given by the repeated identical replicas of the localized potential studied in the previous subsection. Notice that the plane wave outgoing to the right of the nth replica is also the plane wave incoming from the left to the $(n+1)$st replica, so we can write $F_n\, e^{ik(x-nL)} = A_{n+1}\, e^{ik(x-(n+1)L)}$. Similarly, the plane wave incoming from the right to the nth replica is the same as the plane wave outgoing to the left of the $(n+1)$st replica, so we can write $G_n\, e^{-ik(x-nL)} = B_{n+1}\, e^{-ik(x-(n+1)L)}$.

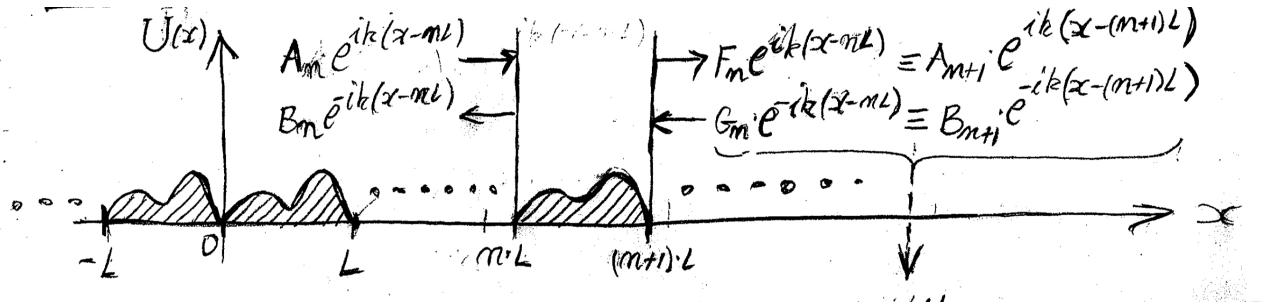


Figure 3: Periodic potential

Thus, $A_{n+1} = F_n\, e^{ikL}$ and $B_{n+1} = G_n\, e^{-ikL}$, which can be written in matrix form as

$$\begin{aligned}
\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} &= \begin{pmatrix} F_n\, e^{ikL} \\ G_n\, e^{-ikL} \end{pmatrix} \\
&= \begin{pmatrix} M_{11}\, e^{ikL}\, A_n + M_{12}\, e^{ikL}\, B_n \\ M_{21}\, e^{-ikL}\, A_n + M_{22}\, e^{-ikL}\, B_n \end{pmatrix} \\
&= \begin{pmatrix} M_{11}\, e^{ikL} & M_{12}\, e^{ikL} \\ M_{21}\, e^{-ikL} & M_{22}\, e^{-ikL} \end{pmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix} \\
&= \begin{pmatrix} e^{ikL} & 0 \\ 0 & e^{-ikL} \end{pmatrix} \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix}, \qquad (7)
\end{aligned}$$

where in the second line we eliminated coefficients F_n and G_n by using Eq. (3),

$$\begin{pmatrix} F_n \\ G_n \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} M_{11}\, A_n + M_{12}\, B_n \\ M_{21}\, A_n + M_{22}\, B_n \end{pmatrix}.$$

Therefore, Eq. (7) gives a connection between the amplitudes of the right– and left–moving plane waves at the nth and the $(n+1)$st sites, which can be expressed as $\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = \underline{P} \begin{pmatrix} A_n \\ B_n \end{pmatrix}$, where we defined the *propagator matrix* as $\underline{P} = \underline{D}\, \underline{M}$ with $\underline{D} = \begin{pmatrix} e^{ikL} & 0 \\ 0 & e^{-ikL} \end{pmatrix}$. Note that $\det(\underline{P}) = \det(\underline{D})\, \det(\underline{M}) = \det(\underline{M}) = 1$ from Eq. (5), whereas $\mathrm{Tr}\,(\underline{P}) = M_{11}\, e^{ikL} + M_{22}\, e^{-ikL} = M_{11}\, e^{ikL} + M_{11}^*\, e^{-ikL} = 2\,\mathrm{Re}\{M_{11}\, e^{ikL}\}$.

For propagation of a plane wave through N replicas of the potential, the right– and left–moving amplitudes at the Nth site are connected with the right– and left–moving amplitudes at the 0th site as

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = \underline{P} \begin{pmatrix} A_{N-1} \\ B_{N-1} \end{pmatrix} = \underline{P}^2 \begin{pmatrix} A_{N-2} \\ B_{N-2} \end{pmatrix} = \cdots = \underline{P}^N \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}. \qquad (8)$$

We must ensure that $\lim_{N\to\infty} \underline{P}^N$ is finite. This can be analyzed by solving the eigen-value problem for the propagator matrix, $\underline{P}\begin{pmatrix} A \\ B \end{pmatrix} = \lambda \begin{pmatrix} A \\ B \end{pmatrix}$. We solve the characteristic equation for this problem,

$$\lambda^2 - \lambda\,\mathrm{Tr}(\underline{P}) + \det(\underline{P}) = 0 \quad \Longrightarrow \quad \lambda_\pm = \frac{1}{2}\left\{\mathrm{Tr}(\underline{P}) \pm \sqrt{[\mathrm{Tr}(\underline{P})]^2 - 4}\right\}.$$

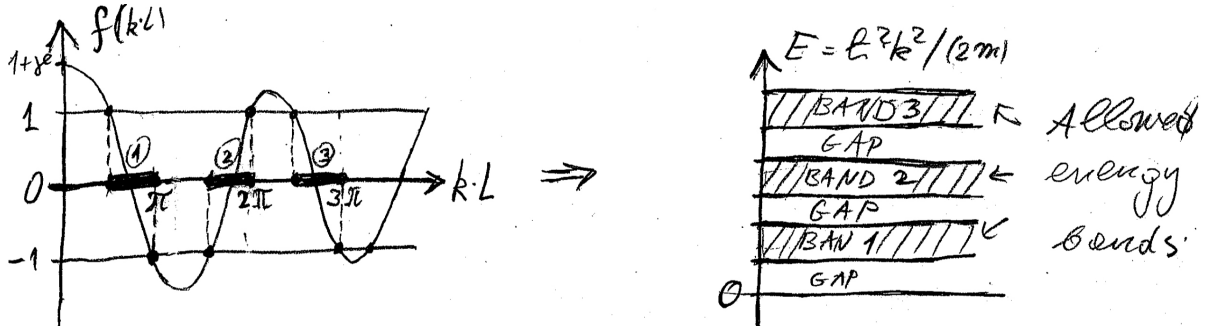
The two eigenvectors, $\begin{pmatrix} A_\pm \\ B_\pm \end{pmatrix}$, corresponding to the eigenvalues $\lambda_\pm$, form an orthonormal basis, so we can use either of them in place of $\begin{pmatrix} A_0 \\ B_0 \end{pmatrix}$ at the 0th site. Because $\underline{P}^N \begin{pmatrix} A_\pm \\ B_\pm \end{pmatrix} = \lambda_\pm^N \begin{pmatrix} A_\pm \\ B_\pm \end{pmatrix}$, Eq. (8) gives the corresponding vectors with amplitudes of a plane wave propagated to the Nth site: $\begin{pmatrix} A_N^{(\pm)} \\ B_N^{(\pm)} \end{pmatrix} = \lambda_\pm^N \begin{pmatrix} A_\pm \\ B_\pm \end{pmatrix}$.

If $|\mathrm{Tr}(\underline{P})| > 2$, both eigenvalues are real and one of them has an absolute value > 1, giving either $\lim_{N\to\infty} \lambda_+^N = \infty$ or $\lim_{N\to\infty} \lambda_-^N = \infty$. Therefore, we must have $|\mathrm{Tr}(\underline{P})| \le 2$, which can be written as $\mathrm{Tr}(\underline{P}) = 2\cos\xi$, where ξ is some real-valued parameter. This gives the eigenvalues in the form $\lambda_\pm = e^{\pm i\xi}$, so that $\lim_{N\to\infty} \lambda_\pm^N =$ finite. By analyzing the dependence of the real-valued function $\mathrm{Tr}(\underline{P})$ on k, the requirement $|\mathrm{Tr}(\underline{P})| \le 2$ generally yields intervals of energy E for the particle to be able to propagate at infinite distances through the periodic potential. Those bands of "favorable" or "allowed" energies are separated by gaps of "forbidden" energies, for which the particle cannot propagate through the periodic potential.

Example 4.0.2. The Kronig-Penney model, or the "Dirac comb", is represented by an infinite periodic lattice of delta-function potentials $\alpha\,\delta(x)$, separated by a distance L. Recalling that $M_{11} = 1 - i\beta$ with $\beta = \dfrac{m\alpha}{\hbar^2\,k}$, we have

$$\mathrm{Tr}(\underline{P}) = 2\,\mathrm{Re}\{(1 - i\beta)e^{ikL}\} = 2[\cos(kL) + \beta\,\sin(kL)].$$

Thus, defining $\gamma = \dfrac{m\alpha L}{\hbar^2}$, we must find all such k-intervals to ensure that the values of the function $f(kL) = \cos(kL) + \gamma\,\dfrac{\sin(kL)}{kL}$ are contained in the interval $[-1, 1]$. As a result, we find multiple bands of allowed energy levels, separated by the gaps of forbidden energy levels.



5 More complex examples of bounded motion

We discuss here some techniques involving bounded motion in a piece-wise continuous potential well, as well as simple harmonic oscillator (SHO) as a typical example of how special DEs and their solutions arise in Mathematical Physics in the form of the so-called orthogonal polynomials.

5.1 Potential well with finite walls

Assume $U_1 > U_2 > 0$ and define

$$U(x) = \begin{cases} U_1, & x < 0 \\ 0, & 0 \le x \le L \\ U_2, & x > L \end{cases}$$

If $E > U_1 \rightarrow$ unbounded motion, no quantization of E, evaluate T & R probability (as in Chapter 4).

$U_2 < E < U_1 \rightarrow$ unbounded motion, no quantization, standing wave with $R = 1$ (as in Chapter 4).

$0 < E < \min(U_1, U_2) \rightarrow$ bounded motion, quantization of E (studied in this section).

Consider solutions of TISE in regions: (1) $x < 0$, (2) $0 < x < L$, and (3) $x > L$:

$$\psi''(x) + \frac{2m}{\hbar^2}[E - U(x)]\psi(x) = 0$$

$$\begin{aligned} (1): &\quad K_1 = \sqrt{2m(U_1 - E)}/\hbar, \quad \psi_1'' - K_1^2\psi_1 = 0 \\ (2): &\quad k = \sqrt{2mE}/\hbar, \quad \psi_2'' + k^2\psi_2 = 0 \\ (3): &\quad K_2 = \sqrt{2m(U_3 - E)}/\hbar, \quad \psi_3'' - K_2^2\psi_3 = 0 \end{aligned}$$

Hence we get

$$\psi(x) = \begin{cases} \psi_1(x) = A\,e^{-K_1 x} + Be^{K_1 x}, & x < 0 \\ \psi_2(x) = C\sin(kx) + D\cos(kx), & 0 \le x \le L \\ \psi_3(x) = Fe^{-K_2 x} + Ge^{K_2 x}, & x > L \end{cases}$$

We can see that $\psi(x)$ is C^1 everywhere $\Rightarrow$ matching/boundary conditions at $x = 0, x = L$:

$$\psi_1(0) = \psi_2(0), \quad \psi_2(L) = \psi_3(L), \quad \psi_1'(0) = \psi_2'(0), \quad \psi_2'(L) = \psi_3'(L)$$

To prevent $\psi(x)$ from "blowing up" when $x \rightarrow \mp\infty$, we must assume $A = 0$ and $G = 0$, respectively. So, we have 4 unknowns (B, C, D, F) and 4 conditions, which can be written as a **homogeneous** system

of 4 equations, $M_{4\times4}\begin{pmatrix} B \\ C \\ D \\ F \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$, where $M_{4\times4}$ is a 4×4 matrix whose coefficients depend on the parameters that define the potential and on the particle energy E. In order to have a non-trivial solution of this system, Linear algebra tells us that we must force the matrix $M_{4\times4}$ to become singular, which is guaranteed by setting $\det(M_{4\times4}) = 0$. This condition produces a (typically transcendental) equation, which involves a nicely "tunable" parameter E. Solving that equation for E yields typically a discrete set of values, say, E_n with $n = 1, 2, 3, \ldots$, giving rise to quantization of the allowed energies.

While setting $E = E_n$ guarantees a nontrivial solution of TISE for bounded motion by making $\det(M_{4\times4}) = 0$, the rank of the system of equations for B, C, D, F is then reduced, i.e., typically one of the equations is a linear combination of the other three equations (again recall Linear algebra). Therefore, only three unknowns may be determined from the system of equations and can be expressed in terms of the fourth unknown (say, B, C and D in terms of F), which remains arbitrary. However, the remaining unknown (F) may be determined from the normalization condition for the solution of TISE, which is always imposed for bounded motion.

For finite $U_{1,2}$, we get a transcendental equation for energy, which can be usually analyzed graphically. Algebraic manipulations of the singularity condition $\det(M_{4\times4}) = 0$ give an equation for $k = \sqrt{2mE}/\hbar$,

$$k\,L = n\pi - \arcsin\left(\frac{\hbar k}{\sqrt{2mU_1}}\right) - \arcsin\left(\frac{\hbar k}{\sqrt{2mU_2}}\right), \quad n = 1, 2, 3\cdots$$

When $U_{1,2} \to \infty$, we get a particle in box (PIB) system, and this equation gives $k\,L \to n\pi \Rightarrow E_n = \left(n\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m}$. Note that then $\psi_{1,3}(x) = 0$, so that $\psi(x)$ is no longer a C^1 function, but is only continuous.

Example 5.0.1. For symmetric well with $U_2 = U_1 = U_0$, define $k_0 = \sqrt{2mU_0}/\hbar$ and look for the solution of the equation

$$Lk_0\xi = n\pi - 2\arcsin(\xi)$$

in the interval $0 \le \xi \le 1$, where $\xi \equiv \frac{k}{k_0} = \sqrt{E/U_0}$, and where we take the principal branch of the inverse sine function, such that $0 \le \arcsin(\xi) \le \pi/2$. Looking for intersections of the line $Lk_0\xi$ with functions $n\pi - 2\arcsin(\xi)$, one can show that the symmetric well with $U_1 = U_2 = U_0$ supports only a finite number of bound states with $n = 1, 2, 3, \ldots, n_{max}$, where

$$n_{max} = \left\lceil \frac{\sqrt{2mU_0}}{\pi\hbar}\,L \right\rceil$$

where $\lceil\cdots\rceil$ is the ceiling function.

5.2 Simple harmonic oscillator in 1D

Bounded motion in a 1D potential that depends quadratically on the particle position is of interest for modeling many Physical systems. For example, interatomic potential energy $U(r)$ in a diatomic molecule typically exhibits a minimum at some equilibrium distance r_0. Then, we can develop a QM description for low-energy vibrations of a diatomic molecule by considering small displacements $|r - r_0|$ and expanding the potential into truncated Taylor series up the second order,

$$U(r) \approx U(r_0) + U'(r_0)(r - r_0) + \frac{1}{2}U''(r_0)(r - r_0)^2 + \cdots$$

where $U'(r_0) = 0$ at equilibrium.

Let $x = r - r_0$ and truncate the Taylor series after the second order term. Defining the total energy relative to the minimum potential energy as $E = E_0 - U(r_0)$, and defining the potential energy of a simple harmonic oscillator as $U(x) = \frac{1}{2}\kappa x^2$ where $\kappa = U''(r_0) > 0$, we may write the corresponding TISE for simple harmonic oscillator (SHO) as

$$-\frac{\hbar^2}{2m}\psi''(x) + \frac{\kappa}{2}x^2\psi(x) = E\psi(x)$$

which is to be solved subject to the BCs: $\psi(x) \to 0, x \to \pm\infty$.

Non-dimensional form of this equation is found by changing the variable according to $\xi = \alpha x$ for some α, and letting $\psi(x) = \phi(\xi)$. Then the Chain Rule shows that the function $\phi(\xi)$ satisfies the equation

$$\phi''(\xi) - \frac{2m}{\hbar^2}\frac{\kappa}{2}\frac{1}{\alpha^4}\xi^2\phi(\xi) + \frac{2m}{\hbar^2}\frac{E}{\alpha^2}\phi(\xi) = 0$$

We want $\frac{2m}{\hbar^2}\frac{\kappa}{2}\frac{1}{\alpha^4} = 1$ in the above equation, so that $\alpha = \left[\frac{\sqrt{m\kappa}}{\hbar}\right]^{\frac{1}{2}} = \sqrt{\omega\frac{m}{\hbar}}$, where we defined the natural frequency of the corresponding classical mechanical oscillator as $\omega = \sqrt{\frac{\kappa}{m}}$. Then, the factor in the last term that contains energy E (as separation constant from the solution of TDSE) may be written as $\frac{2m}{\hbar^2}\frac{E}{\alpha^2} = \frac{2m}{\hbar^2}E\frac{\hbar}{m\omega} = \frac{2E}{\hbar\omega} \equiv \lambda$, where λ is arbitrary, and the dimensionless TISE for SHO becomes

$$\phi''(\xi) - \xi^2\phi(\xi) + \lambda\phi(\xi) = 0 \qquad (*)$$

We may find asymptotic form of the solution $|\xi| \to \infty$ of the above equation by solving the approximate DE $\phi''(\xi) - \xi^2\phi(\xi) \approx 0$. Changing the variable according to $\eta = \xi^2$ and letting $\phi(\xi) = u(\eta)$ yields another

approximate DE, where we further assume $\eta \to \infty$,

$$4\eta u''(\eta) + 2u'(\eta) - \eta u(\eta) \approx 0 \Rightarrow u''(\eta) + \frac{1}{2\eta}u'(\eta) - \frac{1}{4}u(\eta) \approx 0 \Rightarrow u''(\eta) - \frac{1}{4}u(\eta) \approx 0,$$

which has a general solution

$$u(\eta) = Ae^{\frac{\eta}{2}} + Be^{-\frac{\eta}{2}}.$$

We must reject the exponentially growing solution by letting $A = 0$ to ensure normalizability, which then gives the desired asymptotic solution of (*) in the form $\phi(\xi) \sim e^{-\frac{\xi^2}{2}}$.

Assume that the exact solution of the TISE (*) has the form

$$\phi(\xi) = H(\xi)\, e^{-\frac{\xi^2}{2}}$$

where the asymptotic behavior $e^{-\frac{\xi^2}{2}}$ has been "peeled off", and substitute it into $(*)$ to obtain

$$(H'' - 2\xi H' + \xi^2 H - H - \xi^2 H + \lambda H)e^{-\frac{\xi^2}{2}} = 0 \quad \Rightarrow \quad H'' - 2\xi H' + (\lambda - 1)H = 0$$

which gives the famous Hermite's DE for the new function $H(\xi)$.

Define $2n = \lambda - 1 = \dfrac{2E}{\hbar\omega} - 1$ as a new, real-valued parameter, and use the series solution, or the Frobenius method (AMATH 351) for Hermite's DE,

$$H''(\xi) - 2\xi H'(\xi) + 2nH(\xi) = 0$$

Assume $H = \displaystyle\sum_{l=0}^{\infty} c_l \xi^l$, so that $H' = \displaystyle\sum_{l=1}^{\infty} c_l\, l\, \xi^{l-1} = \sum_{k=0}^{\infty} c_{k+1}(k+1)\xi^k$, and $H'' = \displaystyle\sum_{l=2}^{\infty} c_l\, l(l-1)\xi^{l-2} = \sum_{k=0}^{\infty} c_{k+2}(k+1)(k+2)\xi^k$. Substitute everything into the Hermite's DE to get

$$\sum_{k=0}^{\infty}[c_{k+2}(k+1)(k+2) - 2c_k k + 2c_k n]\xi^k = 0$$

So, for each power ξ^k, we require $c_{k+2}(k+1)(k+2) - 2c_k k + 2c_k n = 0$, giving a recurrence relation for c_k:

$$c_{k+2} = c_k \frac{2(k-n)}{(k+1)(k+2)}, \quad k = 0, 1, 2, \ldots$$

where we assume c_0 and c_1 to be arbitrary constants. Using c_0 and c_1 as the "seeds" for the recurrence relation, we generate two linearly independent solutions of the Hermite's DE, which are given in the form

of infinite series. Specifically, we have even and odd solutions depending on the parity of the index k:

$$\begin{aligned} k=2m \quad &: \quad c_2 = c_0\,\frac{2(-n)}{1\cdot 2}, c_4 = c_2\frac{2(2-n)}{3\cdot 4} = c_0\frac{2^2(2-n)(-n)}{4!},\ldots \\ &\qquad c_{2m} = c_0 2^m \frac{(2m-2-n)(2m-4-n)\cdots(-n)}{(2m)!} \\ k=2m+1 \quad &: \quad c_3 = c_1\frac{2(1-n)}{2\cdot 3},\ldots,\ldots \\ &\qquad c_{2m+1} = c_1\cdot 2^m \frac{(2m-1-n)(2m-3-n)\cdots(1-n)}{(2m+1)!} \end{aligned}$$

So, the general solution of the Hermite's DE may be written as

$$H(\xi) = c_0\left[1+\sum_{m=1}^{\infty}\frac{2^m(2m-2-n)\cdots(-n)}{(2m)!}\xi^{2m}\right] + c_1\left[\xi+\sum_{m=1}^{\infty}\frac{2^m(2m-1-n)\cdots(1-n)}{(2m+1)!}\xi^{2m+1}\right] \qquad (**)$$

Both series in (**) are convergent, and they give Hermite's functions for arbitrary $n\in\mathbb{R}$. However, in general, we have $|H(\xi)|\to\infty$ as $|\xi|\to\infty$, and so we must examine the normalizability of the full solution of our non-dimensional TISE $\phi(\xi) = H(\xi)e^{-\frac{\xi^2}{2}}$.

From the recurrence relation for c_k we find that the ratio among any two consecutive terms in the above series behaves as $\frac{c_{k+2}}{c_k}\to\frac{2}{k}$ for large k, which is the same behavior as the ratio of any two consecutive terms in a power series representation of the function $\xi^p e^{\xi^2}$ for some $p\in\mathbb{R}$. This implies that, for arbitrary n, the solution of the TISE would behave asymptotically as $\phi(\xi)\sim\xi^p e^{\frac{\xi^2}{2}}$ when $|\xi|\to\infty$, and so it would not be normalizable.

