Lecture notes for
ZCT 205
Quantum Mechanics

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Based on the textbook
Introduction to Quantum Mechanics
by David Griffiths, second edition.

Contents

Preface

This set of lecture notes are prepared for the ZCT 205 course offered to mainly second year students in the school of physics, Universiti Sains Malaysia, Penang. It is basically a set of notes on selected parts of the first four chapters from the text book “Introduction to Quantum Mechanics” 2ed. by David Griffiths, Pearson Prentice Hall, 2005 [1].

When you enter any class of quantum mechanics at the undergraduate level, it is almost always assumed that you have already familiar with Newtonian mechanics and some introductory level modern physics. You should be familiar with all those fundamental notions such as conservation of energy, movement of a particle in a potential field, momentum, kinetic energy and potential energy of a particle, harmonic oscillation, wave phenomena (you learned this in waves and oscillations), etc. In modern physics class, you should have already gained some preliminary ideas on the rise of quantum phenomena based on a string of experimental discoveries that rocks the fundamental understanding of our physical world based on classical physics. Such counter-intuitive concepts e.g., wave-particle duality, Heisenberg’s uncertainty principle, Bohr’s theory and de Broglie’s postulate are among the key knowledge that are necessarily to understand the content of this course. In order to digest the concepts and calculations you will encounter in this course, a good mastery of the “previous” knowledge you learned in the physics classes in the past (in particular classical mechanics, wave phenomena and modern physics) is almost mandatory. If you have already discarded these after walking out from the exam hall, I strongly urge you to scavenge it from your brain’s trash bin. You can’t afford the failure to recall these required fundamentals in this quantum mechanics course.

Moreover, quantum mechanics ZCT 205 is quite a mathematically demanding subject. You will discover that it makes use of all the knowledge taught in previous (and current) mathematics classes. In particular, you are expected to be familiar with the following topics: vector analysis, vector space, integration (of single variable), differentiation, ordinary differential equations, partial derivatives, complex number, limits, Fourier series, Fourier integral, series, Taylor series expansion, volume integration in spherical coordinates, etc. Going through the content of this course, you will begin to appreciate the usefulness of those "useless heck of" mathematics you have learned in your life all the while. Mathematical training forced upon all physics students are not meant to be a waste of time. You will thank God you know mathematics at time when you really need it (such as now).

In this manuscript, you will find *Exercises* and *Problems* scattered among the in-line texts. *Exercises* are mainly relatively simple mathematical calculations showing the steps leading to a particular results or formula. *Problems* are meant for more elaborated problems requiring lengthier calculations. The solutions to some selected *Exercises* and *Problems* are purposely left out in the notes. These solutions will only be filled up during the lecture. You are right! this is my tactic to lure (or to force, if you may) students to attend lectures.

Each chapter in this lecture is accompanied by a problem set. Students are expected to attempt these problem sets themselves at the end of each chapter. Practicing on problem sets is an integral part in learning a mathematically demanding subject such as QM. You can't really appreciate QM if you don't attempt the calculation problems yourselves (Oh! You may think that this is an nagging statement, but it is also a truth which you can't afford to not to follow).

I also suggest another book to complement Griffiths: *Schaum's Outlines of theory and problems of Quantum Mechanics* by Peleg *et al.*. It provides a huge collection of very useful examples of calculations in great detail.

This is one of the most difficult subjects in your undergraduate year as a physics student, but also one of the most intellectually challenging. The effort you invest in to master this subject would be most intellectually rewarding. Apart from the mundane purpose of passing the examination, understanding QM at the undergraduate level will equip you with one of the most crucial theoretical tools to perform researches in the realm of quantum world.

The late John Wheeler (the physicist who coined the term "black hole") commented

> *If you are not completely confused by quantum mechanics, you do not understand it.*

The great Richard Feynman (Wheeler's graduate student), another great physics figure of our time, said

> *It is safe to say that nobody understands quantum mechanics.*

If you finally comprehend the core issues in QM that renders it such a confusing law, you have understood QM as in the spirit of Feynman and Wheeler. When will be your turn to say something on quantum mechanics? Before you coin your quotation, I'd first suggest you to put in effort to understand the content we are going to learn in this course.

Acknowledgement

I would like to explicitly acknowledge Dr. Myo Thaik for his generous sharing of the notes he personally prepared (in hand writing – a precious piece of effort) for Chapter 4 (QM in three dimensions). Dr. Myo Thaik was once an academic colleague of mine in the School of Physics in USM. Most part of the content in Chapter 4 of this manuscript is primarily based on his contribution. His kindness and generosity to share his intellectual contribution is really something I sincerely appreciated.

Chapter 1

The wave function

1.0.1 The Schroedinger Equation

- Refer to Fig.1.1 of a "particle" constraint to move only in 1D.

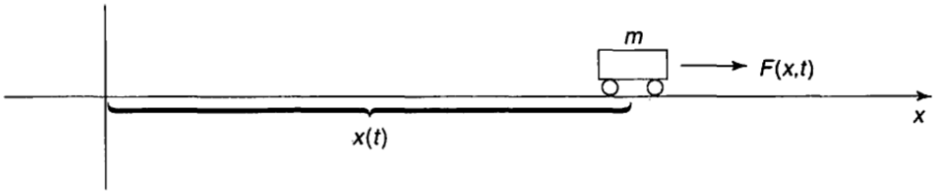


Figure 1.1: A "particle" constrained to move in 1-D under the influence of a specified force.

Classically, the velocity is $v = dx/dt$, momentum $p = mv$, kinetic energy $T = (1/2)mv^2$. $x(t)$ is determined from Newton's law $F = ma$. The force, if conservative, can be derived from the potential via $F = m\frac{\partial^2 x}{\partial t^2} = -\partial V/\partial x$. The complete description of $x(t)$ at any time t can be determined if the initial condition $x(t = 0)$ is provided.

- In quantum mechanics, the program to describe the system is very much different than that by classical mechanics.

- QM looks at the particle's wave function $\Psi(x, t)$ (pronounced a "Psi"). $\Psi(x, t)$

is obtained by solving the **Schroedinger equation**:

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

where $i = \sqrt{-1}$, $\hbar = \frac{h}{2\pi} = 1.054572 \times 10^{-34}$ Js.

- Given the initial condition $\Psi(x,0)$ the Shroedinger equation determines $\Psi(x,t)$ for all future time.

1.0.2 The Statistical Interpretation

- A particle is localised whereas a wave function is spread out in space. How could a wave function provide a description of a particle?
- The answer lies in Born's **statistical interpretation** of the wave function: $|\Psi(x,t)|^2$ gives the probability of finding the particle at point x at time t:

  $$\int_a^b |\Psi(x,t)|^2 dx = \text{probability of finding the particle between } a \text{ and } b \text{ at time } t.$$

- Probability is the area under the graph of $|\Psi|^2$.
- For example, for the wave function shown in Fig. 1.2, since $|\Psi|^2$ large around the vicinity of point A and relatively small around B, it is more likely to find the particle near A relative to B.
- $\Psi(x,t)$ in general is complex. However, $|\Psi(x,t)|^2 = \Psi(x,t)^*\Psi(x,t)$ is real and positive.
- There is an inherent **indeterminacy** in the statistical interpretation of quantum mechanics. Even we know everything about the wave function and the equation governing it, we still can not predict with certainty the outcome of a simple experiment to measure the position. QM only offers statistical information about the *possible* results.
- A measurement act "collapses" the wave function to assume a particular number (e.g., measurement of position results in a particular value of the position). Right after the measurement, repeated measurement on the particle's position will consistently return the same number.
- There are two distinct kinds of physical processes: "ordinary" ones, in which the wave function evolves in a leisurely fashion under the Shroedinger equation,

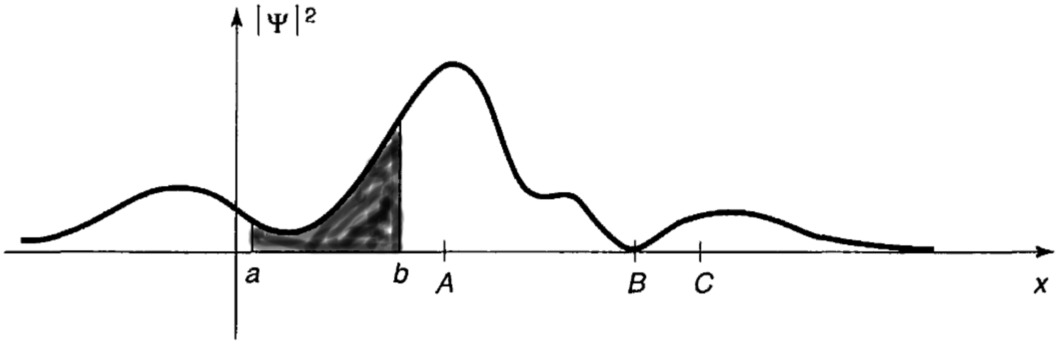


FIGURE 1.2: A typical wave function. The shaded area represents the probability of finding the particle between *a* and *b*. The particle would be relatively likely to be found near *A*, and unlikely to be found near *B*.

and "measurements" in which Ψ suddenly and discontinuously collapses. The former represents the particle before being measured, and the latter represents the particle after measurement.

- What is the particle's position before it is measured? What happen in a measurement process such that a particular position is forced upon a particle's position? What constitute a measurement process?
- These are unsettled questions.

1.1 Probability

1.1.1 Discrete Variables

- Consider a sample comprise of 14 people whose ages are as follows:

one person aged 14,
one person aged 15,
three people aged 16,
two people aged 22,
five people aged 15.

FIGURE 1.3: Collapse of the wave function: graph of $|\Psi|^2$ immediately *after* a measurement has found the particle at point C.

- We represent the above information using the notation $N(j)$

  $N(14) = 1$,
  $N(15 = 1$,
  $N(16) = 3$,
  $N(22) = 2$,
  $N(24) = 2$,
  $N(25) = 5$,
  $N(j) = 0$ for other values of j.

- The age j here takes only integer values. They are discrete variables.
- Total number is $N = \sum_{j=0}^{\infty} N(j)$.
- The histogram of the data is represented in Fig. 1.4:
- $P(j) = N(j)/N$ represents the probability that a person selected randomly from the sample is of age j.
- The sum of all probability must be 1:

$$\sum_{j=0}^{j=\infty} P(j) = 1.$$

  This is known as 'normalisation'. It means the sum of the probability $P(j) = N(j)/N$ over all j must be 1.

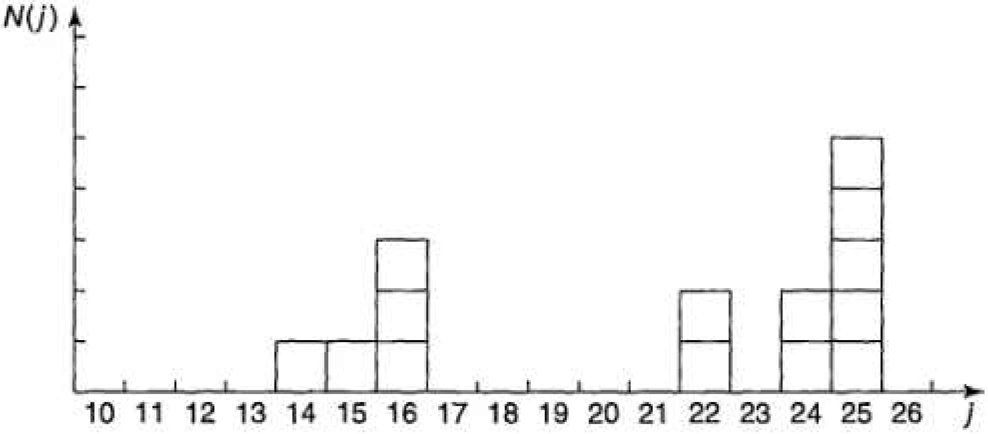


FIGURE 1.4: Histogram showing the number of people, N(j), with age j, for the distribution in Section 1.3.1.

- The most probable age is 25 as $P(j)$ is maximum at $j = 25$.
- The median age is the value of j such that the probability of getting a larger result is the same as the probability of getting a smaller result. In this example, 23 is the median. This value is obtained by working out the value of j_m such that the area under the "curve" before j_m and after j_m equals.
- Average of mean age is given by

$$\langle j \rangle = \frac{\sum jN(j)}{N} = \sum_{j=0}^{\infty} jP(j) = \cdots = 21.$$

- Average value is also known as **expectation value**. It is usually the quantity of interest in QM.
- Average of the squares of the age is given by

$$\langle j^2 \rangle = \frac{\sum j^2 N(j)}{N} = \sum_{j=0}^{\infty} j^2 P(j).$$

- In general, the average value of some function of j, $f(j)$, is given by

$$\langle f \rangle = \sum_{j=0}^{\infty} f(j)P(j).$$

- Apart from the average, $\langle j \rangle$, median and most probable value, a set of discrete statistical data is characterised by a spread in distribution with respect to the average. This is measured by the variance,

  $$\sigma^2 = \langle (\Delta j)^2 \rangle,$$

  which is the average value of the square of Δj, where

  $$\Delta j = j - \langle j \rangle.$$

  measures the deviation of each j from the average value.

- σ is called the **standard deviation**, a customary measure of the spread about $\langle j \rangle$.

- The histogram of the discrete data set $\{j, N(j)\}$ is a very useful graphical representation of it, see Figure 1.5.

