

The Schrödinger Equation: First Steps

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1 Historical

Following *Aberty* and *Silby* [Alb-92], we provide here a very brief review of some of the major breakthroughs that finally lead to the discovery of the Schrödinger equation.

1.1 Balmer’s Law

A major problem for scientists towards the end of the 19th century was that the *spectra* of atoms could not be explained by *Classical Laws*. This was because classical theories involving positive and negative charges predicted that radiation should be continuous. But in 1885, Balmer [Bal-85] discovered that the wavelength λ [m] of the *lines* in the visible region of the emission spectrum of hydrogen atoms could be expressed by the following simple expression,

$$\frac{1}{\lambda} = \nu = R \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right), \quad (1.1)$$

where n_2 represents an integer greater than 2, ν = wave number [m^{-1}] and R is the *Rydberg constant* [Ryd-90] given by,

$$R = \frac{e^4 \mu}{8 \varepsilon_0^2 h^3 c} [= 10,973,731.6 \text{ m}^{-1} \text{ for hydrogen}], \quad (1.2)$$

where, e = fundamental unit of charge, h = Planck’s constant, μ is the reduced mass for the atom and ε_0 is the permittivity of a vacuum. The reduced mass for an atom with one electron is given by,

$$\mu = \frac{m_{\text{nuc}} m_e}{m_{\text{nuc}} + m_e}, \quad (1.3)$$

where m_{nuc} = mass of nucleus and m_e = mass of electron.

The success of Balmer’s equation, 1.1, was soon followed by the discovery of additional lines in the atomic hydrogen spectrum which could be represented by,

$$\nu = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad (1.4)$$

where n_1 also represents an integer and $n_2 > n_1$. Further discoveries showed that the frequencies of the lines of more complicated atoms, with multiple electrons, could also be represented by the difference between a small set of numbers associated with the atom. This meant that each atom has a set of energies E_n called energy levels such that in the associated line spectrum the line spectrum can be calculated as,

$$\nu = \frac{1}{h} (E_n - E_m), \quad (1.5)$$

where $E_n > E_m$ and $h = \text{Planck's constant}$. Here we see that $\Delta E = h\nu$, which is the same as in Planck's theory of blackbody radiation, except that in this case it is assumed that atoms can only have certain specific energy levels, and hence only certain spectral frequencies.

1.2 Bohr's Breakthrough

The acceptance of Balmer's equation resulted in various models of the atom being proposed, built largely upon classical mechanics, but all were found to have unrealistic characteristics. Most notable was Ernest Rutherford's model which failed, primarily because it predicted an orbiting electron would lose energy by emitting electromagnetic radiation when it would spiral into the nucleus. Then, in 1913 Niels Bohr [Boh-13] broke with classical mechanics and developed a successful theory for hydrogen-like atoms (that have one electron). In Bohr's model, the angular momentum p , of an orbital electron was assumed to only have integer multiples of a quantum momentum of magnitude $\hbar = h/2\pi$. It also provided a theoretical justification for the Rydberg equation and a justification for its fundamental physical constants.

To overcome the problems of Rutherford's atom, Bohr proposed three postulates that sum up most of his model:

1. The electron is able to revolve in certain stable orbits around the nucleus without radiating any energy, contrary to what classical electromagnetism suggests. These stable orbits are called stationary orbits and are attained at certain discrete distances from the nucleus. The electron cannot have any other orbit in between the discrete ones.
2. The stationary orbits are attained at distances for which the angular momentum of the revolving electron is an integer multiple of the reduced Planck constant:

$$m_e v r = n \hbar, \quad (1.6)$$

where $m_e = \text{electron mass}$, $v = \text{velocity}$, $r = \text{radius}$, $n = 1, 2, 3, \dots$ is called the principal quantum number and $\hbar = h/2\pi$. The lowest value of n is 1; this gives the smallest possible orbital radius of $r = 0.0529 \text{ nm} (= 0.529 \text{ \AA})$, known as the Bohr radius - see appendix 2. Once an electron is in this lowest orbit, it can get no closer to the nucleus².

3. Electrons can only gain or lose energy by jumping from one allowed orbit to another. During this process they absorb or emit electromagnetic radiation with a frequency ν , determined by the energy difference of the levels according to the Planck relation:

$$\Delta E = E_2 - E_1 = h\nu, \quad (1.7)$$

where $h = \text{Planck's constant}$ and $\nu = \text{frequency}$.

In 1922 Niels Henrik David Bohr was awarded the Nobel Prize in Physics:

for his services in the investigation of the structure of atoms and of the radiation emanating from them.

However, Bohr's model assumed that an electron moves in a circular orbit about the positively charged nucleus; and, whilst this worked for hydrogen and introduced new useful concepts, it could not be extended successfully to other atoms having more than one electron.

²Starting from the angular momentum quantum rule, previously given by Nicholson, Bohr was able to calculate the energies of the allowed orbits of the hydrogen atom and other hydrogen-like atoms and ions. These orbits are associated with definite energies and are also called energy shells or energy levels. In these orbits, the electron's acceleration does not result in radiation and energy loss. The Bohr model of an atom was based upon Planck's quantum theory of radiation.

1.3 Einstein's Photoelectric Effect

Experiments showed that when light is absorbed by a metal surface it results in an electron being ejected, and that the kinetic energy of the fasted ejected electron is independent of the intensity of light. Also, that there is a cutoff frequency below which no electrons are ejected. This is contrary to what would be expected from classical mechanics which predicts that the energy absorbed by the surface should be proportional to the intensity of light. In 1905, Einstein [Ein-05] pointed out that whilst these effects could not be explained using the classical theory of light, they could be explained if the energy of light is transferred in particle-like bundles, later named *photons*³. Thus, as an electron moves from one energy level *up* or *down* to the next, a photon is either *absorbed* or *emitted* by the electron. Einstein assumed that the energy of a photon is given by,

$$E = h\nu, \tag{1.8}$$

where h represents Planck's constant and ν frequency. Previously, Planck [Pla-00] had proposed that the emission and absorption of light in black body radiation is quantized in units of $h\nu$. Einstein extended this work by assuming that the energy of light is quantized with each photon having energy $h\nu$.

In 1921 Albert Einstein was awarded the Nobel Prize in Physics:

for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect.

Confirmation that radiation consists of packets of energy called photons came in 1923 when Arthur Compton [Com-23] studied X-ray scattering by a graphite target, subsequently named the *Compton scattering*. In 1927 Arthur Holly Compton was awarded the Nobel Prize in Physics:

“for his discovery of the effect named after him.”

1.4 De Broglie's Wave Theory for The Electron

Following Balmer's discovery of eqn(1.1), and that each atom had an associated set of spectral lines representing energy levels, the scientific community gradually came to accept the quantization of energy. During this time Einstein had shown, using his *special theory of relativity*, that the momentum of a photon is given by $p = E/c$, from which it follows that

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}, \tag{1.9}$$

where $E =$ the energy of a photon [J] and $c =$ the speed of light [m/s].

Then in 1924 *De Broglie*⁴ was the first to develop a wave theory for the behavior of an electron which he published in his Ph.D. thesis [DeB-24]. He postulated that the wavelength of *any matter* obeyed the relationship $\lambda = h/p$, where h is Planck's constant and p is momentum. Table (2.1) lists some data derived from de Broglie's ideas. His thesis also included the hypothesis that a *standing wave* some how guided the electrons in the Bohr model of the atom, see Figure(1.1). It is clear that for a circular standing wave to exist, it must consist of an integer number of wavelengths. This is the reason that the electron energy is *quantized*.

³A photon consists of a quantum of *energy* (electromagnetic radiation) and has properties of *frequency* ν , *wavelength* λ and *momentum* p .

⁴Full name: *Louis-Victor, Pierre, Raymond 7th duc de Broglie*, usually shortened to de Broglie.

De Broglie’s approach successfully solved some simple problems, but his theory did not adequately explain the behavior of an electron when subjected to different types of external potential fields.

In 1929 Prince Louis-Victor Pierre Raymond de Broglie was awarded the Nobel prize in Physics:

“for his discovery of the wave nature of electrons.”

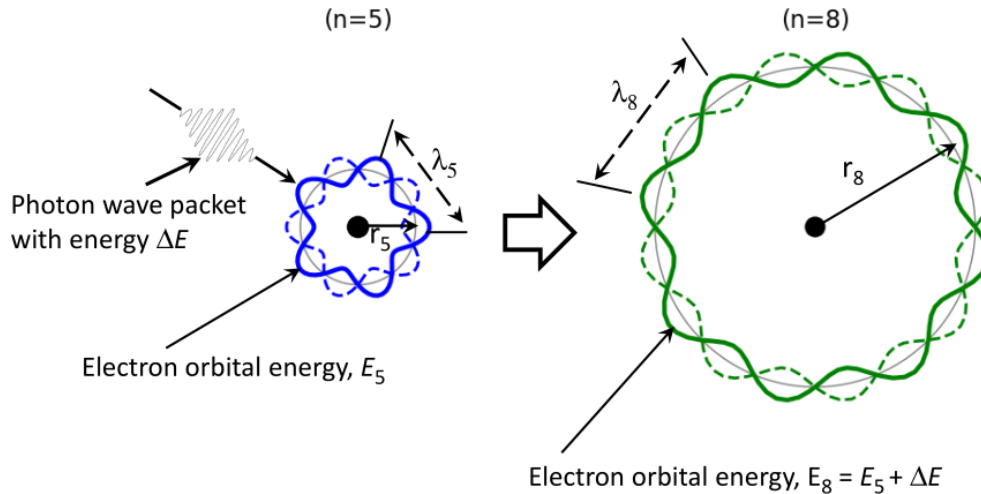


Figure 1.1: Illustration of de Broglie’s *matter waves* for a hydrogen-like atom, consisting of a single positively charged proton with a negatively charged electron circling around it. (left) The situation shows an orbital standing wave electron with energy E_5 being struck by a photon with energy ΔE . (right) The photon has imparted its energy ΔE to the electron. This resulted in it *transitioning* to a higher orbital level, see appendix(E). The new energy level is $E_8 = E_5 + \Delta E$, as predicted by Niels Bohr, see Section (1.2). Tables (2.1) and (2.2) list useful data relating to the hydrogen atom.

Matter waves were first demonstrated in 1927 by George Paget Thomson using a cathode ray apparatus [Tho-27]. In 1937 Thomson, along with Clinton Joseph Davisson, was awarded the Nobel Prize in Physics:

“for their experimental discovery of the diffraction of electrons by crystals.”

2 The Bohr Model

Niels Bohr in 1913 formulated a model of hydrogen-like atoms [Boh-13] based on a mixture of *classical mechanics* and some quantum mechanical ideas that were just developing. He postulated that the hydrogen atom consisted of an *electron* in a *circular orbit* about its nucleus which consisted of a single *proton*, see Figure (8.1). With the proton having a positive unit charge $q_1 = +e$, and the electron having a negative unit charge $q_2 = -e$, they were attracted by an electrostatic force due to *Coulomb’s law*. The Coulomb force is given by

$$F = k_e \frac{|e^2|}{r^2}, \quad (2.1)$$

where $k_e = 1/(4\pi\epsilon_0)$, $\epsilon_0 =$ vacuum permittivity, and r represents the orbit radius.

Bohr then equated the electrostatic force with the centripetal force, giving

$$k_e \frac{e^2}{r^2} = \frac{m_e v^2}{r}. \quad (2.2)$$

Bohr had studied Maxwell’s theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse

into the nucleus. He was also aware of the Planck-Einstein relation $E = h\nu = h/\lambda$, where E represents the quantized energy of a *photon*, ν frequency and λ wavelength. He then postulated that *angular momentum* L , must also be quantized, such that $L = m_e v r = n\hbar$, where n represents the *principal quantum number*. Substituting this relationship into equation 2.2 and rearranging we obtain,

$$r = \frac{4\pi\epsilon_0(n\hbar)^2}{m_e e^2}. \quad (2.3)$$

It therefore follows that

$$r_n = n^2 r_1. \quad (2.4)$$

Substituting values from appendix I and setting $n = 1$ (the ground state), we get

$$a_0 = \frac{4\pi \times 8.85418782 \times 10^{-12} \times (1 \times 1.054571817 \times 10^{-34})^2}{9.1093837 \times 10^{-31} \times (1.602176634 \times 10^{-19})^2}, \quad (2.5)$$

$$\therefore a_0 = 0.052918 \text{ [nm]} = 0.52918 \text{ [\AA]},$$

where a_0 is the standard symbol used for ground state radius. This value of a_0 was later confirmed to be very close to the *most probable* ground state radius, as predicted by the hydrogen atom solution to Schrödinger's equation. The Bohr radius including the effect of reduced mass in the hydrogen atom is given by

$$a_0^* = \frac{m_e}{\mu} a_0, \quad (2.6)$$

where $\mu = m_e m_p / (m_e + m_p)$ is the *reduced* mass of the electron-proton system (with m_p being the mass of proton). The use of reduced mass is a generalization of the classical two-body problem when the mass of the orbiting body is **not** negligible compared to the mass of the central body. In this case, the reduced mass of the electron-proton system is slightly less than the electron mass, so the *reduced* Bohr radius is slightly larger than the Bohr radius, i.e. $a_0^* \approx 1.00054 a_0 \approx 0.052947 \text{ [nm]}$.

From eqns (2.1) and (2.2) we can obtain the electron's orbital velocity now that r is known, i.e.

$$v = \sqrt{\frac{|F| r}{m_e}} = \sqrt{\frac{e^2}{4\pi\epsilon_0 m_e r}} = \frac{k_e e^2}{n\hbar}; \quad (2.7)$$

from which it follows that

$$v_n = \frac{v_1}{n}. \quad (2.8)$$

In addition, from eqns (2.2) and (2.7) we can determine the energy E of the electron which is equal to the sum of its kinetic and potential energies, i.e.

$$\begin{aligned} \text{KE} &= \frac{1}{2} m_e v^2 &= \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}, \\ \text{PE} &= \int_r^\infty k_e \frac{|e^2|}{r^2} dr &= -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}, \\ \therefore E &= \text{KE} + \text{PE} &= -\frac{1}{8\pi\epsilon_0} \frac{e^2}{r}. \end{aligned} \quad (2.9)$$

It therefore follows from eqns. (2.3) and (2.4) that

$$E_n = \frac{E_1}{n^2}. \quad (2.10)$$

Or, in terms of fundamental constants

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}, \quad n = 1, 2, 3, \dots \quad (2.11)$$

Table (2.1) lists Bohr electron radii, velocities, energies, wavelengths and frequencies for various principal quantum numbers. Hydrogen atom energy levels are also plotted in Figure (2.1).

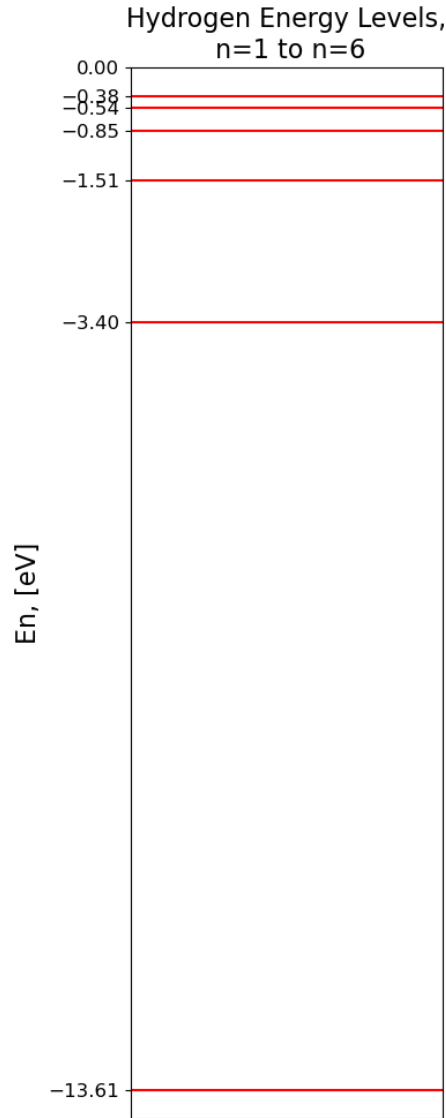


Figure 2.1: Hydrogen atom energy levels.

When an electron in an atom moves from a higher energy level orbital to a lower one, a photon is emitted with energy $\Delta E = hc/\lambda$. Similarly, when an electron absorbs a photon it moves from a lower energy level orbital to a higher one, gaining energy $\Delta E = hc/\lambda$. Thus, from Section (1.4) we have

$$\Delta E = E_j - E_i = E_{\text{photon}} = \frac{hc}{\lambda} = h\nu, \quad E_j > E_i, \quad (2.12)$$

where h is Planck's constant, c is the speed of light [m/s], λ represents wavelength [m] and ν represents frequency [Hz]. The hydrogen atom can emit different wavelengths of

light ν , depending on the initial and final energy levels of the electron. These are known collectively as *spectral emission lines*, see Table (2.2). This phenomena are described by the Rydberg equation (1.1), which was confirmed by Bohr. Bohr's derivation of the Rydberg constant, see Section (1.1), as well as the excellent agreement of Bohr's equation with experimentally observed hydrogen spectral lines, and also the successful theoretical prediction of other lines not yet observed, was the major reason that his model was quickly accepted by the physics community.

Table 2.1: Some Bohr Electron Orbit Data for the Hydrogen Atom.

	Radius	Velocity	Energy		Wavelength	Frequency
n	r_n [m]	v_n [m/s]	E_n [J]	E_n [eV]	λ_n [m]	ν_n [s ⁻¹]
1	5.292E-11	2.188E+06	-2.180E-18	-13.6068	3.3242E-10	3.2900E+15 †
2	2.117E-10	1.094E+06	-5.450E-19	-3.4017	6.6484E-10	8.2251E+14
3	4.763E-10	7.292E+05	-2.422E-19	-1.5119	9.9745E-10	3.6553E+14
4	8.467E-10	5.469E+05	-1.362E-19	-0.8504	1.3299E-09	2.0555E+14
5	1.323E-09	4.375E+05	-8.719E-20	-0.5443	1.6625E-09	1.3159E+14
6	1.905E-09	3.646E+05	-6.055E-20	-0.3780	1.9949E-09	9.1381E+13
∞	∞	0	0	0	-	- ‡

† ground state, ‡ ionized state (free electron)

Table 2.2: Some Photon Transition Energies, Wavelengths and Frequencies for the Hydrogen Atom.

Transition	E_{photon}	Wavelength, λ	Frequency, ν
ΔE	[J]	[m]	[Hz]
$E_2 - E_1$	1.6349E-18	1.21502E-07	2.46738E+15
$E_3 - E_2$	3.0276E-19	6.56112E-07	4.56922E+14
$E_4 - E_3$	1.0597E-19	1.87461E-06	1.59923E+14
$E_5 - E_4$	4.9047E-20	4.05008E-06	7.40214E+13

The Bohr model of the hydrogen atom, consisting of an electron orbiting the nucleus (proton), provides a useful conceptual picture. However, it must be appreciated that these orbits do not conform to reality - the Bohr radii actually represent the *most probable* values as determined from the associated *wave function* solutions to the Schrödinger equation, see Section (8).

Subsequently, de Broglie extended Bohr's idea into a *wave theory of matter* [DeB-24], and Schrödinger developed the ideas further [Sch-26], to include his famous equation which still forms the theoretical basis of quantum mechanics.

3 The Schrödinger Equation

The partial success of de Broglie's wave theory led *Erwin Schrödinger* to investigate alternatives and, ultimately, to derive a *wave function* solution to describe the electron that, crucially, conserved energy [Sch-26]. He then systematically applied his equation, the so called *Schrödinger Equation* (3.1), to problems involving different potentials applied to the electron, and the solutions were subsequently confirmed experimentally. The *time dependent Schrödinger equation*, shown below, is an evolutionary *partial differential equation* (PDE) that describes the behaviour of ψ , the *wave function* of *Quantum*

Mechanics,

$$\boxed{\begin{aligned} i\hbar \frac{\partial}{\partial t} \Psi(t, x) &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi(t, x), \\ 0 < t \leq \infty, x \in \mathbb{R}^s, s \in \{1, 2, 3\}; \end{aligned}} \quad (3.1)$$

where $\hbar = h/2\pi$, the *reduced Planck constant*, also known as the *Dirac constant*⁵, $m =$ mass of particle and $V(x) =$ potential.

The wave function describes the *quantum state* of an isolated *quantum system*. It is a fundamental postulate of Quantum Mechanics [Lib-22, McQ-97] i.e., it cannot be formally derived from first principles. It is the basis for our current understanding of the electron.

The above Schrödinger's equation can also be written as:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle, \quad (3.2)$$

or

$$H |\psi(t)\rangle = E |\psi(t)\rangle, \quad (3.3)$$

where H represents the *Hamiltonian*, $E =$ the *energy of the particle* and $|\psi(t)\rangle$ is the *Dirac notation for quantum state*. Care has to be taken when manipulating H , also written as \hat{H} , as it is a mathematical operator and does not *commute*, i.e. order of operation is important. These forms are discussed in Appendices (B.2) and (C).

In 1933 Erwin Schrödinger, along with Paul Adrien Maurice Dirac, was awarded the Nobel Prize in Physics:

“for the discovery of new productive forms of atomic theory.”

3.1 Time Independent Schrödinger Equation

For the situation where the solution is constant over time, we have the *time independent Schrödinger equation* which is defined as,

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi,} \quad (3.4)$$

with symbols as previously defined. In this form the wave function ψ represents *stationary states*, and is not dependent on time only upon its location.

The first term on the left hand side of eqn(3.4) represents *kinetic energy* of the particle and the second term represents *potential energy*, due to its location within its environment. The right hand term represents *total energy*. So we can consider this equation to be equivalent to:

$$\text{kinetic energy} + \text{potential energy} = \text{total energy}$$

where the total energy does not change with time, t .

3.2 The Born Interpretation

Schrödinger could not come to a conclusion about what the wave function ψ actually represented. It took Max Born [Bor-26] to interpret ψ ; and he concluded that it could be used to calculate a measurable quantity.

⁵Planck's constant, $h = 6.62607015 \times 10^{-34}$ [m²kg/s].

Whilst the wave function Ψ does not actually represent a real measurable quantity, Born postulated that when multiplied by its complex conjugate Ψ^* , it represented a *probability density function*, ρ , for the *particle's position*. This proved to be correct and has so far passed all experimental tests. Consequently, this is now referred to as the *Born Interpretation*.

It therefore follows that,

$$\boxed{\rho(x) = \Psi^* \Psi = |\Psi|^2}, \quad (3.5)$$

which represents the *probability density function* $\rho(x)$, for a particle to be located in $\delta x \subset \mathbb{R}$.