The only way out of this conundrum is to convert the series in (**) into polynomials by forcing n to be positive integer, which would truncate the series in (**), one at a time. Specifically, choosing n odd, we may set $c_0=0$ in (**) to "kill" the first series, while the second series gives a polynomial of degree n called Hermite's Polynomial $H_n(\xi)$, which is multiplied by an arbitrary constant c_1. Similarly, choosing n even, we may set $c_1=0$ in (**) to "kill" the second series, while the first series then gives another Hermite's polynomial of degree n, which is multiplied by an arbitrary constant c_0.

For example, the first few Hermite's polynomials are given by $H_0(\xi)=1$, $H_1(\xi)=2\xi$, $H_2(\xi)=4\xi^2-2$, $H_3(\xi)=8\xi^3-12\xi$, ... Notice that the parity of the polynomial $H_n(\xi)$ as a function of the non-dimensional position ξ is the same as the parity of its order n, as expected, because the Hamiltonian of our SHO commutes with the parity operator $\hat{P}$.

Recall that $2n = \dfrac{2E}{\hbar\omega} - 1$, so that the eigenenergies for SHO are given by

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right), \qquad n = 0, 1, 2, 3, \ldots$$

Sturm-Liouville's theory implies that the corresponding eigenfunctions (recall $\alpha = \sqrt{\omega m/\hbar} = \sqrt{\sqrt{\kappa m}/\hbar}$),

$$\psi_n(x) = C_n\, H_n(\alpha x)\, e^{-\alpha^2 x^2/2}, \qquad n = 0, 1, 2, 3, \ldots$$

constitute an orthonormal basis, such that

$$\langle\psi_{n'}|\psi_n\rangle = C_{n'}C_n\frac{1}{\alpha}\int_{-\infty}^{\infty} H_{n'}(\xi)\, H_n(\xi)\, e^{-\xi^2}\, d\xi = \delta_{n'n}$$

indicating that the Hermite's polynomials are orthogonal with respect to the weight function $e^{-\xi^2}$.

In order to find the normalization coefficients C_n, one may use the so-called generating function $G(\xi, s)$ for Hermite's polynomials, defined by

$$G(\xi, s) \equiv e^{-s^2+2s\xi} = \sum_{n=0}^{\infty}\frac{H_n(\xi)}{n!}\, s^n.$$

One can easily show that

$$\int_{-\infty}^{\infty} G(\xi, s)\, G(\xi, t)\, e^{-\xi^2}\, d\xi = \sqrt{\pi}e^{2st} \equiv \sqrt{\pi}\sum_{n=0}^{\infty}\frac{(2st)^n}{n!}.$$

Comparing this result with

$$\int_{-\infty}^{\infty} G(\xi, s)\, G(\xi, t)\, e^{-\xi^2}\, d\xi = \sum_{n'=0}^{\infty}\sum_{n=0}^{\infty}\frac{s^{n'}\, t^n}{n'!\, n!}\int_{-\infty}^{\infty} H_{n'}(\xi)\, H_n(\xi)\, e^{-\xi^2}\, d\xi$$

yields

$$C_n = \sqrt{\frac{\alpha}{\sqrt{\pi}2^n\, n!}}$$

Example 5.0.2. One can easily show that, in the n-th stationary state of a SHO, $\langle x\rangle_n = 0$ and $\langle\hat{p}\rangle_n = 0$, whereas

$$\langle x^2\rangle_n = \frac{\hbar}{\sqrt{\kappa m}}\left(n + \frac{1}{2}\right) \quad \text{and} \quad \langle\hat{p}^2\rangle_n = \hbar\sqrt{\kappa m}\left(n + \frac{1}{2}\right)$$

so that $\Delta x\, \Delta p = \hbar\left(n + \frac{1}{2}\right) \geq \hbar/2$, showing that equality in the corresponding HUR is reached for the ground state with $n = 0$.

6 Mathematical framework

In this chapter we provide a slightly more formal summary of the ideas developed thus far. Most of the summary is formulated for the case of bounded motion in 1D, with only a few comments pertaining to the case of unbounded motion.

6.1 Axiom 1: state vectors and Hilbert space

Axiom 1 Any physical system is completely described by a normalized wave function $f(x)$ (state vector $|f\rangle$) in a Hilbert space $\mathcal{H}$. (Note: $f(x)$ may depend on time as well, but we ignore that fact for now.)

Explicit dependence of wave functions on the coordinate x arises in the position representation of quantum states for 1D problems. However, **Dirac notation** suppresses the dependence on x and emphasizes analogy between $\mathcal{H}$ and vector spaces in Linear Algebra, so that $f(x)$ corresponds to a column-vector ("ket") $|f\rangle$ and $f^*(x)$ corresponds to a row-vector ("bra") $\langle f| = |f\rangle^\dagger$ (the Hermitian conjugate of $|f\rangle$).

Hilbert space $\mathcal{H}$ is a linear vector space over the field of complex numbers $\mathbb{C}$ whose elements are complex-valued functions $f(x)$ of real variable x, which are square-integrable.

Properties of $\mathcal{H}$:

1. Linearity (superposition principle): For all $|f\rangle$, $|g\rangle \in \mathcal{H}$ and a, $b \in \mathbb{C} \Rightarrow a|f\rangle + b|g\rangle \in \mathcal{H}$.
2. Inner product is a complex number defined by $\langle f|g\rangle = \int f^*(x)\, g(x)\, dx$. Note: $\langle f|g\rangle^* = \langle g|f\rangle$.
3. Norm of $|f\rangle$ is defined by $\|f\| = \sqrt{\langle f|f\rangle} \geq 0$. Note: $\|f\| = 0 \Rightarrow |f\rangle = |0\rangle$, the zero-vector.
4. Completeness of Hilbert space is expressed by the statement: "$\mathcal{H}$ contains all its limit points."
5. $\mathcal{H}$ is N-dimensional iff there exist N linearly independent vectors $\{|f_n\rangle\}_{n=1}^N$ but no $N+1$ vectors are linearly independent.
6. There exists orthonormal basis set of vectors $\{|\psi_n\rangle\}_{n=1}^N$, such that $\langle\psi_m|\psi_n\rangle = \delta_{mn}$, which spans $\mathcal{H}$.

   Gram-Schmidt orthogonalization procedure guarantees that it is always possible to generate an orthonormal basis set $\{|\psi_n\rangle\}$ in an N-dimensional $\mathcal{H}$ from any given set of N linearly independent vectors $\{|f_n\rangle\}$ in $\mathcal{H}$, which are not necessarily orthogonal to each other. The steps of the procedure:

   a) Let $|\phi_1\rangle = |f_1\rangle$ and define $|\psi_1\rangle = |\phi_1\rangle/\|\phi_1\|$.

   b) Let $|\phi_2\rangle = |f_2\rangle + c_{21}|\phi_1\rangle$ and demand that $\langle\phi_1|\phi_2\rangle = 0$, so that $c_{21} = -\langle\phi_1|f_2\rangle/\|\phi_1\|^2$.

c) In general, for $k = 2, 3, \ldots, N$, one obtains $|\psi_k\rangle = |\phi_k\rangle / \|\phi_k\|$, where

$$|\phi_k\rangle = |f_k\rangle - \sum_{l=1}^{k-1} \frac{\langle \phi_l | f_k \rangle}{\|\phi_l\|^2} |\phi_l\rangle \equiv |f_k\rangle - \sum_{l=1}^{k-1} |\psi_l\rangle\langle\psi_l | f_k\rangle.$$

7. In an infinite-dimensional $\mathcal{H}$, we require **completeness** of the orthonormal basis set $\{|\psi_n\rangle\}_{n=1}^{\infty}$ which guarantees that every $|f\rangle \in \mathcal{H}$ can be expanded in a generalized Fourier series

$$|f\rangle = \sum_{n=1}^{\infty} c_n |\psi_n\rangle.$$

Definition 6.1. $\{|\psi_n\rangle\}_{n=1}^{\infty}$ is complete iff there exist c_n such that the partial sums $\sum_{n=1}^{N} c_n |\psi_n\rangle$ converge to $|f\rangle$ in the mean, $\lim_{N\to\infty} \left\| f - \sum_{n=1}^{N} c_n \psi_n \right\| = 0$.

Theorem 6.1. If $\{|\psi_n\rangle\}_{n=1}^{\infty}$ is complete, then $c_n = \langle \psi_n | f \rangle$ in the generalized Fourier series; we also have $\|f\|^2 = \sum_{n=1}^{\infty} |c_n|^2$ (generalized Parseval's formula) and $\sum_{n=1}^{\infty} |c_n|^2 = 1$ (closure relation for normalized $|f\rangle$).

6.2 Axiom 2: physical observables and Hermitian operators

Axiom 2 To every physical observable A there corresponds a linear, self-adjoint (Hermitian) operator $\hat{A}$ on $\mathcal{H}$. The average (expectation) value of A in a (normalized) state $|f\rangle \in \mathcal{H}$ is real number given by

$$\langle \hat{A} \rangle \equiv \langle f | \hat{A} | f \rangle \equiv \langle f | \hat{A} f \rangle = \int f^*(x) \Big(\hat{A} f(x) \Big) \, dx.$$

Definition 6.2. Hermitian conjugate (or adjoint) of $\hat{A}$ is an operator $\hat{A}^\dagger$, such that for any $|f\rangle, |g\rangle \in \mathcal{H}$,

$$\langle f | \hat{A}^\dagger | g \rangle = \langle g | \hat{A} | f \rangle^* \iff \langle f | \hat{A}^\dagger g \rangle = \langle \hat{A} f | g \rangle \iff \int f^*(x) \Big(\hat{A}^\dagger g(x) \Big) \, dx = \int \Big(\hat{A} f(x) \Big)^* g(x) \, dx.$$

Definition 6.3. $\hat{A}$ is a Hermitian (or self-adjoint) operator iff $\hat{A} = \hat{A}^\dagger$.

Properties of operators:

1. Endomorphism of $\mathcal{H}$: If $|f\rangle \in \mathcal{H}$ then $\hat{A}|f\rangle \equiv |\hat{A} f\rangle \in \mathcal{H}$.
2. Linearity: $\hat{A}(c_1 |f_1\rangle + c_2 |f_2\rangle) = c_1 \hat{A} |f_1\rangle + c_2 \hat{A} |f_2\rangle$.
3. Hermiticity is required to ensure that $\langle \hat{A} \rangle$ is real.

4. Some operations and combinations involving operators in $\mathcal{H}$:

   a) $(\hat{A}+\hat{B})|f\rangle = \hat{A}|f\rangle + \hat{B}|f\rangle$ and $\hat{A}\hat{B}|f\rangle = \hat{A}\Big(\hat{B}|f\rangle\Big)$

   b) The inverse of $\hat{A}$ is $\hat{A}^{-1}$, such that $\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{1}$, the identity operator.

   c) $(\hat{A}+\hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$ and $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$

   d) If c is complex number, then $(c\hat{A})^\dagger = c^*\hat{A}^\dagger$

   e) Transposition of operator equation: If $\hat{A}|f\rangle \equiv |\hat{A}f\rangle = |f'\rangle$, then $\langle f'| = \langle \hat{A}f| \equiv \langle f|\hat{A}^\dagger$.

   f) Function of an operator, e.g., $\exp(\hat{A}) = \sum_{k=0}^{\infty} \frac{1}{k!}\hat{A}^k$

Example 6.3.1. Given $\hat{D} = \frac{\partial}{\partial x}$, find $\hat{D}^\dagger$. We use Def. 6.2 in the position representation.

$$\begin{aligned}\langle g|\hat{D}|f\rangle^* &= \langle g|\hat{D}f\rangle^* = \left(\int_{-\infty}^{\infty} g^*(x)\frac{\partial}{\partial x}f(x)dx\right)^* = \int_{-\infty}^{\infty} g(x)\,\frac{\partial}{\partial x}f^*(x)dx = g(x)f^*(x)\Big|_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} f^*\frac{\partial}{\partial x}g(x)dx \\ &= \int_{-\infty}^{\infty} f^*(x)\left(-\frac{\partial}{\partial x}\right)g(x)dx \equiv \langle f|\hat{D}^\dagger|g\rangle\end{aligned}$$

Note: $g(x)f^*(x)|_{-\infty}^{\infty}$ vanishes due to BCs coming from square integrability. Hence $\hat{D}^\dagger = -\frac{\partial}{\partial x}$, by Def. 6.2.

Example 6.3.2. Show that $\hat{p}$ is self-adjoint, or Hermitian operator. Using the property $(c\hat{A})^\dagger = c^*\hat{A}^\dagger$,

$$\hat{p}^\dagger = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^\dagger = \left(\frac{\hbar}{i}\hat{D}\right)^\dagger = -\frac{\hbar}{i}\hat{D}^\dagger = -\frac{\hbar}{i}\left(-\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}\frac{\partial}{\partial x} = \hat{p}$$

Example 6.3.3. Prove $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$. Using Def. 6.2 for two arbitrary states $|f\rangle$ and $|g\rangle$ in $\mathcal{H}$,

$$\langle f|(\hat{A}\hat{B})^\dagger|g\rangle \equiv \langle f|(\hat{A}\hat{B})^\dagger g\rangle = \langle \hat{A}\hat{B}f|g\rangle = \langle \hat{A}(\hat{B}f)|g\rangle = \langle \hat{B}f|\hat{A}^\dagger g\rangle = \langle f|\hat{B}^\dagger(\hat{A}^\dagger g)\rangle = \langle f|\hat{B}^\dagger\hat{A}^\dagger g\rangle \equiv \langle f|\hat{B}^\dagger\hat{A}^\dagger|g\rangle$$

6.3 Axiom 3: measurements and eigenvalue problems

Axiom 3 The only result of a measurement of the observable A, performed on a system in state $|f\rangle$, is one of the eigenvalues A_n of the operator $\hat{A}$. The probability of measuring the value A_n is given by $|\langle\psi_n|f\rangle|^2$, where $|\psi_n\rangle$ is the eigenvector corresponding to A_n obtained by solving the eigenvalue equation $\hat{A}|\psi_n\rangle = A_n|\psi_n\rangle$.

Definition 6.4. Uncertainty in the measurement of A is given by standard deviation:

$$\Delta A = \sqrt{\langle(\Delta\hat{A})^2\rangle} = \sqrt{\langle(\hat{A}-\langle\hat{A}\rangle)^2\rangle} = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$$

Eigenvalue problem for a Hermitian operator $\hat{A}$ on $\mathcal{H}$, $\hat{A}|\psi_n\rangle = A_n|\psi_n\rangle$, gives all states $|\psi_n\rangle \in \mathcal{H}$ for which the uncertainty in a measurement of the observable A vanishes. This can be shown for some state $|\psi\rangle$ by defining the operator $\Delta\hat{A} = \hat{A} - \langle\hat{A}\rangle = \hat{A}^\dagger - \langle\hat{A}\rangle^* = (\Delta\hat{A})^\dagger$, where $\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle$, and considering

$$\begin{aligned}(\Delta A)^2 &= \langle\psi|(\Delta\hat{A})^2|\psi\rangle = \langle\psi|\Delta\hat{A}\Delta\hat{A}|\psi\rangle = \langle\psi|(\Delta\hat{A})(\Delta\hat{A})^\dagger\psi\rangle = \langle(\Delta\hat{A})\psi|(\Delta\hat{A})\psi\rangle \\ &= \|\Delta\hat{A}\psi\|^2 = \int_{-\infty}^{\infty}|(\Delta\hat{A})\psi|^2dx = \int_{-\infty}^{\infty}|\hat{A}\psi(x) - \langle\hat{A}\rangle\psi(x)|^2dx = 0\end{aligned}$$

Thus, a sufficient condition for $\Delta A = 0$ is that $\psi(x)$ is an eigenfunction of $\hat{A}$ so that $\hat{A}\psi_n(x) = A_n\psi_n(x)$.

Definition 6.5. Eigenvalues A_m and A_n are said to be non-degenerate iff $A_m = A_n \Rightarrow |\psi_m\rangle = |\psi_n\rangle$.

Definition 6.6. An eigenvalue A_n is said to be N_n-fold degenerate iff there exist N_n linearly independent eigenvectors $|\psi_{nj}\rangle$ such that $\hat{A}|\psi_{nj}\rangle = A_n|\psi_{nj}\rangle$ for $j = 1, 2, \ldots, N_n$.

Properties of the solutions of the eigenvalue problem for a Hermitian operator with discrete spectrum are based on the Sturm-Liouville theory:

1. Eigenvalues A_n are real and they form a spectrum which may be discrete and/or continuous.
2. Eigenfunctions (eigenvectors) $\{|\psi_n\rangle\}$ are linearly independent.
3. Eigenfunctions belonging to non-degenerate eigenvalues are orthogonal.
4. Eigenfunctions $\{|\psi_{nj}\rangle\}_{j=1}^{N_n}$ belonging to a degenerate eigenvalue A_n are generally not orthogonal, but can be always made orthogonal by using the Gram-Schmidt procedure.
5. Eigen-functions $\{|\psi_n\rangle\}$ of the observable A form a **complete orthonormal basis set** which spans $\mathcal{H}$, thus giving rise to the **superposition principle** of quantum mechanics.

Theorem 6.2. The eigenvalues of a Hermitian operator $\hat{A}$ are real, and the eigenfunctions corresponding to non-degenerate eigenvalues are orthogonal.

Proof: Let $\hat{A}|\psi_k\rangle = A_k|\psi_k\rangle$ and $\hat{A}|\psi_n\rangle = A_n|\psi_n\rangle$ and consider the following matrix elements

$$\begin{aligned}\langle\psi_k|\hat{A}|\psi_n\rangle &= A_n\langle\psi_k|\psi_n\rangle, \\ \langle\psi_k|\hat{A}^\dagger|\psi_n\rangle &= \langle\psi_n|\hat{A}|\psi_k\rangle^* = (A_k\langle\psi_n|\psi_k\rangle)^* = A_k^*\langle\psi_n|\psi_k\rangle^* = A_k^*\langle\psi_k|\psi_n\rangle.\end{aligned}$$

Because $\hat{A}^\dagger = \hat{A}$, the left-hand sides of the above equations are equal, and so must be their rightmost sides:

$$A_n\langle\psi_k|\psi_n\rangle = A_k^*\langle\psi_k|\psi_n\rangle \quad \Rightarrow \quad (A_n - A_k^*)\langle\psi_k|\psi_n\rangle = 0.$$

First let $k = n$. Then, since $\|\psi_n\| = 1$, we must have $A_n = A_n^*$, so A_n is real. Next, when $k \neq n$, we must have $\langle\psi_k|\psi_n\rangle = 0$ for the states corresponding to distinct eigenvalues, such that $A_k^* = A_k \neq A_n$. □

Superposition principle Every physical state $|f\rangle \in \mathcal{H}$ of a system can be represented by a generalized Fourier series

$$|f\rangle = \sum_{n=1}^{\infty} c_n \, |\psi_n\rangle$$

where $|\psi_n\rangle$ are eigenvectors of an observable A, and $c_n = \langle\psi_n|f\rangle$ are **probability amplitudes** for measuring A_n in the state $|f\rangle$. Writing the above series in the form

$$|f\rangle = \sum_{n} |\psi_n\rangle\langle\psi_n|f\rangle$$

allows one to express the completeness of the eigenfunction basis as a "resolution of the identity operator",

$$\sum_{n} |\psi_n\rangle\langle\psi_n| = \hat{1}$$

In the position representation, for square-integrable $f(x) = \langle x|f\rangle$ we have $c_n = \int_{-\infty}^{\infty} \psi_n^*(x') \, f(x') \, dx'$, giving

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \int_{-\infty}^{\infty} \left[\sum_{n=1}^{\infty} \psi_n^*(x') \psi_n(x) \right] f(x') \, dx' = f(x)$$

so that the completeness of the basis $\{\psi_n(x)\} = \{\langle x|\psi_n\rangle\}$ may be expressed via Dirac's delta function as

$$\sum_{n=1}^{\infty} \psi_n^*(x') \psi_n(x) = \delta(x' - x).$$

In the case of an observable A with **continuous spectrum** of eigenvalues $\alpha \in \mathbb{R}$, such that $\hat{A}|\psi_\alpha\rangle = \alpha|\psi_\alpha\rangle$, the eigenvectors are delta-function normalized, $\langle\psi_{\alpha'}|\psi_\alpha\rangle = \delta(\alpha' - \alpha)$. In that case, the probability for measuring the value of the observable in the interval $(\alpha, \alpha + d\alpha)$ for an ensemble in a state $|f\rangle$ is given by $|\langle\psi_\alpha|f\rangle|^2 \, d\alpha$. Completeness of the eigenvectors allows expanding every state-vector $|f\rangle \in \mathcal{H}$ via a generalized Fourier transform,

$$|f\rangle = \int |\psi_\alpha\rangle \, \langle\psi_\alpha|f\rangle \, d\alpha, \quad \text{so that} \quad \|f\|^2 = \int |\langle\psi_\alpha|f\rangle|^2 \, d\alpha = 1 \quad \text{and} \quad \int |\psi_\alpha\rangle \, \langle\psi_\alpha| \, d\alpha = \hat{1}$$

6.4 Axiom 4: time evolution and Schrödinger equation

Axiom 4 The time evolution of the wave function (state vector) $|\Psi(t)\rangle$ of a system is determined by the time-dependent Schrödinger equation, which is expressed in terms of the Hamilton's operator $\hat{H}$ as

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle.$$

If the Hamiltonian is time-independent, then the solution of TDSE is given by

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar}t\hat{H}}\,|\Psi(0)\rangle = \sum_n |\psi_n\rangle\, e^{-\frac{i}{\hbar}E_n t}\,\langle\psi_n|\Psi(0)\rangle,$$

where we have expressed the initial condition as $|\Psi(0)\rangle = \sum_n |\psi_n\rangle\langle\psi_n|\Psi(0)\rangle$ and used the fact that $|\psi_n\rangle$ and E_n are solutions of the energy eigenvalue problem for Hamiltonian, $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$. In the position representation, the time-independent $\hat{H}$ is a second-order differential operator, and the differential equation $\hat{H}\psi_n(x) = E_n\psi_n(x)$ with the appropriate boundary conditions constitutes a special case of the Sturm-Liouville eigen-value problem known as the **time-independent Schrödinger equation**.