- The normalised version of the histogram,

  $$\rho(j) = \frac{N(j)}{N} \text{ vs. } j,$$

  where $\sum_j \rho(j) = 1$. $\rho(j)$ is referred to as the 'probability distribution function', or simply the 'distribution'.

- For discrete variable j, $\Delta j = 1$ on the normalised histogram. Δj is the width of the interval on the j variable axis. (When we generalise to a continuous variable, say x, the width of the interval in the variable axis Δx is taken to be very tiny $\Delta x \to 0$. We will see this in subsection 1.1.2.)

  Normalisation for the discrete PDF is expressed as

  $$\sum_j \rho(j) \Delta j = 1.$$

- One could show that the variance is given by

  $$\sigma^2 = \cdots = \langle j^2 \rangle - \langle j \rangle^2,$$

- The standard deviation is simply

  $$\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}.$$

- Note that $\langle j^2 \rangle \geq \langle j \rangle^2$.

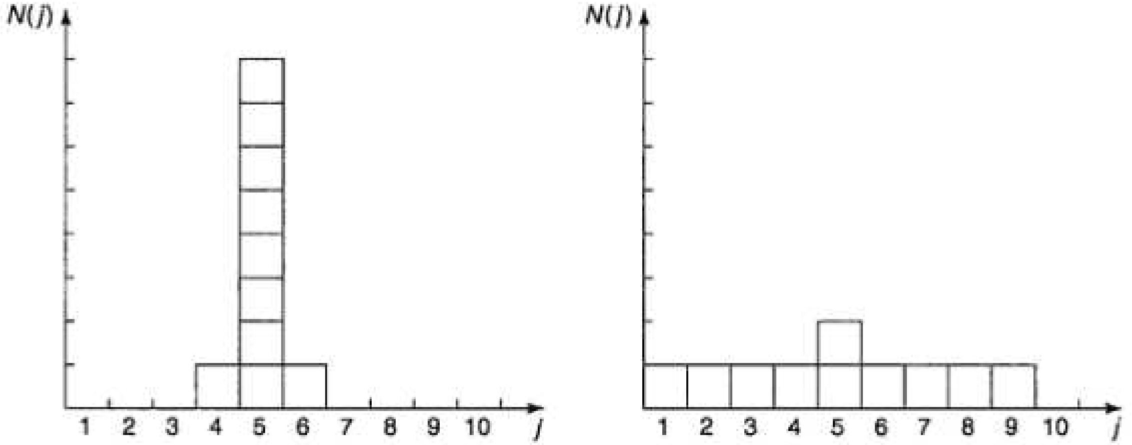


FIGURE 1.5: Two histograms with the same median, same average, and same most probable value, but different standard deviations.

- In short, a discrete statistical data set, $\{j, N(j)\}$ for the discrete variable j, is represented by a discrete probability distribution function (PDF), $\rho(j)$. Given a PDF, we then calculate the variance σ^2 (or equivalently, its standard deviation σ) and min $\langle j \rangle$ for the discrete data set. We could also easily derive the most probable value (mpv) for j and the median j_m from the PDF but these quantities are relatively unimportant in QM.

- Most importantly, given a PDF, we can derive the expectation value for any j-dependent variable $Q(j) = \sum_j \rho(j)Q(j)$.

1.1.2 Continuous Variables

- We could generalise the description of probability distribution of discrete variable to continuous one,

  probability that an individual (chosen at random) lies between x and $(x + dx)$ $= \rho(x)dx$.

- $\rho(x)$ is called the **probability density**.

- The probability that x lies between a and b (a finite interval) is given by

$$P_{ab} = \int_a^b \rho(x)dx,$$

$$
\begin{aligned}
1 &= \int_{-\infty}^{\infty} \rho(x)dx, \\
\langle x\rangle &= \int_{-\infty}^{\infty} x\rho(x)dx, \\
\langle f(x)\rangle &= \int_{-\infty}^{\infty} f(x)\rho(x)dx, \\
\sigma^2 &\equiv \langle(\Delta x)^2\rangle = \langle x^2\rangle - \langle x\rangle^2
\end{aligned}
$$

Example 1.1

Suppose I drop a rock off a cliff of height h. As it falls. I snap a million photographs, at random intervals. On each picture I measure the distance the rock has fallen. Question: What is the average of all these distances? That is to say, what is the time average of the distance traveled?

Solution: The rock starts out at rest and picks up speed as it falls; it spends more time near the top, so the average distance must be less than $h/2$. Ignoring air resistance, the distance x at time t is

$$x(t) = \frac{1}{2}gt^2.$$

The velocity is $dx/dt = gt$, and the total flight time is $T = \sqrt{2h/g}$. The probability that the camera flashes in the interval dt is dt/T.

$$\frac{dt}{T} = \frac{dx}{gt}/T = \frac{dx}{gt}\sqrt{\frac{g}{2h}} = \frac{dx}{g\sqrt{2x/g}}\sqrt{\frac{g}{2h}} = \frac{1}{2\sqrt{hx}}dx \equiv \rho(x)dx$$

- $\rho(x)$ is the probability density to find the particle in position x.
- $\rho(x)dx$ is the probability to find the particle between the position x and $x+dx$.
- We can check this result by finding the total probability (which must be equal 1 when integrating over all x),

$$\int_0^h \frac{1}{2\sqrt{hx}}dx = \frac{1}{2\sqrt{h}}\left(2x^{1/2}\right)\Big|_0^h = 1.$$

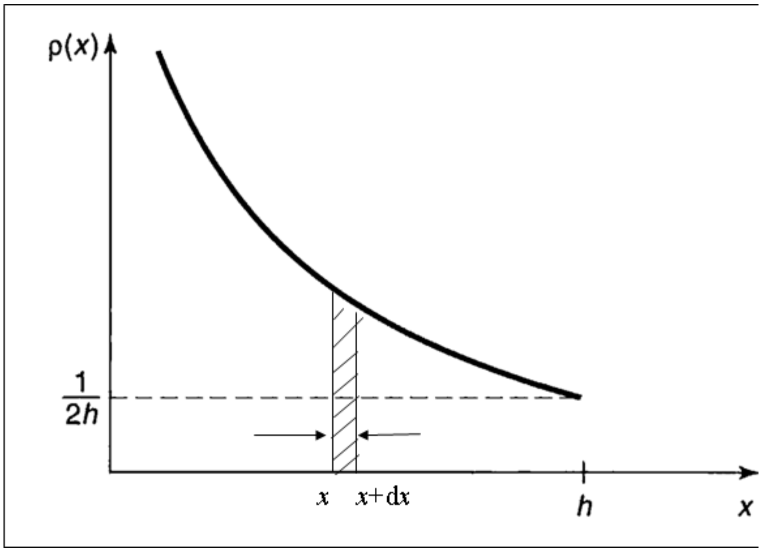


Figure 1.2: The probability density in Example 1.1: $\rho(x) = \frac{1}{2\sqrt{hx}}$. The shaded area is the probability to find the particle between x and $x + dx$.

The average distance is

$$\langle x \rangle = \int_0^h x \frac{1}{2\sqrt{hx}} dx = \frac{1}{2\sqrt{h}} \left(\frac{2}{3} x^{3/2} \right) \Big|_0^h = \frac{h}{3} < \frac{h}{2}.$$

1.2 Normalisation

- According to the statistical interpretation, $|\Psi(x,t)|^2$ represent the probability density for finding the particle at point x at time t.
- If the wave function were to represent physical states, it must be **square-integrable** and **normalisable**:
- square-integrable:

  $$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx < \infty.$$

  To be so, $\Psi(x,t)$ must go to zero faster than $1/\sqrt{|x|}$ as $|x| \to \infty$.
- In relevance to this, $\Psi(x,t) \to 0$ as $|x| \to \infty$. This is demanded by the fact that, if the wave function were to represent a physical state, it must vanish at infinity.

- Normalisation: The probability to find the particle must be 1 when integrating the probability density over all space:
$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1.$$
- The time-dependent wave function is $\Psi(x,t)$. We can prove that (in problem 2, Problem Set 1) the normalisation condition of the wave function, is time-independent, i.e.,
$$\frac{d}{dt}\left(\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx\right) = 0.$$
- This is the result of the mathematical feature of the Schroedinger equation. Due to such a property in the Schroedinger equation, the normalisation condition is preserved for all t.
- What that means is that once the wave function is normalised at the beginning ($t = 0$), it will remain normalised at all future time, i.e., If $|\Psi(x,0)|^2 = 1, \Rightarrow |\Psi(x,t)|^2 = 1$ for all $t > 0$ with the same normalisation constant (a number independent of x and t). See the example 1.4 for how to adjust the normalisation constant A to normalise the wave function.

Example 1.4

At time $t = 0$ a particle is represented by the wave function
$$\Psi(x,0) = \begin{cases} A\frac{x}{a}, & \text{if } 0 \leq x \leq a, \\ A\frac{(b-x)}{(b-a)}, & \text{if } a \leq x \leq b, \\ 0, & \text{otherwise,} \end{cases}$$
where A, a and b are constants.

(a) Normalize Ψ (that is, find A in terms of a and b).

(b) Sketch $\Psi(x,0)$ as a function of x.

(c) Where is the particle most likely to be found, at $t = 0$?

(d) What is the probability of finding the particle to the left of a? Check your result in the limiting cases $b = a$ and $b = 2a$.

(e) What is the expectation value of x?

1.3 Momentum

- For a particle in state Ψ, the expectation value of x is

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

- The expectation value is the average of repeated measurements on an ensemble of identically prepared systems, not the average of repeated measurements on one and the same system.

- Since the wave function is evolving in time, so will the expectation value in general. We wish to know what is $\frac{d}{dt}\langle x\rangle$.

- Using integration-by-parts and applying the boundary condition that the wave function vanishes at infinity, (limits of the the integration will be suppressed for the sake of brevity)

$$\begin{aligned}\frac{d}{dt}\langle x\rangle &= \int x\frac{\partial}{\partial t}|\Psi|^2 dx = \cdots = \frac{-i\hbar}{2m}\int\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)dx = \cdots \\ &= \frac{1}{m}\int\Psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi\right)dx \equiv \frac{\langle p\rangle}{m}.\end{aligned}$$

  The expectation value of momentum is postulated as m times the time derivative of the expectation value of x.

- Exercise: Show this. *Hint:* Integration by parts:

$$\int_a^b f\frac{dg}{dx}dx = fg\bigg|_a^b - \int_a^b \frac{df}{dx}g dx.$$

  Sometimes integration by parts is also expressed in terms of

$$\int u dv = uv - \int v du.$$

- Summarising the previous two results for x, p,

$$\begin{aligned} \langle x \rangle &= \int \Psi^* x \Psi dx, \\ \langle p \rangle &= \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx. \end{aligned} \tag{1.1}$$

- We say that the **operator** x "represents" position, and the operator $(\frac{\hbar}{i})(\frac{\partial}{\partial x})$ "represents" momentum in quantum mechanics. To calculate the expectation values we "sandwich" the appropriate operator between Ψ^* and Ψ, and integrate.

- In other words, in QM, the dynamical variables x, p are represented by operators. Sometimes we use a hat to distinguish a variable and the operator representing it, e.g., x is a variable while $\hat{x}$ a position operator (so is p and the corresponding operators $\hat{p}$). But in most cases we can easily infer whether its a variable or operator from the mathematical context.

- An operator is an instruction to do something to the function that follows it. For example, in $x\Psi$, x is an operator that transforms Ψ to $x\Psi$; while in $\frac{\partial}{\partial x}\Psi$, the operator $\frac{\partial}{\partial x}$ transforms the function Ψ to another function $\frac{\partial}{\partial x}\Psi$.

- All other classical dynamical variables such as energy, angular momentum, kinetic energy, can be expressed in terms of position and momentum, e.g., kinetic energy $T = p^2/(2m)$, angular momentum $\mathbf{L} = \mathbf{r} \times m\mathbf{v} = \mathbf{r} \times \mathbf{p}$.

- Generalising Eq. 1.1 to a generic dynamical variable Q which can always be "assembled" by the two basic variables x, p,

$$\langle Q(x,p) \rangle = \int \Psi^* Q\left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx \tag{1.2}$$

- Once can think Eq. (1.2) is an axiom in QM.

- For example,

$$\langle T \rangle = -\frac{\hbar^2}{2m} \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx.$$

- Exercise: Show this.

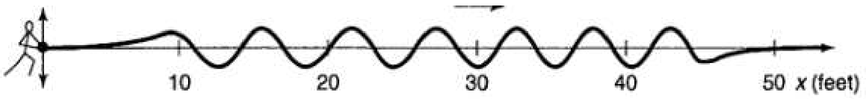


FIGURE 1.7: A wave with a (fairly) well-defined *wavelength*, but an ill-defined *position*.

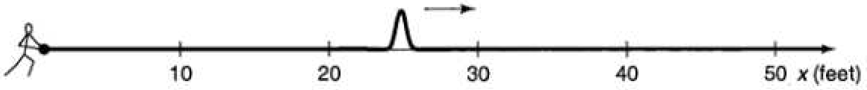


FIGURE 1.8: A wave with a (fairly) well-defined *position*, but an ill-defined *wavelength*.