In 1954 Max Born was awarded the Nobel Prize in Physics:

“for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wavefunction.”

3.2.1 Normalization

From eqn(3.5), probability theory dictates that we must have

$$\boxed{\int_{\Omega} \rho(\mathbf{x}) \, d\mathbf{x} = \int_{\Omega} |\Psi|^2 \, d\mathbf{x} = 1, \quad \mathbf{x} = \mathbf{x}(x, y, z)}, \quad (3.6)$$

where Ω represent the domain within which it is feasible for the particle to be located. It is this property that provides a key to unlocking a *physical* solution to the Schrödinger equation. This calculation is referred to as *normalization*.

There are some important practical restrictions on wave function:

- Ψ must be square integral
- $\int_{-\infty}^{\infty} \Psi \, dx$ must be finite
- $\Psi \rightarrow 0$ as $x \rightarrow \pm\infty$

Also, if Ψ is *normalizable* and solves the time dependent Schrödinger equation, then $A\Psi$ will also solve the same time dependent Schrödinger equation, where A is a constant. This is because the A 's will all cancel when $A\Psi$ is substituted into eqn(3.1). Similarly, if $A\Psi$ solves the time independent Schrödinger equation then $A\psi$ will also solve the same time dependent Schrödinger equation. Again, because the A 's will all cancel when $A\psi$ is substituted into eqn(3.4). Thus, eqn. (3.6) becomes

$$A^2 \int_{\Omega} |\Psi|^2 \, d\mathbf{x} = 1, \quad (3.7)$$

and

$$\therefore A = \frac{1}{\sqrt{\int_{\Omega} |\Psi|^2 \, d\mathbf{x}}}, \quad (3.8)$$

where A is called the *normalization constant*, which is then subsumed into Ψ .

We now need to look at time evolution of $\rho(x)$, and we do this by investigating its time derivative, which according to eqn. (3.6) should equal zero. Consider

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} |\Psi|^2 \, dx = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} \Psi^* \Psi \, dx. \quad (3.9)$$

Bringing the time derivative under the integral sign and applying the product rule, we obtain

$$\int_{-\infty}^{\infty} \frac{\partial}{\partial t} (\Psi^* \Psi) dx = \int_{-\infty}^{\infty} \left(\frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t} \right) dx. \quad (3.10)$$

But from eqn. (3.1) we have

$$\frac{\partial}{\partial t} \Psi(t, x) = \int_{-\infty}^{\infty} \left[\frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - i \frac{V}{\hbar} \Psi \right] dx. \quad (3.11)$$

So, eqn. (3.9) becomes

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} |\Psi|^2 dx = \int_{-\infty}^{\infty} \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) dx, \quad (3.12)$$

where terms containing the potential V have canceled. We note that the right hand side of eqn. (3.12) can be evaluated so that we have,

$$\frac{i\hbar}{2m} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{\infty}. \quad (3.13)$$

But, if Ψ is normalizable, from the above we have $\Psi \rightarrow 0$ as $x \rightarrow \pm\infty$. So, finally, we end up with

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} |\Psi(t, x)|^2 dx = 0, \quad \text{and} \quad \therefore \int_{-\infty}^{\infty} |\Psi(t, x)|^2 dx = \text{constant}. \quad (3.14)$$

This analysis has shown that 1) the constant A above can be chosen to ensure that eqn. (3.6) is true, and 2) that time evolution does not affect normalization.

3.3 Degeneracy

An orbital energy level of a quantum mechanical system is said to be *degenerate* if it corresponds to two or more different measurable states of a quantum system [Wik-22]. Or, alternatively, two or more different states of a quantum mechanical system are said to be degenerate if they give the same value of energy upon measurement. The number of different states corresponding to a particular orbital energy level is known as the degree of degeneracy of the level.

See Section (8.1) for how the possible number of degeneracy levels is calculated.

3.4 Wavelength of matter

De Broglie postulated in 1924 that the wavelength of *any matter* obeyed the relationship $\lambda = h/p$, where h is Planck's constant and p is momentum. This is now accepted - see Section (1.4). However, the wave properties of matter are only observable for very small objects.

4 Infinite Potential Well

4.1 1D Particle in a Box

Consider the time dependent Schrödinger equation (3.1) but in one dimension, and with potential defined as,

$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq L, \\ \infty, & \text{otherwise.} \end{cases} \quad (4.1)$$

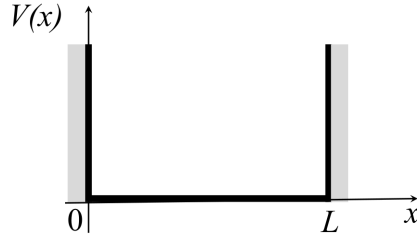


Figure 4.1: The infinite square well potential.

See Figure (4.1).

We now postulate a separable solution of the form,

$$\boxed{\Psi(t, x) = f(t)\psi(x)}, \quad (4.2)$$

so that on substituting into the Schrödinger equation we obtain

$$\frac{\partial f(t)\psi(x)}{\partial t} = \frac{\partial^2 f(t)\psi(x)}{\partial \psi(x)^2} + V(x)f(t)\psi(x). \quad (4.3)$$

Dividing through by $f(t)\psi(x)$ and rearranging, we obtain

$$i\hbar \frac{\partial f(t)}{\partial t} \frac{1}{f(t)} = \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \right) \frac{1}{\psi(x)}. \quad (4.4)$$

Now, because $f(t)$ is a function of t only, and $\psi(x)$ is a function of x only, both sides of eqn(4.4) must be equal to a constant (to be evaluated), which we call E . This results in two separate *ordinary differential equations* equations,

$$i\hbar \frac{df(t)}{dt} = Ef(t). \quad (4.5)$$

and

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x). \quad (4.6)$$

Eqn(4.5) can be integrated directly to give,

$$f(t) = \exp(-iEt/\hbar), \quad (4.7)$$

from which we obtain

$$\Psi(t, x) = \exp(-iEt/\hbar) \psi(0, x) \quad (4.8)$$

where $\psi(0, x) = \psi(x)$.

We now consider a zero potential situation in the box i.e., $V(x) = 0$ where $0 \leq x \leq L$, and eqn (4.6) reduces to,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x). \quad (4.9)$$

Outside the box where $0 > x > L$ we assume that $V(x) = \infty$, which implies the $\psi = 0$. This is because we have

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0; \quad (4.10)$$

so that when $V(x) = \infty$, it follows that

$$\psi = \frac{1}{\infty} \frac{d^2\psi(x)}{dx^2} = 0. \quad (4.11)$$

The standard solution to eqn(4.9) where we impose zero boundary conditions is [Han-97],

$$\psi(x) = \begin{cases} A \cosh(\sqrt{2m|E|}x/\hbar) + B \sinh(\sqrt{2m|E|}x/\hbar), & \text{if } E < 0; \\ A + Bx, & \text{if } E = 0; \\ A \cos(\sqrt{2mE}x/\hbar) + B \sin(\sqrt{2mE}x/\hbar), & \text{if } E > 0; \end{cases} \quad (4.12)$$

where A and B are constants.

For positive energy $E > 0$ and boundary conditions $\psi(0) = \psi(L) = 0$, we see that for the cos term A must be equal to zero. For the sin term we must have $\sqrt{2mE}x/\hbar = n\pi$, which on rearranging yields the following expression for E ,

$$E = E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \left(= \frac{n^2h^2}{8mL^2} \right), \quad (4.13)$$

where $n \in \mathbb{N}$. Thus, we see that the permitted energies, the so called *eigen energies*, depend upon the integer, n . As indicated in section (1.3), a particle can move between different energy levels E_n when it is interacting with its environment. If a particle moves from say, a lower energy level to the next higher energy level, it has to absorb an amount of energy $\Delta E = E_n - E_{n-1}$ from an external source. It can absorb a photon with energy $h\nu = \Delta E$, or it can receive the required energy from another particle in a collision. If the particle moves from a higher energy level to say, the next lower energy level, it has to release an amount of energy $\Delta E = E_n - E_{n-1}$ to the environment. This can be achieved by emitting a photon of energy $h\nu = \Delta E$, e.g.

$$\Delta E = E_n - E_{n-1} = (n^2 - (n-1)^2) \left(\frac{h^2}{8mL^2} \right). \quad (4.14)$$

The frequency ν and wavelength λ of the photon can then be obtained using eqns (2.12) and (1.9).

Some energy levels are listed in Table(4.1), where we have used a value for the mass of the electron, $m = 9.1093837 \times 10^{-31}$ [kg].

With the energy levels known, the third equation of eqns(4.12) reduces to

$$\psi(x) = B \sin(n\pi x/L). \quad (4.15)$$

To find a value for B we invoke the *normalization condition* of eqn(3.6), from which we obtain

$$\int_0^L |B|^2 \sin^2 \left(\frac{n\pi x}{L} \right) dx = \frac{L}{2} |B|^2 = 1 \quad (4.16)$$

and

$$B = \sqrt{\frac{2}{L}}. \quad (4.17)$$

$$\therefore \psi_n(x) = \sqrt{\frac{2}{L}} \sin \left(\frac{n\pi x}{L} \right). \quad (4.18)$$

Equation (4.18) represents the *eigenfunctions* of the Schödinger equation for the 1D potential well that also satisfy the boundary conditions.

The *ground state* or *zero-point* energy occurs when $n = 1$ in eqn(4.13) which represents the *stationary state* of *lowest energy*. For any $n > 1$, this represents an *excited state* where the energy is greater than the ground state.

Table 4.1: Energy Levels for an electron in a 1D box of length, $L = 10$ [nm]. Note: $1 \text{ [J]} = 6.242 \times 10^{18} \text{ [eV]}$.

n	Energy	
	$E_n \text{ [J]}$	$E_n \text{ [eV]}$
16	1.5423E-19	9.6271E-01
15	1.3556E-19	8.4613E-01
14	1.1808E-19	7.3708E-01
13	1.0182E-19	6.3554E-01
12	8.6755E-20	5.4153E-01
11	7.2898E-20	4.5503E-01
10	6.0247E-20	3.7606E-01
9	4.8800E-20	3.0461E-01
8	3.8558E-20	2.4068E-01
7	2.9521E-20	1.8427E-01
6	2.1689E-20	1.3538E-01
5	1.5062E-20	9.4015E-02
4	9.6395E-21	6.0170E-02
3	5.4222E-21	3.3845E-02
2	2.4099E-21	1.5042E-02
1	6.0247E-22	3.7606E-03

From eqn(3.5) it should be noted that

$$\Psi^* \Psi = |\Psi|^2 = \psi(x)^* \psi(x) = |\psi(x)|^2. \quad (4.19)$$

This is because the complex exponential term of eqn(4.8) cancels with its complex conjugate, and the time component disappears. It is only true for "separable solutions".

We can now combine the temporal and spatial solutions, eqns (4.7) and (4.18), to obtain the following time dependent separable solution,

$$\Psi_n = \exp\left(-\frac{iE_n t}{\hbar}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (4.20)$$

or, equivalently

$$\Psi_n = \exp\left(-\frac{i n^2 \pi^2 \hbar t}{2mL^2}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \quad (4.21)$$

Example plots of 1D wave functions ψ , and probability density functions ρ , are shown in Fig (4.2).

4.2 2D Particle in a Box

The same approach used for the 1D box can be used for a 2D box.

Thus we have a zero potential inside the box i.e., where $V(x, y) = 0$, $0 \leq x, y \leq L$, and an infinite potential outside the box i.e., where $V(x, y) = \infty$, $0 > x, y > L$. We now seek a separable solution by separating the temporal and spatial portions of the wavefunction i.e., $\Psi(t, x, y) = f(t)\psi(x, y)$; and, as for the 1D case, the time varying part becomes

$$f(t) = \exp(-iEt/\hbar), \quad (4.22)$$

from which we obtain

$$\Psi(t, x, y) = \exp(-iEt/\hbar) \psi(0, x, y) \quad (4.23)$$

where $\psi(0, x, y) = \psi(x, y)$.

Wave Functions and Probability Density Functions Superimposed on Energy Levels.

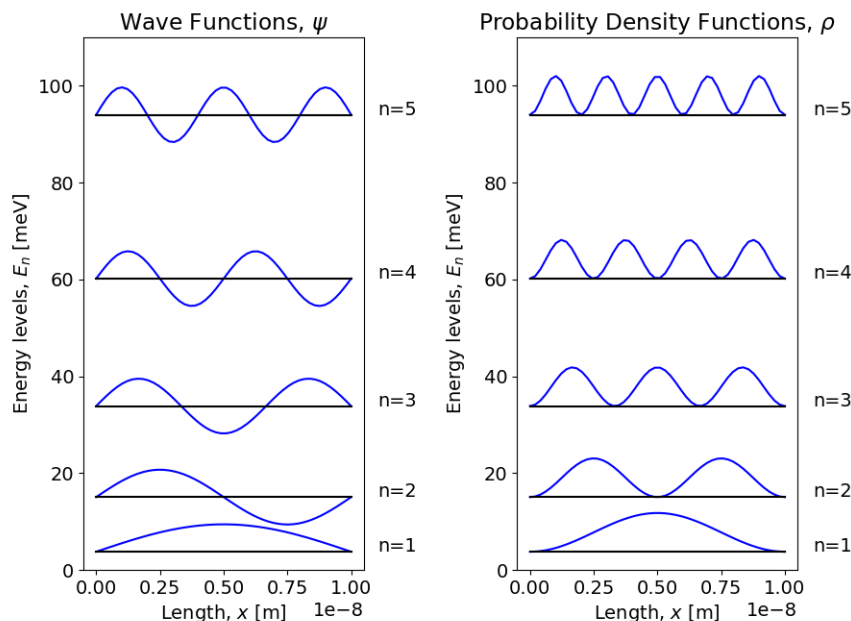


Figure 4.2: Example showing solutions to the Schödinger equation for a particle in a 1D box of length $L = 10$ [nm]. Plots shown superimposed on energy level lines - ψ and ρ are not to scale.

This enables us to recover the time-independent Schrödinger equation, which therefore becomes

$$\boxed{-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} \right) = E \psi(x, y).} \quad (4.24)$$

We can again seek a separable solution by assuming that,

$$\psi(x, y) = X(x)Y(y). \quad (4.25)$$

Also that the energy term consists of individual energies, one for each dimension i.e.,

$$E = E_x + E_y. \quad (4.26)$$

This enables us to split eqn(4.24) into the following two separate *ordinary differential equations*

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} &= E_x X; \\ -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} &= E_y Y; \end{aligned} \quad (4.27)$$

These equations are similar to the 1D box problem eqn(4.9) and have the same solutions i.e.,

$$\begin{aligned} X(x) &= B_x \sin \left(\frac{\sqrt{2m|E_x|} x}{\hbar} \right); \\ Y(y) &= B_y \sin \left(\frac{\sqrt{2m|E_y|} y}{\hbar} \right). \end{aligned} \quad (4.28)$$

And on imposing the *zero* boundary conditions, as for the 1D case,

$$\begin{cases} \sin\left(\frac{\sqrt{2m|E_x|}x}{\hbar} = L_x\right) = \sin(n_x\pi) = 0 \\ \sin\left(\frac{\sqrt{2m|E_y|}y}{\hbar} = L_y\right) = \sin(n_y\pi) = 0. \end{cases} \quad (4.29)$$

the energies E_x and E_y become,

$$E_{n_x} = \frac{n_x^2\pi^2\hbar^2}{2mL_x^2}, \quad E_{n_y} = \frac{n_y^2\pi^2\hbar^2}{2mL_y^2}, \quad (4.30)$$

where $n_x \in \mathbb{N}$, $n_y \in \mathbb{N}$.

Thus, the permitted energies, the so called *eigen energies*, depend upon the two integers, n_x, n_y , such that

$$\boxed{E_{n_x, n_y} = \frac{\pi^2\hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)}. \quad (4.31)$$

The *ground state* or *zero-point* energy occurs when $n_x = 1$ and $n_y = 1$ in eqn(4.31), which represents the *stationary state of lowest energy*. For any $n_x > 1$ or $n_y > 1$, this represents an *excited state* where the energy is greater than the ground state.

From eqns (4.25), (4.28) and (4.30) we obtain,

$$\psi(x, y) = U \sin\left(\frac{n_x\pi x}{L_x}\right) \sin\left(\frac{n_y\pi y}{L_y}\right), \quad (4.32)$$

where $U = B_x B_y$.

To find a value for U we invoke the *normalization condition* of eqn(3.6), from which we obtain

$$U^2 \int_0^{L_x} \sin^2\left(\frac{n_x\pi x}{L_x}\right) dx \int_0^{L_y} \sin^2\left(\frac{n_y\pi y}{L_y}\right) dy = |U|^2 \frac{L_x}{2} \frac{L_y}{2} = 1 \quad (4.33)$$

and

$$U = \sqrt{\frac{4}{L_x L_y}}. \quad (4.34)$$

$$\boxed{\therefore \psi_{n_x, n_y}(x, y) = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_x\pi x}{L_x}\right) \sin\left(\frac{n_y\pi y}{L_y}\right)}. \quad (4.35)$$

Equation (4.35) represents the *eigenfunctions* of the Schödinger equation for the 2D potential well that also satisfy the boundary conditions.

4.3 3D Particle in a Box

The same approach used for the 1D box can be used for a 3D box.

Thus we have a zero potential inside the box i.e., where $V(x, y, z) = 0$, $0 \leq x, y, z \leq L$, and an infinite potential outside the box i.e., where $V(x, y, z) = \infty$, $0 \leq x, y, z \geq L$.

We now seek a separable solution by separating the temporal and spatial portions of the wavefunction i.e., $\Psi(t, x, y, z) = f(t)\psi(x, y, z)$; and, as for the 1D case, the time varying part becomes

$$f(t) = \exp(-iEt/\hbar), \quad (4.36)$$

from which we obtain

$$\Psi(t, x, y, z) = \exp(-iEt/\hbar) \psi(0, x, y, z) \quad (4.37)$$

where $\psi(0, x, y, z) = \psi(x, y, z)$.

This enables us to recover the time-independent Schrödinger equation, which therefore becomes

$$\boxed{-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right) = E\psi(x, y, z).} \quad (4.38)$$

We can again seek a separable solution by assuming that,

$$\psi(x, y, z) = X(x)Y(y)Z(z). \quad (4.39)$$

Also that the energy term consists of individual energies, one for each dimension i.e.,

$$E = E_x + E_y + E_z. \quad (4.40)$$

This enables us to split eqn(4.38) into the following three separate equations

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 X}{\partial x^2} &= E_x X; \\ -\frac{\hbar^2}{2m} \frac{\partial^2 Y}{\partial y^2} &= E_y Y; \\ -\frac{\hbar^2}{2m} \frac{\partial^2 Z}{\partial z^2} &= E_z Z; \end{aligned} \quad (4.41)$$

These equations are similar to the 1D box problem eqn(4.9) and have the same solutions i.e.,

$$\begin{aligned} X(x) &= B_x \sin \left(\frac{\sqrt{2m|E_x|} x}{\hbar} \right); \\ Y(y) &= B_y \sin \left(\frac{\sqrt{2m|E_y|} y}{\hbar} \right); \\ Z(z) &= B_z \sin \left(\frac{\sqrt{2m|E_z|} z}{\hbar} \right); \end{aligned} \quad (4.42)$$

And on imposing the *zero* boundary conditions, as for the 1D and 2D cases, the energies E_x , E_y and E_z become,

$$E_{n_x} = \frac{n_x^2 \pi^2 \hbar^2}{2mL_x^2}, \quad E_{n_y} = \frac{n_y^2 \pi^2 \hbar^2}{2mL_y^2}, \quad E_{n_z} = \frac{n_z^2 \pi^2 \hbar^2}{2mL_z^2}, \quad (4.43)$$

where $n_x \in \mathbb{N}$, $n_y \in \mathbb{N}$, $n_z \in \mathbb{N}$.

Thus, the permitted energies, the so called *eigen energies*, depend upon the three integers, n_x, n_y, n_z , such that

$$\boxed{E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right),} \quad (4.44)$$

The *ground state* or *zero-point* energy occurs when $n_x = 1$, $n_y = 1$ and $n_z = 1$ in eqn(4.44), which represents the *stationary state* of *lowest energy*. For any $n_x > 1$, $n_y > 1$ or $n_z > 1$, this represents an *excited state* where the energy is greater than the ground state.

From eqns (4.39), (4.42) and (4.43) we obtain,

$$\psi(x, y, z) = U \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right). \quad (4.45)$$

where $U = B_x B_y B_z$.

To find a value for U we invoke the *normalization condition* of eqn(3.6), from which we obtain

$$U^2 \int_0^{L_x} \sin^2\left(\frac{n_x \pi x}{L_x}\right) dx \int_0^{L_y} \sin^2\left(\frac{n_y \pi y}{L_y}\right) dy \int_0^{L_z} \sin^2\left(\frac{n_z \pi z}{L_z}\right) dz = |U|^2 \frac{L_x}{2} \frac{L_y}{2} \frac{L_z}{2} = 1 \quad (4.46)$$

and

$$U = \sqrt{\frac{8}{L_x L_y L_z}}. \quad (4.47)$$

$$\therefore \psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right). \quad (4.48)$$

Equation (4.48) represents the *wave functions* of the Schödinger equation for the 3D potential well that also satisfy the boundary conditions.

Example plots are shown in Figures (4.3) and (4.4).

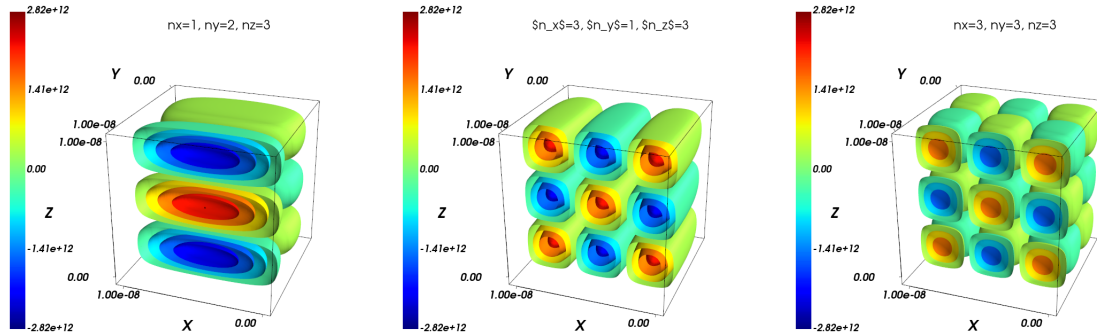


Figure 4.3: Examples showing *wave function* solutions $\psi_{n_x n_y n_z}$ to the Schödinger equation for a particle in a 3D potential well having sides of length $L_x = 10[\text{nm}]$, $L_y = 10[\text{nm}]$, $L_z = 10[\text{nm}]$. Plots were generated in *python* using the *mayavi* package, and include 3D isosurfaces of the solution.