Example 6.6.1. Prove that $|\Psi(t)\rangle = e^{-\frac{i}{\hbar}t\hat{H}}\,|\Psi(0)\rangle$ is the solution of the time-dependent Schrödinger equation.

$$\begin{aligned}\frac{\partial}{\partial t}e^{-\frac{i}{\hbar}t\hat{H}} &= \lim_{\Delta t\to 0}\frac{e^{-\frac{i}{\hbar}(t+\Delta t)\hat{H}} - e^{-\frac{i}{\hbar}t\hat{H}}}{\Delta t} = \lim_{\Delta t\to 0}\sum_{\ell=0}^{\infty}\frac{1}{\ell!}\left(-\frac{i}{\hbar}\hat{H}\right)^{\ell}\frac{(t+\Delta t)^{\ell} - t^{\ell}}{\Delta t}\\ &= \sum_{\ell=0}^{\infty}\frac{1}{\ell!}\left(-\frac{i}{\hbar}\hat{H}\right)^{\ell}\frac{d\,t^{\ell}}{dt} = -\frac{i}{\hbar}\hat{H}\sum_{\ell=1}^{\infty}\frac{1}{(\ell-1)!}\left(-\frac{i}{\hbar}\hat{H}\right)^{\ell-1}t^{\ell-1} = -\frac{i}{\hbar}\hat{H}e^{-\frac{i}{\hbar}t\hat{H}}\end{aligned}$$

Therefore

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = i\hbar\left(\frac{\partial}{\partial t}e^{-\frac{i}{\hbar}t\hat{H}}\right)|\Psi(0)\rangle = -i\hbar\frac{i}{\hbar}\hat{H}e^{-\frac{i}{\hbar}t\hat{H}}|\Psi(0)\rangle = \hat{H}|\Psi(t)\rangle$$

6.5 Commutation of operators

Definition 6.7. Commutator of operators $\hat{A}$ and $\hat{B}$ is an operator, denoted by $[\hat{A},\hat{B}]$ and defined as $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. We say that $\hat{A}$ and $\hat{B}$ commute iff $[\hat{A},\hat{B}] = 0$.

Example 6.7.1. Commuting operators: consider $\hat{H} = \hat{K} + U(x)$ where $\hat{K} = \frac{\hat{p}^2}{2m}$ with $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$. Then $[\hat{K},\hat{p}] = 0$, $[x, U(x)] = 0$, $[\hat{H}, e^{-\frac{i}{\hbar}t\hat{H}}] = 0$, etc.

Example 6.7.2. Non-commuting operators: show that $[\hat{x},\hat{p}] = i\hbar$.

In the position representation, for an arbitrary wavefunction $\psi(x)$, we have

$$\begin{aligned}[x,\hat{p}]\psi(x) &= (x\hat{p}-\hat{p}x)\psi(x) = \left(x\frac{\hbar}{i}\frac{\partial}{\partial x} - \frac{\hbar}{i}\frac{\partial}{\partial x}x\right)\psi(x) = \frac{\hbar}{i}x\frac{\partial\psi}{\partial x} - \frac{\hbar}{i}\frac{\partial}{\partial x}\left(x\psi(x)\right) \\ &= \frac{\hbar}{i}x\frac{\partial\psi}{\partial x} - \frac{\hbar}{i}\psi(x) - \frac{\hbar}{i}x\frac{\partial\psi}{\partial x} = -\frac{\hbar}{i}\psi(x) = i\hbar\,\psi(x).\end{aligned}$$

In the momentum representation, for an arbitrary wavefunction $b(p)$, we have

$$[\hat{x},p]b(p) = \left[i\hbar\frac{\partial}{\partial p},p\right]b(p) = i\hbar\frac{\partial}{\partial p}(pb(p)) - i\hbar p\frac{\partial}{\partial p}b(p) = i\hbar b(p) + i\hbar\frac{\partial b}{\partial p} - i\hbar p\frac{\partial b}{\partial p} = i\hbar\, b(p).$$

So, we get $[\hat{x},p] = i\hbar$ and $[x,\hat{p}] = i\hbar$, or $[\hat{x},\hat{p}] = i\hbar\,\hat{1}$, independent of representation.

Important remark: in order to find an expression for the commutator $[\hat{A},\hat{B}]$ of two non-commuting operators, which is also an operator on $\mathcal{H}$, adopt a suitable representation and apply the corresponding operators $\hat{A}$ and $\hat{B}$ on an arbitrary wavefunction (i.e., state vector in the adopted representation).

Example 6.7.3. Show that $[\hat{H},x] = -i\frac{\hbar}{m}\hat{p}$

$$\begin{aligned}[\hat{H},x]\psi(x) &= \Big\{[\hat{K},x] + [U(x),x]\Big\}\psi(x) = [\hat{K},x]\psi(x) = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2},x\right]\psi(x) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}(x\psi) - x\frac{\partial^2\psi}{\partial x^2}\right) \\ &= -\frac{\hbar^2}{2m}\left(2\frac{\partial\psi}{\partial x} + x\frac{\partial^2\psi}{\partial x^2} - x\frac{\partial^2\psi}{\partial x^2}\right) = -\frac{\hbar^2}{m}\frac{\partial}{\partial x}\psi = -i\frac{\hbar}{m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi = -i\frac{\hbar}{m}\hat{p}\,\psi(x).\end{aligned}$$

Example 6.7.4. Show that $[\hat{H},\hat{p}] = -\frac{\hbar}{i}\frac{dU(x)}{dx}$. We have $[\hat{H},\hat{p}] = [\hat{K},\hat{p}] + [U(x),\hat{p}] = [U(x),\hat{p}]$ where

$$[U(x),\hat{p}]\psi(x) = U(x)\frac{\hbar}{i}\frac{\partial\psi}{\partial x} - \frac{\hbar}{i}\frac{\partial}{\partial x}\left(U(x)\psi(x)\right) = U(x)\frac{\hbar}{i}\frac{\partial\psi}{\partial x} - \frac{\hbar}{i}\frac{\partial U}{\partial x}\psi(x) - \frac{\hbar}{i}U(x)\frac{\partial\psi}{\partial x} = -\frac{\hbar}{i}\frac{dU(x)}{dx}\,\psi(x).$$

6.5.1 Mutually compatible observables

Simultaneous measurement of two observables, A and B, will make the uncertainties ΔA and ΔB both vanish only if the corresponding operators share the same set of eigenvectors, $\hat{A}|\psi_n\rangle = A_n|\psi_n\rangle$ and $\hat{B}|\psi_n\rangle = B_n|\psi_n\rangle$, and if the measurement is made in one of their common eigenstates, $|\psi_n\rangle$, which may be appropriately labeled by the two eigenvalues: $|\psi_n\rangle \equiv |\psi_{A_nB_n}\rangle$.

Theorem 6.3. $\hat{A}$ and $\hat{B}$ share the same set of eigenvectors iff $[\hat{A},\hat{B}] = 0$.

Proof:
Necessary Condition: Assume $\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$ and $\hat{B}|\psi_n\rangle = b_n|\psi_n\rangle$, where $\{|\psi_n\rangle\}$ is a compete basis, so

that an arbitrary state vector can be expressed as $|f\rangle = \sum_n c_n|\psi_n\rangle$. Then, the action of the commutator on that state yields zero vector,

$$[\hat{A},\hat{B}]|f\rangle = \sum_n c_n(\hat{A}\hat{B}-\hat{B}\hat{A})|\psi_n\rangle = \sum_n c_n(a_n\,b_n - b_n\,a_n)|\psi_n\rangle = |0\rangle.$$

Sufficient Condition: Assume that $[\hat{A},\hat{B}]=0$ and let $|\psi\rangle$ be an eigenvector of $\hat{A}$ with the eigenvalue a, i.e., $\hat{A}|\psi\rangle = a|\psi\rangle$.
(1) `Non-degenerate case`: From $\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle = \hat{B}a|\psi\rangle = a\hat{B}|\psi\rangle$, we conclude that $\hat{A}(\hat{B}|\psi\rangle) = a(\hat{B}|\psi\rangle)$, i.e., $\hat{B}|\psi\rangle$ is also an eigenvector of $\hat{A}$ with the same eigenvalue a. For a non-degenerate eigenvalue a the corresponding eigenvector $|\psi\rangle$ must be unique (up to a multiplicative constant), i.e., $\hat{B}|\psi\rangle = b|\psi\rangle$, so we conclude that $|\psi\rangle$ is also an eigenvector of $\hat{B}$ with some (generally different) eigenvalue b.
(2) `Degenerate case`.
Let a be an N-fold degenerate eigenvalue, associated with N linearly independent eigenvectors $|\psi_i\rangle$ with $i=1,2,\ldots,N$, i.e., $\hat{A}|\psi_i\rangle = a|\psi_i\rangle$. As in the non-degenerate case, using $[\hat{A},\hat{B}]=0$ we can show that every $\hat{B}|\psi_i\rangle$ is also an eigenvector of $\hat{A}$ with the same eigenvalue a, but generally $\hat{B}|\psi_i\rangle \neq b|\psi_i\rangle$ in the degenerate case. Noting that any linear combination $|\phi\rangle = \sum_{l=1}^N c_l|\psi_l\rangle$ is also an eigenvector of $\hat{A}$ with the same a, we seek coefficients c_l such that $\hat{B}|\phi\rangle = b|\phi\rangle$. Multiplying this equality by $\langle\psi_k|$ for some $k=1,2,\ldots,N$, we get

$$\langle\psi_k|\hat{B}|\phi\rangle = \sum_{l=1}^N c_l \underbrace{\langle\psi_k|\hat{B}|\psi_l\rangle}_{B_{kl}} = b\,\langle\psi_k|\phi\rangle = b\sum_{l=1}^N c_l \underbrace{\langle\psi_k|\psi_l\rangle}_{\delta_{kl}} \quad\Longrightarrow\quad \sum_{l=1}^N (B_{kl}-b\,\delta_{kl})c_l = 0.$$

Hence we need to diagonalize an $N\times N$ matrix with elements B_{kl} by solving an algebraic eigenvalue problem for a vector with the coefficients c_l, corresponding to an eigenvalue b. Because $\hat{B}$ is Hermitian, there will be N eigenvectors with the coefficients c_{jl}, labeled by $j=1,2,\ldots,N$, giving rise to N linear combinations $|\phi_j\rangle = \sum_{l=1}^N c_{jl}|\psi_l\rangle$, accompanied by N eigenvalues b_j. We may conclude that the states $|\phi_j\rangle$ are eigenvectors of both $\hat{A}$ (with the eigenvalue a) and $\hat{B}$, such that $\hat{B}|\phi_j\rangle = b_j|\phi_j\rangle$ with $j=1,2,\ldots,N$. Note that (some of) the eigenvalues b_j (may) have distinct values, so that they are no longer degenerate.

Definition 6.8. A complete set of commuting observables includes the largest set of commuting operators $\hat{A},\hat{B},\hat{C},\ldots$ which share a set of simultaneous eigenvectors $\{|\psi_{A_nB_nC_n\cdots}\rangle\}$. Then, the observables $A,B,C,\ldots$ are said to be mutually compatible and the eigenvalues $A_n,B_n,C_n,\ldots$ are called good quantum numbers, whereas the state $|\psi_{A_nB_nC_n\cdots}\rangle$ gives the maximum possible information about the system.

A **corollary** of Theorem 6.3 enables one to "lift the degeneracy" that may exist for any eigenvalue A_n of the operator $\hat{A}$, such that $\hat{A}|\psi_{nj}\rangle = A_n|\psi_{nj}\rangle$ for $j=1,2,\ldots,N_n$, by introducing another operator $\hat{B}$ that commutes with $\hat{A}$, and by diagonalizing the $N_n\times N_n$ matrix with elements $B_{jk}=\langle\psi_{nj}|\hat{B}|\psi_{nk}\rangle$ with $j,k=1,2,\ldots,N_n$ in the subspace of the Hilbert space spanned by the (orthonormal) basis vectors $\{|\psi_{nj}\rangle\}$.

Example 6.8.1. Recall free particle in 1D with $\hat{H} = \hat{K} = \frac{\hat{p}^2}{2m}$ where $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$. Clearly $[\hat{H}, \hat{p}] = 0$. Energy $E_k = \dfrac{\hbar^2 k^2}{2m}$ is a doubly-degenerate eigenvalue of $\hat{H}$ for some $k \in \mathbb{R}$, corresponding to two eigenstates given by

$$\{\psi_1, \psi_2\} = \{\cos(kx), \sin(kx)\} \quad \text{where} \quad \hat{H}\psi_1 = E_k\psi_1, \quad \hat{H}\psi_2 = E_k\psi_2.$$

Note that $\{\psi_1, \psi_2\}$ are not the eigenstates of $\hat{p}$ because $\hat{p}\psi_{1,2} \neq p\psi_{1,2}$. However, the linear combinations

$$\{\phi_+, \phi_-\} = \{\psi_1 + i\psi_2, \psi_1 - i\psi_2\} = \{e^{ikx}, e^{-ikx}\}$$

are eigenstates of both $\hat{H}$ and $\hat{p}$, namely, $\hat{H}\phi_\pm = E_k\phi_\pm$ and $\hat{p}\phi_\pm = \pm\hbar k\phi_\pm$. While the degeneracy is still present in the eigenvalue E_k of $\hat{H}$, the sign of the eigenvalues $\pm\hbar k$ of $\hat{p}$ lifts the degeneracy by specifying the **direction** of motion of free particle at energy E_k.

Example 6.8.2. Consider the Parity operator, defined in the position representation by $\hat{P}\psi(x) = \psi(-x)$. It is Hermitian and has only two eigenvalues, $\alpha = \pm 1$

$$\hat{P}\psi_\alpha(x) = \alpha\psi_\alpha \Rightarrow \hat{P}^2\psi_\alpha(x) = \alpha^2\psi_\alpha = \psi_\alpha \Rightarrow \alpha^2 = 1 \Rightarrow \alpha = \pm 1$$

So, all even and odd functions are eigenfunctions of $\hat{P}$ with eigenvalues $+1$ and -1, respectively. Moreover, this basis is complete because any function $f(x)$ may be written as linear combination of an even and an odd function,

$$f(x) = \frac{1}{2}[f(x) + f(-x)] + \frac{1}{2}[f(x) - f(-x)]$$

Consider a 1D TISE with symmetrical potential $U(-x) = U(x)$. Then we have $[\hat{P}, \hat{H}] = 0$ because

$$\left[\hat{P}, -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right] = -\frac{\hbar^2}{2m}\left[\hat{P}, \frac{\partial^2}{\partial x^2}\right] + \Big[\hat{P}, U(x)\Big] = 0$$

Recall Assignment 2, particle in a box that is symmetrically positioned with respect to the origin of the x axis. We found there that all the eigenfunctions may be classified into even or odd, because they are simultaneously the eigenfunctions of $\hat{H}$ and $\hat{P}$, which commute.

6.5.2 Heisenberg's uncertainty relation

Heisenberg uncertainty relation for two Hermitian operators $\hat{A}$ and $\hat{B}$ in $\mathcal{H}$ expresses the fact that, if $[\hat{A}, \hat{B}] \neq 0$, then there are no such states in $\mathcal{H}$ for which both uncertainties ΔA and ΔB can vanish simultaneously. Instead, the inequality

$$\Delta A\, \Delta B \geq \frac{1}{2}\Big|\langle[\hat{A}, \hat{B}]\rangle\Big|$$

holds for expectation values taken in any state $|f\rangle \in \mathcal{H}$.

Proof:
Define the "displaced" operators $\widetilde{A} = \hat{A} - \langle \hat{A} \rangle$ and $\widetilde{B} = \hat{B} - \langle \hat{B} \rangle$ and note that $[\,\widetilde{A}, \widetilde{B}\,] = [\hat{A}, \hat{B}]$. Moreover, the uncertainties of the operators $\hat{A}$ and $\hat{B}$ in an arbitrary state $|f\rangle$ can be expressed as

$$\Delta A = \sqrt{\left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2} = \sqrt{\left\langle \widetilde{A}^2 \right\rangle} \quad \text{and} \quad \Delta B = \sqrt{\left\langle \hat{B}^2 \right\rangle - \left\langle \hat{B} \right\rangle^2} = \sqrt{\left\langle \widetilde{B}^2 \right\rangle}.$$

Define a non-Hermitian operator $\hat{C} = \widetilde{A} + i\lambda\widetilde{B}$ where λ is a real-valued parameter, and consider the function of λ, defined by by the expectation value of $\hat{C}\hat{C}^+$ in the state $|f\rangle$,

$$F(\lambda) = \left\langle \hat{C}\hat{C}^+ \right\rangle = \left\langle \left(\widetilde{A} + i\lambda\widetilde{B}\right)\left(\widetilde{A} - i\lambda\widetilde{B}\right) \right\rangle = (\Delta A)^2 - \lambda \left\langle i[\hat{A}, \hat{B}] \right\rangle + \lambda^2 (\Delta B)^2.$$

Notice the following facts:
1: $F(\lambda)$ is real-valued because $i[\hat{A}, \hat{B}]$ is a Hermitian operator.
2: $F(\lambda) \geq 0$ for all λs because $\langle \hat{C}\hat{C}^+ \rangle = \langle f|\hat{C}\hat{C}^+|f\rangle = \langle f|\hat{C}\hat{C}^+ f\rangle = \langle \hat{C}^+ f|\hat{C}^+ f\rangle = \|\hat{C}^+ f\|^2 \geq 0$.
3: $F(\lambda)$ is a quadratic polynomial taking a minimum value $F_{\min}$ at $\lambda_c = \dfrac{\left\langle i[\hat{A}, \hat{B}] \right\rangle}{2(\Delta B)^2}$.

Thus, $F_{\min} = F(\lambda_c) = (\Delta A)^2 - \dfrac{\left\langle i[\hat{A}, \hat{B}] \right\rangle^2}{4(\Delta B)^2} \geq 0$ implies $\Delta A\, \Delta B \geq \dfrac{1}{2}\left|\left\langle [\hat{A}, \hat{B}] \right\rangle\right|$.

Comment: Note that the expectation value $\langle [\hat{A}, \hat{B}] \rangle$ is generally a purely imaginary number (WHY?), so that the vertical bars in the right hand side of the above inequality refer to the modulus of that number, that is, they ultimately yield the absolute value of the imaginary part of that number.

Example 6.8.3. $\Delta x \Delta p \geq \frac{1}{2}|\langle [\hat{x}, \hat{p}] \rangle| = \frac{1}{2}|i\hbar| = \frac{\hbar}{2}$

Example 6.8.4. $\Delta E = \Delta H = \sqrt{\left\langle \hat{H}^2 \right\rangle - \left\langle \hat{H} \right\rangle^2}$ so

$$\Delta E\, \Delta x \geq \frac{1}{2}|\langle [\hat{H}, x] \rangle| = \frac{1}{2}\left| -i\frac{\hbar}{m} \langle \hat{p} \rangle \right| = \frac{\hbar}{2m}|\, \langle \hat{p} \rangle\, |$$

For bounded motion in the n-th stationary state, $\Psi_n(x,t) = \psi_n(x) e^{-\frac{i}{\hbar}E_n t}$, the expectation values are

$$\begin{aligned} \Delta E_n &= \sqrt{\left\langle \hat{H}^2 \right\rangle_n - \left\langle \hat{H} \right\rangle_n^2} = \sqrt{E_n^2 - E_n^2} = 0 \\ \Delta x_n &> 0 \end{aligned}$$

But $\Delta E_n \Delta x_n \geq \frac{\hbar}{2m} |\langle \hat{p} \rangle_n|$, so we must conclude $\langle \hat{p} \rangle_n = 0$, i.e., the average momentum vanishes in a stationary state of bounded motion.

6.5.3 Equation of motion

Consider the expectation value $\langle \hat{A} \rangle_t \equiv \langle \Psi(t) | \hat{A} | \Psi(t) \rangle$ of a (generally, time-dependent) operator $\hat{A}$ taken in an arbitrary time-dependent state $|\Psi(t)\rangle$ of some QM system. Then, its time dependence is governed by the Equation of motion,

$$\frac{d}{dt}\langle \hat{A} \rangle_t = \frac{i}{\hbar} \left\langle [\hat{H}, \hat{A}] \right\rangle_t + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle_t . \qquad (\bigstar)$$

Proof:
Working in the position representation, the time-dependent state is described by a wave function $\Psi(x,t)$, so that

$$\langle \hat{A} \rangle_t = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle = \int \Psi^*(x,t) \hat{A} \Psi(x,t)\, dx.$$

Differentiating both sides with respect to time and applying the product rule under the integral in the right-hand side gives

$$\frac{d}{dt}\langle \hat{A} \rangle_t = \int \frac{\partial \Psi^*}{\partial t} \hat{A}\Psi \, dx + \int \Psi^* \hat{A} \frac{\partial \Psi}{\partial t} \, dx + \int \Psi^* \frac{\partial A}{\partial t} \Psi \, dx. \qquad (\otimes)$$

Note that the last term stems from the fact that $\hat{A}$ may depend on time explicitly (eg., a time-dependent potential $U(x,t)$). We can express the derivatives of the wavefunction and its complex conjugate by using the TDSE, $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \Rightarrow \frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar}\hat{H}\Psi$, and its complex conjugate, $-i\hbar \frac{\partial \Psi^*}{\partial t} = \hat{H}\Psi^* \Rightarrow \frac{\partial \Psi^*}{\partial t} = \frac{i}{\hbar}\hat{H}\Psi^*$. Substituting those two expressions into Eq. ($\otimes$) we obtain (recall that $\hat{H}$ is Hermitian):

$$\frac{d}{dt}\langle \hat{A} \rangle_t = \frac{i}{\hbar} \underbrace{\langle \hat{H}\Psi | \hat{A}\Psi \rangle}_{\langle \Psi | \hat{H}\hat{A}\Psi \rangle} - \frac{i}{\hbar}\langle \Psi | \hat{A}\hat{H}\Psi \rangle + \left\langle \Psi \left| \frac{\partial \hat{A}}{\partial t} \right| \Psi \right\rangle .$$

Thus, $\frac{d}{dt}\langle \hat{A} \rangle_t = \frac{i}{\hbar}\langle \Psi | (\hat{H}\hat{A} - \hat{A}\hat{H})\Psi \rangle + \left\langle \Psi \left| \frac{\partial \hat{A}}{\partial t} \right| \Psi \right\rangle$, which can be written more compactly as in Eq. ($\bigstar$).

Comment: Compare the equation of motion in Eq. ($\bigstar$) with the result from Classical Mechanics for arbitrary differentiable function $f(x,p,t)$:

$$\frac{df}{dt} = \{H, f\} + \frac{\partial f}{\partial t} \quad \text{where} \quad \{H, f\} = \frac{\partial H}{\partial p}\frac{\partial f}{\partial x} - \frac{\partial H}{\partial x}\frac{\partial f}{\partial p} = \text{ Poisson's bracket.}$$

A **corollary** of the Equation of motion for a time-independent operator $\hat{A}$, which commutes with the Hamiltonian $\hat{H}$ of the system (which is also time-independent), is that $\langle \hat{A} \rangle_t =$ constant, that is, the observable A is conserved. Moreover, in this case, the probability to measure an eigenvalue A_n of the observable A in a time-dependent state $|\Psi(t)\rangle$ is also independent of time.