1.4 The Uncertainty Principle

- A wave if well defined in wavelength (a small spread in wavelength, i.e., $\sigma_\lambda \ll 1$) is ill-defined in its exact location (a large spread in the position, $\sigma_x \gg 1$), and vice-versa. In other words, a wave having well defined wavelength is associated with a large "spread" ($\sigma_x \gg 1$) that roughly corresponds to the region in space where the wave is to be found.

- The QM wave function Ψ is also a wave phenomena. The wavelength of Ψ is related to the *momentum* of the particle by the **de Broglie formula**

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}.$$

- Hence, the spread in *wavelength* corresponds to a spread in momentum. From the above observation on the antagonistic relation in the spread of wavelength and position, we now says that the more precisely determined a particle's position is, the less precisely is its momentum,

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

  where σ_x (σ_p) is the standard deviation in x (p). This relation will be proven quantitatively later.

- This is the famous **Heisenberg's uncertainty principle**

- "Spread" here requires a more quantitative definition. A non-zero σ_p for example means: in momentum measurements of identically prepared systems, each measurement will yield precise answers but not identical results. The narrower the spread σ_p is, the closer are the results of the measurement in a

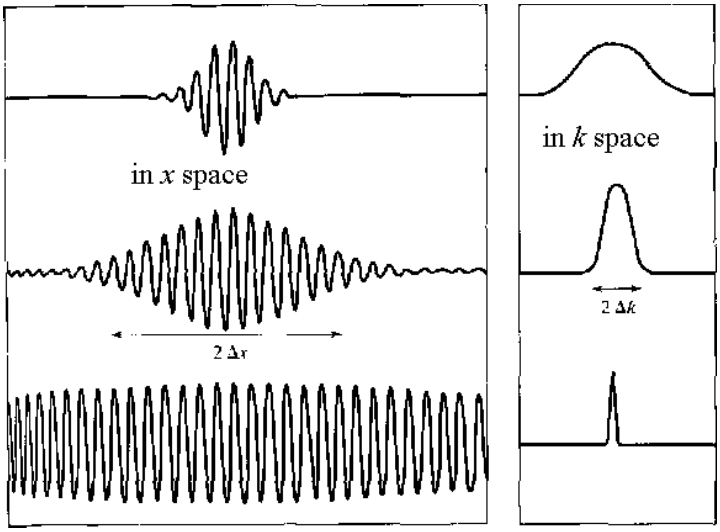


Figure 1.3: The smaller is the spread of the wave in position space, the larger is the spread in momentum space (k-space), and vice versa.

statistical sense. Identical results will be obtained if $\sigma_p = 0$. But in this case, the measurement in position will yield a wildly scattered results.

Here we illustrate the uncertainty principle as applied to a group of waves superimposed to form a "wave packet" using the software package Mathematica. The Mathematica source code and its pdf version for this visual simulation can be accessed at

http://www2.fizik.usm.my/tlyoon/teaching/ZCT205_1112/wave.nb

http://www2.fizik.usm.my/tlyoon/teaching/ZCT205_1112/wave.pdf

In order to install the Mathematica software (legally, bulk purchased by USM), follow the instruction at

http://www2.fizik.usm.my/tlyoon/teaching/ZCE111/1112SEM2/

The whole idea of the Mathematica simulation is to make you appreciate that (i) adding many waves of different wavelength results in a wave packet, (ii) the wave packet's "spread" in x (the "width" of the wave packet) is inversely proportional to the "spread" in wave number ($\Delta k = N_k \Delta$) of the waves that are used to form the wave packet.

- **Example (Problem 1.9)** *Hint*: Error function is defined as $\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du$.

$\mathrm{erf}(x \to \pm\infty) = \pm 1$.

A particle of mass m is in the state

$$\Psi(x,t) = Ae^{-a[(mx^2/\hbar)+it]}$$

where A and a are positive real constants.

(a) Find A.

(b) For what potential energy function $V(x)$ does Ψ satisfy the Schroedinger equation?

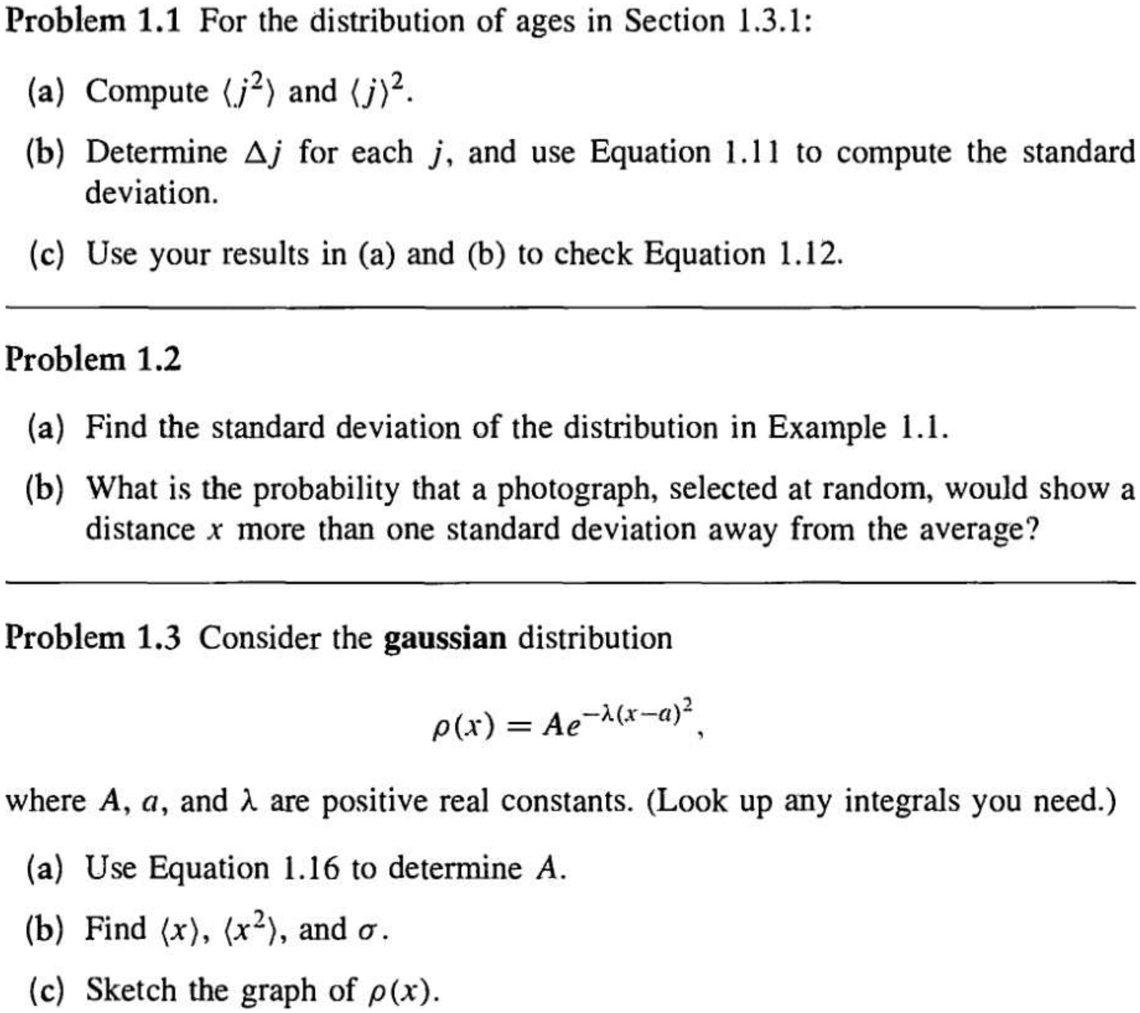
(c) Calculate the expectation values of x, x^2, p and p^2.

(d) Find σ_x and σ_p. Is their product consistent with the uncertainty principle?

1.5 Problem Set

ZCA 205 Quantum Mechanics
Problem set for Chapter 1

1. Prove that $\sigma^2 \equiv \langle (\Delta j)^2 \rangle$, where $\Delta j = j - \langle j \rangle$, j a discrete variable.



Problem 1.1 For the distribution of ages in Section 1.3.1:

(a) Compute $\langle j^2 \rangle$ and $\langle j \rangle^2$.

(b) Determine Δj for each j, and use Equation 1.11 to compute the standard deviation.

(c) Use your results in (a) and (b) to check Equation 1.12.

Problem 1.2

(a) Find the standard deviation of the distribution in Example 1.1.

(b) What is the probability that a photograph, selected at random, would show a distance x more than one standard deviation away from the average?

Problem 1.3 Consider the **gaussian** distribution

$$\rho(x) = Ae^{-\lambda(x-a)^2},$$

where A, a, and λ are positive real constants. (Look up any integrals you need.)

(a) Use Equation 1.16 to determine A.

(b) Find $\langle x \rangle$, $\langle x^2 \rangle$, and σ.

(c) Sketch the graph of $\rho(x)$.

2. Prove that for a wave function that is the solution to the Schroedinger equation, the normalisation of the wave function is time-independent,

$$\frac{d}{dt}\left(\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx\right) = 0.$$

∗**Problem 1.7** Calculate $d\langle p\rangle/dt$. *Answer*:

$$\frac{d\langle p\rangle}{dt} = \left\langle -\frac{\partial V}{\partial x}\right\rangle. \qquad [1.38]$$

Equations 1.32 (or the first part of 1.33) and 1.38 are instances of **Ehrenfest's theorem**, which tells us that *expectation values obey classical laws.*

Problem 1.14 Let $P_{ab}(t)$ be the probability of finding a particle in the range $(a < x < b)$, at time t.

(a) Show that

$$\frac{dP_{ab}}{dt} = J(a,t) - J(b,t),$$

where

$$J(x,t) \equiv \frac{i\hbar}{2m}\left(\Psi\frac{\partial\Psi^*}{\partial x} - \Psi^*\frac{\partial\Psi}{\partial x}\right).$$

What are the units of $J(x,t)$? *Comment:* J is called the **probability current,** because it tells you the rate at which probability is "flowing" past the point x. If $P_{ab}(t)$ is increasing, then more probability is flowing into the region at one end than flows out at the other.

(b) Find the probability current for the wave function in Problem 1.9. (This is not a very pithy example, I'm afraid; we'll encounter more substantial ones in due course.)

Problem 1.16 Show that

$$\frac{d}{dt}\int_{-\infty}^{\infty}\Psi_1^*\Psi_2\,dx = 0$$

for any two (normalizable) solutions to the Schrödinger equation, Ψ_1 and Ψ_2.

Problem 1.17 A particle is represented (at time $t = 0$) by the wave function

$$\Psi(x,0) = \begin{cases} A(a^2 - x^2), & \text{if } -a \leq x \leq +a, \\ 0, & \text{otherwise.} \end{cases}$$

(a) Determine the normalization constant A.

(b) What is the expectation value of x (at time $t = 0$)?

(c) What is the expectation value of p (at time $t = 0$)? (Note that you *cannot* get it from $p = md\langle x\rangle/dt$. Why not?)

(d) Find the expectation value of x^2.

(e) Find the expectation value of p^2.

(f) Find the uncertainty in x (σ_x).

Chapter 2

Time-independent Schroedinger Equation

2.1 Stationary States

- Given a (time-independent) potential $V(x)$ and the starting wave function $\Psi(x,0)$, we wish to find the wave function, $\Psi(x,t)$, for any subsequent time t by solving the (time-dependent) Schroedinger equation.

- How to get $\Psi(x,t)$? By solving the Schroedinger equation:

  $$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial^2 x} + V\Psi$$

  for a specific potential $V(x,t)$. The potential is time-dependent in most situations (not always but mostly). We will restrict ourselves only to potential that is time-independent so that the Schroedinger equation can be solved using **separation of variables** method, in which we assume

  $$\Psi(x,t) = \psi(x)\varphi(t) \tag{2.1}$$

- The most general solution could be constructed from these separable solutions (namely, $\{\psi_n(x),\varphi_n(t)\}$, $n = 1, 2, \cdots$).

- Taking the time partial derivative and second order spatial partial derivative of Eq.(2.1),

  $$\frac{\partial\Psi}{\partial t} = \psi\frac{d\varphi}{dt}, \frac{\partial^2\Psi}{\partial^2 x} = \frac{d^2\psi}{dx^2}\varphi. \tag{2.2}$$

- Plug in $\Psi(x,t) = \psi(x)\varphi(t)$ to the Schroedinger equation,

$$i\hbar\psi\frac{\partial\varphi}{\partial t} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\varphi + V\varphi\psi. \tag{2.3}$$

- Divide both sides of Eq.(2.3) by $\phi\varphi$,

$$i\hbar\frac{1}{\varphi}\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x). \tag{2.4}$$

- LHS is a function of t alone while the RHS is a function of x alone. Equation 2.4 is true only if both sides equal to a *constant*. We will call this constant E, so that

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi, \tag{2.5}$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi.} \tag{2.6}$$

Time-independent Schroedinger equation (TISE)

- Separable method has turned a partial differential equation of two variables into two uncoupled ordinary differential equations.

- The solution to the time-dependent part, Eq. (2.5) is

$$\varphi(t) = e^{-iEt/\hbar}.$$

  The coefficient to $e^{-iEt/\hbar}$ in φ is absorbed into ψ.
  Exercise: Show that $\varphi(t) = e^{-iEt/\hbar}$ is a solution to Eq.(2.5).