4.4 3D Particle in a Box - Spherical Coordinates

We consider now the time dependent Schrödinger equation in a 3D symmetrical situation which, following [Gri-95], can be written as.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi, \quad (4.49)$$

where $\Psi = \Psi(t, \mathbf{r})$ and $V = V(\mathbf{r})$, $\mathbf{r} = (r, \theta, \phi)$ with other symbols as previously defined.

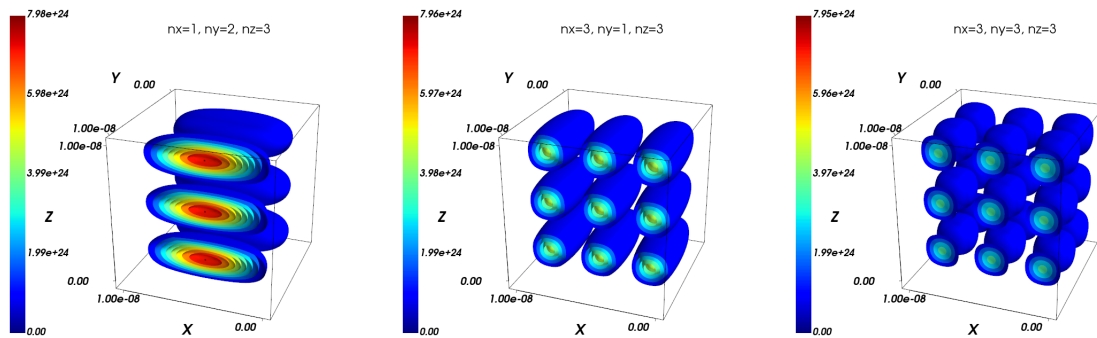


Figure 4.4: Examples showing *probability density function* solutions $\rho = |\psi_{n_x n_y n_z}|^2$ to the Schödinger equation for a particle in a 3D potential well having sides of length $L_x = 10[\text{nm}]$, $L_y = 10[\text{nm}]$, $L_z = 10[\text{nm}]$. Plots were generated in *python* using the *mayavi* package, and include 3D isosurfaces of the solution.

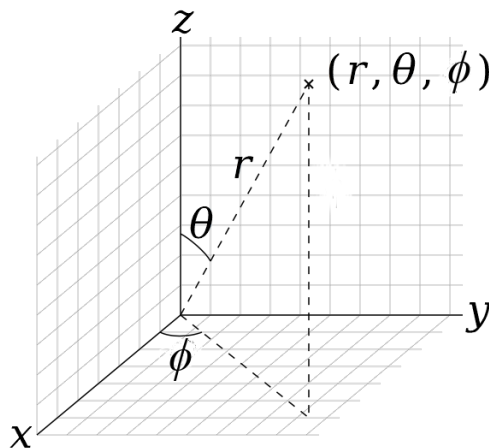


Figure 4.5: Spherical coordinates (r, θ, ϕ) , as commonly defined in *physics* applications, with variables denoted: radial distance r , polar angle θ , and azimuthal angle ϕ . Source: adapted from *wikipedia*.

The Laplacian in spherical coordinates for $\Psi = \Psi(r, \theta, \phi)$, is given by

$$\nabla^2 \Psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2}. \quad (4.50)$$

The same approach used for the 1D box can be used for a 3D box in polar coordinates. This box has a radius, $r = a$. Thus we have a zero potential inside the box i.e., where $V(r, \theta, \phi) = 0$, with radial coordinate $r \leq a$, polar (colatitudinal) coordinate $0 \geq \theta \leq \pi$, azimuthal (longitudinal) coordinate $0 \geq 2\phi \leq \pi$ and an infinite potential outside the box i.e., where $V(r, \theta, \phi) = \infty$, $r > r_0$, see Figure (4.5). **NOTE:** In the *python* programming language, used here for generating plots, θ and ϕ are as commonly defined in physics texts. However, they are interchanged from that shown in most mathematical texts.

We now seek a separable solution by separating the temporal and spatial portions of the wavefunction i.e., $\Psi(t, r, \theta, \phi) = f(t)\psi(r, \theta, \phi)$; and, as for the 1D case, the time varying part becomes

$$f(t) = \exp(-iEt/\hbar), \quad (4.51)$$

from which we obtain

$$\Psi(t, x, y, z) = \exp(-iEt/\hbar) \psi(0, r, \theta, \phi) \quad (4.52)$$

where $\psi(0, r, \theta, \phi) = \psi(r, \theta, \phi)$.

This enables us to recover the time-independent Schrödinger equation, which therefore becomes

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right) - V(r) = E\psi. \quad (4.53)$$

We can again seek a separable solution by assuming that,

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi). \quad (4.54)$$

Also that the energy term is only associated with the radial dimension r , due to rotational symmetry in θ and ϕ i.e.,

On substituting $\psi = R(r)Y(\theta, \phi)$ into eqn (4.53) and rearranging, we obtain the following *ordinary differential equation*,

$$\boxed{\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0.} \quad (4.55)$$

Equation (4.55) consists of two parts; a *radial* part that depends only on r and an *angular* part that depends only on θ and ϕ . This means that each part must be equal to a constant, which enables us to split this equation into the following two separate *radial* and *angular* equations,

$$\begin{aligned} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] &= \ell(\ell + 1); \\ \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} &= -\ell(\ell + 1); \end{aligned} \quad (4.56)$$

where the *separable constant* $\ell(\ell - 1)$ has been chosen to aid later calculations. The parameter ℓ is known as the *angular momentum quantum number* (or *azimuthal quantum number*), with possible values of $0, 1, 2, 3, \dots$

4.4.1 The Angular Equation

On multiplying the second of eqns (4.56) through by $Y \sin^2 \theta$ we obtain,

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -\ell(\ell + 1)Y \sin^2 \theta. \quad (4.57)$$

This equation is again in a form that appears suitable for a separable solution approach, and we try,

$$Y(\theta, \phi) = T(\theta)P(\phi). \quad (4.58)$$

Rearranging eqn (4.57) yields,

$$\left\{ \frac{1}{Y} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) \right] + \ell(\ell + 1)Y \sin^2 \theta \right\} + \frac{\partial^2 Y}{\partial \phi^2} = 0, \quad (4.59)$$

The first term of this equation is a function of only θ and the second only a function of ϕ . This means that each term must be equal to a constant, m , known as the *magnetic*

quantum number, with values ranging from $-\ell$ to ℓ . It should not be confused with the symbol for mass, m .

Substituting eqn (4.58) into eqn (4.59) and rearranging yields two separate *ordinary differential equations*,

$$\begin{aligned} \frac{1}{T} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) \right] + \ell(\ell + 1) \sin^2 \theta &= m^2; \\ \frac{1}{P} \frac{\partial^2 P}{\partial \phi^2} &= -m^2. \end{aligned} \quad (4.60)$$

The solution to the second of eqns. (4.60) is simpler and represented by

$$P(\phi) = e^{im\phi}, \quad m \in \mathbb{Z}. \quad (4.61)$$

Normally, this equation would include a leading constant, but to simplify matters we will subsume it into the solution for $T(\theta)$. Also, because eqn. (4.61) represents a *many-one* relationship with a period of 2π , it follows that the solution must be written as,

$$P(\phi) = e^{im(\phi+2\pi)}, \quad m \in \mathbb{Z}. \quad (4.62)$$

The solution to the first of eqns. (4.60) is more complex and represented by

$$T(\theta) = AP_\ell^m(\cos \theta), \quad \ell \in \mathbb{N}, \quad m \in \mathbb{Z}, \quad |m| \leq \ell, \quad (4.63)$$

where A is a constant to be determined. There are other mathematical solutions to this equation, but they are *physically* unacceptable because they blow up at $\theta = 0$ and/or $\theta = \pi$, and do not yield wave functions that can be normalized.

In eqn. (4.63) P_ℓ^m is the *associated Legendre function*, defined by

$$P_\ell^m(x) = (1 - x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_\ell(x), \quad (4.64)$$

and $P_\ell(x)$ is the ℓ th *Legendre polynomial*. However, for many purposes it will be more convenient to define $P_\ell(x)$ by the *Rodrigues formula*,

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx} \right)^\ell (x^2 - 1)^\ell. \quad (4.65)$$

Some associated Legendre functions of $\cos \theta$ are listed in Table Notice that ℓ must be a

Table 4.2: Some associated Legendre functions, $P_\ell^m(\cos \theta)$ Note: $P_\ell^m = 0$ for $|m| > \ell$.

$P_1^1 = \sin \theta$	$P_3^3 = 15 \sin \theta (1 - \cos^2 \theta)$
$P_1^0 = \cos \theta$	$P_3^2 = 15 \sin^2 \theta \cos \theta$
$P_2^2 = 3 \sin^2 \theta$	$P_3^1 = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$
$P_2^1 = 3 \sin \theta \cos \theta$	$P_3^0 = \frac{1}{2} (\cos^3 \theta - 3 \cos \theta)$
$P_2^0 = \frac{1}{2} (3 \cos^2 \theta - 1)$	

non-negative integer for the Rodrigues formula to make any sense; moreover, if $|m| > \ell$,

then eqn. (4.64) says $P_\ell^m = 0$. For any given ℓ , then, there are $(2\ell + 1)$ possible values of the *magnetic quantum number* m , i.e. we can have

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell. \quad (4.66)$$

Some specific examples of permitted values for m are:

$$\begin{aligned} \ell = 0, & \quad m_\ell = 0 \\ \ell = 1, & \quad m_\ell = -1, 0, +1 \\ \ell = 2, & \quad m_\ell = -2, -1, 0, +1, +2 \\ \ell = 3, & \quad m_\ell = -3, -2, -1, 0, +1, +2, +3 \\ \ell = 4, & \quad m_\ell = -4, -3, -2, -1, 0, +1, +2, +3, +4 \end{aligned}$$

The volume element in spherical coordinates is defined as,

$$d^3\mathbf{r} = r^2 \sin \theta \, dr \, d\theta \, d\phi; \quad (4.67)$$

from which the normalization condition, $|\psi|^2 = 1$, becomes

$$\int |\psi|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = A_{\text{overall}}^2 \int |R|^2 r^2 \, dr \int |Y|^2 \sin \theta \, d\theta \, d\phi = 1. \quad (4.68)$$

We can normalize the radial wave function R , and angular wave function Y , separately by imposing the following conditions

$$\boxed{\begin{aligned} \int_0^\infty A_{\text{radial}}^2 |R|^2 r^2 \, dr &= 1, \quad \rightarrow A_{\text{radial}}, \\ \int_0^{2\pi} \int_0^\pi A_{\text{angular}}^2 |Y|^2 \sin \theta \, d\theta \, d\phi &= 1, \quad \rightarrow A_{\text{angular}}. \end{aligned}} \quad (4.69)$$

So, the overall constant becomes $A_{\text{overall}} = A_{\text{radial}} A_{\text{angular}}$.

The normalized angular wave functions⁶ are called *spherical harmonics*, and are defined as

$$\boxed{Y_\ell^m(\theta, \phi) = \epsilon \sqrt{\frac{(2\ell + 1)(\ell - |m|)!}{4\pi(\ell + |m|)!}} e^{im\phi} P_\ell^m(\cos \theta),} \quad (4.70)$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. It can be proved that the spherical harmonics are orthogonal, so that

$$\int_0^{2\pi} \int_0^\pi [Y_\ell^m(\theta, \phi)]^* [Y_{\ell'}^{m'}(\theta, \phi)] \sin \theta \, d\theta \, d\phi = \delta_{\ell\ell'} \delta_{mm'}, \quad (4.71)$$

which confirms that the normalization condition is met.

4.4.2 The Radial Equation

The first of eqns. (4.56) can be written as,

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = \ell(\ell + 1)R. \quad (4.72)$$

⁶Note: $Y_\ell^{-m} = (-1)^m Y_\ell^m$.

This equation can be simplified by the change of variable

$$u(r) = rR(r), \quad (4.73)$$

when $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$, $(d/dr)[r^2(dR/dr)] = r d^2u/dr^2$, and we obtain

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u = Eu. \quad (4.74)$$

Equation (4.74) is identical to the 1D Schrödinger equation (4.6) except that the effective potential is,

$$V_{\text{eff}} = V(r) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2}, \quad (4.75)$$

which includes the so-called *centrifugal term* $(\hbar^2/2m)/[\ell(\ell+1)/r^2]$. It tends to throw the particle outwards away from the origin, similar to the centrifugal force in classical mechanics.

Following the change of variable, the normalization condition therefore becomes

$$\int_0^\infty |u|^2 dr = 1. \quad (4.76)$$

For the situation under consideration we have,

$$V(r) = \begin{cases} 0, & r \leq a; \\ \infty, & r > a; \end{cases} \quad (4.77)$$

and the radial equation (4.72) becomes

$$\frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2 \right] u, \quad (4.78)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}. \quad (4.79)$$

Case 1: $\ell = 0$

For this situation, eqn. (4.78) simplifies to

$$\frac{d^2u}{dr^2} = -k^2u, \quad (4.80)$$

for the boundary condition $u(L) = 0$, when the solution becomes

$$u(r) = A \sin kr + B \cos kr. \quad (4.81)$$

However, due to $R(r) = u(r)/r$, we must have $B = 0$ because $(\cos ky)/r = \infty$ when $r = 0$. The boundary condition then requires that $\sin kr = 0$, which means that we must have $ka = n\pi$, $n \in \mathbb{N}$. It therefore follows that, for Case 1, the allowed energies are

$$\boxed{E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}}, \quad (4.82)$$

which is the same as for the 1D infinite potential well, eqn. (4.13). Normalizing $u(r)$, i.e.

$$\int_0^a |u(r)|^2 dr = A_{n0}^2 \int_0^a \sin^2(n\pi r/a) dr = 1, \quad (4.83)$$

yields $A_{n0} = \sqrt{2/a}$. Note: The upper limit on the integral is equal to a as the value for $\psi(r > a) = 0$, from the problem statement. Then, including the angular part, which is constant for this case, since from eqn. (4.70) we have $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$, and recalling that $R(r) = u(r)/r$, we arrive at

$$\boxed{\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}}. \quad (4.84)$$

We now use three quantum numbers, n, ℓ , and m to label *stationary states*, i.e. $\psi_{n\ell m}$, but use just two to label energy, which depends only on n and ℓ , i.e. $E_{n\ell}$.

Case 2: The General Solution

The general solution to eqn. (4.78) for arbitrary ℓ is more complex than for Case 1, with the less familiar solution

$$u(r) = A r j_\ell(kr) + B r y_\ell(kr), \quad (4.85)$$

where j_ℓ and y_ℓ are the *spherical Bessel functions* of the *first* and *second* kind. They are defined as,

$$j_\ell = (-z)^\ell \left(\frac{1}{z} \frac{d}{dz} \right)^\ell \frac{\sin z}{z}; \quad y_\ell = -(-z)^\ell \left(\frac{1}{z} \frac{d}{dz} \right)^\ell \frac{\cos z}{z}; \quad (4.86)$$

The first few spherical Bessel functions are listed in Table (4.3) and some plots are shown in Fig. (4.6).

Table 4.3: The first few spherical Bessel functions, j_ℓ and y_ℓ .

$j_0 = \frac{\sin z}{z}$	$y_0 = -\frac{\cos z}{z}$
$j_1 = \frac{\sin z}{z^2} - \frac{\cos z}{z}$	$y_1 = -\frac{\cos z}{z^2} - \frac{\sin z}{z}$
$j_2 = \left(\frac{3}{z^3} - \frac{1}{z} \right) \sin z - \frac{3}{z^2} \cos z$	$y_2 = -\left(\frac{3}{z^3} - \frac{1}{z} \right) \cos z - \frac{3}{z^2} \sin z$
Note: $j_\ell \rightarrow \frac{z^\ell}{(2\ell+1)!!}$, $y_\ell \rightarrow -\frac{(2\ell-1)!!}{z^{\ell+1}}$, for $z \ll 1$.	

On examination of the behavior of spherical Bessel functions as $x \rightarrow 0$, we find that j_ℓ is well behaved, but y_ℓ blows up. Therefore, we conclude that for a physically real solution, we must have $B_\ell = 0$. So that eqn. (4.85) reduces to

$$u(r) = A r j_\ell(kr). \quad (4.87)$$

To ensure that the solution is consistent with the boundary condition $R(L) = 0$, k must be chosen such that

$$j_\ell(ka) = 0. \quad (4.88)$$

This means that (ka) must be equal to one of the n zeros, $\beta_{n\ell}$, of the ℓ^{th} -order spherical Bessel function, i.e. $ka = \beta_{n\ell}$. Because the spherical Bessel functions are oscillatory, and the zeros are not located at regular points along r , they have to be calculated numerically. The parameter n is known as the *principle quantum number*, with possible values of $1, 2, 3, 4, \dots$. Some values for $\beta_{n\ell}$ are given in Table (4.4).

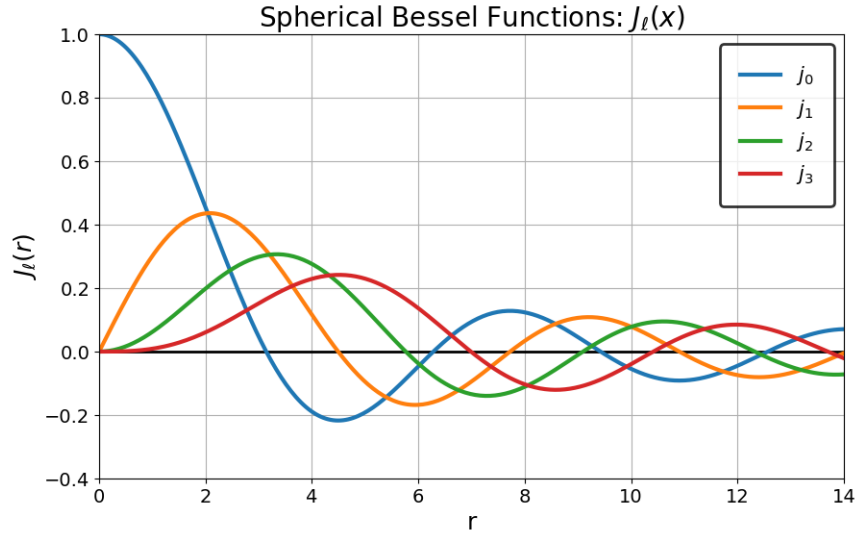


Figure 4.6: Spherical Bessel Function Plots.

Table 4.4: First few values for the n th zeros of order- ℓ spherical Bessel function $j_\ell(z)$, determined numerically. Compare to zero crossings of plots in Fig. (4.6).

Spherical Bessel Function Zeros, $\beta_{n\ell}$					
	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
$n = 1$	3.1416	4.4934	5.7635	6.9879	8.1826
$n = 2$	6.2832	7.7253	9.0950	10.4171	11.7049
$n = 3$	9.4248	10.9041	12.3229	13.6980	15.0397
$n = 4$	12.5664	14.0662	15.5146	16.9236	18.3013

Therefore, to be consistent with the boundary condition we require

$$k = \frac{1}{a}\beta_{n\ell}; \quad \implies j_\ell(\beta_{n\ell} r/a) = 0. \quad (4.89)$$

Some plots of $j_\ell(\beta_{n\ell} r/a)$ are shown in Fig. (4.7), which indicates that the boundary condition at $r = a$ is enforced.

From eqns. (4.79) and (4.89) we see that for Case 2, the allowed energies are given by

$$E_{n\ell} = \frac{\hbar^2}{2ma^2}\beta_{n\ell}^2. \quad (4.90)$$

Some energy levels are included in Table (4.5) that have been calculated using *electron mass*, $m = 9.1093837 \times 10^{-31}$ [kg], *reduced Planck constant*, $\hbar = 1.054571817 \times 10^{-34}$ [m²kg/s] and spherical potential well *radius*, $a = 10^{-8}$ [m]. Note: The energy levels for $\ell = 0$ are the same as those for the 1D potential well, see Table (4.1).

Normalization

Finally, recalling that $R(r) = u(r)/r$, the wave function solutions to the Schrödinger time independent equation (4.55) are

$$\psi_{n\ell m}(r, \theta, \phi) = A_{n\ell m} j_\ell(\beta_{n\ell} r/a) Y_\ell^m(\theta, \phi), \quad (4.91)$$

where the constants $A_{n\ell m}$, have to be determined by normalization. This means that we

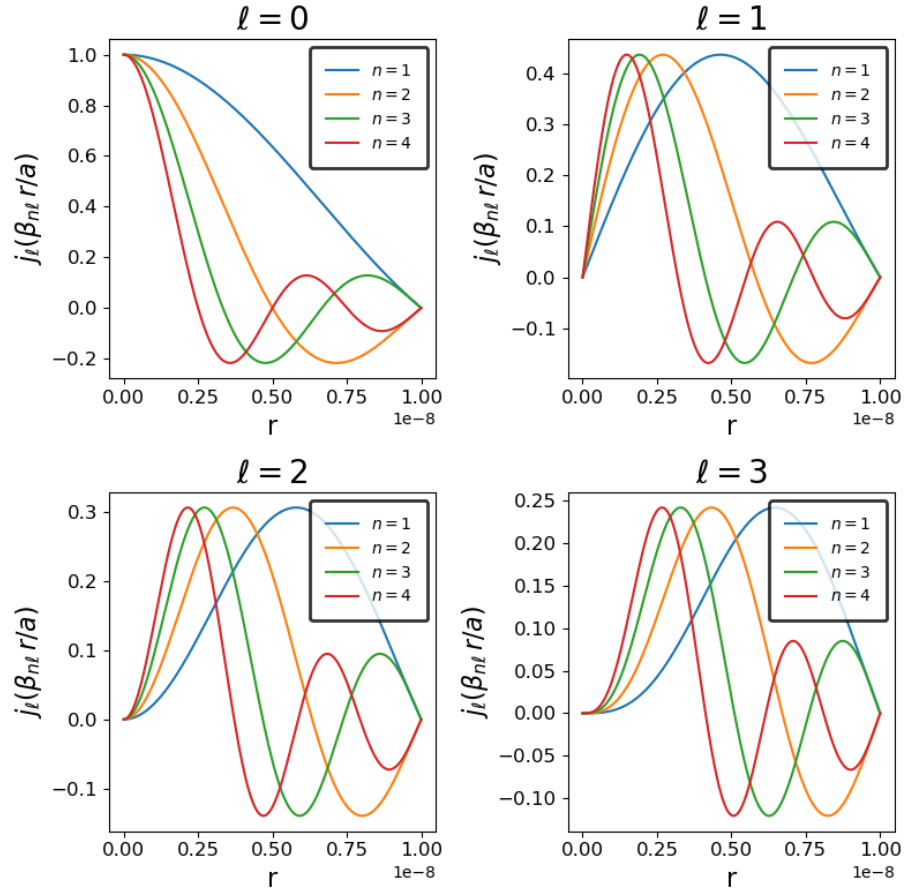


Figure 4.7: Example plots for reduced spherical Bessel functions, $j_\ell(\beta_{nl} r/a)$.

have to choose A_{nml} such that

$$\int_0^a \int_0^{2\pi} \int_0^\pi \psi(r, \theta, \phi)^* \psi(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi = \int_0^a \int_0^{2\pi} \int_0^\pi |\psi|^2 r^2 \sin \theta dr d\theta d\phi = 1, \quad (4.92)$$

where we have employed the infinitesimal volume of eqn. (4.67). Note: The upper limit on the integral radial term is equal to a as the value for $\psi(r > a) = 0$, from the problem statement. As discussed above, we calculate separate *angular* and *radial* normalization constants, so that we have from eqn. (4.69),

$$A_{nml} = A_{nl} A_{ml}. \quad (4.93)$$

Values for A_{ml} and A_{nl} are given in Tables (4.6) and (4.7), and some example plots of associated wave functions ψ_{nlm} , and probability density functions $\rho = |\psi_{nlm}|^2$, are given in Figures (4.8) and (4.9).