In the case of an operator that does not commute with $\hat{H}$, the Equation of motion recovers classical dynamical equation for the corresponding observable.

Example 6.8.5. Recall that $[\hat{H}, x] = -i\frac{\hbar}{m}\hat{p}$ and $[\hat{H}, \hat{p}] = -\frac{\hbar}{i}\frac{dU(x)}{dx}$. So, we have for general 1D motion

$$\frac{d}{dt}\langle x \rangle_t = \frac{i}{\hbar}\left\langle [\hat{H}, x] \right\rangle_t = \frac{1}{m}\langle \hat{p} \rangle_t$$

$$\frac{d}{dt}\langle \hat{p} \rangle_t = \frac{i}{\hbar}\left\langle [\hat{H}, \hat{p}] \right\rangle_t = \left\langle -\frac{dU(x)}{dx} \right\rangle_t = \langle F(x) \rangle_t$$

Note that these equations show that the laws analogous to Classical Mechanics apply to the expectation values of operators in QM. The second of these equations is usually called Ehrenfest's relation, or Ehrenfest's theorem. While it looks like Newton's 2nd law, it certainly does not reproduce Classical Mechanics because generally $\langle F(x) \rangle \neq F(\langle x \rangle)$.

Example 6.8.6. For a free-particle wave packet, $U(x) = 0$, we obtain

$$\begin{aligned} \langle \hat{p} \rangle_t &= \langle \hat{p} \rangle_0 = \text{const} \\ \langle x \rangle_t &= \langle x \rangle_0 + \frac{1}{m}\langle \hat{p} \rangle_0 t \end{aligned}$$

Example 6.8.7. We can analyze the spreading of a free-particle wave packet by calculating time dependent variances $(\Delta p)_t^2$ and $(\Delta x)_t^2$ from the equations of motion for the second moments x^2 and $\hat{p}^2$,

$$\begin{aligned} \frac{d}{dt}\langle x^2 \rangle_t &= \frac{1}{m}\langle x\hat{p} + \hat{p}x \rangle_t \equiv \frac{2}{m}\langle \hat{\Lambda} \rangle_t \quad (\star) \\ \frac{d}{dt}\langle \hat{p}^2 \rangle_t &= 0 \quad \Rightarrow \quad \langle \hat{p}^2 \rangle_t = \langle \hat{p}^2 \rangle_0 = \text{constant} \\ \Rightarrow (\Delta p)_t^2 &= \langle \hat{p}^2 \rangle_t - \langle \hat{p} \rangle_t^2 = \langle \hat{p}^2 \rangle_0 - \langle \hat{p} \rangle_0^2 = (\Delta p)_0^2 = \text{constant} \end{aligned}$$

In $(\star)$ we defined an auxiliary Hermitian operator $\hat{\Lambda} = \frac{1}{2}(x\hat{p} + \hat{p}x)$, with expectation value that satisfies the equation of motion

$$\begin{aligned} \frac{d}{dt}\left\langle \hat{\Lambda} \right\rangle_t &= \frac{1}{m}\langle \hat{p}^2 \rangle = \text{const} = \frac{1}{m}\langle \hat{p}^2 \rangle_0 \\ \Rightarrow \langle \hat{\Lambda} \rangle &= \langle \hat{\Lambda} \rangle_0 + \frac{1}{m}\langle \hat{p}^2 \rangle_0 t \quad (\star\star) \end{aligned}$$

From $(\star)$ and $(\star\star)$,

$$\left\langle x^2 \right\rangle_t = \left\langle x^2 \right\rangle_0 + \frac{2}{m}\langle \hat{\Lambda} \rangle_0 t + \frac{\langle \hat{p}^2 \rangle_0}{m^2} t^2$$

Hence, using $\langle x \rangle_t$ from the preceding example we get the variance (i.e., the squared uncertainty) of the position as

$$(\Delta x)_t^2 = \left\langle x^2 \right\rangle_t - \langle x \rangle_t^2 = (\Delta x)_0^2 + \frac{2}{m}\left(\langle \hat{\Lambda} \rangle_0 - \langle x \rangle_0 \langle p \rangle_0 \right) t + \frac{(\Delta p)_0^2}{m^2} t^2$$

For the Gaussian wave packet in Example 2.2.5, we find $\langle x \rangle_0 = 0$ and $\langle \hat{\Lambda} \rangle_0 = 0$ and recover the result for the time-dependent uncertainty in the position $(\Delta x)_t$ obtained there.

7 TISE in 3 dimensions and hydrogen atom

7.1 TISE in Cartesian coordinates

There are applications of TISE in higher-dimensional problems, which can be easily tackled using the position representation in Cartesian coordinates $\mathbf{r} \equiv \vec{r} = (x, y, z)$, such as, e.g., a particle of mass m in a 3D box with the sides $a \times b \times c$. For such problems, we define the (linear) momentum operator in vector form as $\hat{\mathbf{p}} \equiv \hat{\vec{p}} = \frac{\hbar}{i}\nabla$, where $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$ is the gradient vector. Then the Hamiltonian can be defined by $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})$, where the Laplace operator is given by $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ and the potential is defined as

$$U(\mathbf{r}) \equiv U(x, y, z) = \begin{cases} 0, & \text{for} \quad 0 < x < a \quad \text{and} \quad 0 < y < b \quad \text{and} \quad 0 < z < c; \\ \infty, & \text{otherwise.} \end{cases}$$

To find a time-dependent wavefunction $\Psi(\mathbf{r}, t)$ the separation of time in TDSE proceeds in the same manner as in the 1D problems, so that the general solutions may be written as

$$\Psi(\mathbf{r}, t) = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} C_{n_x n_y n_z} \psi_{n_x n_y n_z}(x, y, z)\, e^{-\frac{i}{\hbar} E_{n_x n_y n_z} t},$$

where the Fourier coefficients $C_{n_x n_y n_z}$ are obtained from initial condition. Here, $\psi_{n_x n_y n_z}(x, y, z)$ is an eigenfunction obtained by solving the 3D TISE, which is easily achieved by the method of separation of variables by writing $\psi(x, y, z) = X(x)\, Y(y)\, Z(z)$. As a result, each of the "component" functions describes a 1D particle in box problem in example 3.1.3 of the Section 3.3. As a result, we find $\psi_{n_x n_y n_z}(x, y, z) = X_{n_x}(x)\, Y_{n_y}(y)\, Z_{n_z}(z)$, where $X_{n_x}(x) = \sqrt{\frac{2}{a}} \sin\left(n_x \frac{\pi}{a} x\right)$, $Y_{n_y}(y) = \sqrt{\frac{2}{b}} \sin\left(n_y \frac{\pi}{b} y\right)$ and $Z_{n_z}(z) = \sqrt{\frac{2}{c}} \sin\left(n_z \frac{\pi}{c} z\right)$ while the total energy of the particle in a 3D box is given by $E = E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z}$, where $E_{n_x} = \frac{\hbar^2}{2m}\left(n_x \frac{\pi}{a}\right)^2$, $E_{n_y} = \frac{\hbar^2}{2m}\left(n_y \frac{\pi}{b}\right)^2$ and $E_{n_z} = \frac{\hbar^2}{2m}\left(n_z \frac{\pi}{c}\right)^2$, with the tree quantum numbers taking the values $n_x = 1, 2, 3, \cdots$, $n_y = 1, 2, 3, \cdots$ and $n_z = 1, 2, 3, \cdots$.

7.2 TISE in spherical coordinates

Spherical coordinates are $\mathbf{r} = (r, \theta, \phi)$ are particularly useful for solving 3D problems in QM involving the so-called central potential, where the potential energy $U(\mathbf{r})$ only depends on the distance $r = \|\mathbf{r}\|$. Typical problems involve Coulomb attraction between two oppositely charged particles, giving rise to the bound state of an electron and proton in a hydrogen atom or the bound state between an electron and "hole" forming the so-called *exciton* in insulator or semiconductor. Since those are typically two-body problems, r is the distance between the particles, while their joint dynamics is governed by the reduced mass μ.

To solve such problems using the position representation, we let $\mathbf{r} \equiv \vec{r}$ define the position relative to the center of a coordinate system, and we define the *linear momentum* in the usual way by the operator $\hat{\mathbf{p}} \equiv \hat{\vec{p}} = \frac{\hbar}{i}\nabla$. However, we also need to define the *angular momentum* by the operator $\hat{\mathbf{L}} \equiv \hat{\vec{L}} = \mathbf{r} \times \hat{\mathbf{p}}$, which generalizes the classical mechanical definition of the angular momentum. Then, the corresponding Hamiltonian may be written in spherical coordinates $\mathbf{r} = (r, \theta, \phi)$ as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + U(r),$$

with the Laplace operator written in a form that separates the dependence on the radial coordinate r,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\,\hat{\vec{L}}^2,$$

and the dependence on the angular coordinates (θ, ϕ), which can be expressed by an operator involving the derivatives with respect to those coordinates,

$$\hat{\vec{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right].$$

While the above two expressions clearly reproduce the form of the Laplacian in spherical coordinates seen in AMATH 231, a bit of a tedious algebra can be used to show that its angular dependence indeed results from using the definition $\hat{\vec{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ to evaluate the operator $\hat{\vec{L}}^2$, which corresponds to the square of magnitude of the corresponding classical-mechanical angular momentum vector $\vec{L}$.

Because (r, θ, ϕ) are independent variables, we may conclude that $\hat{\vec{L}}^2$ commutes with $\hat{H}$ and that each of them commutes with the operator

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi},$$

which describes the component of the quantum-mechanical angular momentum taken along the z-axis. Because $\hat{H}$, $\hat{\vec{L}}^2$ and $\hat{L}_z$ constitute a set of commuting operators,

$$\left[\hat{H}, \hat{\vec{L}}^2\right] = 0, \qquad \left[\hat{H}, \hat{L}_z\right] = 0, \qquad \left[\hat{\vec{L}}^2, \hat{L}_z\right] = 0$$

the corresponding observables are mutually compatible. We may invoke the discussion from Subsections 6.5.1 and 6.5.3 to conclude that:

(1) these operators share the same set of orthonormal eigenfunctions,

(2) it is possible to simultaneously measure, with zero uncertainties, the corresponding physical observables in their shared eigenstates,

(3) their respective eigenvalues form the set of "good quantum numbers", and

(4) their expectation values are constant when taken in any state that solves the corresponding TDSE,

$$\left\langle \hat{H} \right\rangle_t = \text{const.}, \quad \left\langle \hat{\vec{L}}^2 \right\rangle_t = \text{const.}, \quad \left\langle \hat{L}_z \right\rangle_t = \text{const.}$$

Recall that, for a classical-mechanical motion in a central potential, the angular momentum $\vec{L}$ is conserved both in magnitude and direction, which implies that its all Cartesian components are conserved, $L_x = \text{constant}$, $L_y = \text{constant}$, and $L_z = \text{constant}$, and hence $L^2 = L_x^2 + L_y^2 + L_z^2 = \text{constant}$. However, in the corresponding QM problem, we only find $\left\langle \hat{\vec{L}}^2 \right\rangle_t = \text{constant}$ and $\left\langle \hat{L}_z \right\rangle_t = \text{constant}$, whereas expectation values of the operators $\hat{L}_x$ and $\hat{L}_y$ that correspond to the other two Cartesian components of the angular momentum operator are not individually conserved. In fact, it can be easily verified that $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$, so that the uncertainties in measurements of L_x and L_x must generally satisfy the corresponding HUR: $\Delta L_x \Delta L_y \geq \frac{\hbar}{2} \left| \left\langle \hat{L}_z \right\rangle \right|$.

7.3 Separation of variables in spherical coordinates

Assume $\psi(\vec{r}) = \psi(r, \theta, \phi) = R(r)\, Y(\theta, \phi)$ and multiply the TISE $\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$ by $\dfrac{2\mu r^2}{\psi(r, \theta, \phi)}$ to get

$$-\frac{\hbar^2}{2\mu r^2} \frac{2\mu r^2}{RY} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) Y + \frac{2\mu r^2}{2\mu r^2} \frac{1}{RY} \left(\hat{\vec{L}}^2_{\theta,\phi} Y \right) R + \frac{2\mu r^2}{RY} \left[U(r) - E \right] RY = 0,$$

where we have explicitly indicated that the operator $\hat{\vec{L}}^2_{\theta,\phi}$ only differentiates with respect to angles. So we get that a function of r equals a function of θ and ϕ,

$$-\frac{\hbar^2}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + 2\mu r^2 [U(r) - E] = -\frac{\hat{\vec{L}}^2_{\theta,\phi} Y}{Y}.$$

In this equation, the left-hand side is a function of r and the right-hand side is a function of θ and ϕ, which can only be true if both sides are equal to a constant. Therefore, we must let $\dfrac{\hat{\vec{L}}^2_{\theta,\phi} Y}{Y} = \Lambda$, with Λ being a separation constant. Multiplying the r-dependent equation by $\dfrac{R}{2\mu r^2}$, we obtain the so-called radial TISE,

$$-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{\Lambda}{2\mu r^2} + U(r) \right] R = ER,$$

where $\Lambda = \text{constant}$, given by eigenvalues of the EVP for the square of the angular momentum operator,

$$\hat{\vec{L}}^2 Y = \Lambda Y.$$

7.4 Spherical harmonics

To solve the EVP $\hat{\vec{L}}^2 Y = \Lambda Y$, where

$$\hat{\vec{L}}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right],$$

we further pursue separation of variables by assuming $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$, and multiply the EVP by $\dfrac{\sin^2\theta}{\Theta\Phi}$ to find

$$-\frac{\hbar^2}{\Theta\Phi} \sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) \Phi - \frac{\hbar^2}{\Phi\Theta} \frac{d^2\Phi}{d\phi^2} \Theta = \Lambda \sin^2\theta,$$

or after re-arranging

$$\frac{\hbar^2}{\Theta} \sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \Lambda \sin^2\theta = -\frac{\hbar^2}{\Phi} \frac{d^2\Phi}{d\phi^2}$$

In this equation, the left-hand side is a function of θ and the right-hand side is a function of ϕ, which can only be true if both sides are equal to a constant. Notice that the right-hand side of the above equation may be written as $\frac{1}{\Phi}\hat{L}_z^2\Phi$, where $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$ and, because it must be constant, we may use the square of the eigenvalues obtained in solving the EVP $\hat{L}_z\Phi = \zeta\Phi$. This would give then in the right-hand side of the above equation $\frac{1}{\Phi}\hat{L}_z^2\Phi = -\frac{\hbar^2}{\Phi}\frac{d^2\Phi}{d\phi^2} = \zeta^2 = \text{constant}$.

7.4.1 EVP for $\hat{L}_z$

Solutions of the EVP $\hat{L}_z\Phi = \zeta\Phi$ follow from solving the corresponding first-order ODE,

$$\frac{\hbar}{i}\frac{d\Phi}{d\phi} = \zeta\Phi \Rightarrow \Phi(\phi) = Ae^{i\frac{\zeta}{\hbar}\phi},$$

which must be subject to the periodic boundary condition: $\Phi(\phi + 2\pi) = \Phi(\phi)$, so that $e^{i\frac{\zeta}{\hbar}2\pi} = 1$ so that $\zeta = m\hbar$, where

$m = 0, \pm1, \pm2, \cdots$	is called magnetic quantum number.

The normalization constant A in the solution $\Phi_m(\phi) = Ae^{-im\phi}$ is found from

$$\langle \Phi_{m'} | \Phi_m \rangle = |A|^2 \int_0^{2\pi} e^{i(m-m')\phi} d\phi = 2\pi |A|^2 \delta_{m'm} \Rightarrow A = \frac{1}{\sqrt{2\pi}}.$$

Hence, the solution of the EVP $\hat{L}_z\Phi_m(\phi) = \zeta_m\,\Phi_m(\phi)$ gives $\zeta_m = \hbar m$ for eigenvalues of the z-component of the angular momentum with the corresponding set of orthonormal eigenfunctions $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ for $m = 0, \pm1, \pm2, \cdots$.

7.4.2 Legendre polynomials

Going back to the EVP $\hat{\vec{L}}^2 Y = \Lambda Y$, we substitute $\zeta = \hbar m$ to obtain

$$\frac{\hbar^2}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \Lambda\sin^2\theta = m^2\hbar^2,$$

where we define $\Lambda = \hbar^2\lambda$ with λ being an arbitrary real number, and rearrange to obtain a 2nd order ODE for the function $\Theta(\theta)$ on $\theta \in [0, \pi]$,

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0.$$

We proceed by changing the variable to $w = \cos\theta \in [-1, 1]$ and letting $\Theta(\theta) = F(w)$, so that the new function satisfies the ODE, known as the *Legendre equation*

$$(1-w^2)F_m''(w) - 2wF_m'(w) + \lambda F_m(w) - \frac{m^2}{1-w^2}F_m(w) = 0.$$

We first solve the special case with $\boxed{m = 0}$ by the series solution (Frobenius) method assuming $F_0(w) = \sum_{k=0}^{\infty} c_k w^k$, which gives a recurrence relation for the coefficients as

$$c_{k+2} = c_k\frac{k(k+1) - \lambda}{(k+1)(k+2)}.$$

Noticing that $c_{k+2}/c_k \longrightarrow 1$ when $k \to \infty$, we see that for large k the solution behaves as the geometric series $F_0(w) \approx \sum_k w^{2k}$, which is only convergent for $|w| < 1$. To prevent the divergence for $w = \pm 1$, that is for $\theta = 0$ or π, we need to truncate the infinite series for $F_0(w)$ by demanding that the parameter λ in the above recurrence relation has the form $\lambda = l(l+1)$, where

$$\boxed{l = 0, 1, 2, 3, \cdots \quad \text{is called orbital angular quantum number.}}$$

With such choice of the parameter λ, one can see that the above recurrence relation will be terminated after $k = l$, giving rise to a polynomial solution for $F_0(w)$ of degree l.

Solutions for $m = 0$ are thus given by $F_0(w) = C_l\, P_l(w)$, where C_l is normalization constant and $P_l(w)$ is *Legendre polynomial* of degree l. This polynomial can also be defined by the so-called Rodrigues formula, $P_l(w) = \frac{1}{2^l l!}\frac{d^l}{dw^l}(w^2-1)^l$. The orthonormality of the corresponding function $\Theta_{0,l}(\theta) = C_l P_l(\cos\theta)$ for $m = 0$

is expressed as

$$\langle \Theta_{0,l'} | \Theta_{0,l} \rangle = \int_0^\pi \Theta^*_{0,l'}(\theta)\Theta_{0,l}(\theta)\, \sin\theta\, d\theta = C^*_{l'}C_l \int_{-1}^{1} P_{l'}(w)\, P_l(w)\, dw = \delta_{l',l}$$

where one can use the Rodrigues formulas for $P_{l'}(w)$ and $P_l(w)$ along with l' or l (whichever is the larger integer) to show that the last integral in the expression above is zero unless $l' = l$, in which case one can show that $C_l = \sqrt{l + \frac{1}{2}}$. One notices that the functions $\Theta_{0,l}(\theta) = C_l P_l(\cos\theta)$ form an orthonormal basis with the inner product defined on the interval $\theta \in [0, \pi]$ and with the weight function $\sin\theta$.

It is interesting to note that Legendre polynomials $P_l(w)$ constitute an orthonormal basis of polynomials defined on the interval $w \in [-1, 1]$, which can be systematically generated by applying the Gram-Schmidt orthogonalization procedure to the set of linearly independent functions $\{1, w, w^2, w^3, \ldots\}$, with the inner product on the interval $w \in [-1, 1]$, as shown in the Linear algebra courses.

For $\boxed{m \neq 0}$, the solutions are called the *Associated Legendre Functions*, defined by

$$P_l^m(w) = (1 - w^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dw^{|m|}} P_l(w)$$

Hence, to find nontrivial solutions for the θ-dependent problem, $\Theta_{ml}(\theta) = F_{ml}(w) = C_{lm} P_l^m(\cos\theta)$, we must have $|m| \leq l$ giving a relation between the orbital angular and magnetic quantum numbers

$$\boxed{-l \leq m \leq l.}$$

We should note that orthogonality of the functions $\Theta_{m',l'}$ and $\Theta_{m,l}$ only holds when $m' = m$:

$$\langle \Theta_{m,l'} | \Theta_{m,l} \rangle = \int_0^\pi \Theta^*_{m,l'}(\theta)\Theta_{m,l'}(\theta)\, \sin\theta\, d\theta = \delta_{l',l}.$$

Finally, putting everything together, we obtain the famous *spherical harmonics* along with the normalization constant as the eigenfunctions of the operator $\hat{\vec{L}}^2$,

$$Y_{lm}(\theta, \phi) = \Theta_{ml}(\theta)\Phi_m(\phi) = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta)\, e^{im\phi}.$$

[The prefactor with the power of (-1) is merely introduced as a traditional convention.] Spherical har-

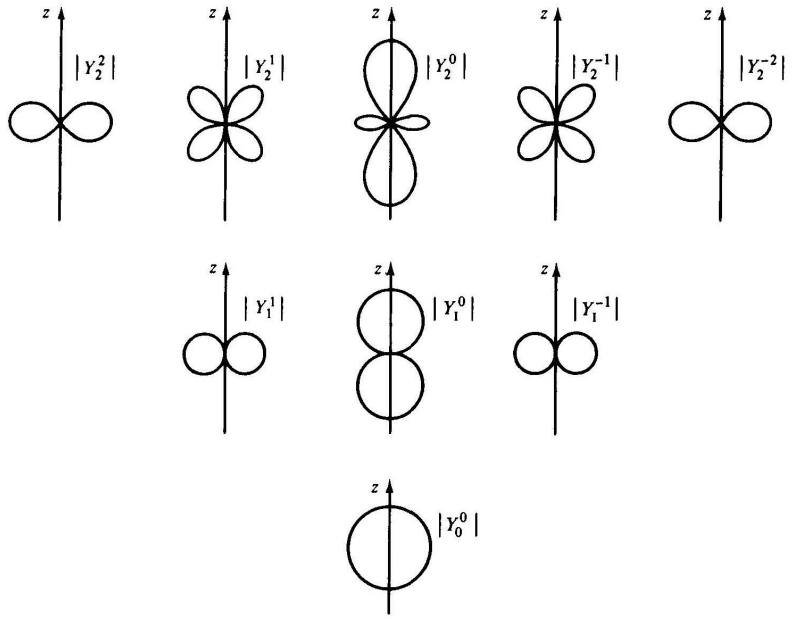


Figure 4: Polar plots of $|Y_{lm}|$ versus θ in any plane passing through z axis.

monics satisfy the orthonormality condition

$$\langle Y_{l'm'}|Y_{lm}\rangle = \int_0^{2\pi}\int_0^{\pi} Y^*_{l'm'}(\theta,\phi)\, Y_{lm}(\theta,\phi)\, \sin\theta\, d\theta\, d\phi = \delta_{m'm}\delta_{l'l}.$$

Note that the proof of this relation rests on first using the orthonormality of the functions $\Phi_m(\phi) = \frac{e^{im\phi}}{\sqrt{2\pi}}$ to generate the Kronecker delta $\delta_{m'm}$, which further enables using the orthonormality of the functions $\Theta_{m,l}(\theta)$ in the subspace of equal quantum numbers m.