- Some important properties of the separable solutions $\psi(x)e^{-iEt/\hbar}$:

  1. $\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$ are stationary states. Despite being time-dependent, the *probability density* does not:

     $$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^* e^{+iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2,$$

     The expectation value of any dynamical variable for the stationary state $\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$ is also time-independent:

     $$\langle Q(x,p)\rangle = \int \Psi^* Q\left(x, -i\hbar\frac{d}{dx}\right)\Psi dx = \int \psi^* Q\left(x, -i\hbar\frac{d}{dx}\right)\psi dx$$

     For a particle in a stationary state, every expectation value is constant in time, as the time-dependent part, $\varphi(t) = e^{-iEt/\hbar}$ drops out when evaluating the probability density or expectation value.

  2. Stationary states are states of definite total energy. Total energy in classical mechanics is called the **Hamiltonian**:

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

     In QM, the corresponding Hamiltonian *operator* is obtained by $p \to \frac{\hbar}{i}\frac{\partial}{\partial x}$:

     $$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

     The time-independent Schroedinger equation, expressed in terms of Hamiltonian, is

     $$\hat{H}\psi = E\psi.$$

     Compare this equation with Eq.(2.6). The expectation value of the total energy is

     $$\langle H\rangle = \int \psi^*(\hat{H}\psi)dx = E\int |\psi|^2 dx = E.$$

     Hence, it is clear now that the separable constant E actually is the total energy. Moreover, the variance of H is

     $$\sigma_H^2 = \langle H^2\rangle - \langle H\rangle^2 = E^2 - E^2 = 0,$$

     where we have made used of the result that $\langle H^2\rangle = E^2$.

     This means measurements of the total energy for a particle in stationary state (a separable solution to the TISE) is certain to return the same value E.

3. The time-independent Schroedinger equation yields an infinite collection of solutions $\{\psi_1(x),\ \psi_2(x), \cdots\}$, each with its associated value of the separation constant $\{E_1,\ E_2, \cdots\}$; thus there is a different wave function for each **allowed energy**:

$$\Psi_1(x,t) = \psi_1(x)e^{-iE_1t/\hbar}, \Psi_2(x,t) = \psi_2(x)e^{-iE_2t/\hbar}, \cdots$$

One can check that the linear combination of solutions,

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-itE_n/\hbar}$$

is itself a solution. In short, the total solution (i.e., the most general solution) is a **linear combination** of separable solutions.

Exercise: Show this.

- In order to completely solve the general time-independent Schroedinger equation, we need to find the coefficients c_n that match the initial condition of a problem at hand. In most cases we will encounter, the initial condition is the profile of the wave function at time $t = 0$, say $f(x)$. We need to solve for the coefficients (which are the unknowns) such that the wave function at zero time $\Psi(x,0)$ is matched to that of $f(x)$.

- The strategy:

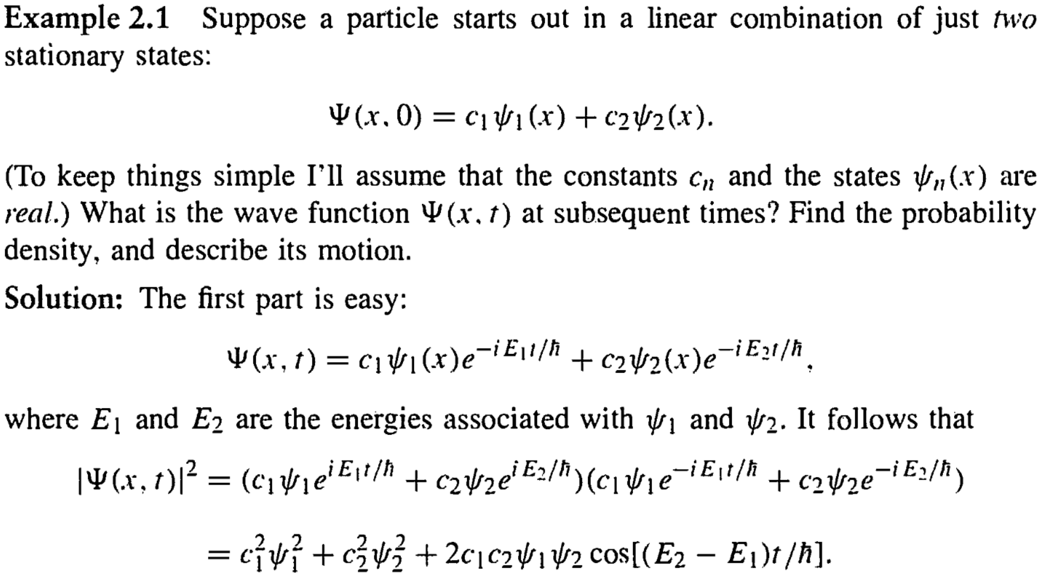
  1. First solve the time-independent Schroedinger equations for the complete set of stationary states, $\{\psi_1(x), \psi_2(x), \cdots\}$, each with its own associated energy $\{E_1, E_2, \cdots\}$.
  2. Find the general solution at $t = 0$, i.e., $\Psi(x,0) = \sum_{n=0}^{\infty} c_n\psi_n(x)$ by finding the coefficients c_n that fit the initial and boundary conditions.

3. Once all the c_n are found, the general time-dependent solution is obtained as

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n \psi_n(x) e^{-itE_n/\hbar} = \sum_{n=0}^{\infty} c_n \Psi_n(x,t) \tag{2.7}$$

- The separable solutions themselves, $\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}$ are stationary states in the sense that all probability and expectation values are time-independent.

- However, for the most general solution, Eq.(2.7), probability density and expectation values are time-dependent as it contains different components of stationary states, which exponents in $e^{-itE_n/\hbar}$ do not cancel.



Example 2.1 Suppose a particle starts out in a linear combination of just *two* stationary states:

$$\Psi(x,0) = c_1\psi_1(x) + c_2\psi_2(x).$$

(To keep things simple I'll assume that the constants c_n and the states $\psi_n(x)$ are *real.*) What is the wave function $\Psi(x,t)$ at subsequent times? Find the probability density, and describe its motion.

Solution: The first part is easy:

$$\Psi(x,t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar},$$

where E_1 and E_2 are the energies associated with ψ_1 and ψ_2. It follows that

$$|\Psi(x,t)|^2 = (c_1\psi_1 e^{iE_1t/\hbar} + c_2\psi_2 e^{iE_2/\hbar})(c_1\psi_1 e^{-iE_1t/\hbar} + c_2\psi_2 e^{-iE_2/\hbar})$$

$$= c_1^2\psi_1^2 + c_2^2\psi_2^2 + 2c_1c_2\psi_1\psi_2\cos[(E_2 - E_1)t/\hbar].$$

- Euler's formula is relevant here,

$$e^{i\theta} = \cos\theta + i\sin\theta.$$

- Note also the probability is oscillating in time, hence, the state represented by

$$\Psi(x,t) = c_1\psi(x)_1 e^{-iE_tt/\hbar} + c_2\psi(x)_2 e^{-iE_tt/\hbar}$$

  is *not* a stationary state. The state $\Psi(x,t)$, also a solution to the TDSE, is formed by a linear combination of two TISE solutions ψ_1, ψ_2 with weights c_1 and c_2 respectively. Although ψ_1 and ψ_1 are stationary state by themselves, the linear combination of them is not.

- Now, be advised to adjust yourself to get familiarised with the following statement which is going to occur repeatedly in the study of QM: A linear combination of solutions to the TISE (TDSE) is also a solution to the TISE (TDSE). such as the example above.

***Problem 2.2** Show that E must exceed the minimum value of $V(x)$, for every normalizable solution to the time-independent Schrödinger equation. What is the classical analog to this statement? *Hint:* Rewrite Equation 2.5 in the form

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi;$$

if $E < V_{\min}$, then ψ and its second derivative always have the *same sign*—argue that such a function cannot be normalized.

Solution

Given $\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar}[V(x) - E]\,\psi(x)$, if $E < V_{\min}$, where $V_{\min}$ the minimal of $V(x)$, $x \in (-\infty, \infty)$, then ψ and $\frac{d^2\psi(x)}{dx^2}$ always have the same sign: If $\psi(x)$ is positive (negative), then $\frac{d^2\psi(x)}{dx^2}$ is also positive (negative). This means that ψ always curves away from the x-axis (see Figure 2.1). In either cases ($\psi(x)$ starts out positive or negative), $|\psi(x)| \to \infty$ as $x \to \pm\infty$. In order for $\psi(x)$ to remain normalisable, this is not to be allowed. Hence, we we must not allow $E < V(x)_{\min}$, $\forall x \in (-\infty, \infty)$.

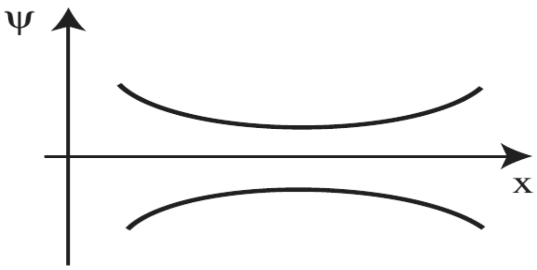


Figure 2.1: Behavior of $\psi(x)$ when ψ and $\frac{d^2\psi(x)}{dx^2}$ always have the same sign.

2.2 The Infinite Square Well

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$$

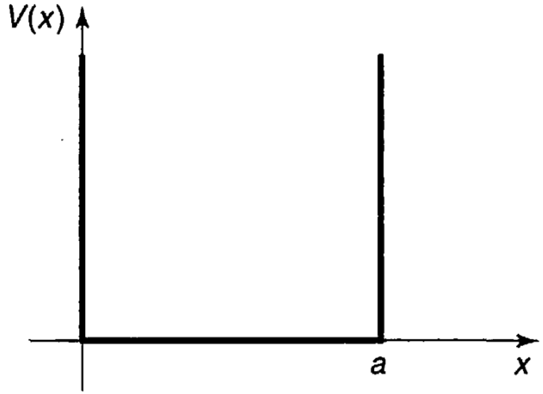


Figure 2.2: The infinite square well potential

- This is the most illustrative example of how the quantum mechanical machinery is used to solve the Schroedinger equation.

- $\psi(x)$ outside the infinite well is zero.

- Inside the well, i.e., $0 \le x \le a, V = 0$. The time-independent Schroedinger equation (TISE) becomes

  $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi,$$

  or

  $$\frac{d^2\psi}{dx^2} = -k^2\psi, \text{ where } k \equiv \frac{\sqrt{2mE}}{\hbar}; k^2 \ge 0 \qquad (2.8)$$

- The energy, E, must be positive (otherwise the wave function would not be normalisable). We have proven this in Problem 2.2 above, i.e., $E > V_{\text{min}} = 0$ ($V_{\text{min}} = 0$ in our case here).

- The general solution to Eq. (2.8) is

  $$\psi(x) = C_1 e^{ikx} + C_2 e^{-ikx} = A \sin kx + B \cos kx.$$

Exercise: Show this.

The arbitrary constants A, B are fixed by the **boundary conditions** of the problem.

- For the infinite square well, where $V \to \infty$ outside the well, there is only one boundary condition, i.e., the wave function $\psi(x)$ must be continuous. For this to be true, it is required that at the boundaries,

  $$\psi(x = 0) = \psi(x = a) = 0;$$

  so as to join onto the solution outside the well, $\psi(x) = 0$ for $x \leq 0, x \geq a$.

- $$\psi(0) = A \sin 0 + B \cos 0 = B$$

  so $B = 0$, and hence

  $$\psi(x) = A \sin kx$$

  Then $\psi(a) = A \sin ka = 0$. Since $A \neq 0$ (or else the solution would become trivial), we must have

  $$ka = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \cdots$$

  $k \neq 0$ (or else it would imply the solution is trivial), hence we obtain a set of distinct solutions, each of them is characterised by an positive integer:

  $$k_n = \frac{n\pi}{a}, \text{ with } n = 1, 2, 3, \cdots$$

- As a result, the possible values of E are

  $$E_n = p_n^2/2m = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

- The energy of a quantum particle in the infinite square well can only be one of these **allowed** values.
- The constant A can be found by normalisation of ψ

  $$\int_0^a |\psi|^2 dx = 1$$

  which gives $A = \sqrt{2/a}$

  Exercise: Show this.

- $$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right).$$

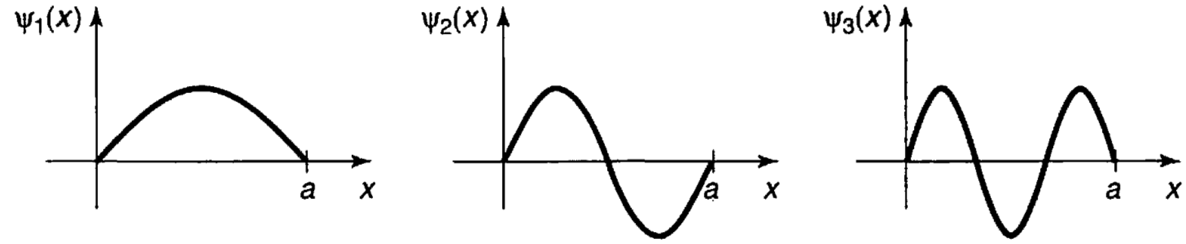


FIGURE 2.2: The first three stationary states of the infinite square well

- The TISE has an infinite set of solutions (one for each positive integer n).
- The $n = 1$ solution is known as the ground state. E_1 is the ground state energy, the lowest of all E_n. For other n, they are known as **excited states**.