Table 4.5: Energy Levels for Spherical Potential Well

	E_{nl} [J]				
	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
$n = 1$	6.0247E-22	1.2325E-21	2.0277E-21	2.9808E-21	4.0871E-21
$n = 2$	2.4099E-21	3.6430E-21	5.0494E-21	6.6241E-21	8.3631E-21
$n = 3$	5.4222E-21	7.2580E-21	9.2696E-21	1.1454E-20	1.3807E-20
$n = 4$	9.6395E-21	1.2078E-20	1.4693E-20	1.7483E-20	2.0445E-20

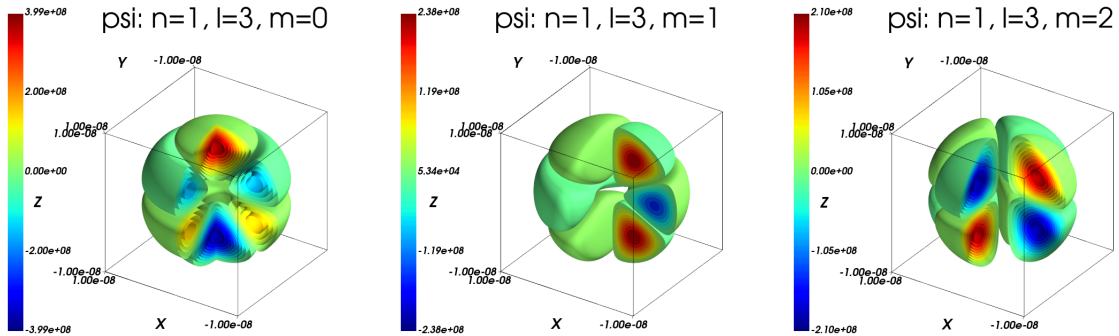
	E_{nl} [eV]				
	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
$n = 1$	3.7606E-03	7.6932E-03	1.2657E-02	1.8606E-02	2.5511E-02
$n = 2$	1.5042E-02	2.2740E-02	3.1518E-02	4.1348E-02	5.2203E-02
$n = 3$	3.3845E-02	4.5304E-02	5.7861E-02	7.1495E-02	8.6185E-02
$n = 4$	6.0170E-02	7.5389E-02	9.1715E-02	1.0913E-01	1.2762E-01

Table 4.6: Normalization Constants - Angular

	$A_{m\ell}, m \leq \ell.$			
	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$
$m = 0$	1.0	1.0	1.0	1.0
$m = 1$	-	1.0	1.0	1.0
$m = 2$	-	-	1.0	1.0
$m = 3$	-	-	-	1.0

Table 4.7: Normalization Constants - Radial, $a = 10^{-8}$

	$A_{n\ell} \times 10^{-8}$			
	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$
$n = 1$	2.506628	3.071142	3.558368	3.997983
$n = 2$	3.544908	3.963508	4.344382	4.697816
$n = 3$	4.341608	4.689527	5.014220	5.320530
$n = 4$	5.013257	5.317384	5.605422	5.880068

**Figure 4.8:** Examples showing *wave function* solutions $\Re(\psi_{n\ell m})$ to the Schödinger equation for a particle in a 3D spherical potential well of radius $r = 10[\text{nm}]$. Plots were generated in *python* using the *mayavi* package, and include 3D isosurfaces of the solution.

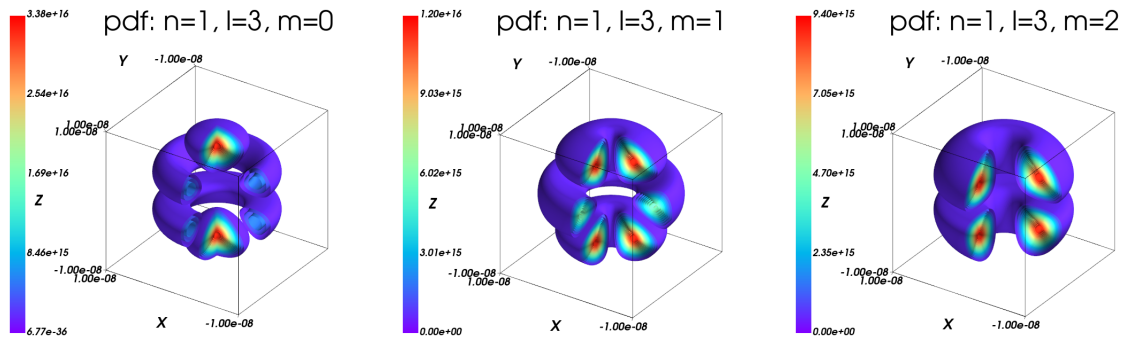


Figure 4.9: Examples showing *probability density* function solutions $\rho = |\psi_{n\ell m}|^2$ to the Schrödinger equation for a particle in a 3D spherical potential well of radius $r = 10[\text{nm}]$. Plots were generated in *python* using the *mayavi* package, and include 3D isosurfaces of the solution.

5 Finite Potential Well

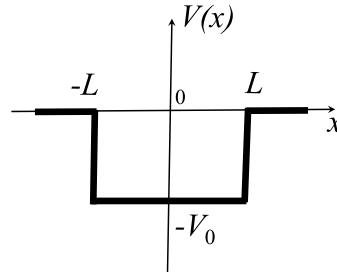


Figure 5.1: The finite square well potential.

Here we follow closely D Griffiths [Gri-95] and consider bound states $E < 0$, with the time independent Schrödinger equation (3.4) in one dimension, i.e.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x), \quad (5.1)$$

where the potential is defined as,

$$V(x) = \begin{cases} -V_0, & \text{for } -L < x < L, \\ 0, & \text{for } |x| > L, \end{cases} \quad (5.2)$$

and V_0 is a positive constant - see Figure (5.1).

In the region $x < -L$ the potential is zero, so the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x), \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = \kappa^2\psi(x), \quad (5.3)$$

where

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}. \quad (5.4)$$

Note: κ will be real and positive as $E < 0$. The general solution to this equation is

$$\psi(x) = A \exp(-\kappa x) + B \exp(\kappa x), \quad (5.5)$$

but the first term blows up as $x \rightarrow -\infty$, so is physically inadmissible, when the solution becomes

$$\psi(x) = Be^{\kappa x}, \quad (x < -a). \quad (5.6)$$

In the region $-L < x < L$, $V(x) = -V_0$, and the Schrödinger equation become,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} - V_0 = E\psi(x), \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = -\ell^2\psi(x), \quad (5.7)$$

where

$$\ell \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar}. \quad (5.8)$$

Although E is negative, for a bound state, it must be greater than $-V_0$, i.e. $E > V_{\min}$. The general solution is

$$\psi(x) = C \sin(\ell x) + D \cos(\ell x), \quad \text{for} \quad (-L < x < L), \quad (5.9)$$

where C and D are arbitrary constants. Finally, in the region $x > L$ the potential is again zero; the general solution is $\psi(x) = F \exp(-\kappa x) + G \exp(\kappa x)$, but the second term blows up (as $x \rightarrow \infty$), so we are left with

$$\psi(x) = Fe^{-\kappa x}, \quad \text{for} \quad (x > L). \quad (5.10)$$

Because we are dealing with a *symmetric* potential, the corresponding stationary states, as determined from the time independent Schrödinger equation (5.1), will exhibit a symmetry property called *parity*, i.e. $\psi(-x) = \pm\psi(x)$. The wave function is then said to exhibit *odd* or *even* parity. Recognizing that a wave function in a symmetric potential must exhibit odd or even parity allows significant simplification in determining permitted energy levels for such situations. Refer to [Fre-92, Chapters 3 and 4] for a more detailed discussion.

We now must solve for the arbitrary constants and we do this by imposing the continuity conditions of $\psi(x)$ and $d\psi(x)/dx$ at the problem boundaries $-L$ and L . Since we are dealing with solutions that exhibit odd and even parity, we look for odd and even solutions separately. We will first look for even solutions. The cosine is even (and sine is odd), so we are looking for solutions of the form,

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & \text{for } (x > L), \\ D \cos(\ell x), & \text{for } (0 < x < L), \\ \psi(-x), & \text{for } (x < 0). \end{cases} \quad (5.11)$$

The continuity of $\psi(x)$, at $x = L$, requires

$$Fe^{-\kappa L} = D \cos(\ell L), \quad (5.12)$$

and the continuity of $d\psi/dx$ requires

$$-\kappa Fe^{\kappa L} = -\ell D \sin(\ell L). \quad (5.13)$$

Dividing eqn. (5.20) by eqn. (5.12) yields

$$\kappa = \ell \tan(\ell L). \quad (5.14)$$

Equation (5.14) can be used to calculate the allowed energies as both κ and ℓ are functions of E with parameter V_0 . At this point it helps to introduce some new notation. Let

$$z \equiv \ell L, \quad \text{and} \quad z_0 \equiv \frac{L}{\hbar} \sqrt{2mV_0}. \quad (5.15)$$

From eqns. (5.4) and (5.8) we see that $(\kappa^2 + \ell^2) = 2mV_0/\hbar^2$, so $\kappa L = \sqrt{z_0^2 - z^2}$, and eqn. (5.14) becomes

$$\tan z = \sqrt{(z_0/z)^2 - 1}. \quad (5.16)$$

This is a *transcendental* equation for z (and hence for E) as a function of z_0 , which is a measure of the size of the well.

It can be solved numerically, or graphically by plotting $\tan z$ and $\sqrt{(z_0/z)^2 - 1}$ on the same grid and looking for points of intersection - see Figure (5.2).

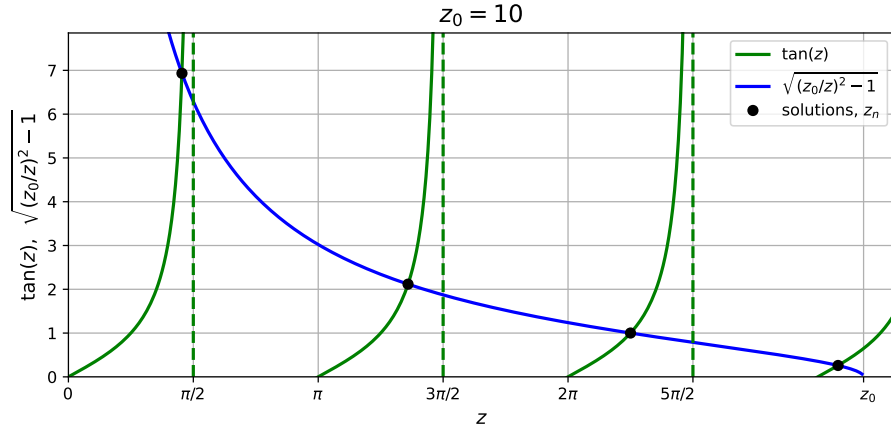


Figure 5.2: Graphical solution to eqn. (5.16), for $z_0 = 8$ (even states).

Once we have solved eqn. (5.16) for z given a particular value of z_0 or V_0 , then from first of eqns. (5.8) along with eqn. (5.15), we can calculate the energy values E_n , using

$$E_n = \frac{1}{2m} \left(\frac{\hbar z_n}{L} \right)^2 - V_0. \quad (5.17)$$

Two limiting cases are of special interest:

1. Wide, deep well. If z_0 is very large, the intersections occur just slightly below $z_n = n\pi/2$, with n odd; it follows that

$$E_n + V_0 \approx \frac{n^2 \pi^2 \hbar^2}{2m(2L)^2}. \quad (5.18)$$

The right hand term of this equation ($E + V_0$) represents the energy above the bottom of the well, and the right hand term the infinite square well energies (see eqn. (4.13)). Thus, for an even parity situation, and a well of width $2L$, we have half the energies of the infinite potential well. The remainder come from the *odd* parity wave functions.

2. Shallow, narrow well. As z_0 decreases, there are fewer and fewer bound states, until finally (for $z_0 < n\pi/2$, where the lowest odd state disappears) only one remains. It is interesting to note, however, that there is always one bound state, no matter how "weak" the well becomes.

We will now look for odd solutions. The sine is odd, so we are looking for solutions of the form,

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & \text{for } (x > L), \\ C \sin(\ell x), & \text{for } (0 < x < L), \\ -\psi(-x), & \text{for } (x < 0). \end{cases} \quad (5.19)$$

The continuity of $\psi(x)$, at $x = L$, requires

$$F e^{-\kappa L} = C \sin(\ell L), \quad (5.20)$$

and the continuity of $d\ell/dx$ requires

$$-\kappa F e^{\kappa L} = \ell C \cos(\ell L). \quad (5.21)$$

Dividing eqn. (5.21) by eqn. (5.20) yields

$$-\kappa = \ell \cot(\ell L). \quad (5.22)$$

Using the previous notation for z and z_0 we arrive at $-\kappa L = \sqrt{(z_0^2 - z^2)}$, which leads to

$$-\cot z = \sqrt{(z_0/z)^2 - 1}, \quad (5.23)$$

for odd parity situations. It can be solved numerically, or graphically by plotting $-\cot z$ and $\sqrt{(z_0/z)^2 - 1}$ on the same grid and looking for points of intersection - see Figure (5.3).

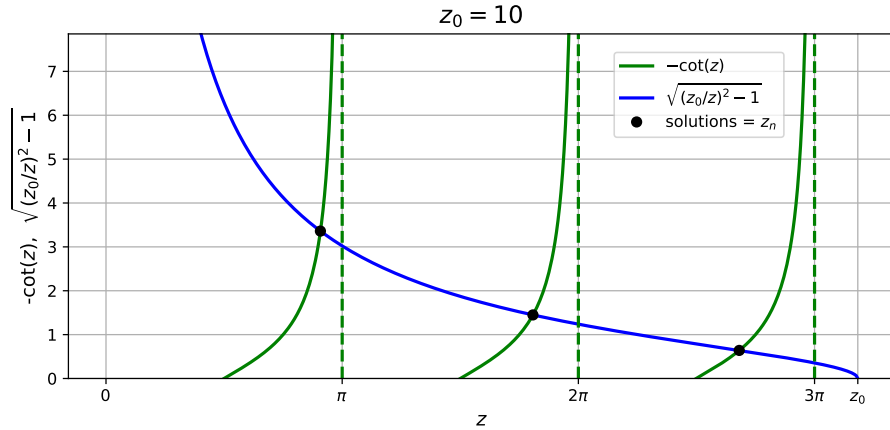


Figure 5.3: Graphical solution to eqn. (5.23), for $z_0 = 10$ (odd states).

Once we have solved eqn. (5.23) for z given a particular value of z_0 or V_0 , then again from eqns. (5.8) and (5.15) we can calculate the energy values E_n , using eqn. (5.17). A combined list of odd and even parity energy levels for $z_0 = 10$, which is equivalent to $V_0 = 6.11 \times 10^{-19}$ [J] (3.81 [eV]), is shown in Table (5.1).

Table 5.1: Energy levels E_n , for the finite potential well.

n	E_n		z
	[J]	[eV]	[-]
7	-3.8589E-20	-0.2438	9.679
6	-1.7748E-19	-1.1098	8.423
5	-3.0562E-19	-1.9092	7.069
4	-4.1387E-19	-2.5842	5.679
3	-4.9945E-19	-3.1180	4.271
2	-5.6119E-19	-3.5030	2.852
1	-5.9842E-19	-3.7354	1.428

The associated wave functions are shown in Figure(5.4). Unlike the situation for the infinite potential well, here there is a probability associated with the particle being found

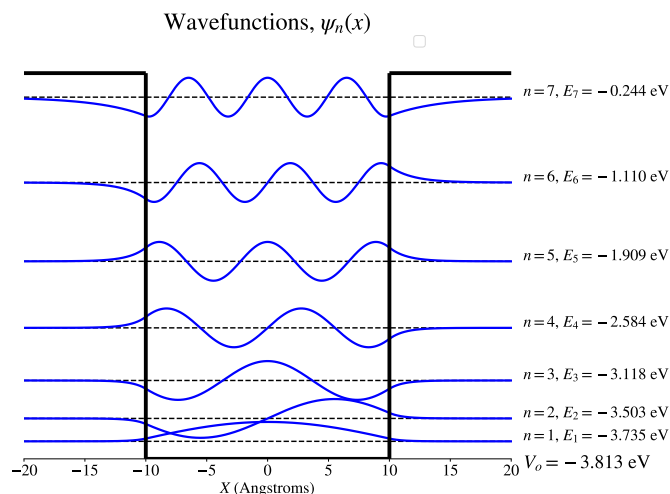


Figure 5.4: Example showing solutions to the Schrödinger equation for a particle in a finite 1D potential well of length $L = 20$ [Å]. Plots shown superimposed on bound state energy level lines - ψ_n are not to scale.

outside the box, even when the energy of the particle is less than the potential energy barrier of the walls. This is an example of *quantum tunneling*.

We again look at two limiting cases.

1. Wide, deep well. If z_0 is very large, the intersections occur just slightly below $z_n = n\pi/2$, this time with n even; it follows again that

$$E_n + V_0 \approx \frac{n^2\pi^2\hbar^2}{2m(2L)^2}. \quad (5.24)$$

As previously, the right hand term of this equation ($E + V_0$) represents the energy above the bottom of the well, and the right term the infinite square well energies for a well of width $2L$. This fills in the rest of the energy levels for the finite, wide, deep well. Thus, we see that these energies closely approximate those of the infinite square well (eqn. (4.13)).

2. Shallow, narrow well. If $z_0 < n/2$, there is no odd bound state. The corresponding condition on V_0 is

$$V_0 < \frac{\pi^2\hbar^2}{8mL^2} \implies \text{no odd bound states.} \quad (5.25)$$

Finally, the even parity constants D and F from eqns. (5.11) can be evaluated by normalization. This is achieved by integrating the associated equations squared, from $-\infty$ to $+\infty$, and setting the result equal to 1, see Section (3.2.1). We will not perform these calculation here, but the results are:

$$D = \sqrt{\frac{\kappa}{1 + \kappa L}} \quad (5.26)$$

$$F = \sqrt{\frac{\kappa}{1 + \kappa L}} \cos(\ell L) e^{\kappa L}, \quad (\text{even parity}).$$

Similarly, the odd parity constant C and F from eqns. (9.6) can also be evaluated by normalization, and the results are:

$$C = \sqrt{\frac{\kappa}{1 + \kappa L}} \quad (5.27)$$

$$F = \sqrt{\frac{\kappa}{1 + \kappa L}} \sin(\ell L) e^{\kappa L}, \quad (\text{odd parity}).$$

6 The Quantum Oscillator

The *classical mechanics* friction-less harmonic oscillator, in its simplest form, is often used as an *analog* for the *quantum oscillator*. For the one dimensional case this is described mathematically as,

$$F = -kx = m \frac{d^2x}{dt^2}, \quad (6.1)$$

where k represents a spring constant and m a mass. Defining the *angular frequency* as

$$\omega \equiv \sqrt{k/m}, \quad (6.2)$$

we find the solution to be,

$$x(t) = A \sin(\omega t) + B \cos(\omega t). \quad (6.3)$$

The potential is

$$V(x) = \frac{1}{2}kx^2, \quad (6.4)$$

which represents a simple parabola. See also Appendix (A).

However, our task here is to solve the *quantum oscillator* problem, and we generally follow [Gri-95]. The quantum oscillator can be represented by the 1D time independent Schrödinger equation with potential

$$V(x) = \frac{1}{2}m\omega^2x^2, \quad (6.5)$$

where the spring constant has been replaced by eqn. (6.2). So we need to solve,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi. \quad (6.6)$$

It will be observed that there is no explicit time dependence. This is because we are solving a *static* problem.

To simplify the analysis we define the dimensionless variable q and transformed energy variable K as

$$q \equiv \sqrt{\frac{m\omega}{\hbar}}x, \quad \text{and} \quad K \equiv \frac{2E}{\hbar\omega}, \quad (6.7)$$

when the Schrödinger equation becomes

$$\frac{d^2\psi}{dq^2} = (q^2 - K)\psi. \quad (6.8)$$

In the process of solving eqn. (6.8) we need to also establish the allowed energy values for E , which we get from K .