For example, several low-order spherical harmonics are:

$$Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}, \quad Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta, \quad Y_{1,\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}.$$

Note that spherical harmonics are the eigenfunctions for both $\hat{\vec{L}}^2$ and $\hat{L}_z$

$$\boxed{\hat{\vec{L}}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1) Y_{lm}(\theta,\phi),}$$

$$\boxed{\hat{L}_z Y_{lm}(\theta,\phi) = \hbar m Y_{lm}(\theta,\phi).}$$

7.5 Rigid rotator

Consider the rotation of a diatomic molecule about its center of mass (CM). Assume that the molecule consists of two atoms with masses m_1 and m_2 at fixed distance r_0 between them, so that the moment of inertia of the molecule with respect to its CM is given by $I = \mu r_0^2$ where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass. This system may be described as rigid rotator (RR).

Comment: If $\vec{r}_1$ and $\vec{r}_2$ are the position vectors of the two masses, and $\vec{R} = (m_1\vec{r}_1 + m_2\vec{r}_2)/(m_1 + m_2)$ is the position vector of the CM, then $I = m_1(\vec{r}_1 - \vec{R})^2 + m_2(\vec{r}_2 - \vec{R})^2 = \cdots = \mu(\vec{r}_1 - \vec{r}_2)^2 = \mu r_0^2 = \text{const.}$

Since there is no radial motion, the Hamiltonian for a RR is simply given by $\hat{H} = \dfrac{\hat{\vec{L}}^2}{2\mu r_0^2} = \dfrac{\hat{\vec{L}}^2}{2I}$. Hence, the eigenfunctions Y_{lm} of the EVP for $\hat{\vec{L}}^2$ will also be the eigenfunctions of the TISE for RR,

$$\hat{H}Y_{lm} = E_l Y_{lm}$$

with the corresponding eigenenergies $E_l = \frac{\hbar^2 l(l+1)}{2I}$ that are $(2l+1)$-fold degenerate because $-l \le m \le l$.

The general solution of the TDSE for RR is given by

$$\Psi(\theta, \phi, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm} Y_{lm}(\theta, \phi)\, e^{-\frac{i}{\hbar} E_l t}$$

where the generalized Fourier coefficients are to be determined from the IC

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm} Y_{lm}(\theta, \phi)$$

whence

$$c_{lm} = \langle Y_{lm} | f \rangle = \int_0^{2\pi} \int_0^{\pi} Y_{lm}^*(\theta, \phi) f(\theta, \phi) \sin\theta d\theta\ d\phi.$$

Recalling that $\hat{H}$, $\hat{\vec{L}}^2$ and $\hat{L}_z$ are mutually commuting operators, the probabilistic interpretation of the generalized Fourier coefficients for simultaneous measurements of the corresponding observables is:

$$|c_{lm}|^2 = p_{lm} = \text{probability that: } \begin{cases} \text{energy takes value } E_l = \hbar^2 l(l+1)/(2I), \\ \textbf{and } \vec{L}^2 \text{ takes value } \hbar^2 l(l+1), \\ \textbf{and } L_z \text{ takes value } \hbar m. \end{cases}$$

Since normalization of the state $\Psi(\theta, \phi, t)$ is conserved, we have the Parseval's formula for RR as

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} p_{lm} = \|f\|^2 = 1$$

Expectation value of energy is

$$\begin{aligned}\langle\Psi(t)|\hat{H}|\Psi(t)\rangle &= \sum_{l'}\sum_{m'}\sum_{l}\sum_{m} c^*_{l'm'}c_{lm}e^{\frac{i}{\hbar}(E_{l'}-E_l)t}\left\langle Y_{l'm'}|\hat{H}|Y_{lm}\right\rangle \\ &= \sum_{l=0}^{\infty} E_l\left[\sum_{m=-l}^{l}|c_{lm}|^2\right] = \sum_l E_l\, p_l\end{aligned}$$

where we have used in the first line the fact that $\left\langle Y_{l'm'}|\hat{H}|Y_{lm}\right\rangle = E_l\,\langle Y_{l'm'}|Y_{lm}\rangle = E_l\delta_{l'l}\delta_{m'm}$.
Notice that the probability for observing E_l in a measurement of energy is given by the marginal probability

$$p_l = \sum_{m=-l}^{l} p_{lm}.$$

Similarly, the probability to find $m\hbar$ in a measurement of L_z regardless of the value of l is also given by a marginal probability p_m defined by

$$p_m = \sum_{l=|m|}^{\infty} p_{lm}.$$

Example 7.0.1. In a measurement of the magnitude of angular momentum, one finds the value $\hbar\sqrt{6}$. What is the smallest angle between $\vec{L}$ and the z-axis that can be observed?

Since we have $\left\langle\hat{\vec{L}}^2\right\rangle = \hbar^2 l(l+1) = \hbar^2 6 \Rightarrow l^2 + l = 6 \Rightarrow l = 2$, so $m = 0, \pm1, \pm2$. There are five possible projections of the angular momentum with the magnitude $\sqrt{\left\langle\hat{\vec{L}}^2\right\rangle} = \hbar\sqrt{6}$ on the z axis, given by: $\langle L_z\rangle = 0, \pm\hbar, \pm2\hbar$. Hence, the smallest angle θ_{min} occurs for $l = 2, m = 2$, and is given by

$$\cos\theta_{\min} = \frac{\left\langle\hat{L}_z\right\rangle_{2,2}}{\sqrt{\left\langle\hat{\vec{L}}^2\right\rangle_{2,2}}} = \frac{\hbar 2}{\hbar\sqrt{6}} = \sqrt{\frac{2}{3}} \Rightarrow \theta_{\min} \approx 48.2^\circ.$$

In general, $\cos\theta_{\min} = \dfrac{l}{\sqrt{l(l+1)}} = \sqrt{\dfrac{l}{l+1}}$. Notice that in the limit $l \to \infty$ we recover classical result, $\theta_{\min} \to 0$.

Example 7.0.2. An RR with the moment of inertia I is in the state given by $f(x, y, z) = N(x + y + z)$, where N is normalization constant. What are the possible values of energy and L_z that can be measured in this state, and with what probabilities?

Express the wave function f in terms of spherical harmonics $Y_{lm}(\theta,\phi)$, recalling

$$Y_{0,0}=\frac{1}{\sqrt{4\pi}},\quad Y_{1,0}(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta,\quad Y_{1,\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$$

Notice $\begin{cases} x=r_0\sin\theta\cos\phi \\ y=r_0\sin\theta\sin\phi \\ z=r_0\cos\theta \end{cases} \Rightarrow f(\theta,\phi)=Nr_0(\sin\theta\cos\phi+\sin\theta\sin\phi+\cos\theta)=\sum_l\sum_m c_{lm}Y_{lm}$. To find the coefficients $c_{lm}=\langle Y_{lm}|f\rangle$ recall $\cos\phi=\frac{e^{i\phi}+e^{-i\phi}}{2}$, $\sin\phi=\frac{e^{i\phi}-e^{-i\phi}}{2i}$ and write

$$\begin{aligned} f(\theta,\phi) &= -Nr_0\left[\sqrt{\frac{2\pi}{3}}(1-i)Y_{1,1}-\sqrt{\frac{2\pi}{3}}(1+i)Y_{1,-1}-\sqrt{\frac{4\pi}{3}}Y_{1,0}\right] \\ &= -\tilde{N}\left[(1-i)Y_{1,1}-(1+i)Y_{1,-1}-\sqrt{2}Y_{1,0}\right],\quad \tilde{N}\equiv Nr_0\sqrt{\frac{2\pi}{3}}=? \end{aligned}$$

Hence, the only non-zero coefficients are $c_{1,1}=-\tilde{N}(1-i)$, $c_{1,-1}=-\tilde{N}(1+i)$, and $c_{1,0}=-\sqrt{2}\tilde{N}$.
The normalization constant follows from

$$|c_{1,-1}|^2+|c_{1,1}|^2+|c_{1,0}|^2=1\Rightarrow\tilde{N}^2(2+2+2)=6\tilde{N}^2=1,$$

giving for the Fourier coefficients

$$c_{1,1}=\frac{1-i}{\sqrt{6}},\qquad c_{1,-1}=-\frac{1+i}{\sqrt{6}},\qquad c_{1,0}=-\frac{1}{\sqrt{3}}.$$

So, a measurement of energy will only find $E_1=\dfrac{2\hbar^2}{2I}=\dfrac{\hbar^2}{I}$ with probability $p_{l=1}=1$, whereas measurement of L_z will find three values: 0 and $\pm\hbar$ with equal probabilities, $p_{m=0}=p_{m=1}=p_{m=-1}=\frac{1}{3}$.

7.6 Radial equation for hydrogen atom

We are going to solve below a 3D TISE for bound states ($E<0$) in a Hydrogen-like ion, that is, in an atom with atomic number Z (= number of protons in its nucleus), which has lost $Z-1$ of its electrons, so that the interaction of the remaining electron and the nucleus is given by the Coulomb potential $U(r)=-k_c\frac{Ze^2}{r}$, where k_c is a universal constant that depends on the system of units. Of course, the case of a Hydrogen atom is recovered by setting $Z=1$.

Recall: $\psi(\vec{r})=R(r)Y_{lm}(\theta,\phi)$, $\hat{\vec{L}}^2Y_{lm}=\hbar^2l(l+2)Y_{lm}$ and $\hat{L}_zY_{lm}=\hbar mY_{lm}$, where the function $R(r)$

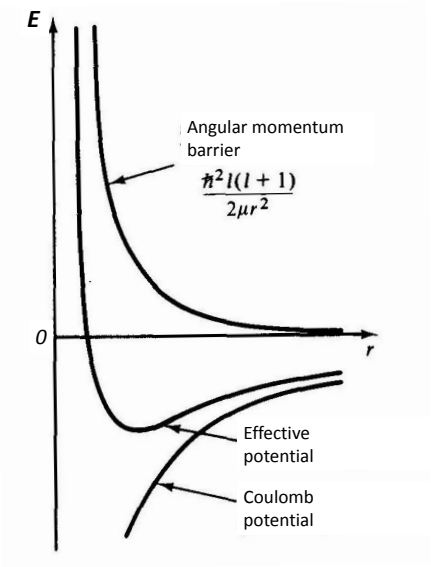


Figure 5: Effective potential well for H atom

satisfies the radial equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\underbrace{\left[-k_c\frac{Ze^2}{r}+\frac{\hbar^2 l(l+1)}{2\mu r^2}\right]}_{\text{Effective potential}}R=ER$$

Notice that this equation includes the orbital angular quantum number $l=0,1,2,\ldots$. Together with the Coulomb potential, the resulting "angular momentum barrier" produces a potential well (see Figure).

We want to solve the above equation on the interval $r\in[0,\infty]$, so we require a BC $R(r)\to 0$ when $r\to\infty$ to ensure normalizability.

Let $R(r)=\dfrac{w(r)}{r}$, multiply the above equation by $\dfrac{2\mu}{\hbar^2}r$, and obtain

$$-w''(r)+\frac{l(l+1)}{r^2}w-\frac{2\mu}{\hbar^2}k_c\frac{Ze^2}{r}w+\frac{2\mu}{\hbar^2}|E|w=0.$$

To reduce the number of parameters in this equation, we let $w(r)=u(\rho)$ and define dimensionless radial distance $\rho=2\kappa r$, where $\kappa=\dfrac{\sqrt{2\mu|E|}}{\hbar}$ includes the binding energy $|E|=-E>0$. Then

$$-4\kappa^2u''+4\kappa^2\frac{l(l+1)}{\rho^2}u-4\kappa^2\frac{2\mu}{\hbar^2}k_c\frac{Ze^2}{2\kappa}\frac{u}{\rho}+\kappa^2u=0,$$

or after simplifications,

$$u''-\frac{l(l+1)}{\rho^2}u+\left(\frac{\lambda}{\rho}-\frac{1}{4}\right)u=0\qquad(*)$$

where we defined the parameter $\lambda = \frac{\mu}{\hbar^2}\frac{k_c Z e^2 \hbar}{\sqrt{2\mu|E|}} \equiv Z\sqrt{\frac{E_R}{|E|}}$ and introduced the so-called *Rydberg energy*

$$E_R = k_c^2 \frac{\mu e^4}{2\hbar^2} \approx 13.6\,\text{eV}.$$

Notice that $\rho = 0$ is a singular point of the DE (*) for function $u(\rho)$, which imposes a BC $u(0) = 0$, in addition to $u(\rho) \to 0$ when $\rho \to \infty$ to ensure normalizability of the solution for TISE.

We proceed by "peeling off" the behavior of the solution at large and small distances:

$\rho \to \infty$: $(*) \Rightarrow u_\infty''(\rho) - \frac{1}{4}u_\infty(\rho) = 0 \Rightarrow u_\infty(\rho) = Ae^{\frac{\rho}{2}} + Be^{-\frac{\rho}{2}}$, where we set $A = 0$;

$\rho \to 0$: $(*) \Rightarrow u_0''(\rho) - \frac{l(l+1)}{\rho^2}u_0(\rho) = 0$.

Assuming $u_0(\rho) = \rho^p$, the latter equation yields indicial equation $p(p-1) - l(l+1) = 0$, which gives

$p = \begin{cases} l+1 \\ -l \end{cases} \Rightarrow u_0(\rho) = C\rho^{l+1} + D\rho^{-l}$, where we set $D = 0$ to avoid divergence at $\rho = 0$.

Hence, assume $u(\rho) = e^{-\frac{\rho}{2}}\rho^{l+1}F(\rho)$ and substitute into the ODE (*) to get an ODE for new function,

$$\rho F''(\rho) + (2l + 2 - \rho)F'(\rho) + (\lambda - l - 1)F(\rho) = 0.$$

Assume series solution $F(\rho) = \sum_{k=0}^{\infty} c_k \rho^k$ with $c_0 \neq 0$, which yields the recurrence relation:

$$c_{k+1} = c_k \frac{k + l + 1 - \lambda}{(k+1)(k+2l+2)}.$$

Notice that $\frac{c_{k+1}}{c_k}$ behaves as $\frac{1}{k}$ when $k \to \infty$, which is characteristic of the series expansion of a function $\sim \rho^p\, e^\rho$. Thus, $F(\rho)$ behaves asymptotically as $F(\rho) \sim e^\rho$, which would result in the asymptotic behaviour of the function $u(\rho)$ as $u(\rho) \sim e^{\frac{\rho}{2}}$. Therefore to prevent the divergence of the series solution for $u(\rho)$ at $\rho \to \infty$, we must truncate the summation at some term with $k_{max} = 0, 1, 2, \cdots$. This is achieved by demanding that the parameter λ in the recurrence relation takes integer values, $\lambda = k_{\max} + l + 1 = n$, where

$$\boxed{n = 1, 2, 3 \cdots \quad \text{is the principal quantum number.}}$$

As a consequence, we find immediately from $\lambda = n = Z\sqrt{\frac{E_R}{|E|}}$ that the bound-state eigenenergies are given by the infinite sequence

$$\boxed{E_n = -Z^2 \frac{E_R}{n^2}.}$$

Moreover, the above truncation shows that the angular orbital quantum number is bounded above according to

$$\boxed{0 \leq l \leq n-1,}$$

which, when combined with the relation $-l \leq m \leq l$ for the magnetic quantum number, shows that E_n has a high degree of degeneracy, given by

$$\sum_{l=0}^{n-1}(2l+1) = 2\frac{1}{2}(n-1)n + n = n^2.$$

The corresponding eigenfunctions of the radial equation are given by

$$R_{nl}(r) = \frac{C_{nl}}{r}w_{nl}(r) = \frac{C_{nl}}{r}u(\rho_n) = C_{nl}e^{-\frac{\rho_n}{2}}\rho_n^l \sum_{k=0}^{n-l-1} c_k \rho_n^k$$

where $\rho_n = 2\kappa_n r$ with $\kappa_n = \frac{\sqrt{2\mu|E_n|}}{\hbar} = \frac{Z}{n}\frac{1}{a_B}$, and where we defined the *Bohr's radius* a_B by

$$a_B = \frac{\hbar^2}{k_c \mu e^2} \approx 0.529\,\mathring{A}.$$

Notice that the polynomial of degree $n-l-1$, which appears in the above solution $R_{nl}(r)$ of the radial equation is called *Associated Laguerre's polynomial* and is denoted by $L_{n-l-1}^{2l+1}(\rho)$. It can be shown that setting the normalization constant to $C_{nl} = (2\kappa_n)^{3/2}A_{nl}$ where $A_{nl} = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}$, ensures the orthonormality of the radial solutions with equal l values, given with respect to the weight function r^2 as

$$\int_0^\infty R_{n'l}^*(r)R_{nl}(r)\,r^2\,dr = \delta_{n'n}.$$

Examples of the radial solution for Hydrogen-like ion:

$$R_{10}(r) = \frac{2}{a_B^{3/2}}e^{-\frac{r}{a_B}}, \quad R_{20}(r) = \frac{2}{(2a_B)^{3/2}}\left(1-\frac{r}{2a_B}\right)e^{-\frac{r}{2a_B}}, \quad R_{21}(r) = \frac{1}{\sqrt{3}(2a_B)^{3/2}}\frac{r}{a_B}e^{-\frac{r}{2a_B}}.$$

Finally, the eigenfunctions of the full TISE for Hydrogen-like ion, $\hat{H}\psi_{nlm} = E_n\psi_{nlm}$, are $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$. Their orthonormality is expressed as

$$\langle\psi_{n'l'm'}|\psi_{nlm}\rangle = \iiint_{\mathbb{R}^3}\psi_{n'l'm'}^*\psi_{nlm}dV = \int_0^\infty\int_0^\pi\int_0^{2\pi} R_{n'l'}^*(r)R_{nl}(r)Y_{l'm'}(\theta,\phi)Y_{lm}(\theta,\phi)r^2\sin\theta d\phi d\theta dr = \delta_{n'n}\delta_{l'l}\delta_{m'm}$$

The general solution of the TDSE is

$$\Psi(r,\theta,\phi,t) = \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} c_{nlm}\psi_{nlm}(r,\theta,\phi)e^{-\frac{i}{\hbar}E_n t}$$

with the generalized Fourier coefficients found from the IC $\Psi(r,\theta,\phi,0) = f(r,\theta,\phi)$ as $c_{nlm} = \langle\psi_{nlm}|\Psi(0)\rangle = \iiint_{\mathbb{R}^3} \psi^*_{nlm}(r,\theta,\phi)f(r,\theta,\phi)\, r^2\,\sin\theta\, dr\, d\theta\, d\phi$. As before, $p_{nlm} = |c_{nlm}|^2 =$ is joint probability for observing E_n for $\hat{H}$ **and** $\hbar^2 l(l{+}1)$ for $\hat{\vec{L}}^2$ **and** $m\hbar$ for $\hat{L}_z$. Marginal probability for observing E_n is $p_n = \sum_{l=0}^{n-1}\sum_{m=-l}^{l}|c_{nlm}|^2$.

Similarly, defining $D_{nlm}(r,\theta,\phi) = |\psi_{nlm}(r,\theta,\phi)|^2$, we get $D_{nlm}(r,\theta,\phi)\, dV$ to be the probability to find the particle in a small volume centered at the point (r,θ,ϕ) in 3D, whereas defining $D_{nl}(r) = r^2\int_0^{\pi}\int_0^{2\pi}|\psi_{nlm}(r,\theta,\phi)|^2\sin\theta d\theta d\phi = r^2|R_{nl}(r)|^2$, we get $D_{nl}(r)\, dr$ to be the marginal probability for observing the particle in the interval of radial distances $(r, r+dr)$.

Spectroscopic Notation of hydrogenic states:

$n=1$	$l=0$	1s
$n=2$	$l=0$	2s
$n=2$	$l=1$	2p
$n=3$	$l=0$	3s
$n=3$	$l=1$	3p
$n=3$	$l=2$	3d
$\cdots$	$\cdots$	$\cdots$

Rydberg's formula for the characteristic spectral lines of Hydrogen atom gives the wavelength $\lambda_{n'n}$ of EM radiation emitted when electron "jumps" from a state with n' to a lower state with $n < n'$, releasing the quantum of energy $E_{n'n} = E_{n'} - E_n = E_R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$. The corresponding frequency of the emitted photon $\omega_{n'n}$ is found from the Planck's formula $E_{n'n} = \hbar\omega_{n'n}$ using the relation $\hbar\omega = h\nu = \frac{hc}{\lambda} \approx \frac{1240\,\text{eV}\times\text{nm}}{\lambda}$. Hence, Rydberg's formula is

$$\frac{1}{\lambda_{n'n}} = \frac{E_R}{hc}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right), \quad n < n' = 1, 2, \cdots$$

Example 7.0.3. Find the expectation value $\langle r\rangle$, the uncertainty Δr and the most probable r for a H-atom in the ground state $(n=1, l=0, m=0)$ using

$$\psi_{100} = R_{10}(r)Y_{00}(\theta,\phi) = \frac{2}{a_B^{3/2}}e^{-\frac{r}{a_B}}\frac{1}{\sqrt{4\pi}}.$$

Because the radial probability density is $D_{1,0}(r) = \left(\int_0^{2\pi}\int_0^{\pi} |\psi_{100}|^2 \sin\theta\, d\theta\, d\phi\right) r^2 = \frac{4}{a_B^3} r^2 e^{-2\frac{r}{a_B}}$, we find the peak position of that density from $\frac{dD_{1,0}(r)}{dr} = 0$, giving the most probable radial distance $r = a_B$.