- Three important properties of ψ_n

  1. They are alternately **even** and **odd**, with respect to the center of the well (i.e., $x = a/2$)
  2. As n increases, each successive states has one more **node**. ψ_1 has none, ψ_2 has one, ψ_3 has two, and so on.
  3. They are mutually **orthogonal**,

$$\int \psi_m(x)^* \psi_n(x) dx = \delta_{mn}.$$

Exercise: Proof this.

δ_{mn} is the so-called **Kronecker delta function**

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n \\ 1, & \text{if } m = n \end{cases}$$

  4. They are **complete**: Any other function $f(x)$ can be expressed as linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right).$$

Loosely, c_n represents how much of ψ_n is contained in $f(x)$. It can be projected out from $f(x)$ using **Fourier's trick** that exploits the orthogonality of $\{\psi_n\}$:

$$c_n = \int \psi_n(x)^* f(x) dx. \tag{2.9}$$

Exercise: Show this.

- The stationary states are:

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-itE_n/\hbar} \tag{2.10}$$

  where $E_n = n^2 \frac{\pi^2\hbar^2}{2ma^2}$.

- The most general solution to the time-dependent Schroedinger equation (TDSE) is a linear combination of stationary states:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-itE_n/\hbar} \tag{2.11}$$

- Note that the stationary states Eq. (2.10) and the most general solution, Eq.(2.11), are two different thing. Make sure that you know their distinction.

  Exercise: Check that indeed $\Psi(x,t)$ is a solution to the TDSE.

- At $t = 0$ the wave function assumes an initial profile $f(x) \equiv \Psi(x,0)$. This is the initial condition to the problem. The initial profile is usually considered a known quantity.

- Given a specific form of the initial condition $f(x)$, we need to work out the coefficients c_n (which are t- and x-independent) such that the wave function at $t = 0$ fits the initial condition. Specifically, we need to find c_n such that the RHS of Eq.(2.11) match the given initial profile $f(x)$

- The coefficients c_n can be obtained via Fourier's trick, Eq.(2.9):

$$c_n = \int \psi_n(x)^* f(x)dx = \int_{-\infty}^{\infty} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) f(x)dx = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) f(x)dx$$

- To summarise the procedure to calculate the wave function in the infinite square well:

  1. Given an initial profile $f(x)$, evaluate the coefficient c_n.
  2. Then plug in these coefficients into Eq.(2.11). That's it. The most general solution of the wave function to the Schroedinger equation for the infinite square well is obtained.
  3. Armed with this solution, we can proceed next to use it to calculate the expectation values for any dynamical variable.

- The procedure of calculation for other form of potentials are exactly the same as for the infinite square well except the functional form of the stationary states $\psi_n(x)$ and the allowed energies E_n would be different in that case.

Example 2.2 A particle in the infinite square well has the initial wave function

$$\Psi(x,0) = Ax(a-x), \quad (0 \leq x \leq a),$$

for some constant A (see Figure 2.3). *Outside* the well, of course, $\Psi = 0$. Find $\Psi(x,t)$.

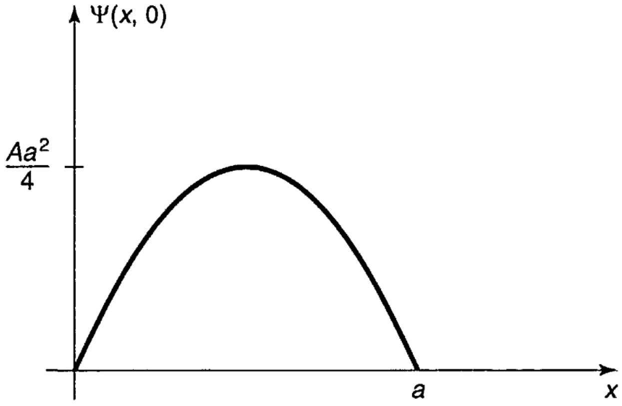


FIGURE 2.3: The starting wave function in Example 2.2.

Solution: First we need to determine A, by normalizing $\Psi(x,0)$:

$$1=\int_0^a |\Psi(x,0)|^2\,dx = |A|^2\int_0^a x^2(a-x)^2\,dx = |A|^2\frac{a^5}{30},$$

so

$$A=\sqrt{\frac{30}{a^5}}.$$

The nth coefficient is (Equation 2.37)

$$\begin{aligned}
c_n &= \sqrt{\frac{2}{a}}\int_0^a \sin\left(\frac{n\pi}{a}x\right)\sqrt{\frac{30}{a^5}}\,x(a-x)\,dx \\
&= \frac{2\sqrt{15}}{a^3}\left[a\int_0^a x\sin\left(\frac{n\pi}{a}x\right)dx - \int_0^a x^2\sin\left(\frac{n\pi}{a}x\right)dx\right] \\
&= \frac{2\sqrt{15}}{a^3}\left\{a\left[\left(\frac{a}{n\pi}\right)^2\sin\left(\frac{n\pi}{a}x\right)-\frac{ax}{n\pi}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right. \\
&\quad \left.-\left[2\left(\frac{a}{n\pi}\right)^2 x\sin\left(\frac{n\pi}{a}x\right)-\frac{(n\pi x/a)^2-2}{(n\pi/a)^3}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right\} \\
&= \frac{2\sqrt{15}}{a^3}\left[-\frac{a^3}{n\pi}\cos(n\pi)+a^3\frac{(n\pi)^2-2}{(n\pi)^3}\cos(n\pi)+a^3\frac{2}{(n\pi)^3}\cos(0)\right] \\
&= \frac{4\sqrt{15}}{(n\pi)^3}\left[\cos(0)-\cos(n\pi)\right] \\
&= \begin{cases} 0, & \text{if } n \text{ is even.} \\ 8\sqrt{15}/(n\pi)^3, & \text{if } n \text{ is odd.}\end{cases}
\end{aligned}$$

Thus (Equation 2.36):

$$\Psi(x,t)=\sqrt{\frac{30}{a}}\left(\frac{2}{\pi}\right)^3\sum_{n=1,3,5\ldots}\frac{1}{n^3}\sin\left(\frac{n\pi}{a}x\right)e^{-in^2\pi^2\hbar t/2ma^2}.$$

- What is the physical meaning of c_n?

- Every time you measure the observable energy of a quantum particle in state Ψ, you will obtain a discrete number E_n. $|c_n|^2$ is the probability of getting the *particular* value E_n when you make a measurement.

- The probability when summed over all allowed states n must be normalised:

$$\sum_{n=1}^{\infty} |c_n|^2 = 1$$

Exercise: Proof this relation for any arbitrary t-dependent state $\Psi(x,t)$.
Hint: Make use of the normalisation condition $\int |\Psi(x,t)|^2 = 1$ *and the orthonormality of the stationary states,* $\int \psi_n^*(x)\psi_m(x)dx = \delta_{mn}$.

- We can also show that the expectation value of the energy $\langle H\rangle$ can be obtained from the knowledge of the coefficients c_n via

$$\langle H\rangle = \sum_{n=0}^{\infty} |c_n|^2 E_n.$$

Exercise: Proof this.
Hint: Make use of (1) the definition $\langle H\rangle = \int \Psi^* H \Psi$, *(2) the TISE in terms of Hamiltonian,* $H\Psi_n = E_n\Psi_n$, *and that the wave function* Ψ *is a linear combination of the stationary states,* $\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-itE_n/\hbar}$.

- Note that the expectation value of energy is a constant. This is a manifestation of **conservation of energy** in QM.

Example 2.3 Calculate the expectation value of energy for the particle in Example 2.2.

The expectation value of the energy, in this example, is

$$\langle H \rangle = \sum_{n=1,3,5,\dots}^{\infty} \left(\frac{8\sqrt{15}}{n^3\pi^3} \right)^2 \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{480\hbar^2}{\pi^4 ma^2} \sum_{n=1,3,5,\dots}^{\infty} \frac{1}{n^4} = \frac{5\hbar^2}{ma^2}.$$

You got to check out the convergence of infinite series $\sum_{n=1,3,5,\cdots} \frac{1}{n^4}$ yourself from either Murray Spiegel or revisit your ZCA 110. Is $\langle H \rangle$ larger, equal or smaller than the ground state energy $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$? Explain why.

2.3 The Harmonic Oscillator

- Quantum harmonic oscillator suffers a potential of the parabolic form $V(x) = \frac{1}{2}m\omega^2x^2$, where ω^2 a positive constant (angular frequency squared), m the mass of the oscillator.
- In practice, in the neighborhood of a local minimum ($x = x_0$), a generic potential (Fig. 2.4) can be approximated by a harmonic potential of the form (by Taylor expanding the potential $V(x)$ about $x = x_0$):

$$V(x) \cong \frac{1}{2}V''(x_0)(x - x_0)^2$$

- As such, quantum harmonic oscillator (QHO) is a very important topic in QM as it provides very useful approximated solutions to many generic problem (such as phonon oscillation in periodic solid crystals, where the *ground state* of the periodic potential can be approximated by a harmonic potential.)
- TISE for a 1D harmonic oscillator:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{2x^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi. \tag{2.12}$$

- We will solve Eq.(2.12) using an analytical method – power series (we will skip the ladder operator method).

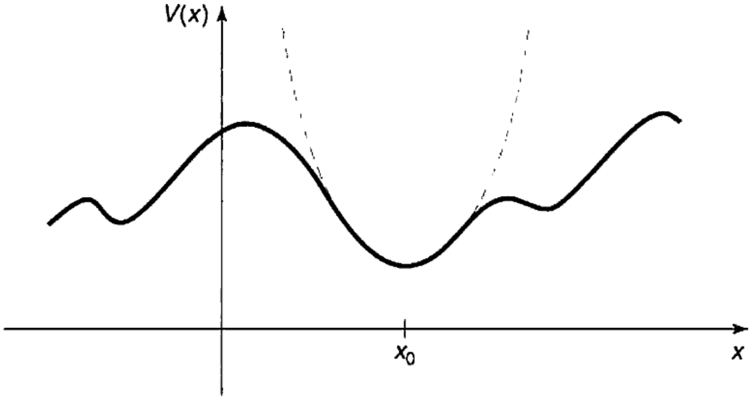


FIGURE 2.4: Parabolic approximation (dashed curve) to an arbitrary potential, in the neighborhood of a local minimum.

2.3.1 Analytical Method

- To simplify the complexity of the equation, we introduce dimensionless variable ξ in place of position variable x,

$$\xi = x\sqrt{\frac{m\omega}{\hbar}}.$$

- ξ is pronounced as "xi".

- The TISE then reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi, \tag{2.13}$$

where K (also dimensionless) is the energy in unit of $(1/2)\hbar\omega$,

$$K \equiv \frac{2E}{\hbar\omega}.$$

Exercise: Show this.

- We wish to solve Eq.2.13 for $\psi(x)$ and obtain the allowed values of K.

- The strategy we would employ in the following is to first look at the behaviour of the wave function solution to the TISE in the $\xi \to \infty$ limit. This will provide very insightful information to how the true solution shall behave. We could 'build up' the true solution based on ξ.

- To begin with, we know that the solution $\psi(\xi)$ must be well-behave (normalisable, finite, continuous) throughout all values in ξ, including in the $\xi \to \infty$ limit.

- In this limit, Eq.(2.13) becomes

$$\frac{d^2\psi}{d\xi^2} = \xi^2\psi, \tag{2.14}$$

- The solution to this second order ordinary different equation is

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{+\xi^2/2},$$

  A, B two arbitrary constants to be fixed by boundary conditions.
  Exercise: Prove this.

.

- The B term has to be dropped as it causes $\psi(\xi)$ not normalisable ($Be^{+\xi^2/2}$ blows up as $|\xi| \to \infty$).

- As such, $\psi(\xi) \sim e^{-\xi^2/2}$ at large ξ.

- In the intermediate range of ξ, we expect $\psi(\xi)$ to be represented by

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}, \tag{2.15}$$

where the (yet unknown) functions $h(\xi)$ behave in such a way that $\psi(\xi) \to e^{-\xi^2/2}$ at large ξ.

- So now the problem is recast into finding the form for $h(\xi)$, which is the solution to the equation (a supposedly easier task than solving $\psi(x)$ directly from the original TISE):

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K-1)h = 0. \tag{2.16}$$

Eq.(2.16) is obtained by substituting Eq.(2.15) into the TISE equation Eq.(2.13). *Exercise:* Show this.

- Eq.(2.16) is to be solved using power series method by assuming the solution could be expanded into the series form

$$h(\xi) = \sum_{j=0}^{\infty} a_j \xi^j. \tag{2.17}$$

- In practice, what we really need to know are the values of the coefficients a_j for all j.

- Differentiating $h(\xi)$ with respect to ξ once and twice, then substitute the results into Eq.(2.16), we obtain the relation

$$\sum_{j=0}^{\infty} \left[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j\right]\xi^j = 0 \tag{2.18}$$

for all powers of j.

- The coefficients to ξ^j must be zero (because ξ^j are not) so that the RHS of Eq.(2.18) is zero. Hence, we obtain the **recursion formula** that relates an a for the present j with previous j:

$$a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)} a_j. \tag{2.19}$$

- The recursion formula allows us to obtain all a_j based on two "seed" coefficients (unknown at this stage), a_0 and a_1.

- a_0 generate all even coefficients $a_j, j = 2, 4, 6, \cdots$.