We observe that at very large q (and hence very large x), q^2 dominates K and we have

$$\frac{d^2\psi}{dq^2} \approx q^2\psi. \quad (6.9)$$

which has the approximate solution,

$$\psi(q) \approx Ae^{-q^2/2} + Be^{q^2/2}. \quad (6.10)$$

The second term on the right hand side blows up at large q , and is therefore non-physical; hence, we must have $B = 0$. We now postulate a solution of the form

$$\psi(q) = h(q)e^{-q^2/2}, \quad \text{at large } q. \quad (6.11)$$

Our hope is that we can, similar to as applied previously, represent $h(q)$ in the form of a simple function. Differentiating eqn. (6.11) once, and then twice, we obtain

$$\frac{d\psi}{dq} = \left(\frac{dh}{dq} - qh \right) e^{-q^2/2}, \quad (6.12)$$

and

$$\frac{d^2\psi}{dq^2} = \left(\frac{d^2h}{dq^2} - 2q \frac{dh}{dq} + (q^2 - 1)h \right) e^{-q^2/2}. \quad (6.13)$$

Substituting these results into eqn. (6.8), the Schrödinger equation becomes

$$\frac{d^2h}{dq^2} - 2q \frac{dh}{dq} + (K - 1)h = 0. \quad (6.14)$$

We now look for a solution in the form of a power series in terms of q , i.e.

$$h(q) = a_0 + a_1q + a_2q^2 + \dots = \sum_0^{\infty} a_j q^j. \quad (6.15)$$

Differentiating once, and then twice, we obtain

$$\frac{dh}{dq} = a_1 + 2a_2q + 3a_3q^2 + \dots = \sum_0^{\infty} j a_j q^{j-1}, \quad (6.16)$$

and

$$\frac{d^2h}{dq^2} = 2a_2 + 2 \cdot 3a_3q + 3 \cdot 4a_4q^2 + \dots = \sum_0^{\infty} (j+1)(j+2)a_{j+2}q^j. \quad (6.17)$$

Substituting these results into eqn. (6.14), we obtain

$$\sum_0^{\infty} [(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j]q^j = 0. \quad (6.18)$$

Now we use our knowledge that the coefficient of each power of q must equal zero. Therefore, on rearranging, this equation simplifies to the following recursive expression,

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)} a_j, \quad (6.19)$$

which is entirely equivalent to the Schrödinger equation. We observe that, given a_0 it recursively generates a_2, a_4, a_6, \dots , and given a_1 , it generates a_3, a_5, a_7, \dots . Thus, we can write the following even and odd functions as

$$h_{\text{even}}(q) = a_0 + a_2q^2 + a_4q^4 + \dots \quad (6.20)$$

and

$$h_{\text{odd}}(q) = a_1 + a_3q^3 + a_5q^5 + \dots \quad (6.21)$$

which leads to

$$h(q) = h_{\text{even}}(q) + h_{\text{odd}}(q) \quad (6.22)$$

It follows, therefore, that eqn. (6.19) determines $h(q)$ in terms of the two arbitrary constants a_0 and a_1 . However, for very large j , the recursive equation leads the situation where

$$a_{j+2} \approx \frac{2}{j} a_j, \quad (6.23)$$

with the approximate solution

$$a_j \approx \frac{C}{(j/2)!}, \quad (6.24)$$

for some constant C . But, for large q , where higher powers dominate, we have

$$h(q) \approx C \sum \frac{1}{(j/2)!} q^j \approx C \sum \frac{1}{k!} q^{2k} \approx C e^{q^2} \quad (6.25)$$

This means that if h grows according to $\exp(q^2)$, then according to eqn. (6.11) ψ grows according to $\exp(q^2/2)$. This would lead to a non-physical solution that cannot be normalized. For a normalizable solution, the power series must terminate. So, we require that at some highest value of j , say n , the recursive equation must yield $a_{n+2} = 0$, which will truncate either the series h_{even} or h_{odd} - the other one must be zero from the start. Thus, for a physically acceptable solution, we must have a situation where for a positive integer n ,

$$K = 2n + 1. \quad (6.26)$$

It follows from the second of eqns. (6.7) that the energy levels are defined by

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega, \quad \text{for } n = 0, 1, 2, \dots \quad (6.27)$$

For the allowed values of K , the recursion equation becomes

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)} a_j. \quad (6.28)$$

So, for a particular value of n , h_n will be described by a polynomial of degree n , each with a completely different set of coefficients a_j , some of which may be equal to zero. If $n = 0$, there is only one term in the series, consequently we must choose $a_1 = 0$ to eliminate h_{odd} , and with $j = 0$ eqn. (6.28) yields $a_2 = 0$,

$$\therefore h_0(q) = a_0, \quad (6.29)$$

and the associated wavefunction becomes

$$\psi_0 = a_0 e^{-q^2/2}. \quad (6.30)$$

For $n = 1$, again there is only one term in the series, consequently we must choose $a_0 = 0$ to eliminate h_{even} , and with $j = 1$ eqn. (6.28) yields $a_3 = 0$,

$$\therefore h_1(q) = a_1 q, \quad (6.31)$$

and the associated wavefunction becomes

$$\psi_1 = a_1 q e^{-q^2/2}. \quad (6.32)$$

For $n = 2$, $j = 0$ yields $a_2 = -2a_0$, and $j = 2$ gives $a_4 = 0$, so

$$h_2(q) = a_0(1 - 2q^2), \quad (6.33)$$

and the associated wavefunction becomes

$$\psi_2 = a_0(1 - 2q^2)e^{-q^2/2}, \quad (6.34)$$

and so on.

Table 6.1: The first few Hermite polynomials, $H_n(x)$

$H_0 = 1,$
$H_1 = 2x,$
$H_2 = 4x^2 - 2,$
$H_3 = 8x^3 - 12x,$
$H_4 = 16x^4 - 48x^2 + 12,$
$H_5 = 32x^5 - 160x^3 + 120x,$
$H_6 = 64x^6 - 480x^4 + 720x^2 - 120.$

In general, $h_n(q)$ will be a polynomial of degree n in q , involving even powers only, if n is an even integer, and odd powers only, if n is an odd integer. Apart from the overall factor (a_0 or a_1) they are the so-called *Hermite polynomials*, defined as

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}. \quad (6.35)$$

The first few Hermite polynomials H_n , are listed in Table (6.1).

By tradition, the arbitrary multiplicative factor is chosen so that the coefficient of the highest power of q is 2^n . With this convention, the normalized stationary states for the harmonic oscillator are

$$\psi_n(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(q) e^{-q^2/2}. \quad (6.36)$$

Plots of wavefunctions $\psi_n(q)$ and probability density functions $|\psi_n(q)|^2$ are given in Figure (6.1).

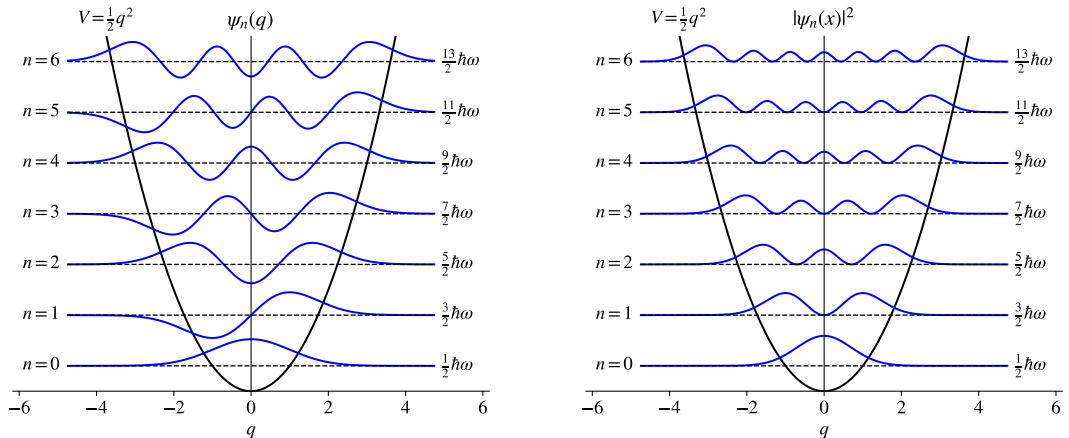


Figure 6.1: *Left:* Wavefunctions $\psi_n(q)$, for the quantum harmonic oscillator with parabolic potential V . *Right:* The corresponding probability density functions $|\psi_n(q)|^2$. The independent *nuclear* spatial variable $q = (mk/\hbar^2)^{1/4}x$, $\omega = \sqrt{k/m}$ and k represents a *spring force constant*. The energy levels $E_n = (n + \frac{1}{2})\omega\hbar$, are shown on the right of each plot. They are equally spaced, with transitional energies $\Delta E = \hbar\omega$. Unlike the classical oscillator, the quantum oscillator has a non-zero probability of occurring outside the classical turning points. The wavefunctions ψ_n , and probability density functions $|\psi(q)|^2$, are not to scale

The quantum and classical oscillators are quite different. The quantum oscillator is only permitted to have quantized energy levels and is described by positions in space. Whereas, the classical oscillator can have continuous energy levels and is described by positions over time. Also, the quantum oscillator has wave-like properties, unlike the classical oscillator. See Appendix (A) for derivation of the probability density function for a classical oscillator. Figure (6.2) shows a plot of the probability density function of

a quantum oscillator with high energy level E_{100} , and superimposed is that of the corresponding classical oscillator. We see that as energy levels increase, a new phenomenon occurs. The particle of the quantum oscillator has higher probability of occurring towards the edges, becoming lower towards the center.

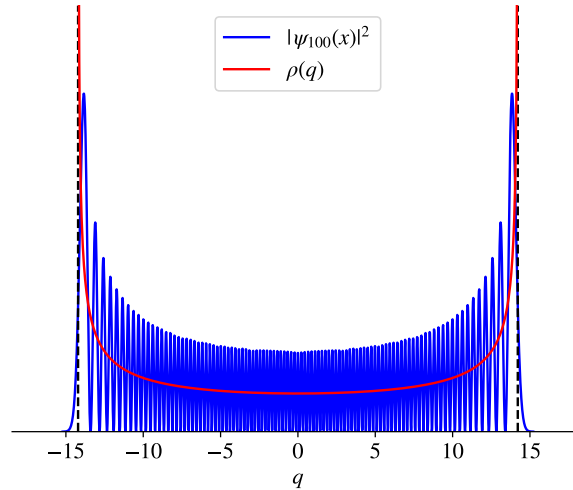


Figure 6.2: Probability density function, $|\psi_{100}(q)|^2$ shown with classical SHM oscillator probability density function $\rho(q)$ superimposed. The classical turning points are indicated by the vertical dashed lines.

It appears from our model that as the energy levels increase, the quantum system begins to more closely resemble macroscopic objects and, in the limit classical behavior will emerge from this quantum description. The process by which an object in a quantum state morphs into a classical object is called *decoherence*. It is part of the crucial transitioning from quantum to classical existence. Explaining why quantum behavior is not observable in classical systems is difficult. But intuition says that at some point the change must occur, and that it should be detectable. However, this is a somewhat simplistic view as, in the quantum world, intuition can often lead us astray from how reality behaves. Consequently, how the quantum world transitions to the classical world is still an open question.

7 Quantum Tunneling

Quantum tunneling is defined as a quantum mechanical process where wave functions can penetrate through a potential barrier. The transmission through the potential barrier can be finite and relies exponentially on the barrier width and barrier height. Wave functions have the genuine probability of disappearing on one side of a barrier and reappearing on the other side.

For a quantum particle to appreciably tunnel through a barrier three conditions must be met:

- The height of the barrier must be finite with a narrow width.
- The potential energy of the barrier must exceed the kinetic energy of the particle.
- The particle must exhibit wave like properties. Because the wave function is able to penetrate through the barrier the implication is that quantum tunneling applies only to microscopic objects such as protons or electrons, and not macroscopic objects.

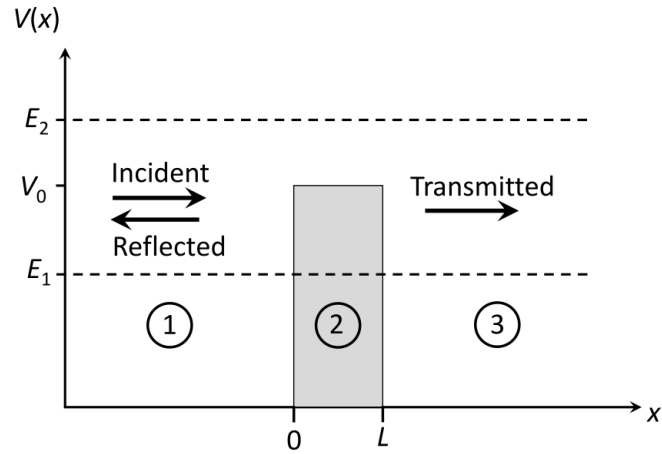


Figure 7.1: Tunneling diagram showing the the domain split into three regions: 1) and 3) with zero potential, and 2) with potential V_0 of width L . Particles can be *incident*, *reflected* or *transmitted*, and the energies considered are $E_1 < V_0$ and $E_2 > V_0$.

If these conditions are met, there is some finite probability of the particle transitioning to the other side of the barrier.

Consider a quantum system having a potential $V(x)$, see Figure (7.1), defined as,

$$V(x) = \begin{cases} 0, & \text{for } (-\infty < x < 0) \\ V_0, & \text{for } (0 \leq x \leq L) \\ 0, & \text{for } (L < x < \infty) \end{cases} \quad (7.1)$$

with our task of solving the one dimensional Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi_1(x). \quad (7.2)$$

For the different regions, where $V(x)$ is defined by eqn. (7.1) and after rearranging, the one dimensional time independent Schrödinger equation takes the following forms:

Region 1: $-\infty < x < 0$,

$$\frac{d^2\psi_1(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi_1(x) = 0. \quad (7.3)$$

Region 2: $0 \leq x \leq L$,

$$\frac{d^2\psi_2(x)}{dx^2} - \frac{2m(V_0 - E)}{\hbar^2}\psi_2(x) = 0. \quad (7.4)$$

Region 3: $L < x < \infty$,

$$\frac{d^2\psi_3(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi_3(x) = 0. \quad (7.5)$$

The general solution for regions 1 and 3, before applying the boundary conditions, will be in the form,

$$\begin{aligned} \psi_1(x) &= Ae^{+ik_0x} + Be^{-ik_0x} \\ \psi_3(x) &= Ce^{+ik_0x} + De^{-ik_0x} \end{aligned} \quad (7.6)$$

where $k_0 = \sqrt{2mE}/\hbar$ represents a *wave number*, and the complex exponent implies the solution is oscillatory due to Euler's formula,

$$e^{ikx} = \cos(kx) + i \sin(kx), \quad i = \sqrt{-1}. \quad (7.7)$$

The complex exponentials in eqns. (7.6) each represent two traveling waves. The terms with positive exponents represent right-traveling waves and terms with a negative exponent represent left-traveling waves. This is important as it allows us to imply certain attributes to regions 1 and 3. In region 1, we can have *incident* waves traveling to the right and *reflected* waves traveling to the left. However, in region 3 we can only have *transmitted* waves traveling to the right, as there is no physical mechanism for there to be waves traveling to the left. Therefore, for region 3, the constant D must equal zero. This situation is indicated in Figure (7.1)

We now consider region 2 where $E < V_0$. For this situation the general solution, before applying the boundary conditions, will be in the form,

$$\psi_{2,1}(x) = Fe^{+k_1x} + Ge^{-k_1x} \quad (7.8)$$

where $k_1 = \sqrt{2m(V_0 - E)}/\hbar$. Because we now have real exponents, the solution is not oscillatory.

Now consider region 2 where $E > V_0$. For this situation the general solution, before applying the boundary conditions, will be in the form,

$$\psi_{2,2}(x) = He^{+ik_2x} + Ke^{-ik_2x} \quad (7.9)$$

where $k_2 = \sqrt{2m(E - V_0)}/\hbar$. Because we again have complex exponents, the solution will be oscillatory.

Continuity conditions at region boundaries require:

$$\begin{aligned} \psi_1(0) &= \psi_2(0) \\ \psi_2(L) &= \psi_3(L) \end{aligned} \quad (7.10)$$

Smoothness conditions at region boundaries require:

$$\begin{aligned} \left. \frac{d\psi_1(x)}{dx} \right|_{x=0} &= \left. \frac{d\psi_2(x)}{dx} \right|_{x=0} \\ \left. \frac{d\psi_2(x)}{dx} \right|_{x=L} &= \left. \frac{d\psi_3(x)}{dx} \right|_{x=L} \end{aligned} \quad (7.11)$$

We will now use the above boundary conditions to simplify the problem.

Case a. $E < V_0$

The continuity conditions yield at $x = 0$,

$$A + B = F + G, \quad (7.12)$$

and smoothness conditions yield at $x = 0$,

$$ik_0A - ik_0B = k_1F - k_1G. \quad (7.13)$$

We also have for continuity conditions at $x = L$

$$Fe^{k_1L} + Ge^{-k_1L} = Ce^{ik_0L}, \quad (7.14)$$

and smoothness conditions yield at $x = L$,

$$k_1Fe^{k_1L} - k_1Ge^{-k_1L} = ik_0Ce^{ik_0L}. \quad (7.15)$$

Recall that constant D has been set to zero as left-traveling waves are not possible in region 3. This means we only have 4 equations but 5 unknowns: A , B , C , F and G . So the system is under-determined.

Even though the particle energy E is less than the barrier potential V_0 , the above equations show that there is a *non-zero* chance of a right-moving particle, the *incident* particle, passing through the barrier. Now the intensity of a wave is proportional to its amplitude squared. Therefore, defining the right traveling wavefunction in region 1 as

$$\psi_{1,R} = Ae^{ik_0x} \quad (7.16)$$

the amplitude squared is simply equal to the wavefunction multiplied by its complex conjugate. Let's define the *probability* of the right-moving particle in region 1 as being equal to its intensity; therefore, its *probability density function* becomes,

$$P_{1,R} = \psi_{1,R}^* \psi_{1,R} = (A^* e^{-ik_0x})(Ae^{ik_0x}) = A^* A. \quad (7.17)$$

Similarly, let's define the probability density function of a left-moving particle in region 1 as being equal to

$$P_{1,L} = \psi_{1,L}^* \psi_{1,L} = (B^* e^{ik_0x})(Be^{-ik_0x}) = B^* B. \quad (7.18)$$

Finally, let's define probability density function of a right-moving particle in region 3 as being equal to

$$P_{3,R} = \psi_{3,R}^* \psi_{3,R} = (C^* e^{-ik_0x})(Ce^{ik_0x}) = C^* C. \quad (7.19)$$

A particle traveling to the right in region 3 must have experienced *transmission* through the barrier of region 2. Conversely, a particle traveling to the left in region 1 must have experienced *reflection* from the barrier of region 2. This is illustrated in Figure (7.1). To move forward in our analysis, we introduce the concept of *transmission* and *reflection* coefficients; namely, T and R respectively. We define these coefficients as being equal to the ratios of their respective probabilities with respect to of the probability of the particle moving to the right in region 1. Thus, we obtain

$$T = \frac{P_{3,R}}{P_{1,R}} = \frac{C^* C}{A^* A}, \quad (7.20)$$

which represents the probability that particle passes through the barrier (*quantum tunneling*); and

$$R = \frac{P_{1,L}}{P_{1,R}} = \frac{B^* B}{A^* A}, \quad (7.21)$$

which represents the probability that the particle has been reflected from the barrier (*quantum reflection*).

If the energy of the incident particle is significantly lower than the barrier height V_0 , then it is to be expected that there will be a large reflectivity coefficient and a small transmission coefficient.

After performing some rather lengthy algebraic manipulation on eqns. (7.12), (7.13), (7.14) and (7.15), and making use of the hyperbolic relationships

$$\cosh(x) = \frac{e^x + e^{-x}}{2}, \quad \sinh(x) = \frac{e^x - e^{-x}}{2}, \quad (7.22)$$

we obtain

$$T = \frac{1}{\frac{V_0^2}{4E(V_0 - E)} \sinh^2(k_1 L) + 1}. \quad (7.23)$$

We know that the incident particle must be either transmitted or reflected as there are no alternative possibilities. Therefore, $T + R = 1$ and the reflectivity coefficient is given by

$$R = 1 - T \quad (7.24)$$

Case b. $E > V_0$

The continuity conditions yield at $x = 0$,

$$A + B = H + K, \quad (7.25)$$

and smoothness conditions yield at $x = 0$,

$$ik_0A - ik_0B = k_2H - k_2K. \quad (7.26)$$

We also have for continuity conditions at $x = L$

$$He^{ik_2L} + Ke^{-ik_2L} = Ce^{ik_0L}, \quad (7.27)$$

and smoothness conditions yield at $x = L$,

$$k_2He^{k_2L} - k_2Ke^{-k_2L} = ik_0Ce^{ik_0L}. \quad (7.28)$$

Similar to Case a, after performing some rather lengthy algebraic manipulation on eqns. (7.25), (7.26), (7.27) and (7.28), we obtain

$$T = \frac{1}{\frac{V_0^2}{4E(E - V_0)} \sin^2(k_2L) + 1}. \quad (7.29)$$

Again we have $T + R = 1$, and the reflectivity coefficient is given by

$$R = 1 - T \quad (7.30)$$

We can now explore how T and R change as E varies from being very much smaller than V_0 to being much larger. To facilitate this we introduce the new variable $\eta = E/V_0$. Consider a system with the following parameters:

$$\begin{aligned} L &= 4.5 \times 10^{-10}, & [\text{m}] \\ V_0 &= 1.6 \times 10^{-18}, & [\text{J}] \\ m &= 9.11 \times 10^{-31}, & [\text{kg}] \\ \hbar &= 1.055 \times 10^{-34}, & [\text{J s}] \end{aligned} \quad (7.31)$$

We now let η vary from 0 to 4 and plot T and R in Figure (7.2), using eqn. (7.23) when $\eta < 1$ and eqn. (7.29) when $\eta > 1$. We avoid $\eta = 1$ as this produces a *divide-by-zero* error. Transmission T , clearly starts before $E = 1$ and reflection R , continues even when E is much larger than V_0 . This demonstrates the difference between *classical* mechanics and *quantum* mechanics, because in the latter situation reflection would stop abruptly and transmission would only start when $\eta > 1$. The oscillations are due to the $\sin()$ term in eqn. (7.29) as opposed to the $\sinh()$ term in eqn. (7.23).

We now consider a problem taken from [Wan-06] with the same parameters as in eqn. (7.31), except that we reduce the barrier width to

$$L = 1.8 \times 10^{-10}. \quad (7.32)$$

The system has an *incident* particle with *unit intensity* and an energy $E = 0.6V_0$. This means that we are now able to solve eqns. (7.12), (7.13), (7.14) and (7.15), because variable A is equal to 1, which reduces the problem to four equations and four unknowns.

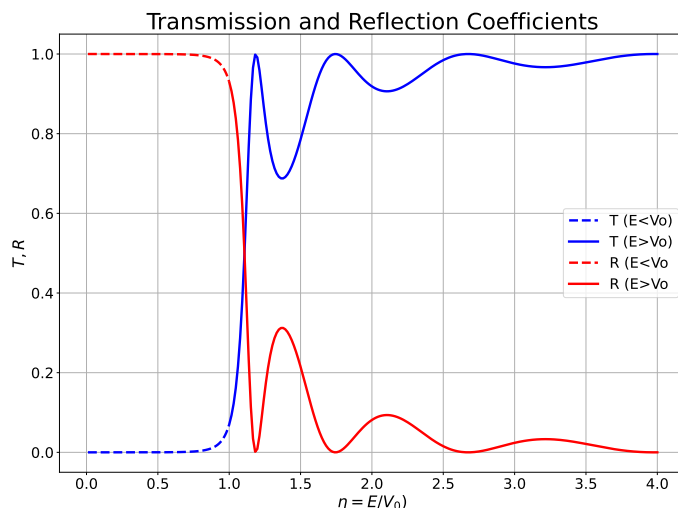


Figure 7.2: Plots showing how the *transmission* and *reflection* coefficients T and R change as the particle energy ratio $\eta = E/V_0$, varies from 0 to 4. Transmission T , clearly starts before $E = 1$ and reflection R , continues even when E is much larger than V_0 .