Since for the kth moment of r,

$$\langle r^k \rangle = \int_0^\infty r^k D_{1,0}(r) dr = \frac{4}{a_B^3}\int_0^\infty r^{k+2} e^{-2\frac{r}{a_B}} dr = \begin{cases} \frac{3}{2}a_B, & k=1 \\ 3a_B^2, & k=2 \end{cases}$$

we find $\langle r\rangle = \frac{3}{2}a_B$ and $\Delta r = \sqrt{\langle r^2\rangle - \langle r\rangle^2} = \frac{\sqrt{3}}{2}a_B$.

Example 7.0.4. Assume that a H-atom starts out in the state $\Psi(\vec{r},0) = A(\psi_{2,1,1} + \psi_{2,1,-1})$.

(a) Find A to normalize $\Psi(\vec{r},0)$;

(b) Find $\Psi(\vec{r},t)$;

(c) Evaluate $\langle U(r)\rangle_t$ and $\left\langle \hat{K} \right\rangle_t$.

(a) $\iiint |\Psi(\vec{r},0)|^2\, dV = A^2\left[\int |\psi_{2,1,1}|^2\, dV + \int |\psi_{2,1,-1}|^2\, dV + 0 + 0\right] = 2A^2 = 1 \Rightarrow A = \frac{1}{\sqrt{2}}$.

(b) This is a doubly degenerate state with only one eigenenergy, E_2, so the general solution of TDSE is

$$\begin{aligned} \Psi(\vec{r},t) &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,1}(\vec{r}) + \psi_{2,1,-1}(\vec{r})\right) e^{-\frac{i}{\hbar}E_2 t} \\ &= \frac{1}{\sqrt{2}} R_{21}(r)\left[-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} + \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}\right] e^{-\frac{i}{\hbar}E_2 t} \\ &= -\frac{ire^{-\frac{r}{2a_B}}}{\sqrt{2\pi a_B}4a_B^2}\sin\theta\sin\phi\, e^{-\frac{i}{\hbar}E_2 t}. \end{aligned}$$

(c) The expectation value of the Coulomb potential $U(r) = -k_c\frac{e^2}{r}$ is

$$\begin{aligned} \langle U(r)\rangle_t &= -\iiint k_c\frac{e^2}{r}|\Psi|^2 dV = -\frac{k_c e^2}{32\pi a_B^5}\int_0^\infty r^3 e^{-\frac{r}{a_B}}\, dr \int_0^\pi \sin^3\theta\, d\theta \int_0^{2\pi}\sin^2\phi\, d\phi \\ &= -\frac{k_c}{4}\frac{e^2}{a_B} = -\frac{1}{2}E_R \approx -6.8\,\text{eV}. \end{aligned}$$

From the total energy being $E_2 = -\frac{E_R}{2^2} = -\frac{E_R}{4} = \langle U\rangle + \left\langle \hat{K}\right\rangle$, we obtain the expectation value of kinetic energy $\left\langle \hat{K}\right\rangle = E_2 - \langle U\rangle = -\frac{1}{2}\langle U\rangle \approx 3.4\,\text{eV}$, as expected from the Virial theorem for motion in the Coulomb potential.

7.7 Effects of magnetic field

We wish to study the effects of constant external magnetic field with the induction $\vec{B}$ on a H-atom. This problem will require the inclusion of electron spin, but we wish here to only show the effects of magnetic field on the orbital angular momentum of electron. Notice that the reduced mass of this atom is $\mu = m_e m_p/(m_e + m_p) \approx m_e$ because $m_p \gg m_e$, where m_e and m_p are the bare electron and proton masses. Referring to the classical planetary model of H-atom (due to Bohr), the orbital motion of electron constitutes an electric current loop, which produces a magnetic dipole with the moment $\vec{\mu} = \frac{-|e|}{2m_e c}\vec{L}$, where $e < 0$ is electron charge and c speed of light in the Gaussian units. When the field is oriented along the z axis, we may write $\vec{B} = (0, 0, B_0)$ so that the classical expression for the change in electron energy is $H_{mag} = -\vec{\mu} \cdot \vec{B} = -\mu_z B_0$.

Imposing the quantization of the orbital angular momentum, we see that the electron in a H-atom acquires an addition to its Hamiltonian that is given by

$$\hat{H}_{mag} = -\hat{\vec{\mu}} \cdot \vec{B} = \frac{|e|}{2m_e c}\hat{\vec{L}} \cdot \vec{B} = \frac{|e|}{2m_e c} B_0 \hat{L}_z$$

showing that the direction of the magnetic field is a natural choice for the z axis as the interaction of electron with that field is governed by $\hat{L}_z$. Accordingly, spherical harmonics are also the eigenfunctions of $\hat{H}_{mag}$, so that

$$\hat{H}_{mag} Y_{lm} = \frac{|e|B_0}{2m_e c}\hat{L}_z Y_{lm} = m\mu_B B_0 Y_{lm}$$

where m is the usual magnetic quantum number, and μ_B is the so-called *Bohr's magneton*, defined by

$$\mu_B = \frac{\hbar|e|}{2m_e c} \approx 9 \times 10^{-24}\ \mathrm{A\,m^2}.$$

It is therefore tempting to write the full H-atom Hamiltonian in magnetic field as $\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - k_c\frac{e^2}{r} + \frac{\mu_B}{\hbar}B_0\hat{L}_z$ noticing that we could use the same eigenfunctions ψ_{nlm} found in the case without magnetic field. However, there are two problems. First, we should start from a classical Hamiltonian written in the form of the so-called minimal coupling (to be discussed latter) and, second, we need to introduce the spin angular momentum of electron into the Hamiltonian. While the first problem is easily handled by generalizing our quantization procedure based on assigning quantum mechanical operators to classical observables (such as the potential energy, kinetic energy, orbital angular momentum, etc.), the situation is more challenging with the spin operator because it does not have its classical counterpart. Nevertheless, both the *orbital angular momentum operator* and the *spin angular momentum operator* are subject to the same set of algebraic rules, which we shall outline in the following subsection by re-considering the orbital angular momentum in terms of the so-called lowering and raising operators, or simply the *Ladder Operators*.

7.8 Ladder operators

Consider angular momentum operator $\hat{\vec{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$, with its Cartesian components being Hermitian operators that satisfy the commuting relations $[\hat{L}_i, \hat{L}_j] = \epsilon_{ijk} i\hbar \hat{L}_k$, where ϵ_{ijk} is the Levi-Civitta symbol. Choosing $\hat{\vec{L}}^2$ and $\hat{L}_z$ as mutually commuting (compatible) operators, recall that they share the same eigenstates, $\hat{\vec{L}}^2 Y_{\lambda\mu} = \lambda Y_{\lambda\mu}$, and $\hat{L}_z Y_{\lambda\mu} = \mu Y_{\lambda\mu}$, where we pretend that we do not know what the corresponding eigenvalues λ and μ are.

This leaves $\hat{L}_x$ and $\hat{L}_y$ as incompatible operators because $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$, but we use them to define Ladder operators as

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y.$$

It is easy to show that their commutators with $\hat{\vec{L}}^2$ and $\hat{L}_z$ are

$$[\hat{\vec{L}}^2, \hat{L}_\pm] = 0, \quad \text{and} \quad [\hat{L}_z, \hat{L}_\pm] = [\hat{L}_z, \hat{L}_x] \pm i[\hat{L}_z, \hat{L}_y] = i\hbar \hat{L}_y \pm \hbar \hat{L}_x \equiv \pm \hbar \hat{L}_\pm.$$

Let us see what happens when $\hat{L}_\pm$ are applied to $Y_{\lambda\mu}$.

a) $\hat{\vec{L}}^2(\hat{L}_\pm Y_{\lambda\mu}) = \hat{L}_\pm \hat{\vec{L}}^2 Y_{\lambda\mu} = \lambda(\hat{L}_\pm Y_{\lambda\mu})$, so $\hat{L}_\pm Y_{\lambda\mu}$ is also an eigenstate of $\hat{\vec{L}}^2$ with unchanged eigenvalue λ.

b) $\hat{L}_z \hat{L}_\pm Y_{\lambda\mu} = [\hat{L}_z, \hat{L}_\pm] Y_{\lambda\mu} + \hat{L}_\pm \hat{L}_z Y_{\lambda\mu} = (\mu \pm \hbar)(\hat{L}_\pm Y_{\lambda\mu})$, so $\hat{L}_\pm Y_{\lambda\mu}$ is an eigenstate of $\hat{L}_z$ with the eigenvalue μ changed to $\mu \pm \hbar$.

Hence, $\hat{L}_\pm$ are called the raising/lowering operators. We may use those operators repeatedly for any fixed λ to generate all the states with different μ values, which may only differ by integer multiples of $\hbar$. Those states can be written as $\hat{L}_\pm Y_{\lambda,\mu} = C^\pm_{\lambda\mu} Y_{\lambda,\mu\pm\hbar}$, $\hat{L}^2_\pm Y_{\lambda,\mu} = C^\pm_{\lambda\mu} C^\pm_{\lambda\mu\pm\hbar} Y_{\lambda,\mu\pm 2\hbar}$, etc., with constants $C^\pm_{\lambda\mu}$ to be determined later.

However, this climbing the ladder of μ values cannot go forever because of the relation $-\sqrt{\lambda} \leq \mu \leq \sqrt{\lambda}$ between the eigenvalues λ and μ, which follows from the fact $\left\langle Y_{\lambda\mu} | \hat{\vec{L}}^2 - \hat{L}_z^2 | Y_{\lambda\mu} \right\rangle = \lambda - \mu^2 = \left\langle Y_{\lambda\mu} | \hat{L}_x^2 + \hat{L}_y^2 | Y_{\lambda\mu} \right\rangle \geq 0$. Therefore, using the raising/lowering properties of the operators $\hat{L}_\pm$, we may claim that, for any fixed λ, there exist $\mu_{\max} \equiv \hbar l$ and $\mu_{\min} \equiv \hbar l'$ such that $\hat{L}_+ Y_{\max} = 0$ and $\hat{L}_- Y_{\min} = 0$, or written compactly, $\hat{L}_\pm Y_{\max\,\min} = 0$, where we simplified the notation to $Y_{\max\,\min} \equiv Y_{\lambda,\mu_{\max\,\min}}$.

We want to find what values may be taken by the parameters l' and l. It will be useful to use the following identity

$$\hat{L}_\pm \hat{L}_\mp = \left(\hat{L}_x \pm i\hat{L}_y\right)\left(\hat{L}_x \mp i\hat{L}_y\right) = \hat{L}_x^2 + \hat{L}_y^2 \mp i[\hat{L}_x, \hat{L}_y] = \hat{\vec{L}}^2 - \hat{L}_z^2 \pm \hbar \hat{L}_z \Rightarrow \hat{\vec{L}}^2 = \hat{L}_\pm \hat{L}_\mp + \hat{L}_z^2 \mp \hbar \hat{L}_z$$

Since both $Y_{\min\max}$ are the eigenstates of $\hat{\vec{L}}^2$ with the same eigenvalue λ, the above identity gives

$$\hat{\vec{L}}^2 Y_{\min\max} = \lambda Y_{\min\max} = \hat{L}_\pm(\hat{L}_\mp Y_{\min\max}) + \hat{L}_z^2 Y_{\min\max} \mp \hbar \hat{L}_z Y_{\min\max} = \left\{ \begin{array}{c} \mu_{\min}^2 \\ \mu_{\max}^2 \end{array} \right\} Y_{\min\max} \mp \hbar \left\{ \begin{array}{c} \mu_{\min} \\ \mu_{\max} \end{array} \right\} Y_{\min\max}$$

So, $\lambda = \hbar^2 l(l+1) = \hbar^2 l'(l'-1)$, with the second equality giving quadratic equation $l'^2 - l' - l(l+1) = 0$, which can be solved for l'. The two roots of this equation are $l' = \left\{ \begin{array}{c} l+1 \\ -l \end{array} \right\}$, but we must choose $l' = -l$ because $\mu_{\min} = \hbar l' \leq \mu_{\max} = \hbar l$, giving the difference $\mu_{\max} - \mu_{\min} = \hbar(l - l') = 2\hbar l$. On the other hand, referring to the raising/lowering properties of the operators $\hat{L}_\pm$, the difference $\mu_{\max} - \mu_{\min}$ must occur in $N = 0, 1, 2, 3, \cdots$ steps. Therefore, $2\hbar l = \hbar N$ implies that $l = \frac{N}{2}$ **can only be an integer or half-integer!** We have seen that, for the orbital angular momentum $l = 0, 1, 2, \ldots$, but for the spin of electron l only takes one value, $l \equiv s = \frac{1}{2}$. Particles that have integer values for their spin are called bosons, while the particles with a half-integer spin are called fermions (such as electrons and neutrons).

Moreover, starting from $\mu_{\min} \leq \mu \leq \mu_{\max}$ and setting $\mu = \hbar m$, we recover the relation $-l \leq m \leq l$. So, for bosons and for the orbital angular momentum with $l = 0, 1, 2, \ldots$, the magnetic quantum number m can take zero value, whereas for the fermions we can never have $m = 0$. In particular, for the spin of an electron we only have two values of the magnetic quantum number, which we denote by $m_s = \pm s = \pm\frac{1}{2}$. This implies that components of the spin angular momentum of an electron along the direction of an external magnetic field may only be oriented either "up" or "down" the field.

So, we have found that, in general $Y_{\lambda\mu} \to Y_{lm}$ such that $\hat{\vec{L}}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$ and $\hat{L}_z Y_{lm} = \hbar m Y_{lm}$, and we wish to prove now that the constant in the relation

$$\hat{L}_\pm Y_{lm} = C_{lm}^\pm Y_{l,m\pm1}$$

has the value $C_{lm}^\pm = \hbar\sqrt{l(l+1) - m(m\pm1)}$.

The proof proceeds in two steps:

1. Since $\hat{L}_\mp^\dagger = (\hat{L}_x \mp i\hat{L}_y)^\dagger = \hat{L}_x^\dagger \pm i\hat{L}_y^\dagger = \hat{L}_x \pm \hat{L}_y = \hat{L}_\pm$, we have

$$\langle Y_{lm}|\hat{L}_\mp \hat{L}_\pm|Y_{lm}\rangle = \langle Y_{lm}|\hat{L}_\mp(\hat{L}_\pm Y_{lm})\rangle = \langle \hat{L}_\mp^\dagger Y_{lm}|\hat{L}_\pm Y_{lm}\rangle = \langle \hat{L}_\pm Y_{lm}|\hat{L}_\pm Y_{lm}\rangle = |C_{lm}^\pm|^2 \langle Y_{l,m\pm1}|Y_{l,m\pm1}\rangle = \left(C_{lm}^\pm\right)^2$$

2. Recalling $\hat{L}_\mp \hat{L}_\pm = \hat{\vec{L}}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z$, the left-hand side of the above expression can also be written as

$$\langle Y_{lm}|\hat{L}_\mp \hat{L}_\pm|Y_{lm}\rangle = \langle Y_{lm}|\hat{\vec{L}}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z|Y_{lm}\rangle = \langle Y_{lm}|\hbar^2 l(l+1) - \hbar^2 m^2 \mp \hbar^2 m|Y_{lm}\rangle = \hbar^2\left[l(l+1) - m(m\pm1)\right]\langle Y_{lm}|Y_{lm}\rangle$$

Comparing the right-hand sides of the above two expressions, we find $C_{lm}^\pm = \hbar\sqrt{l(l+1) - m(m\pm1)}$.

8 Spin

8.1 Stern-Gerlach experiment

In response to an experiment by Stern and Gerlach (1922), where the beam of Ag atoms (having zero total angular momentum from its electrons' orbital motions) was passed through a region with magnetic field, Goudsmit and Uhlenbeck (1925) hypothesized that each electron must carry intrinsic angular momentum called spin, whose projection along the direction of magnetic field can only take two values, $\pm\frac{\hbar}{2}$.

We shall introduce mathematical representation of the spin for electron in close analogy with the theory for orbital angular momentum, which produces magnetic dipole moment $\hat{\vec{\mu}}_L$ and the interaction Hamiltonian $\hat{H}_L$ with a magnetic field of inductance $\vec{B} = (0, 0, B_0)$ given by

$$\hat{\vec{\mu}}_L = -\frac{|e|}{2m_e c}\hat{\vec{L}}, \quad \hat{H}_L = -\hat{\vec{\mu}}_L \cdot \vec{B} = \frac{|e|B_0}{2m_e c}\hat{L}_z$$

with the eigenvalues of $\hat{L}_z$ being $\hbar m, m = 0, \pm 1, \cdots, \pm l$. Notice, however, that, unlike the the orbital angular momentum quantum number l, which takes a range of integer values in a H-atom bounded by $0 \leq l \leq n-1$, the spin angular momentum quantum number of an electron is fixed at $s = \frac{1}{2}$. Referring to the section on Ladder operators, we recall that the quantum number s and the associated quantum number m_s for the z component of the spin angular moment satisfy the same algebraic relations, e.g., m_s jumps in unit steps from $-s$ to s, thereby taking only two values, $m_s = \pm\frac{1}{2}$, describing the electrin spin orientation "up" or "dawn" relative to the direction of the z axis (usually adopted to be parallel to an external magnetic field vector).

Making the changes

$$\hat{\vec{L}} \to \hat{\vec{S}}, \qquad l \to s = \frac{1}{2}, \qquad -l \leq m \leq l \quad \to \quad -s \leq m_s \leq s \quad \Rightarrow \quad m_s = \pm\frac{1}{2}$$

we may write magnetic dipole moment due to spin and its interaction energy with the magnetic field as

$$\hat{\vec{\mu}}_s = -g\frac{|e|}{2m_e c}\hat{\vec{S}}, \quad \hat{H}_s = -\hat{\vec{\mu}}_s \cdot \vec{B} = g\frac{|e|B_0}{2m_e c}\hat{S}_z \approx \frac{|e|B_0}{m_e c}\hat{S}_z$$

where g is the so-called *Lande's gyromagnetic factor* that has a value very close to 2 for electron, and the eigenvalues of $\hat{S}_z$ are $\hbar m_s = \pm\frac{\hbar}{2}$.

We want to find a *matrix representation* of the spin vector components, $\hat{\vec{S}} = \left(\hat{S}_x,\ \hat{S}_y,\ \hat{S}_z\right)$, by first considering the EVPs for the commuting operators $\hat{\vec{S}}^2$ and $\hat{S}_z$ in analogy with the EVPs for $\hat{\vec{L}}^2$ and $\hat{L}_z$:

$$\begin{cases} \hat{\vec{S}}^2|sm_s\rangle = \hbar^2 s(s+1)|sm_s\rangle = \dfrac{3}{4}\hbar^2|sm_s\rangle \\ \hat{S}_z|sm_s\rangle = \hbar m_s|sm_s\rangle = \pm\dfrac{\hbar}{2}|sm_s\rangle \end{cases}$$

Thus, there are only two eigenvectors shared by $\hat{\vec{S}}^2$ and $\hat{S}_z$, which can be written as Dirac's kets or as two-component column vectors in matrix representation :

$$|sm_s\rangle = \begin{cases} |\frac{1}{2},\frac{1}{2}\rangle = |\frac{1}{2}\rangle = |\chi_+\rangle \mapsto \boldsymbol{\chi}_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} & \text{spin up} \\ |\frac{1}{2},-\frac{1}{2}\rangle = |-\frac{1}{2}\rangle = |\chi_-\rangle \mapsto \boldsymbol{\chi}_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} & \text{spin down} \end{cases}$$

for which the operators $\hat{\vec{S}}^2$ and $\hat{S}_z$ can be represented by the following 2×2 diagonal matrices:

$$\begin{aligned} \hat{\vec{S}}^2\boldsymbol{\chi}_\pm &= \frac{3}{4}\hbar^2\boldsymbol{\chi}_\pm \quad \Rightarrow \quad \hat{\vec{S}}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \equiv \frac{3}{4}\hbar^2\hat{1} \\ \hat{S}_z\boldsymbol{\chi}_\pm &= \hbar m_s\boldsymbol{\chi}_\pm = \pm\frac{\hbar}{2}\boldsymbol{\chi}_\pm \quad \Rightarrow \quad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \equiv \frac{\hbar}{2}\hat{\sigma}_z \end{aligned}$$

where $\hat{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ is identity matrix and where we introduced the matrix $\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

To find the corresponding matrix representations for $\hat{S}_x$ and $\hat{S}_y$, we use the properties of the corresponding ladder operators $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$. If we let $\mu_{\max} = \hbar m_{s\max} = \frac{\hbar}{2}$, then

$$\hat{S}_+\boldsymbol{\chi}_+ = 0, \quad \text{and} \quad \hat{S}_-\boldsymbol{\chi}_+ = C^-_{s,m_{s\max}}\boldsymbol{\chi}_- = \hbar\sqrt{\underbrace{s(s+1)}_{3/4} - \underbrace{m_{s\max}(m_{s\max}-1)}_{-1/4}}\boldsymbol{\chi}_- = \hbar\boldsymbol{\chi}_- \Rightarrow \hat{S}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Similarly, letting $\mu_{\min} = \hbar m_{s\min} = -\frac{\hbar}{2}$ gives

$$\hat{S}_-\boldsymbol{\chi}_- = 0, \quad \text{and} \quad \hat{S}_+\boldsymbol{\chi}_- = C^+_{s,m_{s\min}}\boldsymbol{\chi}_+ = \hbar\sqrt{\underbrace{s(s+1)}_{3/4} - \underbrace{m_{s\min}(m_{s\min}+1)}_{-1/4}}\boldsymbol{\chi}_+ = \hbar\boldsymbol{\chi}_+ \Rightarrow \hat{S}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

Therefore,

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\hat{\sigma}_x \quad \text{and} \quad \hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-) = \frac{\hbar}{2i}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar}{2}\hat{\sigma}_y$$

where we introduced the matrices $\hat{\sigma}_x$ and $\hat{\sigma}_y$, which are together with $\hat{\sigma}_z$ known as the Pauli Spin Matrices.