- a_1 generate all odd coefficients $a_j, j = 3, 5, 7, \cdots$.

- Hence we write the solution $h(\xi)$ in terms of the sum of two parts with definite parity,

$$h(\xi) = h_{even}(\xi) + h_{odd}(\xi),$$

  where

$$h_{even}(\xi) \equiv a_0 + a_2\xi^2 + a_4\xi^4 + \cdots ,$$
$$h_{odd}(\xi) \equiv a_1 + a_3\xi^3 + a_5\xi^5 + \cdots .$$

- The exact values of the arbitrary constant a_0, a_1 are to be fixed by normalisation condition but usually not of much interest.

- But this is not the end of the story. In order to guarantee normalisation in $\psi(\xi)$, the functions $h(\xi)$ must behave in such a ways that $\psi(\xi)$ never blow up in the large ξ limit.

- Indeed, $\psi(\xi) = h(\xi)e^{-\xi^2/2}$, with $h(\xi)$ as defined in Eq. 2.17, does blow up at large $|\xi|$,

$$\psi(\xi) \to e^{\xi^2/2} \text{ as } \xi \to \infty.$$

  (See the textbook Griffth for discussion on this.)

- How to avoid $\psi(\xi)$ from blowing up? This can be achieved if the coefficients a_j in the series expansion $h(x) = \sum a_j\xi^j$ terminates at a cut-off (i.e., a "highest" j), say, $j = n$, i.e, $a_j = 0$ for all $j > n$.

- If we truncate the series after the n-th term, the solution would look like

$$\psi(\xi) = (a_0\xi^0 + a_1\xi^1 + a_2\xi^2 + a_3\xi^3 + \cdots + a_n\xi^n)e^{-\xi^2/2}.$$

- Look at the recursion formula, Eq. (2.19). We can impose automatic truncation into the series of $h(\xi)$ by introducing a non-negative integer n (i.e., 0,1,2,3,...) and tying it with the allowed energy E via

$$K = 2n + 1.$$

- In this way, either the odd or even terms in the power series will terminate for $j > n$.

- Note that the power series $\sum a_j \xi^j = h_{odd}(\xi) + h_{even}(\xi)$ comprises of both an even and odd part. The condition $K = 2n + 1$ only truncates either the odd or even part (but not both). For example, if n is even, only the even series is truncated but not the odd series.

- To truncate the series of the opposite parity, we need to impose by hand another condition: that if n is odd, the even parity part must be set to zero "by hand", $h_{even}(\xi) = 0$, i.e, $a_0 = 0$ (Hence the subsequent even coefficients $a_2 = a_4 = a_6 = \cdots = 0$.); if n is even, the odd parity part $h_{odd}(\xi) = 0$, i.e, $a_1 = 0$ (Hence the subsequent odd coefficients $a_3 = a_5 = a_7 = \cdots = 0$.);

- For example, if n is an odd value, $n = 5$, $a_7 = a_9 = \cdots = 0$. a_1, a_3, a_5 are non-zero. $a_0 = a_2 = a_4 = \cdots = 0$. (The latter is imposed "by hand").

- For example, if n is an even value, $n = 4$, $a_6 = a_8 = a_{10} = \cdots = 0$. a_0, a_2, a_4 are non zero. $a_1 = a_3 = a_5 = \cdots = 0$. (The latter is imposed "by hand").

- To summarise: If we (1) impose the condition $K = 2n + 1$, and (2) shut off the power-series of the opposite parity, the solution

$$\psi_n(x) = e^{-\xi^2/2}(a_0\xi^0 + a_2\xi^2 + a_0\xi^0 + \cdots a_n\xi^n)(\text{ for } n \text{ even}),$$

  or

$$\psi_n(x) = e^{-\xi^2/2}(a_1\xi^1 + a_3\xi^3 + a_5\xi^5 + \cdots a_n\xi^n)(\text{ for } n \text{ odd})$$

  will be well behaved (i.e., normalisable).

- We have not proved this (normalisation of $\psi_n(x)$) with mathematical rigor, but we can investigate the numerical behavior of $\psi_n(x)$ to show that indeed $\psi_n(x)$ is well behave for arbitrary n.

- As a result the normalisation condition forces the energy E to assume only discrete values according to

  $$K = 2n + 1 \rightarrow E_n = (\frac{1}{2} + n)\hbar\omega,\ n = 0, 1, 2, 3, \cdots$$

  We say that the energies of the QHM is quantised. It can not assume a continuous value as like in classical mechanics. Now each solution is characterised by a non-negative integer n, $\psi_n(\xi)$.

- One can show numerically that if E assume a value other that allowed, (say $E = 0.49\hbar\omega$ or $0.51\hbar\omega$), the solution $\psi(\xi)$ will not be normalisable (they blow up at large $|\xi|$), see Figure 2.3.

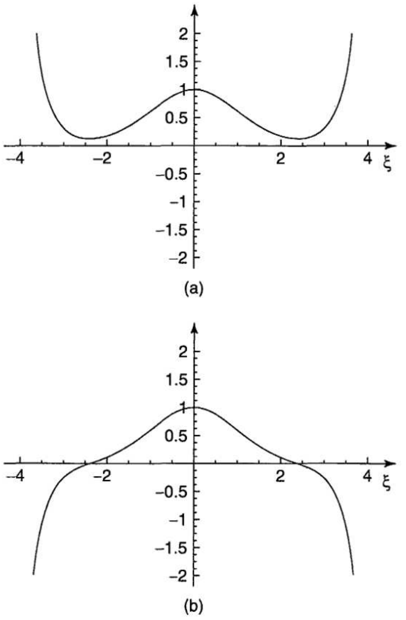


Figure 2.3: Solutions to the TISE for (a) $E = 0.49\hbar\omega$, and (b) $E = 0.51\hbar\omega$

Exercise: Assume n is 1, write down $h(\xi)$, hence the stationary wave function, $\psi_1(x)$. We denote the $h(\xi)$ function characterised by $n = 1$ as $h_1(\xi)$.

Exercise: Assume n is 2, write down $h(\xi)$, hence, $\psi_2(x)$. We denote the $h(\xi)$ function characterised by $n = 2$ as $h_2(\xi)$.

- The functions $h_n(\xi)$ is a polynomial of degree n in ξ, involving either even or odd powers only (depend on whether n is even or odd). Apart from overall factor a_0 or a_1, h_n are known as **Hermite polynomials**. See Table 2.1.

TABLE 2.1: The first few Hermite polynomials, $H_n(\xi)$.

$$H_0 = 1,$$
$$H_1 = 2\xi,$$
$$H_2 = 4\xi^2 - 2,$$
$$H_3 = 8\xi^3 - 12\xi,$$
$$H_4 = 16\xi^4 - 48\xi^2 + 12,$$
$$H_5 = 32\xi^5 - 160\xi^3 + 120\xi.$$

- In general, the normalised stationary states are given by the form

$$\psi_n(x) = h_n(\xi)e^{-\xi^2/2} = \frac{1}{\sqrt{2^n n!}} H_n(\xi)e^{-\xi^2/2}$$

- Figure 2.7(a) plots $\psi_n(x)$ for the first few n's.
- The Hermite polynomials can be generated from the **Rodrigues formula**:

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}.$$

- Higher order Hermite polynomials H_{n+1} can be easily generated from the lower order ones, H_n, using the recursion relation:

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi).$$

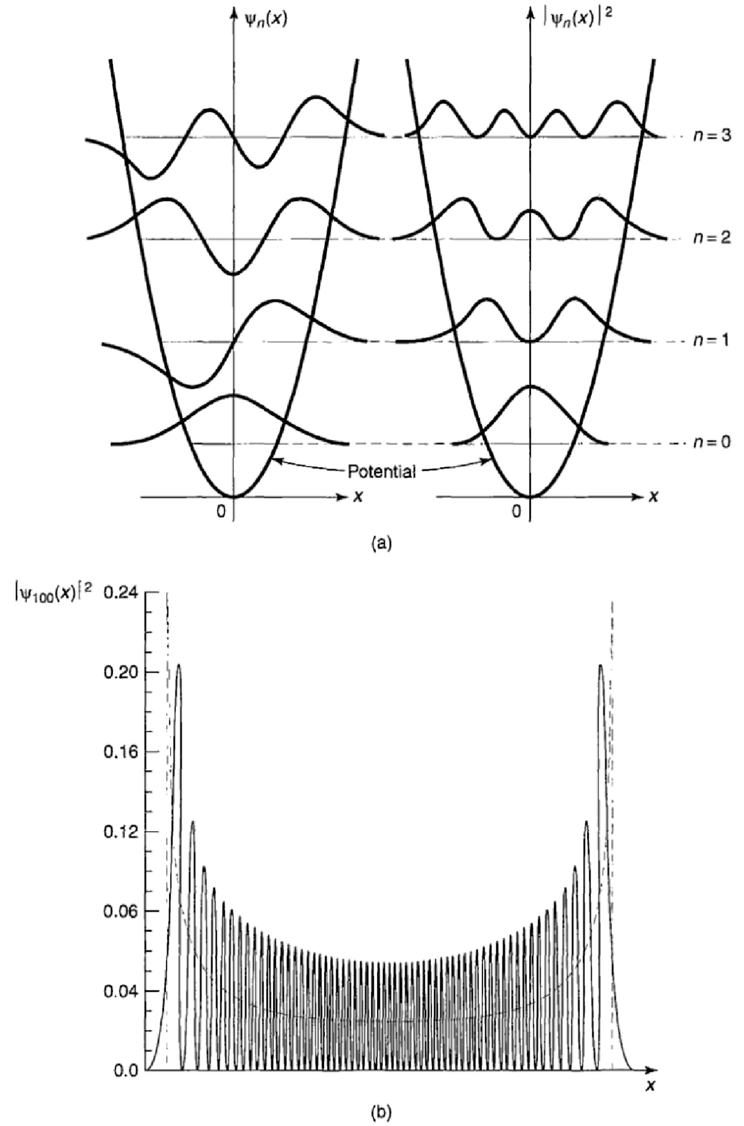


FIGURE 2.7: (a) The first four stationary states of the harmonic oscillator. T

Exercise: Derive H_1, H_2, H_3 from the Rodrigues formula.

Exercise: Derive H_3, H_4 from H_1, H_2 using the recursion relation. As a check, the function H_3 derived using both methods must agree.

- Three features of the QM solutions for the harmonic oscillator:

  1. $|\psi_n|^2 \neq 0$ outside the harmonic well. These are classically forbidden regions of x. Recall that classically, the energy of a harmonic oscillator is given by $E = K + V = (1/2)m\omega^2 x^2 + (1/2)m\omega^2(A^2 - x^2) = (1/2)m\omega^2 A^2$. The kinetic energy $K = (1/2)m\omega^2 x^2$ can never be larger than $E = (1/2)m\omega^2 A^2$ because $-A \leq x \leq A$. A is the amplitude of the oscillator.
  2. In the odd states, probability to find the oscillator is always zero at the center ($x = 0$) of the potential.
  3. Figure 2.7(b) plots $|\psi_{100}(x)|^2$. As $n \to \infty$, $|\psi_n|^2$ behaves much like what is expected of a classical harmonic oscillator if one plots the probability density of finding the oscillator as a function of position x. This is an particular example of the correspondence principle that says: in the $n \to \infty$ limit, results of a quantum calculation must reduce to that of classical calculation.

2.4 The Free Particle

- TISE for a free particle:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

  or, equivalently,

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \text{ where } k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

- This is similar to the case of particle in the infinite square well (except that now the width $a \to \infty$.)

- The general solution to the TISE

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx}$$

- There is no boundary condition to restrict the possible value of k (hence E) as in the infinite square well; the energy of the free particle E can take any positive value (recall why E can't be negative?).

- In relation to this, there is no quantization of states characterised by the integer n as in the the case of infinite square well or the QHO. k or E is not quantised in this case.

- Tacking on the time-dependence function $e^{-iEt/\hbar}$ to $\psi_k(x)$, the "stationary" state for the free particle is

$$\Psi_k(x,t) = \psi_k(x)e^{-itE/\hbar} = \psi_k(x)e^{-\frac{it\hbar k^2}{2m}} = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)}. \quad (2.20)$$

- The first term in the RHS represents a traveling plane wave in the $+x$ direction, whereas the second term a traveling plane wave in the -x direction.

- Rewrite Eq.(2.20) compactly as

$$\begin{aligned}\Psi_k(x,t) &= Ae^{ik(x-\frac{\hbar k}{2m}t)};\\ k &\equiv \pm\frac{\sqrt{2mE}}{\hbar},\ \text{with}\ \begin{cases} k>0 \Rightarrow \text{traveling to the positive direction}\\ k<0 \Rightarrow \text{traveling to the negative direction}\end{cases}\end{aligned} \quad (2.21)$$

- The "stationary states" of the free particle are traveling waves (this is unlike the cases of QHO or infinite square well) with a wavelength $\lambda = 2\pi/|k|$ and a corresponding momentum $p = \hbar|k|$.

- An disturbing feature: the wave function is not normalisable,

$$\int_{-\infty}^{\infty} \Psi_k^*\Psi_k dx \to \infty.$$

- This means the "stationary" wave function $\Psi_k(x,t)$ does not represents a physical state. In other words, there is nothing such as a free particle with a definite energy. To find a way out of this disturbing feature for the free particle, we turn to the most general solution to the TDSE for the free particle (instead of looking at the "stationary states" $\Psi_k(x)$ per se.