Table 7.1: Tunneling problem parameter values

A	=	1.0	(specified)	
B	=	0.1815481747	-	$i0.9352973513$,
C	=	-0.1436753713	-	$i0.2676126167$,
F	=	0.0180237704	+	$i0.03354866193$,
G	=	1.1635244040	-	$i0.96884601320$.

The parameter solution values are given in Table (7.1), and a plot of the resulting wavefunction as it transitions through the barrier is shown in Figure (7.3).

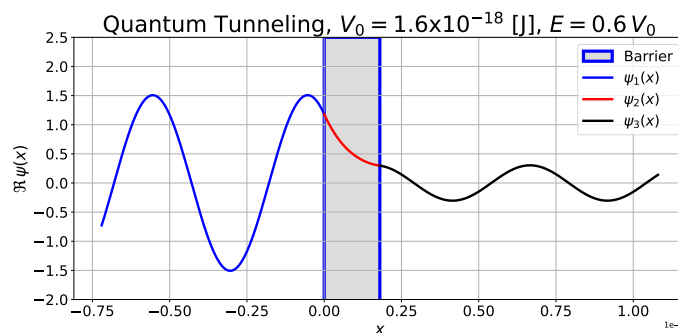


Figure 7.3: Plot of the *real part* of the tunneling problem solutions $\psi_1(x)$, $\psi_2(x)$ and $\psi_3(x)$ for regions 1, 2 and 3 respectively. It illustrates how the incident wavefunction transitions through a potential barrier. Note how the wavefunction is non-oscillatory as it is attenuated through the barrier, and becomes oscillatory again once it exits the barrier. Also, how the three wavefunctions form a continuous smooth curve throughout, as demanded by the continuity conditions at region boundaries.

8 The Hydrogen Atom

In the hydrogen atom analysis below we largely follow D. Griffiths [Gri-95]. The model we will use is a positively charged proton with a negatively charged electron circling around it. We will consider the proton to be essentially stationary, as its mass is very much greater than that of the electron. This means that we do not have to use the reduced mass of the proton, as discussed in Appendix (2). They are held together by

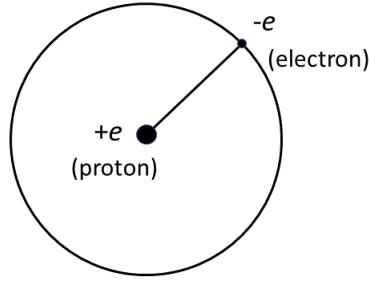


Figure 8.1: The Hydrogen Atom.

Coulomb's law, eqn. (2.1), such that the potential energy of the electron is

$$V(r) = \int_r^\infty \frac{|e^2|}{4\pi\epsilon_0 r^2} dr = -\frac{e^2}{4\pi\epsilon_0 r}, \quad (8.1)$$

where e represents unit charge, r the orbit radius, and ϵ_0 vacuum permittivity. The calculations are performed in *spherical coordinates*, see Figure (4.5), and follow essentially the same analysis as that outlined in Section (4.4), where a *separable* approach is adopted. This assumes the solution for the wave function to be of the form,

$$\boxed{\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)}. \quad (8.2)$$

The *angular* part of the Hydrogen atom wave function solution takes the the same form as the *spherical harmonics* of eqn. (4.70), i.e.

$$Y_\ell^m(\theta, \phi) = \epsilon \sqrt{\frac{(2\ell + 1)(\ell - |m|)!}{4\pi(\ell + |m|)!}} e^{im\phi} P_\ell^m(\cos \theta), \quad (8.3)$$

where $\epsilon = (-1)^m$ for *magnetic quantum number* $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$.

The *radial* part of the Hydrogen atom Schrödinger equation is the same as eqn(4.72), i.e.

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = \ell(\ell + 1)R. \quad (8.4)$$

However, this equation now needs to account for the non-zero potential $V(r)$; and, after applying the change of variable

$$u(r) \equiv rR(r), \quad (8.5)$$

it simplifies to,

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m} \frac{\ell(\ell + 1)}{r^2} \right] u = Eu. \quad (8.6)$$

Equation (8.6) can be further simplified by letting

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}, \quad (8.7)$$

when it becomes

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{(\kappa r)} + \frac{\ell(\ell + 1)}{(\kappa r)^2} \right] u. \quad (8.8)$$

We now let

$$\rho \equiv \kappa r, \quad \text{and} \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa}, \quad (8.9)$$

when we obtain,

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u. \quad (8.10)$$

This is a difficult equation to solve, and we start by examining the asymptotic form of the solutions.

As $\rho \rightarrow \infty$ the constant term in the brackets dominates, and problem becomes approximately

$$\frac{d^2u}{d\rho^2} = u, \quad (8.11)$$

with general solution,

$$u(\rho) = Ae^{-\rho} + Be^{\rho}. \quad (8.12)$$

But e^{ρ} blows up as $\rho \rightarrow \infty$, so $B = 0$, and for large ρ we have

$$\boxed{u(\rho) \approx Ae^{-\rho}.} \quad (8.13)$$

However, when $\rho \rightarrow 0$, the centrifugal term dominates and we have approximately

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u, \quad (8.14)$$

with general solution,

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}. \quad (8.15)$$

But for this case $\rho^{-\ell}$ blows up as $\rho \rightarrow 0$, so $D = 0$, and for small ρ we have

$$\boxed{u(\rho) \approx C\rho^{\ell+1}.} \quad (8.16)$$

It should be noted that whilst this argument does not hold for $\ell = 0$, the conclusion, eqn. (8.16), is correct.

We now need a function say, $w(\rho)$, that will provide a bridge between $u(\rho)$ for $\rho \rightarrow$ large and $u(\rho) \rightarrow$ small, i.e.

$$\boxed{u(\rho) = \rho^{\ell+1}e^{-\rho}w(\rho).} \quad (8.17)$$

The hope is that this will simplify matters from eqn. (8.10).

Differentiating $u(\rho)$ we obtain

$$\begin{aligned} \frac{du}{d\rho} &= \rho^{\ell}e^{-\rho} \left[(\ell+1-\rho)w + \rho \frac{dw}{d\rho} \right], \\ \frac{d^2u}{d\rho^2} &= \rho^{\ell}e^{-\rho} \left\{ \left[-2\ell - 2 + \rho + \frac{\ell(\ell+1)}{\rho} \right] w + 2(\ell+1-\rho) \frac{dw}{d\rho} + \rho \frac{d^2w}{d\rho^2} \right\} \end{aligned} \quad (8.18)$$

Substituting eqns. (8.10) and (8.17) into the second of eqns.(8.18), we obtain after rearranging,

$$\rho \frac{d^2w}{d\rho^2} + 2(\ell+1-\rho) \frac{dw}{d\rho} + [\rho_0 - 2(\ell+1)]w = 0. \quad (8.19)$$

We now assume that $w(\rho)$ can be expressed as the following power series in ρ ,

$$w(\rho) = \sum_{j=0}^{\infty} a_j \rho^j. \quad (8.20)$$

The problem now reduces to evaluating the coefficients (a_0, a_1, a_2, \dots) . Differentiating term by term and manipulating the final form,

$$\frac{dw}{d\rho} = \sum_{j=0}^{\infty} j a_j \rho^{j-1} = \sum_{j=-1}^{\infty} (j+1) a_{j+1} \rho^j = \sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^j. \quad (8.21)$$

Differentiating again,

$$\frac{d^2 w}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^{j-1}. \quad (8.22)$$

Inserting these equations into eqn.(8.19) yields

$$\begin{aligned} \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^j + 2(\ell+1) \sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^j \\ - 2 \sum_{j=0}^{\infty} j a_j \rho^j + [\rho_0 - 2(\ell+1)] \sum_{j=0}^{\infty} a_j \rho^j = 0. \end{aligned} \quad (8.23)$$

On equating the coefficients of like powers of ρ we obtain,

$$j(j+1) a_{j+1} + 2(\ell+1)(j+1) a_{j+1} - 2j a_j + [\rho_0 - 2(\ell+1)] a_j = 0 \quad (8.24)$$

which, on rearranging, yields the following recursive equation

$$\boxed{a_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} a_j.} \quad (8.25)$$

The process starts with $a_0 = A$ (an overall constant that will eventually be fixed by normalization) and eqn. (8.25) gives us a_1 . Then from a_1 and eqn. (8.25) we get a_2 and so on.

Now, for large j , which corresponds to large ρ , the coefficients become

$$a_{j+1} \approx \frac{2j}{j(j+1)} a_j = \frac{2}{j+1} a_j; \quad (8.26)$$

and, therefore

$$a_j \approx \frac{2^j}{j!} A. \quad (8.27)$$

If we were to take this result to be the answer we are seeking, our bridging function would become

$$w(\rho) = A \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = A e^{2\rho}, \quad (8.28)$$

when eqn. (8.17) yields

$$u(\rho) = A \rho^{\ell+1} e^\rho, \quad (8.29)$$

which blows up for large ρ . The resulting positive exponential is precisely the asymptotic behavior we didn't want in eqn. (8.17), even though it is to be expected. This is because it does represent the asymptotic form of some solutions to the radial equation. However, they are not ones we require because they cannot be normalized. For the result of eqn. (8.28) to be useful, it is clear that the series must terminate. This means there must be some $j = j_{\max}$ such that

$$\boxed{a_{j_{\max}+1} = 0.} \quad (8.30)$$

The effect of this, due to recursive eqn. (8.25), is that coefficients $a_j = 0$, $j > j_{\max}$, and this provides the key to unlocking a solution to the radial equation.

For the foregoing argument to be true, we see from eqn. (8.25) that we must have

$$2(j_{\max} + \ell + 1) - \rho_0 = 0. \quad (8.31)$$

Defining

$$n = j_{\max} + \ell + 1, \quad (8.32)$$

the so-called *principal quantum number*, we obtain

$$\boxed{\rho_0 = 2n.} \quad (8.33)$$

But from eqns. (8.7) and (8.9)

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}, \quad (8.34)$$

so we are now able define the allowed orbital energies as

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots} \quad (8.35)$$

This is the famous *Bohr energy equation* (2.11), derived in Section (2). A list of energy levels for the hydrogen atom is given in Table (2.1) and plotted in Figure (2.1).

Combining eqns. (8.9) and (8.33) we find that

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} = \frac{1}{an}, \quad (8.36)$$

where

$$\boxed{a \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m},} \quad (8.37)$$

is the so-called *Bohr radius*. It also follows from eqn. (8.9) that

$$\rho = \frac{r}{an}. \quad (8.38)$$

We now have reached a point where the spatial wave functions for hydrogen are labeled by three quantum numbers, namely n, ℓ, m , so that eqn (8.2) becomes

$$\psi_{n,\ell,m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell}^m(\theta, \phi), \quad (8.39)$$

where, from eqns. (8.5) and (8.17)

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} w(\rho), \quad (8.40)$$

and $w(\rho)$ is a polynomial of degree $j_{\max} = n - \ell - 1$ in ρ , whose coefficients are determined by the recursion equation

$$\boxed{a_{j+1} = \frac{2(j + \ell + 1 - n)}{(j + 1)(j + 2\ell + 2)} a_j.} \quad (8.41)$$

We are now in a position to calculate the state of lowest energy, the *ground state*, when $n = 1$. Using standard physical constant values, we obtain

$$E_1 = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ [eV]}. \quad (8.42)$$

Thus, 13.6 [eV] corresponds to the *binding energy* of hydrogen, or the energy that would need to be imparted to the electron in order to *ionize* the atom. From eqn. (8.32) we see that this result means that $\ell = 0$ and, from eqn. (4.66), we must also have $m = 0$. Therefore, the wave function becomes

$$\psi_{100}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi). \quad (8.43)$$

The recursion formula truncates after the first term (Equation (8.41) with $j = 0$ yields $a_1 = 0$), so $w(\rho)$ is a constant, a_0 , and

$$R_{10}(r) = \frac{a_0}{a} e^{-r/a}. \quad (8.44)$$

Normalizing this equation in accordance with eqn. (3.6) we have

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|a_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr = |a_0|^2 \frac{a}{4} = 1, \quad (8.45)$$

so $a_0 = 2/\sqrt{a}$. Since from eqn. (4.70) we have $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$, so

$$\boxed{\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}.} \quad (8.46)$$

From eqn. (8.35) we see that for $n = 2$ we have

$$E_2 = \frac{-13.6}{4} = -3.4 \text{ [eV]}; \quad (8.47)$$

which represents the first *excited states*, where we can have $\ell = 0$, when $m = 0$, or $\ell = 1$, when $m = -1, 0, 1$. Thus, there are four different states that all have the same energy. For $\ell = 0$ the recursive relation, eqn. (8.41) gives

$$a_1 = -a_0 \text{ (using } j = 0\text{)}, \quad \text{and } a_2 = 0 \text{ (using } j = 1\text{)}, \quad (8.48)$$

so $w(\rho) = a_0(1 - \rho)$, and hence

$$R_{20}(r) = \frac{a_0}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a}. \quad (8.49)$$

For $\ell = 1$ the recursive equation terminates the series after just one term, so $w(\rho)$ is a constant and we find

$$R_{21}(r) = \frac{a_0}{4a^2} r e^{-r/2a}. \quad (8.50)$$

For each case of R_{20} and R_{21} , the constant a_0 is to be determined by normalization.

For arbitrary n . the possible values of ℓ consistent with eqn (8.41) are

$$\ell = 0, 1, 2, \dots, n - 1. \quad (8.51)$$

For each ℓ , we see from eqn. (4.66) that there are $(2\ell + 1)$ possible values of m , so the total *degeneracy* (see Section (3.3)) of the energy level E_n is

$$d(n) = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2. \quad (8.52)$$

The polynomial $w(\rho)$, with coefficients defined by recursion eqn. (8.41), is a function well known to applied mathematicians. Apart from normalization, it can be written as

$$w(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho), \quad (8.53)$$

where

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_q(x) \quad (8.54)$$

is an *associated Laguerre polynomial* and

$$L_q(x) \equiv e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q) \quad (8.55)$$

is the q th *Laguerre polynomial*. So the radial part of the wave function, eqn. (8.40), becomes

$$R_{n\ell}(r) = \frac{1}{r} \left(\frac{r}{an} \right)^{\ell+1} e^{-r/an} L_{n-\ell-1}^{2\ell+1}(2r/na), \quad (8.56)$$

The first few Laguerre polynomials are listed in Table (8.1) and some associated Laguerre polynomials are listed in Table (8.2). The first few radial wave functions are listed in Table (8.3) and plotted in Figure (8.2).

Substituting eqn. (8.56) into eqn. (8.2), the normalized hydrogen wave functions become

$$\psi_{n\ell m} = \sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-r/na} \left(\frac{2r}{na} \right)^\ell L_{n-\ell-1}^{2\ell+1}(2r/na) Y_\ell^m(\theta, \phi), \quad (8.57)$$

where $a = 0.529^{-10}$, see eqn. (8.37).

Note: Equation (8.57) is a corrected version of the wave function given on page 139 of [Gri-95]. It is one of the very few realistic systems that can be solved in exact closed form. They are also mutually orthogonal, i.e.

$$\int \psi_{n\ell m}^* \psi_{n'\ell'm'} r^2 \sin \theta \, dr \, d\theta \, d\phi = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}. \quad (8.58)$$

Some example 3D plots of the hydrogen *wave functions* $\psi(r, \theta, \phi)$, and *probability density functions* $\rho = |\psi(r, \theta, \phi)|^2$, are included below in Figures (8.3) and (8.4).

Table 8.1: The first few Laguerre polynomials, $L_q(x)$.

$L_0 = 1$
$L_1 = -x + 1$
$L_2 = x^2 - 4x + 2$
$L_3 = -x^3 + 9x^2 - 18x + 6$
$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$
$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$
$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 750$

Table 8.2: Some associated Laguerre polynomials, $L_{q-p}^p(x)$.

$L_0^0 = 1$	$L_0^2 = 2$
$L_1^0 = -x + 1$	$L_1^2 = -6x + 18$
$L_2^0 = x^2 - 4x + 2$	$L_2^2 = 12x^2 - 96x + 144$
$L_0^1 = 1$	$L_0^3 = 6$
$L_1^1 = -2x + 4$	$L_1^3 = -24x + 96$
$L_2^1 = 3x^2 - 18x + 18$	$L_2^3 = 60x^2 - 600x + 1200$

Table 8.3: The first few radial wave functions for hydrogen, $R_{n\ell}(r)$.

$R_{10} = 2a^{-3/2} \exp(-r/a)$
$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a}\right) \exp(-r/2a)$
$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \left(\frac{r}{a}\right) \exp(-r/2a)$
$R_{30} = \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right) \exp(-r/3a)$
$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a}\right) \left(\frac{r}{a}\right) \exp(-r/3a)$
$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$
$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4} \frac{r}{a} + \frac{1}{8} \left(\frac{r}{a}\right)^2 - \frac{1}{192} \left(\frac{r}{a}\right)^3\right) \exp(-r/4a)$
$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a}\right)^2\right) \frac{r}{a} \exp(-r/4a)$
$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12} \frac{r}{a}\right) \left(\frac{r}{a}\right)^2 \exp(-r/4a)$
$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$

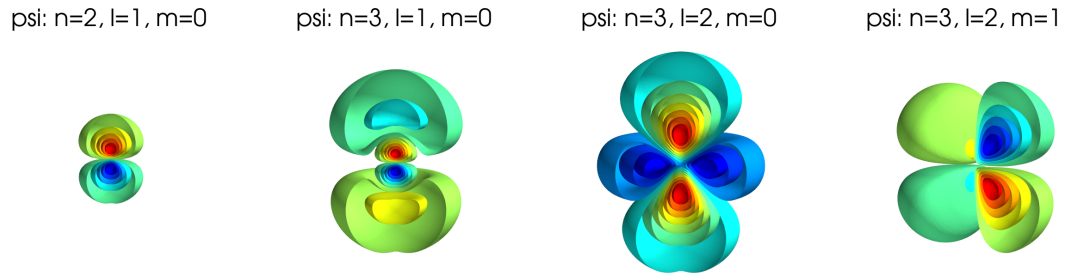


Figure 8.3: Examples showing *wave function* solutions $\Re(\psi_{n\ell m})$ to the Schödinger equation for a hydrogen atom. Plots were generated in *python* using the *mayavi* package, and include 3D isosurfaces of the solution.

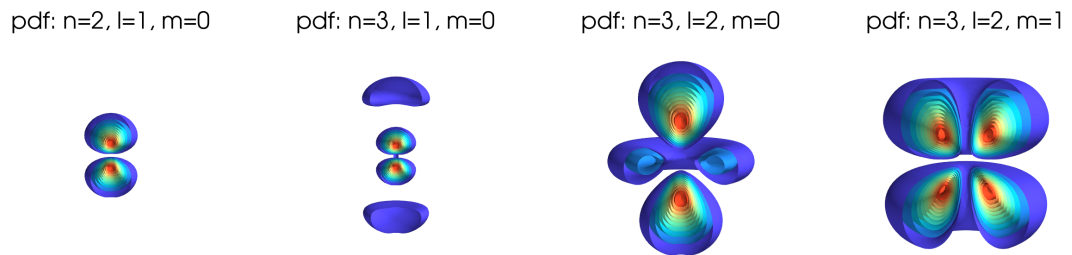


Figure 8.4: Examples showing *probability density function* solutions $\rho = |\psi_{n\ell m}|^2$ to the Schödinger equation for a hydrogen atom. Plots were generated in *python* using the *mayavi* package, and include 3D isosurfaces of the solution.

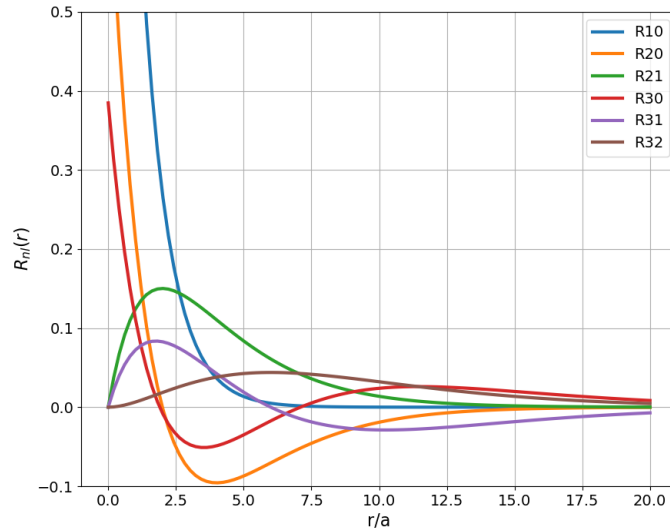


Figure 8.2: Plots of the first few hydrogen radial wave functions, $R_{nl}(r)$.

It is worth emphasizing the following paragraph by D. Griffiths [Gri-95]:

In principle, if you put a hydrogen atom into some stationary state ψ_{nlm} , it should stay there forever. However, if you tickle it slightly (by collision with another atom, say, or by shining light on it), then the atom may undergo a transition to some other stationary state - either by absorbing energy and moving up to a higher-energy state, or by giving off energy (typically in the form of electromagnetic radiation) and moving down⁷. In practice such perturbations are always present; transitions (or, as they are sometimes called, "quantum jumps") are constantly occurring, and the result is that a container of hydrogen gives off light (photons), whose energy corresponds to the *difference* in energy between the initial and final states:

$$E_{\text{end}} = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right). \quad (8.59)$$

8.1 Hydrogen atom degeneracy

The degree of degeneracy of a Hydrogen atom is calculated from the number of possible linearly independent energy eigenstates corresponding to the energy E_n of the atom. For a hydrogen atom, the energy eigenstates are derived from its wave function $\Psi_{n\ell m}$, where:

- Principal quantum number $n = 1, 2, 3, \dots$
- Azimuthal or Orbital Angular momentum quantum number $\ell = 0, 1, 2, \dots, n - 1$. So there are n possibilities.
- Magnetic Quantum number $m = 0, \pm 1, \pm 2, \dots, \pm \ell$. So there are $(2\ell + 1)$ possibilities.