8.2 Pauli spin matrices

$$\hat{S}_u = \frac{\hbar}{2}\hat{\sigma}_u,\ u = x, y, z: \quad \hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\ \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad \hat{\vec{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$$

Properties

(1) $\hat{\sigma}_u^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{1}, u = x, y, z \Rightarrow \hat{\vec{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{\hbar^2}{4}\left(\hat{\sigma}_x^2 + \hat{\sigma}_y^2 + \hat{\sigma}_z^2\right) = \frac{3}{4}\hbar\hat{1}$

(2) $[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z$, and two more relations with cyclically permuted indices $\Rightarrow \left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z$

(3) $\hat{\sigma}_x\hat{\sigma}_y = -\hat{\sigma}_y\hat{\sigma}_x = i\hat{\sigma}_z$, and two more relations with cyclically permuted indices, show anti-commutation of Pauli matrices $\Rightarrow \{\hat{\sigma}_x, \hat{\sigma}_y\} = [\hat{\sigma}_x, , \hat{\sigma}_y]_+ = \hat{\sigma}_x\hat{\sigma}_y + \hat{\sigma}_y\hat{\sigma}_x = 0$

(4) $\mathrm{tr}\{\hat{\sigma}_u\} = 0,\ u = x, y, z$

(5) $\det[\hat{\sigma}_u] = -1,\ u = x, y, z$

$(\cdots)$

Example 8.0.1. Solve the EVP for $\hat{\sigma}_x$. Consider $\hat{\sigma}_x\boldsymbol{\chi}^{(x)} = \lambda\boldsymbol{\chi}^{(x)}$, let $\boldsymbol{\chi}^{(x)} = \begin{pmatrix} a \\ b \end{pmatrix}$ and impose normalization $\|\boldsymbol{\chi}^{(x)}\|^2 = \begin{pmatrix} a^* & b^* \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = |a|^2 + |b|^2 = 1$. Assuming a, b real, we can write $a^2 + b^2 = 1$. Then

$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \lambda\begin{pmatrix} a \\ b \end{pmatrix} \Rightarrow \det\begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} = \lambda^2 - 1 = 0$. So, for $\lambda = \pm 1$, we have $b = \lambda a$.

$\lambda = 1: \quad b = a$, so from $a^2 + b^2 = 1 \Rightarrow 2a^2 = 1 \Rightarrow a = \frac{1}{\sqrt{2}}, \quad b = \frac{1}{\sqrt{2}} \quad \Rightarrow \quad \boldsymbol{\chi}_+^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$\lambda = -1: \quad b = -a$, so from $a^2 + b^2 = 1 \Rightarrow 2a^2 = 1 \Rightarrow a = \frac{1}{\sqrt{2}}, \quad b = -\frac{1}{\sqrt{2}} \quad \Rightarrow \quad \boldsymbol{\chi}_-^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

Example 8.0.2. Solve the EVP for $\hat{S}_u$, which is the spin component in the direction of arbitrary unit vector $\vec{u} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ that is given by $\hat{S}_u = \vec{u}\cdot\hat{\vec{S}} = \frac{\hbar}{2}\vec{u}\cdot\hat{\vec{\sigma}} = \frac{\hbar}{2}\hat{\sigma}_u$, where we define

$$\hat{\sigma}_u = \hat{\sigma}_x\sin\theta\cos\phi + \hat{\sigma}_y\sin\theta\sin\phi + \hat{\sigma}_z\cos\theta = \begin{pmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{pmatrix}$$

The solution of the EVP $\hat{\sigma}_u\boldsymbol{\chi}^{(u)} = \lambda\boldsymbol{\chi}^{(u)}$ gives $\lambda = \pm 1$ with the corresponding orthonormal eigenvectors $\boldsymbol{\chi}_\pm^{(u)}$ given by

$$\lambda = 1: \quad \boldsymbol{\chi}_+^{(u)} = \begin{pmatrix} \cos(\theta/2) \\ e^{i\phi}\sin(\theta/2) \end{pmatrix} \to \begin{cases} \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, & u = x \\ \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}, & u = y \\ \begin{pmatrix} 1 \\ 0 \end{pmatrix} \equiv \boldsymbol{\chi}_+, & u = z \end{cases}$$

$$\lambda = -1: \quad \boldsymbol{\chi}_-^{(u)} = \begin{pmatrix} -\sin(\theta/2) \\ e^{i\phi}\cos(\theta/2) \end{pmatrix} \to \begin{cases} \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix}, & u = x \\ \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ i \end{pmatrix}, & u = y \\ \begin{pmatrix} 0 \\ 1 \end{pmatrix} \equiv \boldsymbol{\chi}_-, & u = z \end{cases}$$

8.3 Electron in magnetic field

We consider here an electron in constant magnetic field and describe the precession of its spin vector. Using the magnetic dipole moment for the spin of electron,

$$\hat{\vec{\mu}}_s = -g\frac{|e|}{2m_e c}\hat{\vec{S}} = -g\frac{|e|}{2m_e c}\frac{\hbar}{2}\hat{\vec{\sigma}}, \quad g \approx 2$$

the classical EM theory gives the Hamiltonian

$$\hat{H}_s = -\hat{\vec{\mu}}_s \cdot \vec{B} = \frac{|e|\hbar}{2m_e c}\vec{B} \cdot \hat{\vec{\sigma}}.$$

Assuming $\vec{B} = (0, 0, B_0)$, we have $\hat{H}_s = -\hat{\vec{\mu}}_s \cdot \vec{B} = \mu_B B_0 \hat{\sigma}_z$ where $\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ and $\mu_B = \dfrac{|e|\hbar}{2m_e c}$ is the Bohr's magneton.

First solve the TISE with $\hat{H}_s$ by using the solution of the EVP $\hat{\sigma}_z\boldsymbol{\chi}_\pm = \pm\boldsymbol{\chi}_\pm$, which gives eigenvectors $\boldsymbol{\chi}_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\boldsymbol{\chi}_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Thus, the solution of TISE is given by $\hat{H}_s\boldsymbol{\chi}_\pm = E_\pm\boldsymbol{\chi}_\pm$ with eigenenergies $E_\pm = \pm\mu_B B_0$.

General solution of the TDSE $\hat{H}_s\boldsymbol{\chi}(t) = i\hbar\dfrac{\partial}{\partial t}\boldsymbol{\chi}(t)$ is

$$\boldsymbol{\chi}(t) = a\boldsymbol{\chi}_+ e^{-\frac{i}{\hbar}E_+ t} + b\boldsymbol{\chi}_- e^{-\frac{i}{\hbar}E_- t} = \begin{pmatrix} a\, e^{-i\omega_L t} \\ b\, e^{i\omega_L t} \end{pmatrix}$$

where we defined the so-called *Larmor frequency* by

$$\omega_L = \frac{\mu_B}{\hbar} B_0 = \frac{|e| B_0}{2 m_e c}.$$

The probability to observe the "spin up" with energy E_+ is $p_+ = |a|^2$ and "spin down" with energy E_- is $p_- = |b|^2$, where $|a|^2 + |b|^2 = 1$. The average energy is then $\bar{E} = \langle \chi(t) | \hat{H}_s | \chi(t) \rangle = \cdots = \mu_B B_0 (|a|^2 - |b|^2)$.

Assume IC with some normalized vector $\boldsymbol{\chi}(0) = \begin{pmatrix} a \\ b \end{pmatrix}$ such that $|a|^2 + |b|^2 = 1$. We may define $a = \cos\frac{\theta}{2}$ and $b = \sin\frac{\theta}{2}$ with θ being an arbitrary, initially prescribed angle. Then, $\bar{E} = \mu_B B_0 \cos\theta$, while the time-dependent expectation values of the Cartesian components of the electron spin vector $\hat{\vec{S}} = \left(\hat{S}_x,\ \hat{S}_y,\ \hat{S}_z \right)$ are

$$\begin{aligned}
\left\langle \hat{S}_z \right\rangle &= \langle \chi(t) | \hat{S}_z | \chi(t) \rangle = \frac{\hbar}{2} \begin{pmatrix} \cos(\frac{\theta}{2}) e^{i\omega_L t} & \sin(\frac{\theta}{2}) e^{-i\omega_L t} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \cos(\frac{\theta}{2}) e^{-i\omega_L t} \\ \sin(\frac{\theta}{2}) e^{i\omega_L t} \end{pmatrix} = \frac{\hbar}{2} \cos\theta \\
\left\langle \hat{S}_x \right\rangle &= \langle \chi(t) | \hat{S}_x | \chi(t) \rangle = \frac{\hbar}{2} \langle \chi(t) | \hat{\sigma}_x | \chi(t) \rangle = \cdots = \frac{\hbar}{2} \sin\theta \cos(2\omega_L t) \\
\left\langle \hat{S}_y \right\rangle &= \langle \chi(t) | \hat{S}_y | \chi(t) \rangle = \frac{\hbar}{2} \langle \chi(t) | \hat{\sigma}_y | \chi(t) \rangle = \cdots = \frac{\hbar}{2} \sin\theta \sin(2\omega_L t)
\end{aligned}$$

8.4 Weak Zeeman effect

Consider Classical Mechanical motion of a point charge e in the presence of both electric field $\vec{E}$ and magnetic field of induction $\vec{B}$. Maxwell's equations imply that those fields may be generally written as

$$\vec{E} = -\nabla\phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \nabla \times \vec{A}$$

where ϕ is the electrostatic potential and $\vec{A}$ is the magnetic vector potential. However, those potentials are not uniquely defined because including any scalar field $\Lambda(\vec{r}, t)$ transforms the potentials to $\phi' = \phi - \frac{1}{c}\frac{\partial \Lambda}{\partial t}$ and $\vec{A}' = \vec{A} + \nabla\Lambda$ without changing the values of the electric and magnetic fields. Therefore, we may apply suitable constraints to the vector potential that are referred to as gauge transformations.

The classical Hamilton's function for this problem is written in the so-called minimal coupling as

$$H_{cl}(\vec{p}, \vec{r}) = \frac{1}{2m_e} \left(\vec{p} - \frac{e}{c}\vec{A} \right)^2 + e\phi(\vec{r}).$$

Using Hamilton's equations $\begin{cases} \dot{\vec{p}} = -\nabla_{\vec{r}} H_{cl} \\ \dot{\vec{r}} = \nabla_{\vec{p}} H_{cl} = \frac{1}{m_e}(\vec{p} - \frac{e}{c}\vec{A}) \end{cases}$, one finds $\underbrace{m_e \dot{\vec{r}}}_{\text{kinetic mom}} = \underbrace{\vec{p}}_{\text{canonical mom}} - \frac{e}{c}\vec{A}$, which

may be differentiated with respect to time to show that the position vector $\vec{r} = \vec{r}(t)$ of charged particle satisfies the Newtonian DE $m_e\ddot{\vec{r}} = e\left(\vec{E} + \frac{1}{c}\dot{\vec{r}} \times \vec{B}\right)$, with the total force in the right-hand side called Lorentz force.

The Quantum Mechanical Hamiltonian in time-independent fields is therefore given by

$$\hat{H}_Q = \frac{1}{2m_e}\left(\hat{\vec{p}} - \frac{e}{c}\vec{A}\right)^2 + e\phi(\vec{r}) = \frac{\hat{\vec{p}}^2}{2m_e} - \frac{e}{2m_e c}(\hat{\vec{p}} \cdot \vec{A} + \vec{A} \cdot \hat{\vec{p}}) + \frac{e^2\vec{A}^2}{2m_e c^2} + e\phi(r)$$

where $\hat{\vec{p}} = \frac{\hbar}{i}\nabla_{\vec{r}}$ in the position representation. It can be shown that, for arbitrary wavefunction $\psi(\vec{r})$,

$$\hat{\vec{p}} \cdot (\vec{A}\psi(\vec{r})) = \frac{\hbar}{i}\nabla_{\vec{r}} \cdot (\vec{A}\psi) = \frac{\hbar}{i}(\nabla \cdot \vec{A})\psi + \frac{\hbar}{i}\vec{A} \cdot \nabla\psi = \frac{\hbar}{i}(\nabla \cdot \vec{A})\psi + \vec{A} \cdot \hat{\vec{p}}\psi$$

so that, by adopting the so-called *Coulomb gauge*, $\nabla \cdot \vec{A} = 0$, we have $\hat{\vec{p}} \cdot \vec{A} = \vec{A} \cdot \hat{\vec{p}}$, giving

$$\hat{H}_Q = \frac{\hat{\vec{p}}^2}{2m_e} - \frac{e}{m_e}\vec{A} \cdot \hat{\vec{p}} + \frac{e^2\vec{A}^2}{2m_e c^2} + e\phi(r).$$

We wish to study the effect of weak magnetic field on hydrogen atom, known as weak Zeemen effect. Hence, in the above Hamiltonian we let $e\phi(r) = -k_c\frac{e^2}{r}$ and neglect the quadratic term with $\vec{A}^2$ with respect to the linear term with $\vec{A}$ in the above Hamiltonian. Next, we define $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$, which for the magnetic field $\vec{B} = (0, 0, B_0)$ gives $\vec{A} = \frac{1}{2}\begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ 0 & 0 & B_0 \\ x & y & z \end{pmatrix} = \frac{B_0}{2}(-y, x, 0)$, satisfying both the Coulomb gauge and the definition $\vec{B} = \nabla \times \vec{A}$. Thus, by using properties of a triple mixed vector product from AMATH 231,

$$\vec{A} \cdot \hat{\vec{p}} = \frac{1}{2}(\vec{B} \times \vec{r}) \cdot \hat{\vec{p}} = \frac{1}{2}\vec{B} \cdot (\vec{r} \times \hat{\vec{p}}) = \frac{1}{2}\vec{B} \cdot \hat{\vec{L}}$$

we find that the Hamiltonian for the weak Zeemen effect due to orbital motion of electron may be approximated as $\hat{H}_Q \approx \hat{H}_{\text{orb}}$, where

$$\hat{H}_{\text{orb}} = -\frac{\hbar^2}{2m_e}\nabla^2_{\vec{r}} - \frac{e}{2m_e c}\vec{B} \cdot \hat{\vec{L}} - k_c\frac{e^2}{r}.$$

Notice that we may write the above Hamiltonian as $\hat{H}_{\text{orb}} = \hat{H}_0 - \frac{e}{2m_e c}\vec{B} \cdot \hat{\vec{L}} = \hat{H}_0 + \omega_L\hat{L}_z$, where $\hat{H}_0$ is the Hamiltonian of the H-atom without magnetic field, and $\omega_L = \frac{|e|B_0}{2m_e c}$ is the Larmor frequency.

Now we want to include spin in the weak Zeeman effect for the H-atom by noticing that its interaction

with the magnetic field may be similarly written as

$$\hat{H}_s = -\vec{B}\cdot\vec{\mu}_s = \frac{|e|B_0}{m_e c}\hat{S}_z = \omega_L \hbar \hat{\sigma}_z; \quad \text{where} \quad \hat{S}_z = \frac{\hbar}{2}\hat{\sigma}_z, \quad \hat{\sigma}_z \boldsymbol{\chi}_\pm = \pm\boldsymbol{\chi}_\pm, \quad \boldsymbol{\chi}_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \ \boldsymbol{\chi}_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

So, we may attempt to write the full Hamiltonian for the weak Zeemen effect as the sum $\hat{H}_Z = \hat{H}_{\text{orb}} + \hat{H}_s$, but the problem is that $\hat{H}_{\text{orb}} = \hat{H}_0 + \omega_L \hat{L}_z$ is a scalar operator expressed in the position representation, whereas $\hat{H}_s = \hbar\omega_L\hat{\sigma}_z$ is a 2×2 matrix operator.

This problem may be rectified if we simply multiply $\hat{H}_{\text{orb}}$ by a 2×2 identity matrix $\hat{1}$ and write the Zeeman Hamiltonian as

$$\hat{H}_Z = \left(\hat{H}_0 + \omega_L \hat{L}_z\right)\hat{1} + \hbar\omega_L\hat{\sigma}_z.$$

Accordingly, the TISE for such Hamiltonian, $\hat{H}_Z\boldsymbol{\psi} = E\boldsymbol{\psi}$, must be expressed in mixed representation involving a column vector $\boldsymbol{\psi}$ called spinor, which has two components for the electron spin oriented up or down that are functions of the electron position describing its orbital motion.

8.5 Spinor eigenstates

For a H-atom in constant external magnetic field oriented along the z axis, notice that the spin component $\hat{S}_z$ and hence $\hat{H}_s$ commute with the rest of the Hamiltonian, $\left(\hat{H}_0 + \omega_L\hat{L}_z\right)\hat{1}$, within $\hat{H}_Z$, so we may include $m_s = \pm\frac{1}{2}$ from the EVP $\hat{S}_z\boldsymbol{\chi}_\pm = \hbar m_s \boldsymbol{\chi}_\pm$ as good quantum number whose value describes the state of the electron's spin component along the direction of the magnetic field being either "up" or "down". Hence, we define the spinor $\boldsymbol{\psi}(r,\theta,\phi)$ for the H-atom as

$$\boldsymbol{\psi}(r,\theta,\phi) = \begin{pmatrix} \psi_+(r,\theta,\phi) \\ \psi_-(r,\theta,\phi) \end{pmatrix} = \psi_+(r,\theta,\phi)\boldsymbol{\chi}_+ + \psi_-(r,\theta,\phi)\boldsymbol{\chi}_-,$$

where the spinor components, $\psi_\pm(r,\theta,\phi) = c_\pm\psi_{nlm}(r,\theta,\phi)$, are proportional to the wavefunctions found in solving the H-atom without magnetic field in spherical coordinates, $H_0\psi_{nlm} = E_n\psi_{nlm}$ with $E_n = -E_R/n^2$.

Notice that the normalization of a spinor requires

$$\|\boldsymbol{\psi}\|^2 = \iiint \begin{pmatrix} \psi_+^* & \psi_-^* \end{pmatrix}\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} dV = \iiint |\psi_+|^2 dV + \iiint |\psi_-|^2 dV = |c_+|^2 + |c_-|^2 = 1,$$

so that, e.g., $|\psi_\pm(r,\theta,\phi)|^2\,dV$ is the probability of finding the electron in a small volume dV at the point (r,θ,ϕ) with its spin oriented up/down, whereas $|c_\pm|^2$ is the probability for the electron spin being oriented up/down regardless of the position of the electron.

The TISE with the full Hamiltonian $\hat{H}_Z$ is equivalent to two coupled scalar TISEs for ψ_+ and ψ_-,

$$\hat{H}_Z\boldsymbol{\psi} = E\boldsymbol{\psi} \Leftrightarrow \begin{cases} \hat{H}_0\psi_+ + \omega_L(\hat{L}_z + \hbar)\psi_+ = E\psi_+ \\ \hat{H}_0\psi_- + \omega_L(\hat{L}_z - \hbar)\psi_- = E\psi_- \end{cases} \quad \rightarrow \quad E_{nlmm_s} = E_n + \hbar\omega_L(m \pm 1).$$

The n^2-fold degeneracy of the eigenenergy E_n of a H-atom without magnetic field is first doubled by adding spin, and then lifted in magnetic field because eigenenergy E_{nlmm_s} depends on all four quantum numbers:

1s state: $n = 1, l = 0, m = 0$ so $E_1 \rightarrow \begin{cases} E_1 + \hbar\omega_L, & m_s = \frac{1}{2} \\ E_1 - \hbar\omega_L, & m_s = -\frac{1}{2} \end{cases}$

2s state: $n = 2, l = 0, m = 0$ so $E_2 \rightarrow \begin{cases} E_2 + \hbar\omega_L, & m_s = \frac{1}{2} \\ E_2 - \hbar\omega_L, & m_s = -\frac{1}{2} \end{cases}$

2p state: $n = 2, l = 1, m = -1, 0, 1$ so $E_2 \rightarrow \begin{cases} E_2 + 2\hbar\omega_L, & m = 1, m_s = \frac{1}{2} \\ E_2 + \hbar\omega_L, & m = 0, m_s = \frac{1}{2} \\ E_2 & m = \pm 1, m_s = \mp\frac{1}{2} \text{ (remains doubly degenerate)} \\ E_2 - \hbar\omega_L, & m = 0, m_s = -\frac{1}{2} \\ E_2 - 2\hbar\omega_L, & m = -1, m_s = -\frac{1}{2} \end{cases}$

8.6 Spin-orbit coupling

Notice that the orbital angular momentum arising from the relative motion of electron and proton in a H-atom produces electric current loop that gives rise to a magnetic field $\hat{\vec{B}} = \dfrac{e}{m_e c^2 r^3}\hat{\vec{L}}$, which couples with electron's own spin, so that the corresponding spin-orbit interaction is governed by the Hamiltonian

$$\hat{H}_{so} = -\hat{\vec{B}} \cdot \hat{\vec{\mu}}_s = \frac{e^2}{m_e^2 c^2 r^3}\hat{\vec{L}} \cdot \hat{\vec{S}}.$$

Therefore, to include this interaction in a H-atom model, we need to add $\hat{H}_{so}$ to the Hamiltonian $\hat{H}_Z$ for the weak Zeeman effect, and solve a TISE with $\hat{H} = \hat{H}_Z + \hat{H}_{so}$. However, $\hat{H}_{so}$ does NOT commute with $\hat{H}_Z$, even in the absence of an external magnetic field, so we can no longer use the previously found eigenfunctions ψ_{nlm} of the H-atom. Luckily, $\hat{H}_{so}$ commutes with the total angular momentum $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$, and we can therefore construct new set of quantum states by adopting the eigenvalues of the operators $\hat{\vec{L}}^2$, $\hat{\vec{S}}^2$, $\hat{\vec{J}}^2$, and $\hat{J}_z$ as good quantum numbers. However, to achieve that goal, one needs to develop algebraic rules for the addition of angular momenta, which go beyond this course. We just mention briefly that, for a given l, with the the electron spin quantum number being fixed at $s = \frac{1}{2}$, the quantum number for the total angular momentum takes two values, $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$, each of which is accompanied with the quantum number for the z-component of the total angular momentum, m_j, jumping in unit steps in the interval $-j \leq m_j \leq j$, thereby giving rise to the total number of quantum states $2(2l + 1)$, as expected.

9 Approximation methods for TISE

Few problems in QM can be solved in an analytically exact manner. On the other hand, numerical computations may be very tedious, especially in many-particle problems. Luckily, it often happens that the problem at hand is "close" to a problem that we know how to solve analytically. In other words, the hamiltonian $\hat{H}$ of a "difficult", or analytically intractable problem may be written as the sum of the Hamiltonian $\hat{H}_0$ of an analytically solvable, or "unperturbed" problem and some "small perturbation" $\hat{H}_1$. We study here how to develop systematic series-like solutions to such problems in the "powers" of $\hat{H}_1$ that are hoped to give reasonable approximation to the "difficult" problem upon truncation of such series.

9.1 Non-degenerate perturbation theory

We want to solve TISE of the form $\hat{H}\psi_n = E_n\psi_n$ where $\hat{H} = \hat{H}_0 + \hat{H}_1$ with $\hat{H}_1$ being "small", and we know the solution to the unperturbed TISE, $\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, with non-degenerate eigenenergies $E_n^{(0)}$.