- Recall that the most general TDSE solution to quantised systems (e.g., infinite square well, harmonic potential) is a sum over all stationary states each indexed by the quantum number n, i.e., $\Psi(x,t) = \sum_{\text{all } n} c_n\psi_n(x)e^{-itE_n/\hbar}$.

- For the free particle case, the most general solution to the TDSE is not obtained via a discrete sum over all n but an integration over the continuous variable k instead,

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)\psi_k(x,t)e^{-itE/\hbar}dk = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\frac{\hbar k^2}{2m}t)}dk.$$

  Here $\frac{1}{\sqrt{2\pi}}\phi(k)dk$ plays the role of c_n, and instead of $\sum_n c_n(\cdots)$, we have $\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}(\cdots)\phi(k)dk$. The factor $1/\sqrt{2\pi}$ is introduced for the sake of later convenience (so that it is consistent with the definition of Fourier transformation).

- $\Psi(x,t)$ contains a range of k, hence a range of energies and speeds. Hence we understand that $\Psi(x,t)$ is a wave packet.
- Most importantly, $\Psi(x,t)$ is normalisable. It does represent a physical state.
- In other words, in QM, a free particle cannot be in a "stationary state", Ψ_k, because such "stationary states" are not normalisable for a free particle – it is unphysical. Instead, a free particle must be represented as a wave packet that has a large spread of wave number k (hence a large spread in energy E).
- Now, the problem remains to find what is $\phi(k)$ given the initial wave function profile $\Psi(x,0)$. This the equivalence to the determination of c_n, given a known initial profile $\Psi(x,0) = \sum_n c_n\psi_n(x)$, when we discussed the QHO and the infinite square well.
- If we know the initial profile $\Psi(x,0)$, we match it to $\frac{1}{\sqrt{2\pi}}\int \phi(k)e^{ikx}dk$ to find what $\phi(k)$ is.
- This is a classic Fourier analysis problem which answer is provided by Plancherel's theorem,

$$\boxed{f(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} F(k)e^{ikx}dk \Leftrightarrow F(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(x)e^{-ikx}dx.}$$

- $F(k)$ is the Fourier transform of $f(x)$; $f(x)$ inverse Fourier transform of $F(k)$.
- Here, we want to know what $\phi(k)$ is, given $f(x) \equiv \Psi(x,0)$. This could be obtained via the Fourier transforms:

$$\phi(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Psi(x,0)e^{-ikx}dx. \tag{2.22}$$

- $\phi(k)$ is the Fourier transform of $\Psi(x,0)$.
- Warning: Do mind the sign in the exponential factor in these Fourier transform conjugate pair $e^{\pm ikx}$.

Example 2.6

A free particle, which is initially localised in the range $-a < x < a$, is released at time $t = 0$:

$$\Psi(x,0) = \begin{cases} A, & \text{if} - a < x < a, \\ 0, & \text{otherwise,} \end{cases}$$

where A and a are real positive constants. Find $\Psi(x,t)$.

Solution: Refer Figure 2.8. First find the normalisation constant A:

$$\int_{-\infty}^{\infty} |\Psi(x,0)|^2 dx = 1 \Rightarrow A = \frac{1}{\sqrt{2a}}.$$

Then work out $\phi(k)$ using Eq.(2.22):

$$\phi(k) = \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2a}}\int_{-a}^{a} e^{-ikx} dx = \cdots = \frac{1}{\sqrt{a\pi}}\frac{\sin(ka)}{k}. \text{ (show this)}$$

- Then put it back to $\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\frac{\hbar k^2}{2m}t)}dk$, and we obtain

$$\Psi(x,t) = \frac{1}{\pi\sqrt{2a}}\int_{-\infty}^{\infty}\frac{\sin(ka)}{k}e^{i(kx-\frac{\hbar k^2}{2m}t)}dk. \tag{2.23}$$

- The integration cannot be solved analytically (in practice one solves it numerically.)
- From Eq. (2.23), we see that once the time evolution is switched on (i.e., $t > 0$), the initial wave function profile $\Psi(x,t)$ begins to spread in width, moving towards both sides and decreases in amplitude. This is similar to the spreading of a ripple from the center of a water generated by a perturbation. Initially well localised, the wave will become less and less localised as time goes by, see Figure 2.8.
- $\phi(k)$ describes the free particle (at $t = 0$) in terms of $k = p/\hbar$, whereas $\Psi(x,0)$ the free particle (at $t = 0$) in terms of position, x.
- We will consider two limits of the free particle wave function solution at $t = 0$. These limits are (i) $a \ll 1$ and (ii) $a \gg 1$. We will see that in these limits, the position and momentum of the free particle display "antagonistic" behaviour consistent with Heisenberg uncertainty principle: the lesser is the spread in position (momentum) the larger is the spread in momentum (position).
- In the $a \ll 1$ limit,
  -
$$\phi(k) \xrightarrow{a\ll 1} \sqrt{\frac{a}{\pi}}.$$

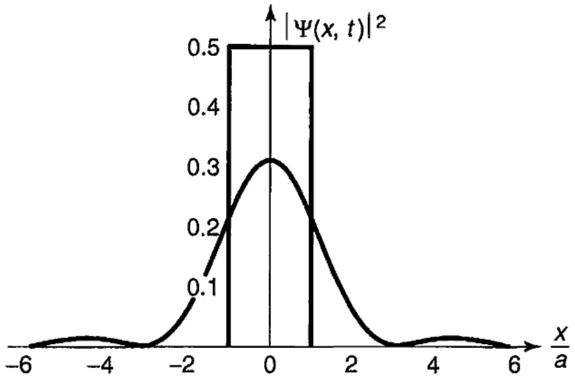


FIGURE 2.8: Graph of $|\Psi(x,t)|^2$ (Equation 2.104) at $t = 0$ (the rectangle) and at $t = ma^2/\hbar$ (the curve).

- Note that this limiting behavior is obained with the help of L'Hopital's rule, $\lim_{x\to 0}\frac{\sin x}{x} = 1$.
- Compare this with

$$\Psi(x,0) = \begin{cases} A, & \text{if} -a < x < a, \\ 0, & \text{otherwise.} \end{cases}$$

- See Figure 2.9. A small spread in position space, $\sigma_x \simeq a$ (where $a \ll 1$) is associated with a large spread in momentum space, i.e., $\sigma_k \to \infty$.
- In other words, in the limit $a \ll 1$, where the particle is sharply localised in position (with a narrow width in $\Psi(x,0)$), it's spread in momentum must be large (seen from the fact that $\phi(k)$ a flat constant throughout all values k).

- Now consider $\phi(k)$ in the $a \gg 1$ limit: Multiply the RHS of $\phi(k)$ by a factor of $\frac{a}{a}$,
  -
$$\phi(k) = \sqrt{\frac{a}{2\pi}}\frac{\sin(ka)}{ka}.$$
  - For a fixed value of a, $\phi(k)$ peaks around $k = 0$ with a width $\sigma_k \approx \frac{2\pi}{a}$, see Figure 2.10. The width of $\phi(k)$ in momentum space is inversely proportional to a.
  - If we take $a \to \infty$, $\Psi(x,0)$ becomes a flat constant (i.e. the spread in position becomes infinitely large), yet this results in a much narrower $\phi(k)$ in momentum space. Again, we see the HUP is in action here.

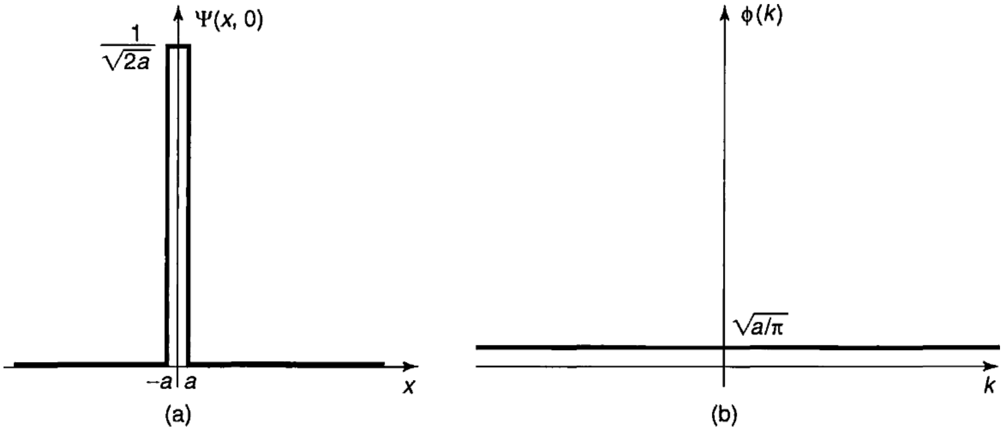


FIGURE 2.9: Example 2.6, for small a. (a) Graph of $\Psi(x,0)$. (b) Graph of $\phi(k)$.

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- When time evolution is switched on:
  - Initially the wave is well located within $\sigma_x(t=0)=2a$ (with a tiny spread in position) [(a) in Figure 2.9]. From the viewpoint of Fourier analysis, the highly localised wave (in terms of position space x) is made up of many waves with various wavelengths, hence the spread in σ_k is huge ("it is made up of many, many wave numbers"). Mathematically, this is translated into the statement $\sigma_k(t=0)\to\infty$, [see (b) in Figure 2.9].
  - When t begins, the wave starts to spread, and $\sigma_x(t\to\infty)\to\infty$. The wave tends toward a constant throughout all x [(a) in Figure 2.10]. From the view point of Fourier analysis, it takes much less number of waves with different wavelength to make up such a "flat" wave ("it is made up of only a few wave numbers"). In other words, the wavelength is now better defined (sharper), hence the spread in k, $\sigma_k\to 2\pi/a$, [(b) in Figure 2.10].
  - To summarise, for a fixed a, the time-development behavior of the wave function is such that,

$$\sigma_x(t=0)=2a\longrightarrow\sigma_x(t\to\infty)\to\infty$$

$$\sigma_k(t=0)\to\infty\longrightarrow\sigma_k(t\to\infty)\to 2\pi/a$$

Exercise (Problem 2.8):

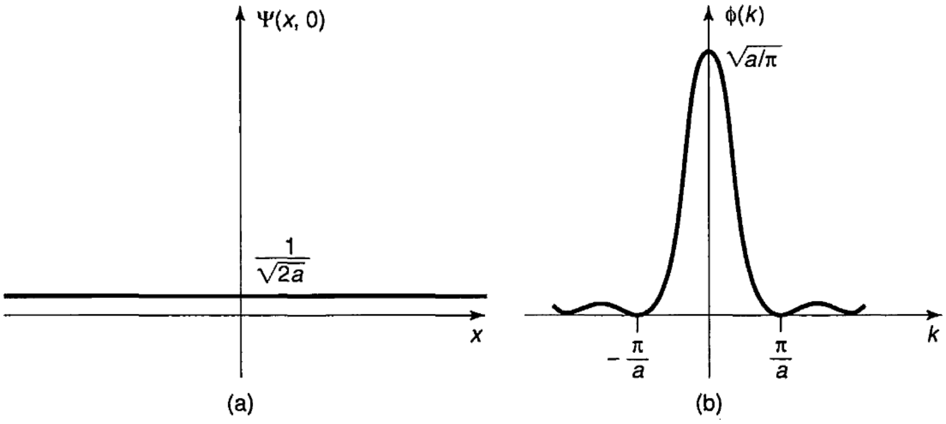


FIGURE 2.10: Example 2.6, for large a. (a) Graph of $\Psi(x, 0)$. (b) Graph of $\phi(k)$.

Show that $Ae^{ikx} + Be^{-ikx}$ and $C \cos kx + D \sin kx$ are equivalent ways of writing the same function of x, and determine the constants C and D in terms of A and B, and vice versa. *Hint:* Use Euler's equation, $e^{ix} = \sin x + i \cos x$.

Comment: In quantum mechanics, when $V = 0$, the exponentials represent traveling waves, and are most convenient in discussing the free particle, whereas sines and cosines correspond to standing waves, which arise naturally in the case of the infinite square well.

2.5 The Delta-Function Potential

2.5.1 Bound states and scattering states

- **Recap**
  - Two different kind of TISE solutions $\psi(x)$ (stationary states) were encountered so far:
    1. $\psi_n(x)$, renormalisable, labeled by a *discrete index* n, as in QHO, infinite square well;
    2. $\psi_k(x)$, non-renormalisable, labeled by *continuous variable* k, as in the free particle.
  - In both cases, the general solution to the TDSE is a linear combination of these stationary states, i.e., $\Psi(x,t) = \sum_{n=0}^{\infty} c_n \psi_n(x) e^{-itE_n/\hbar}$ for case 1, $\Psi(x,t) = \int_{k=-\infty}^{k=\infty} \phi(k)\psi_k(x) e^{-i\frac{\hbar k^2}{2m}t} dk$ for case 2.
  - What is the significance of this distinction (continuous variable k vs. discrete index n)?
  - It turns out that a state indexed by a continuous variable is a **scattering state**, whereas that by discrete index a **bound state**.