Hence for a given Principal quantum number n ,

- The total number of possible energy eigenstates associated with $\Psi_{n\ell m}$, is given by,

⁷By its nature, this involves a time-dependent interaction, so will be governed by the *time-dependent* Schrödinger equation.

$$\begin{aligned}
d &= \sum_{\ell=0}^{n-1} (2\ell + 1) = 1 + 2 \sum_{\ell=1}^{n-1} \ell \pm \sum_{\ell=1}^{n-1} 1 = 1 + 2 \left(\frac{(n-1)n}{2} \right) + (n-1), \\
&= n^2.
\end{aligned} \tag{8.60}$$

Therefore,

$$\boxed{\text{The degree of degeneracy of a Hydrogen atom} = n^2.} \tag{8.61}$$

9 Wave Packet

In quantum mechanics the term *wave packet* is used to denote a wave function describing an *atomic particle* or a *quantum* of energy. In this context it was first introduced in a series of papers in 1926 by Erwin Schrödinger [Kar-09]. Applying the *superposition principle*, he introduced the idea of constructing a wave packet from a weighted sum of wave functions⁸.

It is essential that for a physically realizable wave packet to be represented by a solution to the Schrödinger equation, Ψ , it must conform to the *normalization* restrictions defined in section (3.2.1). i.e.

- Ψ must be square integral
- $\int_{-\infty}^{\infty} \Psi \, dx$ must be finite
- $\Psi \rightarrow 0$ as $x \rightarrow \pm\infty$

Charles Galton Darwin was the first person to investigate Schrödinger's equation for an electron in free space. He published his ideas in 1927 [Dar-27], assuming an initial Gaussian wave packet.

9.1 Free Particle

When we investigated the 1D Infinite Square Well in section (4.1), where $V = 0$, we found that the time independent Schrödinger equation became,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E\psi(x) = 0; \tag{9.1}$$

with the solution,

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{9.2}$$

where we have let $k^2 = \frac{2mE}{\hbar^2}$.

Because we do not have a pair of boundary conditions to impose, this solution represents a *plain wave* where A and B are constants, $k = \sqrt{2mE}/\hbar$, and E can take any positive value.

We also found in section (4.1) that the separable solution gave the time dependence to be,

$$f(t) = \exp(-iEt/\hbar) = e^{-\frac{ik^2\hbar}{2m}t}. \tag{9.3}$$

⁸This is possible because wave functions are solutions to the *linear* Schrödinger equation, so the *superposition principle* applies. The result being that the wave functions *interfere constructively* to form a wave packet confined to a small volume in space, with zero elsewhere. It means that the wave packet itself will also be a solution to the Schrödinger equation.

Combining this with eqn. (9.2) we have, $\Psi(t, x) = \psi(x) * f(t)$, which yields

$$\Psi(t, x) = Ae^{ik(x - \frac{\hbar k}{2m}t)} + Be^{-ik(x - \frac{\hbar k}{2m}t)}. \quad (9.4)$$

The first term of eqn. (9.4) represents a wave traveling to the right and the second term a wave traveling the the left. If we allow k to take on positive and negative values, we can write

$$\Psi(t, x) = Ae^{i(kx - \frac{\hbar k^2}{2m}t)}, \quad (9.5)$$

so that we have

$$k = \pm \frac{\sqrt{2mE}}{\hbar} \begin{cases} k > 0 \implies \text{traveling to the right,} \\ k < 0 \implies \text{traveling to the left.} \end{cases} \quad (9.6)$$

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The speed the wave travels at is equal to the coefficient of t divided by the coefficient of x , i.e. for quantum mechanics

$$v_q = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}. \quad (9.7)$$

The equivalent *classical* velocity of a free particle with kinetic energy $E = \frac{1}{2}mv_c^2$ is,

$$v_c = \sqrt{\frac{2E}{m}} = 2v_q. \quad (9.8)$$

Thus, we see that the velocity of a particle described by a wave function is half that of a particle described by classical theory.

See also the discussion on *group* and *phase* velocities in Section (9.2).

While the above is correct mathematically, unfortunately, plain waves do not conform to the normalization requirements defined above. Therefore, they cannot be normalized, so cannot properly represent a physically realizable wave packet. However, because the Schrodinger equation is linear, any linear combination of wave function solutions will also be a solution. This indicates that *Fourier analysis* may provide a way forward.

It is clear that the square of the absolute value of the time dependent part of eqn. (9.5) will always be equal to unity⁹ and not affect normalization. So, in order to achieve normalization, it only remains to ensure that the wave function at $t = 0$ can be normalized. So, a Fourier series solution over the interval $[-L, +L]$ at time zero would be

$$\Psi(0, x) = \sum_{-\infty}^{\infty} c_n e^{ik_n x}, k_n = n\pi/L, \quad (9.9)$$

where c_n are weighting constants. This gets us closer to a real solution, but it uses discrete values of k_n and a characteristic of Fourier series solutions is that they are periodic; therefore, eqn. (9.9) cannot be normalized as it still does not meet normalization requirements. However, if we use an integral over a continuous variable k instead of a summation of discrete values k_n , we can describe a wave packet that is localized and zero elsewhere. This would be in the form of an *inverse Fourier Transform*, i.e.

$$\Psi(0, x) = \mathcal{F}^{-1}(\phi(k)) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} dk. \quad (9.10)$$

⁹This is because $\exp(-iEt) * \exp(-Et) = \exp(+iEt) \exp(-Et) = 1$, where $*$ implies *conjugation* of the preceding term.

We do not yet know the form of $\phi(k)$, but we can invoke the *Fourier transform* of $\Psi(0, x)$ to obtain it, i.e.

$$\phi(k) = \mathcal{F}(A\Psi(0, x)) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A\Psi(0, x)e^{ikx} dx, \quad (9.11)$$

where A is the normalization constant. Once we know $\phi(k)$ we can use it to find the time dependent Schrödinger equation. This is achieved by including $f(t) = e^{-ik^2\hbar t/2m}$ in the integrand of the inverse Fourier transform of eqn. (9.10), when we obtain

$$\Psi(t, x) = \mathcal{F}^{-1}(\phi(k)f(t)) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)e^{-ik^2\hbar t/2m} e^{ikx} dk. \quad (9.12)$$

So, to construct a time dependent solution $\psi(t, x)$, to the Schrödinger equation for a given wave packet with initial wave function $\psi(0, x)$, we apply the following steps:

- 1 Define initial wave function, $\Psi(0, x)$.
- 2 Calculate normalization constant A from $\Psi(0, x)$, see eqn. (3.8).
- 3 Calculate $\phi(k)$ from the Fourier transform of $A\Psi(0, x)$.
- 4 Calculate $\Psi(t, x)$ from the inverse Fourier transform of $\phi(k)f(t)$.
- 5 Calculate probability density function from $\rho(t, x) = |\Psi(t, x)|^2$.

Example

Step 1: We begin by defining the wave function $\Psi(0, x)$ for the wave packet starting condition (the solution to TISE). We choose it to be,

$$\Psi(0, x) = e^{ik_0x} e^{-x^2/(2\sigma_x^2)} = e^{ik_0x - x^2/(2\sigma_x^2)}, \quad (9.13)$$

where k_0 represents the center of the amplitude function $\phi(k)$ and σ_x the width of the wave packet. The first term above represents the oscillatory component and ensures the wave packet moves from left to right. The second term enforces a Gaussian shaped wave packet. Without the first term the probability density function $\rho(t, x)$, calculated in Step 5, would just spread out over time and not move from left to right - see Figure (9.2).

Step 2: Now we solve for the normalization constant A , from

$$\int_{-\infty}^{\infty} (A\Psi(0, t))^2 dx = 1. \quad (9.14)$$

This yields,

$$A = \left(\frac{1}{\pi\sigma_x^2} \right)^{1/4} \quad (9.15)$$

So, incorporating A into $\psi(0, x)$ the TISE becomes,

$$\Psi(0, x) = \left(\frac{1}{\pi\sigma_x^2} \right)^{1/4} e^{ik_0x - x^2/(2\sigma_x^2)}. \quad (9.16)$$

Step 3: Perform a Fourier transform on normalized $\psi(0, x)$ to obtain $\phi(k)$,

$$\begin{aligned}
\phi(k) &= \mathcal{F}(\Psi(0, x)), \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(0, x) e^{ikx} dx, \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left(\frac{1}{\pi\sigma_x^2} \right)^{1/4} e^{ik_0 x - x^2/(2\sigma_x^2)} e^{ikx} dx, \\
&= \left(\frac{\sigma_x^2}{\pi} \right)^{1/4} e^{-\sigma_x^2 \frac{(k_0 - k)^2}{2}}.
\end{aligned} \tag{9.17}$$

In deriving the above, the computer algebra system Maple was used to solve the integral. Whilst this integral looks formidable, it can be solved manually by manipulating it into the following standard form,

$$I = \int_{-\infty}^{\infty} c e^{-ax^2 - bx} dx = \sqrt{\frac{\pi}{a}} c e^{b^2/4a}, \tag{9.18}$$

where a, b and c are constants.

The key to evaluating this standard form integral is to complete the square in x , i.e.

$$I \rightarrow c e^{\frac{b^2}{4a}} \int_{-\infty}^{\infty} e^{-a(x + \frac{b}{2a})^2} dx \tag{9.19}$$

The solution is finally obtained by evaluating the resulting integral by applying the change of variable $u = x + b/2a$.

Step 4: We now obtain the TDSE by performing the inverse Fourier transform on $\phi(k)f(t)$ to obtain $\Psi(t, x)$,

$$\begin{aligned}
\Psi(t, x) &= \mathcal{F}^{-1}(\phi(k)f(t)) \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)f(t)e^{ikx} dk, \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left(\frac{\sigma_x^2}{2\pi} \right)^{1/4} e^{-\sigma_x^2 \frac{(k_0 - k)^2}{2}} e^{-\frac{ik^2 \hbar t}{2m}} e^{ikx} dk, \\
&= \frac{e^{\frac{i(x - \frac{k_0 \hbar t}{2m})k_0 - \frac{x^2}{2\sigma_x^2}}{1 + i\frac{\hbar t}{\sigma_x^2 m}}}}{(\pi\sigma_x^2)^{1/4} \sqrt{1 + i\frac{\hbar t}{\sigma_x^2 m}}}.
\end{aligned} \tag{9.20}$$

Again, we used maple to perform the integration. Plots of $\Psi(t, x)$ are included in Figure (9.1).

Step 5: The final calculation is to obtain the probability density function,

$$\begin{aligned}
\rho(x, t) &= |\Psi(t, x)|^2, \\
&= \frac{\left(x - \frac{k_0 \hbar t}{m} \right)^2}{\sigma_x \left(1 + \frac{\hbar^2 t^2}{\sigma_x^4 m^2} \right)} \\
&= \frac{1}{\sqrt{\pi} \sigma_x \sqrt{1 + \frac{\hbar^2 t^2}{\sigma_x^4 m^2}}}.
\end{aligned} \tag{9.21}$$

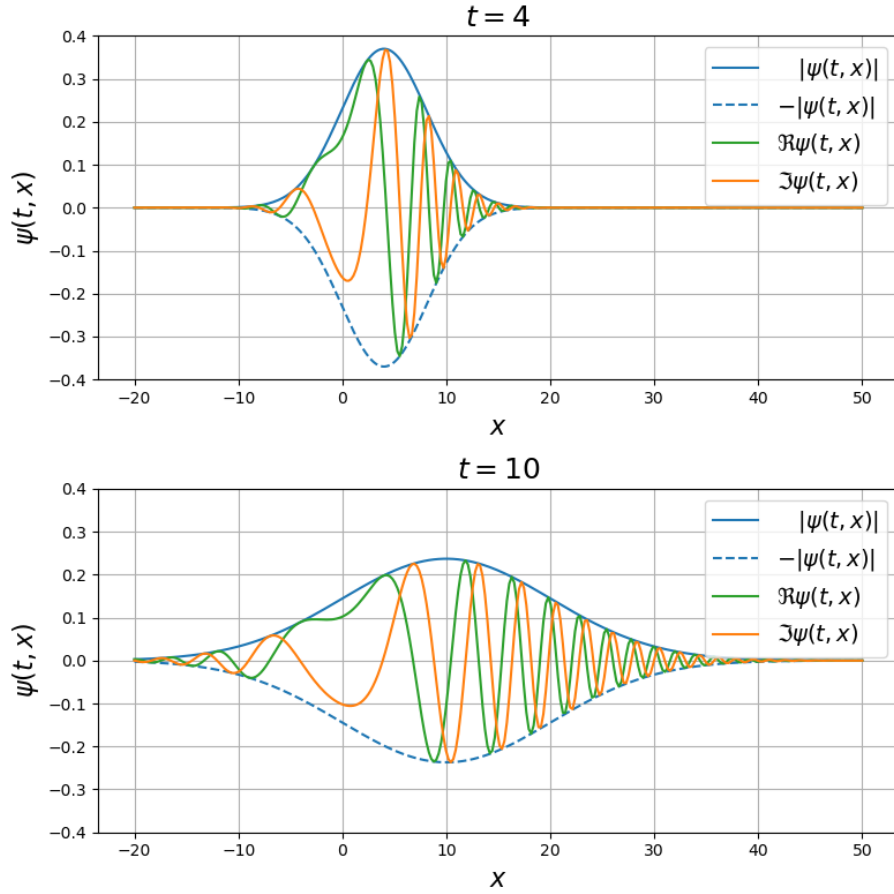


Figure 9.1: Absolute, real and imaginary value plots of wave function $\Psi(t, x)$ at times: $t = [4, 10]$, calculated using *Hartree* units where $k_o = 1$, $\sigma = 1$, $\hbar = 1$ and $m = 1$. The central peak location moves to the right at constant velocity, and its width widens and peak reduces as time increases.

To check that our calculations are correct we need to integrate $\rho(t, x)$ over all space to confirm that it is equal to 1, i.e.

$$\int_{-\infty}^{\infty} \rho(t, x) dx = \int_{-\infty}^{\infty} \left[\frac{e^{-\frac{(x - \frac{k_o \hbar t}{m})^2}{\sigma_x (1 + \frac{\hbar^2 t^2}{\sigma_x^4 m^2})}}}{\sqrt{\pi} \sigma_x \sqrt{1 + \frac{\hbar^2 t^2}{\sigma_x^4 m^2}}} \right] dx = 1. \quad (9.22)$$

Plugging eqn. (9.22) into Maple confirms that indeed it does equate to unity.

Plots of $\rho(t, x)$ are provided in Figure(9.2) for various values of t . The probability density function describes the time-evolving spatial distribution of the Gaussian wave packet, which moves to the right and spreads out over time. The term $\frac{k_o \hbar t}{m}$ in the numerator of the exponential exponent governs the left-to-right movement of its central peak, whilst the terms $\frac{\hbar^2 t^2}{\sigma_x^4 m^2}$ govern its reducing peak and the spreading out of the wave.

9.2 Group and Phase Velocities

The term *group velocity* refers to the speed of a *wave packet* consisting of a low frequency signal modulated (or multiplied) by a higher frequency wave [Gwg-16, p277-8]. The result is a low frequency wave, consisting of a fundamental plus harmonics (a wave packet), that moves along a continuum with group velocity v_g . From De Broglie's wave theory, $E = \hbar \omega$

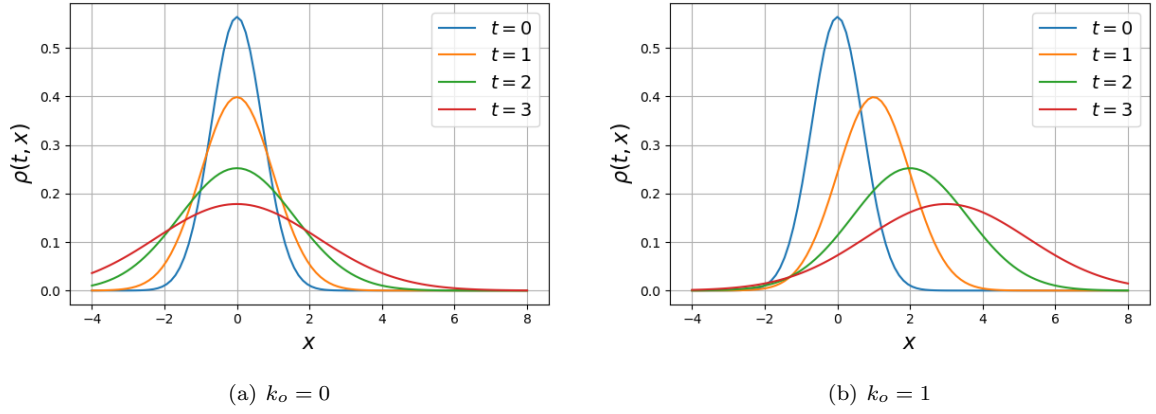


Figure 9.2: Probability density plots at times: $t = [0, 1, 2, 3]$, calculated using *Hartree* units where $\sigma = 1$, $\hbar = 1$ and $m = 1$. (a) With $k_o = 0$ the central peak location remains fixed and its width widens as time increases. This is a physically non-realizable situation. (b) With $k_o = 1$ the central peak location moves to the right at constant velocity and its width widens as time increases.

(see Section (1.4)), and eqn. (9.6), we find that $\omega(k) = \frac{\hbar k^2}{2m}$. *Wave energy* and *information signals* propagate at group velocity, which is defined as being equal to the derivative of the frequency ω , with respect to wavenumber k , i.e.

$$v_g = \left. \frac{d\omega(k)}{dk} \right|_{k=k_o} = \frac{\hbar k_o}{m}. \quad (9.23)$$

If there are a number of spatial dimensions then the group velocity is equal to the gradient of frequency with respect to the wavenumber vector, i.e. $v_g = \nabla\omega(k)|_{k=k_o}$.

The complementary term to group velocity is *phase velocity*, and this refers to the speed of propagation of an individual frequency component of the wave. It is defined as being equal to the ratio of frequency to wavenumber, i.e.

$$v_p = \frac{\omega(k)}{k} = \frac{\hbar k_o}{2m}, \quad (9.24)$$

which is equal to the velocity defined by eqn. (9.7) above.

A wave packet can be thought of as a weighted set of single frequency plane waves, each moving at its own phase velocity. It can also be viewed as the speed at which a particular phase of a wave propagates. In one wave period T , the crest advances one wave length λ , therefore the phase velocity is also given by $v_p = \lambda/T$. We see that this second form is equal to eqn. (9.24) due to the following relationships: wavenumber $k = \frac{2\pi}{\lambda}$ (radians per unit distance) and frequency $\omega = 2\pi\nu$ (radians per second), where $\nu = \frac{1}{T}$ (1/seconds).

Note: For a non-dispersive wave $v_g = v_p$.

Appendices

Appendix A Classical Harmonic Oscillator - Position Probability Density

The *classical harmonic oscillator* is a useful analog for the *quantum oscillator*, see section (6). We assume a friction-less system with weight m , attached to a spring with spring

constant k . From conservation of energy, we have total energy = potential energy + kinetic energy, i.e.

$$\text{P.E.} = \int F dx = \int kx dx = \frac{1}{2}kx^2, \quad (\text{A.1})$$

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{1}{2}m \left(\frac{dx}{dt} \right)^2, \quad (\text{A.2})$$

where x represents displacement and t time. Therefore, total energy becomes,

$$E = \text{P.E.} + \text{K.E.} = \frac{1}{2}kx^2 + \frac{1}{2}m \left(\frac{dx}{dt} \right)^2 = \text{constant}. \quad (\text{A.3})$$

But at the *turning points* when $x = \pm a$, the particle will be stationary for an instant and the kinetic energy will be zero. This gives

$$E = \frac{ka^2}{2}. \quad (\text{A.4})$$

Substituting back into the total energy equation gives

$$\frac{dx}{dt} = \sqrt{\frac{k(a^2 - x^2)}{m}} = v, \quad (\text{A.5})$$

where v represents the particle's velocity. But the particle goes from $-a$ to $+a$, and then back to $-a$ for a complete cycle. Therefore, we can integrate to obtain an expression for the oscillator period T in terms of x , where we obtain

$$T = \int_{-a}^{+a} \sqrt{\frac{m}{k(a^2 - x^2)}} dx = 2\pi \sqrt{\frac{m}{k}}. \quad (\text{A.6})$$

We now let the probability of finding the particle in a narrow region of length Δx at position x be $\rho(x)\Delta x$, and let Δt be the time required for the particle to cross Δx . Here, $\rho(x)$ is the probability density function for the particle's position, x . Since the particle crosses Δx twice during each complete cycle of the oscillation, we have $\rho(x)\Delta x = 2\Delta t/T$ or, $\rho(x) = 2/(vT)$. Rearranging using eqn. (A.5), we finally arrive at

$$\boxed{\rho(x) = \frac{1}{\pi\sqrt{a^2 - x^2}}}. \quad (\text{A.7})$$

As a check, we see that

$$\int_{-a}^a \rho(x) dx = 1. \quad (\text{A.8})$$

This is correct as the particle must be found somewhere within the domain $-a \leq x \leq a$. Also, because the particle travels more slowly towards the turning points and is fastest at the center, the probability of finding the particle at $\pm a$ is greatest. Conversely, the probability of finding the particle at the center is lowest. This is shown clearly in Figure (A.1) for different turning point values.

Appendix B Vector Spaces

A *vector space* is defined as:

*A set of objects (**vectors**) that satisfy the following rules:*

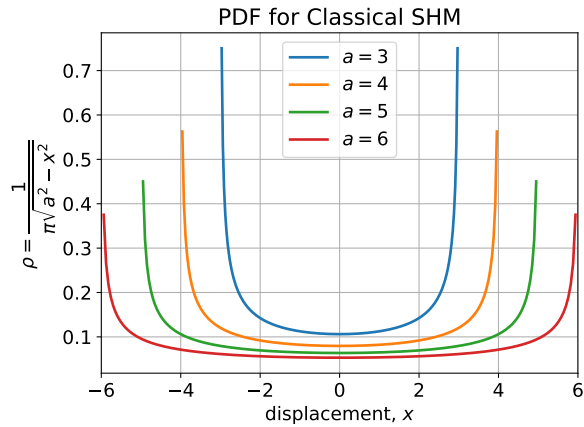


Figure A.1: Some plots showing probability density curves for the classical SHM oscillator, for various turning point values.

For any vectors u, v, w and scalars a, b :

- $u + v$ is also a vector
- au is also a vector
- $u + (v + w) = (u + v) + w$
- $u + v = (v + u) + w$
- 0 (the zero vector) exists
- $-u$ exists
- $a(bu) = ab(u)$
- $1u = u$
- $a(u + v)u = au + av$
- $(a + b)u = au + bu$

The above *rules* make no reference to *numbers* or *arrows/pointers*. This is because, for a vector space, the term *vector* can apply to any set of *objects*. A vector space consists of a set of abstract objects with a defined *structure* and/or *pattern*, not only numerical vectors having the properties of *length* and *direction*. So vector spaces can include real- and complex-valued objects.