Introduce a "book-keeping" parameter λ (consider it small, but let $\lambda = 1$ in the end), write $\hat{H} = \hat{H}_0 + \lambda\hat{H}_1$, and assume the following series for the n-th eigenstate and the corresponding eigenenergy

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots ; \quad \text{and} \quad E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots .$$

We insert those series in the full TISE,

$$\left(\hat{H}_0 + \lambda\hat{H}_1\right)\left(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \cdots\right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \cdots\right)\left(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \cdots\right)$$

and collect terms with equal powers of λ,

$$\lambda^0\left(\hat{H}_0\psi_n^{(0)} - E_n^{(0)}\psi_n^{(0)}\right) + \lambda\left(\hat{H}_1\psi_n^{(0)} + \hat{H}_0\psi_n^{(1)} - E_n^{(1)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(1)}\right) + \lambda^2(\cdots) + \cdots = 0.$$

Notice that the term with $\lambda^0 = 1$ vanishes by the unperturbed TISE, and consider the term linear in λ, which gives

$$\left(\hat{H}_0 - E_n^{(0)}\right)\psi_n^{(1)} = -\left(\hat{H}_1 - E_n^{(1)}\right)\psi_n^{(0)}. \qquad (*)$$

Multiply equation (*) by $\psi_n^{(0)*}$ and integrate to get

$$\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle - E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = -\langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle + E_n^{(1)}$$

but since $\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle = \langle\hat{H}_0\psi_n^{(0)}|\psi_n^{(1)}\rangle = E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle$, the left-hand side of the above equation vanishes

and we get

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle.$$

Therefore, to the first order, we may approximate the eigenenergy by $E_n \approx E_n^{(0)} + \lambda E_n^{(1)} \equiv E_n^{(0)} + E_n^{(1)}$.

To find the first-order approximation for the corresponding eigenfunction, $\psi_n \approx \psi_n^{(0)} + \lambda \psi_n^{(1)} \equiv \psi_n^{(0)} + \psi_n^{(1)}$, we use the completeness and orthonormality of the solutions $\{\psi_n^{(0)}\}_{n=1}^{\infty}$ of the unperturbed TISE, and write

$$\psi_n^{(1)} = \sum_{k=1, k\neq n}^{\infty} c_k \psi_k^{(0)} \qquad (**)$$

where we exclude the $k = n$ term because it is already included in the zeroth order term when we write $\psi_n \approx \psi_n^{(0)} + \lambda \psi_n^{(1)}$.

Comment: Notice that the approximate eigenfunction will automatically remain normalized to the first order because

$$\|\psi_n\|^2 = \left\langle \psi_n^{(0)} + \lambda \sum_{k\neq n} c_k \psi_k^{(0)} + \cdots \middle| \psi_n^{(0)} + \lambda \sum_{k'\neq n}^{\infty} c_{k'} \psi_{k'}^{(0)} + \cdots \right\rangle = \|\psi_n^{(0)}\|^2 + \lambda^2(\cdots) = 1 + \lambda^2(\cdots),$$

where we used the orthogonality relations $\langle \psi_n^{(0)} | \psi_{k'}^{(0)} \rangle = 0$ and $\langle \psi_k^{(0)} | \psi_n^{(0)} \rangle = 0$.

Next, substitute the expansion (**) into equation (*) to get

$$\sum_{k\neq n} c_k \left(\underbrace{\hat{H}_0 \psi_k^{(0)}}_{E_k^{(0)} \psi_k^{(0)}} - E_n^{(0)} \psi_k^{(0)} \right) = \sum_{k\neq n} \left(E_k^{(0)} - E_n^{(0)} \right) c_k \psi_k^{(0)} = - \left(\hat{H}_1 - E_n^{(1)} \right) \psi_n^{(0)}. \qquad (***)$$

Multiply equation (***) by $\psi_l^{(0)*}$ with some $l \neq n$ and integrate to get

$$\sum_{k\neq n} c_k \left(E_k^{(0)} - E_n^{(0)} \right) \underbrace{\langle \psi_l^{(0)} | \psi_k^{(0)} \rangle}_{\delta_{kl}} = E_n^{(1)} \underbrace{\langle \psi_l^{(0)} | \psi_n^{(0)} \rangle}_{0} - \langle \psi_l^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle.$$

Therefore, $(E_l^{(0)} - E_n^{(0)}) c_l = -\langle \psi_l^0 | \hat{H}_1 | \psi_n^0 \rangle$ gives $c_l = -\frac{\langle \psi_l^0 | \hat{H}_1 | \psi_n^0 \rangle}{E_l^0 - E_n^0}$, so that the first-order correction to the eigenfunction $\psi_n^{(0)}$ is given by

$$\psi_n^{(1)} = \sum_{k=1, k\neq n}^{\infty} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)}.$$

Example 9.0.1. Find $E_n^{(1)}$ and $\psi_n^{(1)}$ for $U(x) = \begin{cases} 0, & 0 \leq x \leq a \\ V_0, & a \leq x \leq b \\ \infty, & \text{elsewhere} \end{cases}$, where V_0 is small.

Use $\hat{H}_0$ for a particle-in-box system for the interval $0 \le x \le b$ with $\begin{cases} \psi_n^{(0)}(x) = \sqrt{\frac{2}{b}} \sin(n\frac{\pi}{b}x) \\ E_n^{(0)} = \left(n\frac{\pi}{b}\right)^2 \frac{\hbar^2}{2m} \end{cases}$, and let $\hat{H}_1 = V_0$ for $a \le x \le b$. Then,

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle = V_0 \frac{2}{b} \int_a^b \sin^2\left(n\frac{\pi}{b}x\right) dx = V_0 \left[1 - \frac{a}{b} + \frac{1}{2n\pi} \sin\left(2n\pi\frac{a}{b}\right)\right],$$

$$\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle = V_0 \frac{2}{b} \int_a^b \sin\left(k\frac{\pi}{b}x\right) \sin\left(n\frac{\pi}{b}x\right) dx = \frac{V_0}{\pi} \left\{ \frac{\sin\left[(k+n)\pi\frac{a}{b}\right]}{k+n} - \frac{\sin\left[(k-n)\pi\frac{a}{b}\right]}{k-n} \right\}, \quad k \ne n.$$

9.2 Degenerate perturbation theory

Assume that, for some n, the unperturbed TISE has an eigenenergy $E_n^{(0)}$, which is N-fold degenerate, i.e.,

$$\hat{H}_0 \psi_{n\alpha}^{(0)} = E_n^{(0)} \psi_{n\alpha}^{(0)} \quad \text{for} \quad \alpha = 1, 2, 3, \cdots, N.$$

Notice that the eigenfunctions $\{\psi_{n\alpha}^{(0)}\}_{\alpha=1}^N$ are linearly independent, but are not necessarily orthogonal. However, we may always apply Gram-Schmidt procedure to those functions and obtain an orthonormal basis for the subspace of states corresponding to the eigenenergy $E_n^{(0)}$. Thus, we may safely assume $\langle \psi_{n\alpha} | \psi_{n\beta} \rangle = \delta_{\alpha\beta}$.

Consider the perturbed TISE, $\left(\hat{H}_0 + \hat{H}_1\right) \phi_n = E_n \phi_n$, for n fixed and assume $\phi_n = \sum_{\alpha=1}^N c_\alpha \psi_{n\alpha}^{(0)}$ giving upon substitution

$$\sum_\alpha \left(c_\alpha \underbrace{\hat{H}_0 \psi_{n\alpha}^{(0)}}_{E_n^{(0)} \psi_n^{(0)}} + c_\alpha \hat{H}_1 \psi_{n\alpha}^{(0)} \right) = E_n \sum_\alpha c_\alpha \psi_{n\alpha}^{(0)}.$$

Multiply this by $\psi_{n\beta}^{(0)*}$ and integrate to get

$$\sum_\alpha c_\alpha E_n^{(0)} \underbrace{\langle \psi_{n\beta}^{(0)} | \psi_{n\alpha}^{(0)} \rangle}_{\delta_{\beta\alpha}} + \sum_\alpha c_\alpha \langle \psi_{n\beta}^{(0)} | \hat{H}_1 | \psi_{n\alpha}^{(0)} \rangle = E_n \sum_\alpha c_\alpha \underbrace{\langle \psi_{n\beta}^{(0)} | \psi_{n\alpha}^{(0)} \rangle}_{\delta_{\beta\alpha}}.$$

Denote the matrix elements by $H_{\beta\alpha}^{(1)} = \langle \psi_{n\beta}^{(0)} | \hat{H}_1 | \psi_{n\alpha}^{(0)} \rangle$ and re-arrange the above equation into

$$\sum_\alpha \left[H_{\beta\alpha}^{(1)} - \left(E_n - E_n^{(0)}\right) \delta_{\beta\alpha} \right] c_\alpha = 0.$$

Notice that this is an $N \times N$ matrix algebraic eigenvalue problem with an eigenvalue $E_n^{(1)} \equiv E_n - E_n^{(0)}$ and

an eigenvector $\begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$, which we may write as $\begin{pmatrix} H_{11}^{(1)} & H_{12}^{(1)} & \cdots \\ H_{21}^{(1)} & H_{22}^{(1)} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = E_n^{(1)} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$.

Since the matrix $\left(H_{\alpha\beta}^{(1)}\right)$ is Hermitian, we may diagonalize it. First solve the characteristic equation for $E_n^{(1)}$,

$$\det \begin{pmatrix} H_{11}^{(1)} - E_n^{(1)} & H_{12}^{(1)} & \cdots \\ H_{21}^{(1)} & H_{22}^{(1)} - E_n^{(1)} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} = 0.$$

This equation has N real roots that may be written as $E_{n\gamma}^{(1)}$ for $\gamma = 1, 2, \cdots, N$, which represent the first order corrections to the originally N-fold degenerate eigenenergy $E_n^{(0)}$ of the unperturbed TISE. Those eigenvalues $E_{n\gamma}^{(1)}$ will be accompanied by a set of N orthogonal eigenvectors $\begin{pmatrix} c_1^{(\gamma)} \\ c_2^{(\gamma)} \\ \vdots \end{pmatrix}$, giving rise to N orthonormal functions $\phi_n^{(\gamma)}$. So, depending on how many roots among the $E_{n\gamma}^{(1)}$ are distinct, the inclusion of the perturbation $\hat{H}_1$ in the TISE may lift the degeneracy of the unperturbed problem, at least partially.

Example 9.0.2. Consider a square-shaped 2D particle-in-box system with the potential

$$U(x,y) = \begin{cases} 0, & 0 \le x \le L, \quad 0 \le y \le L \\ \infty, & \text{otherwise} \end{cases}$$

Assume that the well is perturbed by a potential of the form of a 2D delta-function peak, $U_1(x,y) = V_0\delta(x-x_0)\,\delta(y-y_0)$, located at the point $(x_0, y_0) = \left(\frac{L}{3}, \frac{L}{6}\right)$. Find the first-order perturbation of the eigenenergy for this system in the (a) ground state and in the (b) first excited state.

Recall the unperturbed eigenfunctions $\psi_{n_x n_y}^{(0)}(x,y) = \frac{2}{L}\sin\left(n_x\frac{\pi}{L}x\right)\sin\left(n_y\frac{\pi}{L}y\right)$ and unperturbed eigenenergies $E_{n_x n_y}^{(0)} = \left(n_x^2 + n_y^2\right)\frac{\pi^2\hbar^2}{2mL^2}$, labeled by two quantum numbers: $n_x = 1, 2, 3, \ldots$ and $n_y = 1, 2, 3, \ldots$

(a) Ground state occurs for $n_x = n_y = 1$, and the the corresponding eigenenergy, $E_{11}^{(0)} = \frac{\pi^2\hbar^2}{mL^2}$ is non-degenerate with $\psi_{11}^{(0)}(x,y) = \frac{2}{L}\sin\left(\frac{\pi}{L}x\right)\sin\left(\frac{\pi}{L}y\right)$. Therefore, by the non-degenerate perturbation theory,

$$E_{11}^{(1)} = \langle\psi_{11}^{(0)}|\hat{H}_1|\psi_{11}^{(0)}\rangle = \iint |\psi_{11}^{(0)}(x,y)|^2\, U_1(x,y)\, dx\, dy = V_0|\psi_{11}^{(0)}(x_0,y_0)|^2 = V_0\frac{4}{L^2}\sin^2\left(\frac{\pi}{6}\right)\sin^2\left(\frac{\pi}{3}\right) = \frac{3}{4}\frac{V_0}{L^2}.$$

(b) 1st excited state occurs for two combinations of quantum numbers, $(n_x, n_y) = (1,2)$ and $(n_x, n_y) = (2,1)$, so the corresponding eigenenergy, $E_{12}^{(0)} = E_{21}^{(0)} = \frac{5\pi^2\hbar^2}{2mL^2} \equiv E_{\text{ex}}^{(0)}$ is doubly degenerate because $\psi_{12}^{(0)}(x,y) = \frac{2}{L}\sin\left(\frac{\pi}{L}x\right)\sin\left(2\frac{\pi}{L}y\right) \neq \psi_{21}^{(0)}(x,y) = \frac{2}{L}\sin\left(2\frac{\pi}{L}x\right)\sin\left(\frac{\pi}{L}y\right)$. Using the notation $\psi_{\text{I}}^{(0)} \equiv \psi_{12}^{(0)}$

and $\psi^{(0)}_{\rm II} \equiv \psi^{(0)}_{21}$, evaluate matrix elements $H^{(1)}_{\alpha\beta} = \langle \psi^{(0)}_\alpha | \hat{H}_1 | \psi^{(0)}_\beta \rangle$, which for $\alpha, \beta = {\rm I}, {\rm II}$ give the matrix $\mathcal{H}^{(1)}$,

$$\begin{aligned} \mathcal{H}^{(1)} &= V_0 \frac{4}{L^2} \begin{pmatrix} \sin^2\left(\frac{\pi}{L}x_0\right)\sin^2\left(2\frac{\pi}{L}y_0\right) & \sin\left(\frac{\pi}{L}x_0\right)\sin\left(2\frac{\pi}{L}y_0\right)\sin\left(2\frac{\pi}{L}x_0\right)\sin\left(\frac{\pi}{L}y_0\right) \\ \sin\left(2\frac{\pi}{L}x_0\right)\sin\left(\frac{\pi}{L}y_0\right)\sin\left(\frac{\pi}{L}x_0\right)\sin\left(2\frac{\pi}{L}y_0\right) & \sin^2\left(2\frac{\pi}{L}x_0\right)\sin^2\left(\frac{\pi}{L}y_0\right) \end{pmatrix} \\ &= V_0 \frac{4}{L^2} \begin{pmatrix} \frac{9}{16} & \frac{3\sqrt{3}}{16} \\ \frac{3\sqrt{3}}{16} & \frac{3}{16} \end{pmatrix} \equiv \frac{3}{4}\frac{V_0}{L^2} \begin{pmatrix} 3 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}. \end{aligned}$$

Now, let $\phi = c_{\rm I}\psi^{(0)}_{\rm I} + c_{\rm II}\psi^{(0)}_{\rm II}$ and solve the EVP for matrix $\mathcal{H}^{(1)}$ with perturbed eigenenergy of the first excited state $E^{(1)}_{\rm ex}$ as

$$\frac{3}{4}\frac{V_0}{L^2} \begin{pmatrix} 3 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix} \begin{pmatrix} c_{\rm I} \\ c_{\rm II} \end{pmatrix} = E^{(1)}_{\rm ex} \begin{pmatrix} c_{\rm I} \\ c_{\rm II} \end{pmatrix}. \qquad (\bigstar)$$

If we define $E^{(1)}_{\rm ex} = \frac{3}{4}\frac{V_0}{L^2}\,\varepsilon$, then solving the equation $\det\begin{pmatrix} 3-\varepsilon & \sqrt{3} \\ \sqrt{3} & 1-\varepsilon \end{pmatrix} = \varepsilon(\varepsilon - 4) = 0$ we get two roots, $\varepsilon_1 = 0$ and $\varepsilon_2 = 4$, giving two values for the perturbation to the first-order eigenenergy, $E^{(1)}_{\rm ex1} = 0$ and $E^{(1)}_{\rm ex2} = \frac{3V_0}{L^2}$. The corresponding orthonormal functions, ϕ_1 and ϕ_2, are obtained by solving the above equations ($\bigstar$) with $\varepsilon_1 = 0$ and $\varepsilon_2 = 4$, giving $\phi_1 = \frac{1}{2}\left(\psi^{(0)}_{\rm I} - \sqrt{3}\,\psi^{(0)}_{\rm II}\right)$ and $\phi_2 = \frac{1}{2}\left(\sqrt{3}\,\psi^{(0)}_{\rm I} + \psi^{(0)}_{\rm II}\right)$, respectively.

Therefore, the first-order degenerate perturbation theory gives now two distinct vales for the corrected eigenenergy in the first excited state, namely, $E^{(0)}_{\rm ex} + E^{(1)}_{\rm ex1} = \frac{5\pi^2\hbar^2}{2mL^2}$ and $E^{(0)}_{\rm ex} + E^{(1)}_{\rm ex2} = \frac{5\pi^2\hbar^2}{2mL^2} + \frac{3V_0}{L^2}$, which are paired with a suitable "rearrangement" of the unperturbed eigenfunctions $\psi^{(0)}_{12}$ and $\psi^{(0)}_{21}$ into $\phi_1 = \frac{1}{2}\left(\psi^{(0)}_{12} - \sqrt{3}\,\psi^{(0)}_{21}\right)$ and $\phi_2 = \frac{1}{2}\left(\sqrt{3}\,\psi^{(0)}_{12} + \psi^{(0)}_{21}\right)$, so that the degeneracy of that state is "lifted" upon perturbation.

9.3 Variational method

Recall that the Sturm-Liouville's theory asserts that, for bounded motion in 1D with the TISE $\hat{H}\psi_n = E_n\psi_n$, the sequence of eigenenergies is bounded below, $E_1 < E_2 < E_3 < \cdots$, while we showed that the expectation value of energy in an arbitrary state with the normalized wavefunction $f(x)$ is given by

$$\langle f|\hat{H}|f\rangle = \sum_{n=1}^{\infty} |c_n|^2\, E_n$$

where $c_n = \langle \psi_n | f \rangle$ are the generalized Fourier coefficients. Hence, by using the inequality $E_1 \le E_n$ in each term of the above series and invoking the normalization $\sum_n |c_n|^2 = 1$ due to Parseval formula, we arrive at the inequality

$$E_1 \le \langle f|\hat{H}|f\rangle.$$

Notice that the above inequality provides $\langle f|\hat{H}|f\rangle$ as an upper bound for the ground state eigenenergy E_1, whereas the equality may only be reached when $f(x)$ **is** the true ground state wavefunction $\psi_1(x)$. This can be used in Calculus of Variations to *deduce* the TISE as a DE whose solution minimizes $\langle f|\hat{H}|f\rangle$.

The above inequality establishes the so-called *Rayleigh-Ritz variational principle*, which states that the lowest-lying, or ground-state eigenenergy E_1 of a TISE with Hamiltonian $\hat{H}$ may be approximated by minimizing the expectation value of $\hat{H}$. This is helpful in cases where we cannot find the ground state wavefunction $\psi_1(x)$. We may use any **normalized** function $f(x,\alpha)$ that "resembles" $\psi_1(x)$ and contains a free, real-valued parameter α, which is simple enough to allow an easy calculation of the expression for $\mathcal{E}(\alpha) = \int f^*(x,\alpha)\hat{H}f(x,\alpha)\,dx$. Then, if we are lucky in our guess for the "trial function" $f(x,\alpha)$, finding the minimum of the function $\mathcal{E}(\alpha)$ with respect to the parameter α may give us a value for energy that is close enough to E_1.

Example 9.0.3. Consider the "Quantum Bouncer" in 1D with mass m, moving in the gravitational force field with acceleration g, which is described by the potential $U(x) = \begin{cases} mgx, & x > 0 \\ \infty, & x \le 0 \end{cases}$. Find an estimate for the ground state energy E_1.

We first review the exact solution of the TISE with the above potential, giving $\psi(x) = 0$ for $x \le 0$ and

$$-\frac{\hbar^2}{2m}\psi''(x) + mgx\,\psi(x) = E\psi(x) \qquad \text{for} \qquad x \ge 0,$$

where the wavefunction $\psi(x)$ must satisfy the BCs: $\psi(0) = 0$ and $\psi(+\infty) = 0$. Changing the position variable to $z = \gamma\left(x - \frac{E}{mg}\right)$ with $\gamma = \left(\frac{2m^2g}{\hbar^2}\right)^{1/3}$ and defining $\psi(x) = \phi(z)$ gives the *Airy differential equation*, $\phi''(z) = z\phi(z)$, which has two linearly independent solutions called Airy functions, $Ai(z)$ and $Bi(z)$, with only $Ai(z) \to 0$ as $z \to +\infty$. This function has infinitely many zeros at points a_n, that is $Ai(a_n) = 0$, which are located at $a_1 = -2.338$, $a_2 = -4.088$, $a_3 = -5.521$, etc. So, we let $\phi(z) = Ai(z)$ and obtain eigenenergies from the BC: $\phi\left(-\gamma\frac{E}{mg}\right) = \psi(0) = 0$, giving $E_n = -a_nE_0$ with $n = 1, 2, 3, \ldots$, where $E_0 = \frac{mg}{\gamma} = \left(\frac{1}{2}mg^2\hbar^2\right)^{1/3}$ is a constant which, e.g., takes the value $\approx 4.9 \times 10^{-14}$ eV for an electron in the Earth's gravitation field. The corresponding eigenfunction is $\psi_n(x) = C_n\,Ai(\gamma x + a_n)$ for $x \ge 0$.

To use the variational method, the trial function should satisfy the same BCs as the solutions $\psi(x)$ of TISE, so we assume $f(x,\alpha) = C(\alpha)\,x\,e^{-\alpha x}$ for $x \ge 0$, where $\alpha > 0$ is a parameter and $C(\alpha) = 2\alpha^{3/2}$ ensures the normalization of f. Taking the expectation value of the Hamiltonian with $f(x,\alpha)$ we find

$$\langle\hat{H}\rangle = \int_0^\infty f(x,\alpha)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + mgx\right)f(x,\alpha)\,dx = \cdots = E_0\frac{2\alpha^3 + 3\gamma^3}{2\alpha\gamma^2}.$$

Solving the equation $\frac{\partial\langle\hat{H}\rangle}{\partial\alpha} = 0$ yields $\alpha = \frac{1}{2}6^{1/3}\gamma$ and substituting this back into $\langle\hat{H}\rangle$ gives an upper bound for the ground state energy, $E_1 \le \frac{3}{4}6^{2/3}E_0 \approx 2.476\,E_0$, which is close to the exact value $E_1 = 2.338\,E_0$.