In quantum mechanics vectors use the *ket* symbol $|\psi\rangle$, and the reasons will be described subsequently.

B.1 Hilbert Space

For our purposes we need to add the following additional rule to those listed above

- Every convergent sum of vectors must converge to an element inside the vector space.

So, we need,

$$\sum_i^{\infty} |E_i\rangle \rightarrow |\psi\rangle \quad (\text{B.1})$$

This is called a *Hilbert Space*, which is denoted as \mathcal{H} . It is defined as:

A vector space equipped with an *inner product* that is *Cauchy complete*.

An inner product is approximately equal to a *dot product*, and Cauchy complete means that:

Every convergent sequence of vectors (e.g. partial sum of infinite linear combination) converges to an element inside the vector space.

B.2 Inner Product

In quantum mechanics, an *inner product* is usually written using the *bra-ket* notation as

$$\langle \psi | \phi \rangle, \quad (\text{B.2})$$

where $|\phi\rangle$ is a general state in *ket-space*. All physical states are vectors in this space. The space is spanned by an infinite set of basis vectors $|j\rangle$ where j can be a discrete index or a continuous index, such as x .

Similarly, $\langle \psi |$ is a vector in *bra-space*. This is the dual space to *ket-space*, and there is a one-to-one correspondence between the two spaces. Because of the one-to-one relationship, the same principles apply to the *bra-space*. There are corresponding basis vectors $\langle j |$, the dual to the basis vectors in *ket-space*.

An inner product $\langle \psi |$ represents a mapping from vectors to scalars that satisfies the following rules for any vectors ψ, ϕ, ξ and scalar a :

- $\langle \psi | \xi + \phi \rangle = \langle \psi | \xi \rangle + \langle \psi | \phi \rangle$
- $\langle \psi | a\phi \rangle = a \langle \psi | \phi \rangle$
- $\langle \psi | \phi \rangle = \langle \phi | \psi \rangle^\dagger$
- for $|\psi\rangle \neq 0$, $\langle \psi | \psi \rangle > 0$

where \dagger represents the complex conjugate transpose. To clarify, given a *ket* $|\phi\rangle$, the corresponding *bra* $\langle \phi |$ is equal to the *transpose* complex conjugate of $|\phi\rangle$, commonly written as $\langle \phi | = |\phi\rangle^\dagger$. For an operator, we have the corresponding situation $\hat{A}^\dagger = (\hat{A}^*)^T$ - see Appendix (C.1).

In the notation above, a *bra* next to a *ket*, implies *matrix multiplication*. For example, let

$$\langle \psi | = [2 + i2, 3 - i2, 2 + i], \quad |\phi\rangle = \begin{bmatrix} 1 - i2 \\ 2 + i3 \\ -1 + i6 \end{bmatrix}, \quad (\text{B.3})$$

then performing a matrix multiplication yields

$$\langle \psi | \phi \rangle = (10 + i14). \quad (\text{B.4})$$

For quantum mechanics, we emphasize that the following special *inner product rule* (the third rule above) is required

$$\langle \psi | \phi \rangle \stackrel{\text{def}}{=} \langle \phi | \psi \rangle^\dagger, \quad (\text{B.5})$$

where \dagger implies the complex conjugate, and the result can be complex. Also, converting from a “ket” to a “bra” requires a complex conjugate matrix transpose and visa versa. This is referred to as an *anti-linear* operation. So, for the above example we have,

$$\langle \phi | = [1 + i2, 2 - i3, -1 - i6], \quad |\psi\rangle = \begin{bmatrix} 2 - i2 \\ 3 + i2 \\ 2 - i \end{bmatrix}, \quad (\text{B.6})$$

Then performing a matrix multiplication and taking the complex conjugate of the result yields

$$\langle \phi | \psi \rangle = (10 + i14), \quad (\text{B.7})$$

as expected.

This special rule ensures that the inner product with its self is always *real*, i.e.

$$\langle \phi | \phi \rangle \stackrel{\text{def}}{=} \langle \phi | \phi \rangle^\dagger \quad (\text{real}) \quad (\text{B.8})$$

Also, if we take the square root of the inner product of a ket with its self, i.e. $\sqrt{\langle\phi|\phi\rangle}$, the result is equal to the *magnitude* of the ket $|\phi\rangle$. In addition, two vectors ψ and ϕ are *orthogonal* if their inner product is equal to zero, i.e. $\langle\psi|\phi\rangle = 0$.

The reason for the special rule is that in quantum mechanics we need to interpret inner products on states as being equal to *probabilities*: $\langle\phi|j\rangle\langle j|\phi\rangle$ for fixed j . This equates to the probability of measuring the value j for a particular observable. It is guaranteed to be real by virtue of the special inner-product rule. Again, using the above example, we have

$$\langle\phi| = [1 + i2, 2 - i3, -1 - i6], \quad |\phi\rangle = \begin{bmatrix} 1 - i2 \\ 2 + i3 \\ -1 + i6 \end{bmatrix}, \quad (\text{B.9})$$

Then performing a matrix multiplication and taking the complex conjugate yields the *real* result,

$$\langle\phi|\phi\rangle = \langle\phi|\phi\rangle^\dagger = 55 + i0. \quad (\text{B.10})$$

When the inner product holds, it can be used for *normalization*. This is achieved by taking the inner product of a state with its self, and setting the result equal to one, i.e.

$$\langle\phi(x)|\phi(x)\rangle = 1 \quad (\text{B.11})$$

Practically, this usually involves determining the value of a constant that makes

$$\int_D \rho \, dx = 1. \quad (\text{B.12})$$

where $\rho = |\phi(x)|^2 = \phi(x)^*\phi(x)$ represents a probability density function - see Section (3.2.1).

Appendix C Operators and Commutators

C.1 Operators

Operators act on functions, and corresponds to how functions act on quantities. However, when an operator acts on a function, it results in another function. For example, when an operator \hat{A} acts on wavefunction $\psi(x)$ we get another function $\phi(x)$, i.e.

$$\hat{A}\psi(x) = \phi(x). \quad (\text{C.1})$$

This is similar to how a function $f(x)$ acts on a quantity $x = a$, when we get another quantity, b .

By convention, operators act on expressions immediately to their right. For two adjacent operators, there are two separate operations: the first by the right hand operator operating on the expression to its right, and the second operation consists of the left hand operator operating on the result of the first operation.

By way of example, consider the following operators $\hat{A}, \hat{B}, \hat{C}$, acting on the particular wavefunction $\psi(t, x) = e^{kx - \omega t}$, where $k = 2\pi/\lambda$ is the wave-vector and λ is the wavelength of the spatial frequency, x represents position and $\omega = 2\pi\nu$ is the angular frequency, with ν the frequency of the wave,

$$\begin{aligned} \hat{A}\psi &= \frac{\partial}{\partial t}\psi &= i\omega\psi(x), \\ \hat{B}\psi &= x\frac{\partial}{\partial x}\psi &= ikx\psi(x), \\ \hat{C}\psi &= \alpha\psi(x). \end{aligned} \quad (\text{C.2})$$

Operators, in general, have the following properties:

- $(\hat{A} + \hat{B})\psi = (\hat{A}\psi + \hat{B}\psi,$
- $\beta\hat{B}\psi = \beta(\hat{B}\psi),$
- $\hat{A}\hat{B}\psi = \hat{A}(\hat{B}\psi),$ \hat{B} operates on ψ , and then \hat{A} operates on $(\hat{B}\psi),$
- $\hat{A} = \hat{A}^\dagger,$ Hermitain (self-adjoint),
- $\hat{A}\hat{B} \neq \hat{B}\hat{A},$ In general, operators do not *commute*,

where $\hat{A}^\dagger = (\hat{A}^*)^T$, and $*$ represent the complex conjugate.

We have seen from eqn. (3.1) that the the *Schrödinger equation* can be written as,

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V(x)\Psi. \quad (\text{C.3})$$

But the *energy operator* is defined as

$$\hat{E} = i\hbar\frac{\partial}{\partial t}; \quad (\text{C.4})$$

and the *momentum operator* is defined as,

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}. \quad (\text{C.5})$$

So, therefore, the Schrödinger equation can also be written as

$$\hat{E}\Psi = \frac{p^2}{2m}\Psi + V(x)\Psi. \quad (\text{C.6})$$

Also, the right hand side of the Schrödinger equation can utilize the *Hamiltonian Operator* notation, defined as

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \quad (\text{C.7})$$

The symbol \hat{H} represents the *total energy* of the particle of mass m in the *potential field* $V(x)$. So, using the Hamiltonian operator, the Schrodinger equation can be written as in eqn. (3.3), i.e.

$$\hat{H}|\psi(t)\rangle = \hat{E}|\psi(t)\rangle, \quad (\text{C.8})$$

C.2 Commutators

Commutators are used in quantum mechanics in the context of operators.

States in quantum mechanics are represented by vectors in a Hilbert space, and operators are maps from states to states.

Given two operators A and B, their commutator is defined as $[A,B] = AB - BA$, where the order of operation is important.

There are various uses of commutators, but probably the most useful one is between *observables*. Given two operators that correspond to physically observable quantities (this means that they must be Hermitian operators), if their commutator is equal to zero, it means we can simultaneously measure both physical quantities. Also, it means that the commutator is a constant of the motion, i.e. its expectation value will be independent of time. However, if the commutator is non-zero, it means that we cannot simultaneously know the values of both the observables. Consequently, there is an *uncertainty* relationship between the observables, with the commutator providing information on how

knowledge of one observable limits how well the other can be measured. For example, the famous *Heisenberg Uncertainty* principle is a direct consequence of the fact that *position* and *momentum* operators do not commute.

Commutators, in general, have the following properties:

$$\begin{aligned}
 \bullet \quad [\hat{A}, c] &= 0, \\
 \bullet \quad [\hat{A}, \hat{A}] &= 0, \\
 \bullet \quad [\hat{A}, \hat{B}] &= -[\hat{B}, \hat{A}], \\
 \bullet \quad [c\hat{A}, \hat{B}] &= [\hat{A}, c\hat{B}] = c[\hat{A}, \hat{B}], \\
 \bullet \quad [\hat{A}, \hat{B} \pm \hat{C}] &= [\hat{A}, \hat{B}] \pm [\hat{A}, \hat{C}], \\
 \bullet \quad [\hat{A}\hat{B}, \hat{C}] &= \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}, \\
 \bullet \quad [\hat{A}, \hat{B}\hat{C}] &= \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C},
 \end{aligned}$$

where \hat{A} , \hat{B} and \hat{C} are operators, and c is a constant.

Appendix D Quantum States

In quantum mechanics we represent a particle by a *vector* in a *vector space*. In this situation, the vector in a vector space represents a *quantum state* of the particle and represents all the physical properties of the particle.

Vector spaces are used extensively in Quantum mechanics to calculate *quantum states* and other quantum properties of a system, such as: position (x_1, x_2, x_3, \dots) , momentum (p_1, p_2, p_3, \dots) , energy (E_1, E_2, E_3, \dots) , etc., as well as all the associated *probabilities*.

Instead of using a standard symbol for a quantum state, such as $\vec{\psi}$, we use a different notation called a *ket* - see Appendix (B.2), which has the symbol $|\psi\rangle$. This symbol was first introduced by *Paul Dirac* [Dir-39] and is therefore known as the Dirac notation. It is still a vector but provides a powerful short hand for calculating and manipulating quantum states.

Because we are dealing primarily with *linear* systems, a quantum state can be represented by the *superposition* of all possible outcomes of a measurement, for example energy. We would therefore have a list of possible energy outcomes represented by energy kets, and could represent our quantum state vector by a linear combination of them. For example, using *ket* notation ,

$$|\psi\rangle = c_1 |E_1\rangle + c_2 |E_2\rangle + c_3 |E_3\rangle + \dots = \sum_{i=1}^{\infty} c_i |E_i\rangle, \quad (\text{D.1})$$

where the coefficients c_i , relate to the probability of the outcome of its associated energy, E_i . However, not all states are discrete, some are *continuous*, e.g. *position*. For the position vector we need a different representation that is suitable for a continuous state, where we use an integral instead of a summation, and a function $c(x)$, instead of coefficients c_i . So the representation becomes,

$$|\psi\rangle = \int dx c(x) |x\rangle. \quad (\text{D.2})$$

The limits for this integral are implicitly $\pm\infty$.

Now consider the position wave function $\psi(x)$. Here the state vector becomes

$$|\psi\rangle = \int dx \psi(x) |x\rangle. \quad (\text{D.3})$$

So we see that wave functions in quantum mechanics represent coefficients to *kets* whenever the list of kets is continuous.

For a state with definite momentum p , we write this using the Dirac bra-ket notation as $|p\rangle$. Similarly, for a state with definite position x , we write this as $|x\rangle$.

We use the *inner product* operating on two abstract states ψ_1 and ψ_2 to determine a probability amplitude of going from one state to the other. This operation is written as,

$$\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} \psi_1^* \psi_2 dx \quad (\text{D.4})$$

where ψ_1^* represents the complex conjugate of ψ_1 . This inner product projects the state ψ_2 onto ψ_1 and determines the amplitude going from ψ_2 to ψ_1 .

To find the probability amplitude for a particle to be at any position x , we take the inner product of the state of definite x with the state ψ , i.e.

$$\psi(x) = \langle x|\psi\rangle \quad (\text{D.5})$$

To find the probability amplitude for a particle to have any momentum p , we take the *inner product* of the state of definite p with the state ψ , i.e.

$$\psi(p) = \langle p|\psi\rangle \quad (\text{D.6})$$

D.1 Stationary States

A *stationary state* is called stationary because the system remains in the same state as time progresses. It is a quantum state that is a solution to the time-independent Schrödinger equation:

$$\hat{H}|\psi\rangle = E|\psi\rangle, \quad (\text{D.7})$$

where \hat{H} is the Hamiltonian operator, ψ is a stationary state that satisfies this equation, and E represents the *eigenvalue* of the state ψ . However, the wavefunction itself is not stationary as it continually changes its overall complex phase. This allows it to form a standing wave. The oscillation frequency ν of the standing wave, times Planck's constant h , is equal to the energy of the state according to the Planck–Einstein relation of eqn. (2.12), i.e.

$$E = h\nu. \quad (\text{D.8})$$

Appendix E Transition Between States

An electron is a quantum object that simultaneously acts as a wave and as a particle. When bound as part of an atom, an electron mostly acts like a wave. The electron locations are described by wave functions that represent cloud-like probability distributions, which are called *orbitals*. These orbitals tend to overlap in space. Thus, when an electron transitions from one energy level to another, it does not jump from one physical location to another; rather, the wave function that it is associated with simply changes shape to that associated with the new energy level. Electron energy level transitions typically occur within a few nanoseconds or less. Wave functions of higher energy states tend to have more complex shapes than those of lower energy states.

Appendix F Emission

F.1 Spontaneous Emission

If a light source, the atom, is in an *excited state* with energy E_2 , it may *spontaneously decay* to a lower energy level (e.g., the ground state) with energy E_1 , releasing the difference in energy between the two states as a *photon* [Spo-23]. The photon will possess a frequency ν and an energy $h\nu$, i.e.

$$E_2 - E_1 = h\nu, \quad (\text{F.1})$$

where h is the Planck constant. The *phase* of the photon in spontaneous emission is random, as is the direction in which the photon propagates, see figure(F.1). This is not true for stimulated emission.

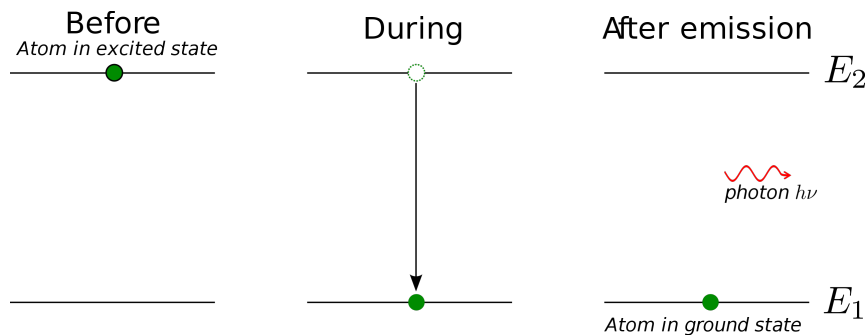


Figure F.1: Spontaneous Emission. Source [Spo-23].

Spontaneous transitions are not explainable solely within the framework of the Schrödinger equation, in which the electronic energy levels are quantized but the electromagnetic field is not. In order to explain this phenomena quantum mechanics must be extended to a *quantum field theory*, where the electromagnetic field is quantized at every point in space. This theory is known as *quantum electrodynamics* [Qua-23], and is beyond the scope of this article.

F.2 Stimulated Emission

Stimulated emission is the process whereby an incoming photon of a specific frequency interacts with an excited atomic electron (or other excited molecular state), causing it to drop to a lower energy level. The liberated energy transfers to the electromagnetic field, creating a new photon with a frequency, polarization, and direction of travel that are all identical to the photons of the incident wave [Sti-22], see figure (F.2). This is in contrast to spontaneous emission, which occurs at a characteristic rate for each of the atoms/oscillators in the upper energy state regardless of the external electromagnetic field.

Appendix G Quantum Numbers

Schrödinger's model describes how the electron occupies three-dimensional space, and it uses three quantum numbers to describe the *orbitals* or *clouds* in which electrons can be found [Qua-23a]. The three coordinates that come from Schrödinger's wave equation $\psi_{n,\ell,m}$, are the *principal* (n), *angular* (ℓ), and *magnetic* (m) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals of an atom - see Sections (4.4, 8)

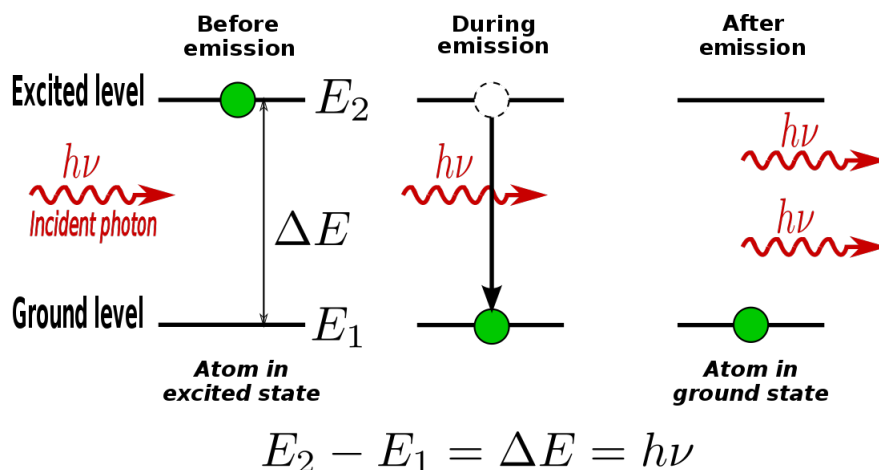


Figure F.2: Stimulated Emission. Source [Sti-22].

Principal Quantum Number. This number, n , describes the electron shell, or energy level, of an electron. The value of n ranges from 1 to the number of the shell containing the outermost electron of the associated atom, i.e.

$$n = 1, 2, \dots \quad (\text{G.1})$$

Angular Quantum Number. This number, ℓ , also known as the *azimuthal momentum quantum number* or *orbital quantum number*, describes the sub-shell, and gives the magnitude of the orbital angular momentum through the relation.

$$L^2 = \hbar^2 \ell(\ell + 1). \quad (\text{G.2})$$

In chemistry and spectroscopy, $\ell = 0$ is called the *s* orbital, $\ell = 1$, the *p* orbital, $\ell = 2$, the *d* orbital, and $\ell = 3$, the *f* orbital.

The value of ℓ ranges from 0 to $n - 1$, so the first *p* orbital ($\ell = 1$) appears in the second electron shell ($n = 2$), the first *d* orbital ($\ell = 2$) appears in the third shell ($n = 3$), and so on. Thus, we have,

$$\ell = 0, 1, 2, \dots, n - 1. \quad (\text{G.3})$$

Magnetic Quantum Number. This number, m_ℓ or plain m when there is no ambiguity, describes the specific *orbital* (or *cloud*) within the associated sub-shell. It yields the projection of the orbital angular momentum along a specified axis, i.e.

$$L_z = m_\ell \hbar. \quad (\text{G.4})$$

The values of m_ℓ take on the following integer values,

$$-\ell, \dots, \ell. \quad (\text{G.5})$$

The *s* sub-shell ($\ell = 0$) contains only one orbital, and therefore the m_ℓ of an electron in an *s* orbital will always be 0. The *p* sub-shell ($\ell = 1$) contains three orbitals (in some systems, depicted as three *dumbbell-shaped* clouds), so the m_ℓ of an electron in a *p* orbital will be -1, 0, or 1. The *d* sub-shell ($\ell = 2$) contains five orbitals, with m_ℓ values of -2, -1, 0, 1, and 2.

Appendix H Some Definitions

Definition 1. The **Kronecker delta** is defined as:

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n; \\ 1, & \text{if } m = n. \end{cases} \quad (\text{H.1})$$

Definition 2. Two vectors are said to be **orthogonal** if they are perpendicular to each other. i.e. the **dot product** of the two vectors evaluates to zero.

Definition 3. A set of vectors $\{\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_n\}$ are said to be mutually **orthogonal** if every pair of vectors is orthogonal. i.e. $\mathbf{v}_i \cdot \mathbf{v}_j = 0$, for all $i \neq j$.

Definition 4. A set of vectors S is said to be **orthonormal** if every vector in S has **unit** magnitude, and the set of vectors are mutually orthogonal.

Definition 5. An **observable** is said to be any physical quantity relating to a particle that can be **measured**. This includes position, momentum, energy, angular momentum, or any combination of these linear operators. Also, the corresponding eigenvalues must be **real** because they represent the values we would measure in the corresponding eigenstate.

Appendix I Data Related to Quantum Mechanics

c	=	Speed of light, 2.99792458×10^8 [m/s]
e	=	Unit charge, 1.602176634^{-19} [C]
E	=	Energy [J]
h	=	Planck's constant, $6.62607015 \times 10^{-34}$ [J s]
\hbar	=	Planck's reduced constant, $h/(2\pi)$, $1.054571817 \times 10^{-34}$ [J s]
m_e	=	Mass of electron, $9.1093837 \times 10^{-31}$ [kg]
m_p	=	Mass of proton, $1.67262192 \times 10^{-27}$ [kg]
ϵ_0	=	Vacuum permittivity, $8.85418782 \times 10^{-12}$ [F/m]

Appendix J Python Source Code

will be available on www.pdecomp.net

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