- *The following discussion on the bound state/scattering states is in the context of classical mechanics:*
  - *Classically*, a particle (with a given constant energy E) subjected to a potential $V(x)$ could be either (a) trapped between two "turning points" separated by a finite distance, or (b) free to roam in one of the following regions: $-\infty \leq x < x_{\text{TP}}$, or $x_{\text{TP}} \leq x \leq \infty$ or $-\infty \leq x \leq \infty$.
  - Case (a) corresponds to the situation as in Figure 2.12(a) and Figure 2.12(c). The energy of the particle, E, is such that $V(x_{\text{TP1}}) \leq E \leq V(x_{\text{TP2}})$. These are classical bound states.
  - Case (b) corresponds to the situations as depicted in Figure 2.12(b). The energy of the particle, E, in the left figure in Figure 2.12(b) is such that $E \geq V(x)$ for $x \leq x_{\text{TP}}$. For the right figure in Figure 2.12(b), $E > V(x)$ for $-\infty \leq x \leq \infty$. These are classical scattering states.
  - Note that in Figure 2.12(c), should the energy E is sufficiently raised, the particle will "overflow" into a scattering state. This shows that whether a particle subjected to a potential $V(x)$ is in a bound or scattering state, in some cases, depend on how large is E.

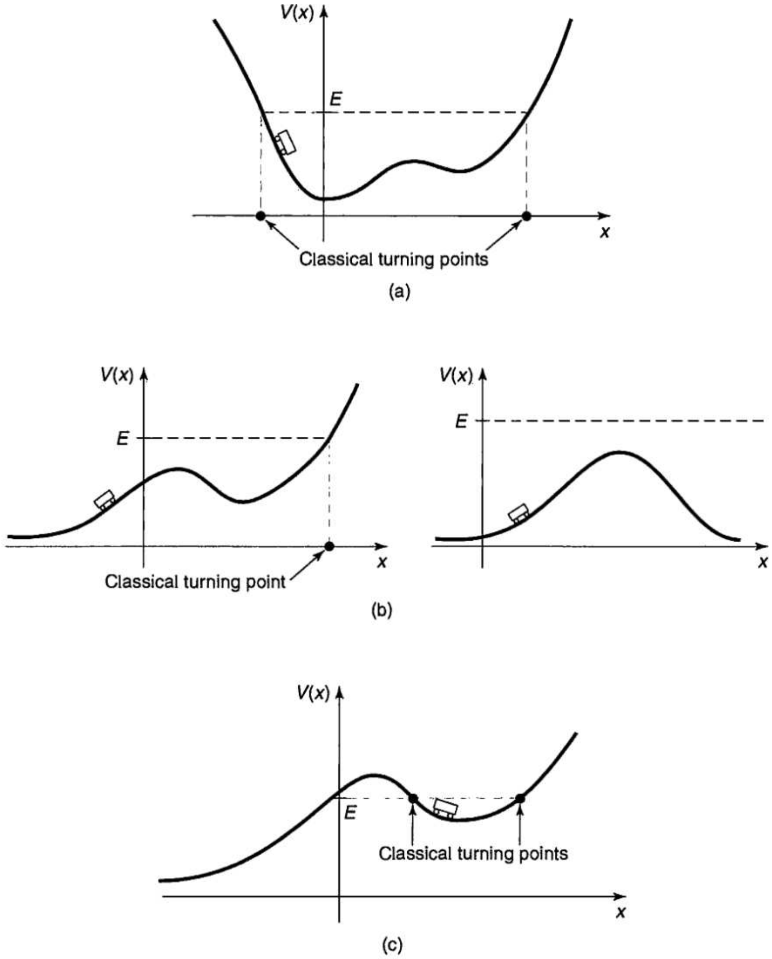


FIGURE 2.12: (a) A bound state. (b) Scattering states. (c) A *classical* bound state, but a quantum scattering state.

  - In classical mechanics, a particle can only exist in a region where the energy of the particle E is such that $E > V(x)$.

- *The following discussion on the bound state/scattering states is in the context of QM:*

  - For a QH oscillator, it is restricted to move around in the restricted region inside the potential well. It admits only bound states. For any given fixed energy E, there always exist a x_{TP} such that $V(x) > E$ when $|x| \geq x_{\text{TP}}$.
  - In the free particle case, the particle is free to move around in all regions. The free particle admits only scattering states (since $E > V(x) = 0$ everywhere).
  - In QM, some potentials admit only bound states, some allow only scattering states. Some permit both, depend on the energy of the particle (example: finite square well).

  - In QM, a quantum phenomena known as **quantum tunneling**, which has no classical analog, allows a particle to leak out from the potential "trap" into regions which are otherwise forbidden in classical mechanics (these are regions in x where $E < V(x)$.) This occurs in, e.g., the QHO, where the a non-zero wave function penetrates beyond the classically forbidden region by a "skin-depth".
  - Two kinds of solutions to the SE correspond to bound state and scattering state:

$$\begin{cases} E < [V(-\infty) \text{ and } V(+\infty)] \Rightarrow \text{ bound state.} \\ E > [V(-\infty) \text{ or } V(+\infty)] \Rightarrow \text{ scattering state.} \end{cases} \tag{2.24}$$

2.5.2 The Delta function

- Defined as

$$\delta(x) = \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0, \end{cases}$$

  with

$$\int_{-\infty}^{\infty} \delta(x) dx = 1.$$

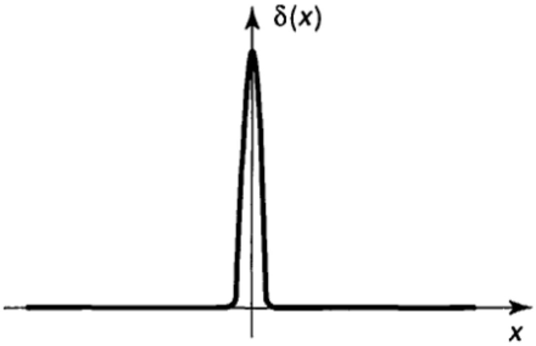


Figure 2.4: The Dirac delta potential well.

Exercise: What is the dimension of the Dirac delta function?
Hint: refer to the normalisation equation of it.

- $\delta(x-a)$ is a sharp spike at $x = a$.

- Multiplying a function $f(x)$ by the Dirac delta function $\delta(x-a)$ and then integrate over all x "projects" out the value of the function $f(x)$ at $x=a$:

$$\int_{-\infty}^{\infty} \delta(x-a)f(x)dx = f(a).$$

- Consider a hypothetical potential well

$$V(x) = -\alpha\delta(x),$$

  α a positive constant.

  Exercise: What is the dimension of α?
  Hint: you need to know what is the dimension of the Dirac delta function to answer this.

- The TISE for this case is

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

- There are two possibilities: either $E > 0$ (this will yield a scattering state) or $E < 0$ (this will yield a bound state). Convince yourself that these cases correspond respectively to a scattering and a bound state by referring to the criteria Eq. (2.24).

- We will solve the TISE for the case of $E < 0$, and as we will see later, the stationary solution is a localised function concentrating around $x = 0$ and drops to zero as $|x| \to \infty$. Hence it is a bound state.

- We need to solve this equation by considering the variable x in three separate regions, namely, $x < 0$, $x > 0$ and $x = 0$.

- Consider the $x < 0$ region:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \equiv \kappa^2\psi, \ \kappa \equiv \sqrt{\frac{-2mE}{\hbar^2}},$$

  κ is real and positive (since $E < 0$ by assumption).

- The general solution is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}.$$

- A has to be set to zero so that $\psi(x)$ remains finite as $x \to -\infty$, otherwise $\psi(x)$ will explode in this limit.

- Hence,
$$\psi(x) = Be^{\kappa x},\ x < 0.$$

- Using similar argument, we obtain the solution
$$\psi(x) = Fe^{-\kappa x},\ x > 0$$

- At $x = 0$, we need to stitch together the solutions from both sides by applying appropriate boundary conditions that:

$$\boxed{\begin{cases} 1.\ \psi \text{ is always continuous} \\ 2.\ \frac{d\psi}{dx}\text{is continuous except at points where the potential is infinite.} \end{cases}} \tag{2.25}$$

- Boundary condition #1 requires that $\lim_{x\to 0^-}\psi(x) = \lim_{x\to 0^+}\psi(x)$, i.e. $\psi(x = 0) = F = B$.

- Hence the full (valid for all x) solution for $\psi(x)$ is
$$\psi(x) = \begin{cases} Be^{\kappa x}, x \leq 0 \\ Be^{-\kappa x}, x \geq 0, \end{cases}$$

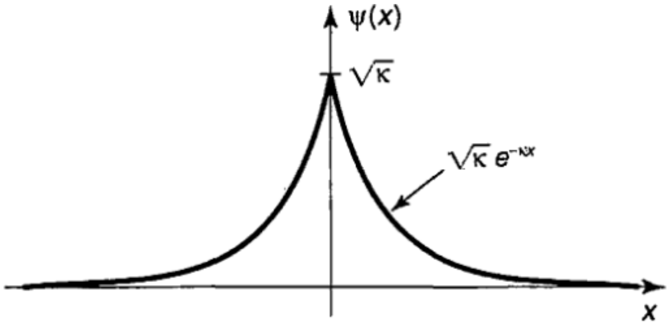


Figure 2.5: Bound state wave function for the delta-function potential.

- Normalisation gives the value of $B = \sqrt{\kappa}$.
Exercise: Show this.

- Now let us look at the boundary condition #2. It does not play a role to determine the solution; it forces energy quantisation upon the bound state solution.

- To see how quantisation arises, integrate the TISE around $x = 0$ for a small region $-\epsilon < x < \epsilon$, ϵ a tiny positive number. At the end we will take the limit $\epsilon \to 0$. As a result, quantisation of energy will arise:

$$\lim_{\epsilon\to 0} -\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon}\frac{d^2\psi}{dx^2}dx + \lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon} V(x)\psi(x)dx = \lim_{\epsilon\to 0} E\int_{-\epsilon}^{+\epsilon}\psi(x)dx.$$

- The first term (apart from the constant $-\frac{\hbar^2}{2m}$) is

$$\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon}\frac{d^2\psi}{dx^2}dx = \lim_{\epsilon\to 0}\left(\left.\frac{d\psi(x)}{dx}\right|_{\epsilon} - \left.\frac{d\psi(x)}{dx}\right|_{-\epsilon}\right) \equiv \Delta$$

- The second term:

$$\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon} V(x)\psi(x)dx = \lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon} -\alpha\delta(x)\psi(x)dx = -\alpha\psi(0).$$

- The last term involving E is zero in the limit $\epsilon \to 0$:

$$\lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}\psi(x)dx = 0$$

  It represents the area of the function $\psi(x)$ about the kink at $x = 0$, and this area shrinks to zero as $\epsilon \to 0$.

- Equating both terms,

$$-\frac{\hbar^2}{2m}\Delta = \alpha\psi(0) = \alpha\sqrt{\kappa} \tag{2.26}$$

- Look more closely at Δ :

$$\Delta = \lim_{\epsilon\to 0}\left(\left.\frac{d\psi(x)}{dx}\right|_{\epsilon} - \left.\frac{d\psi(x)}{dx}\right|_{-\epsilon}\right) = \lim_{x\to 0^+}\frac{d\psi(x)}{dx} - \lim_{x\to 0^-}\frac{d\psi(x)}{dx}$$

- The second term on the RHS is for $x < 0$, where $\psi(x) = Be^{\kappa x}$, $\frac{d\psi(x)}{dx} = \kappa Be^{\kappa x}$,

$$\lim_{\epsilon\to 0}\left.\frac{d\psi(x)}{dx}\right|_{-\epsilon} = \lim_{x\to 0^-}\frac{d\psi(x)}{dx} = \lim_{x\to 0^-}\kappa Be^{\kappa x} = \kappa B$$

- Similarly for the first term, it is for $x > 0$, where $\psi(x) = Be^{-\kappa x}$, $\frac{d\psi(x)}{dx} = -\kappa Be^{-\kappa x}$,

$$\lim_{\epsilon\to 0}\left.\frac{d\psi(x)}{dx}\right|_{\epsilon} = \lim_{x\to 0^+}\frac{d\psi(x)}{dx} = \lim_{x\to 0^+} -\kappa Be^{-\kappa x} = -\kappa B$$

- Put back both expression into Δ:

  $$\Delta = -2\kappa B,$$

  so that now Eq.(2.26) becomes

  $$-2\kappa B = -\frac{2m}{\hbar^2}\alpha\sqrt{\kappa} \Rightarrow \kappa = \frac{m}{\hbar^2}\alpha \Rightarrow \kappa^2 = \frac{m^2}{\hbar^4}\alpha^2 = -2\frac{mE}{\hbar^2},$$

  from which quantisation of energy ensues (recall that from normalisation, we already know $B = \sqrt{\kappa}$),

  $$E = -\frac{m\alpha^2}{2\hbar^2}.$$

  The bound state's energy is quantised in the sense that it admits only one allowed discrete value (which is unlike the bound states of QHM or the infinite square well).

- In terms of α, $\sqrt{\kappa} = \frac{\sqrt{m\alpha}}{\hbar}$.

- The stationary wave function is $\psi(x) = \frac{\sqrt{m\alpha}}{\hbar^2} e^{\frac{-m\alpha}{\hbar^2}|x|}$, which is the only bound state (no other excited states)

What about scattering state, with $E > 0$? This case will not be discussed here. Read the textbook for more detail.

2.6 The Finite Square Well

- $$V(x) = \begin{cases} -V_0, \text{ for } -a \leq x \leq a, \\ 0, \text{ for } |x| > a, \end{cases}$$

  where V_0 is a positive constant.

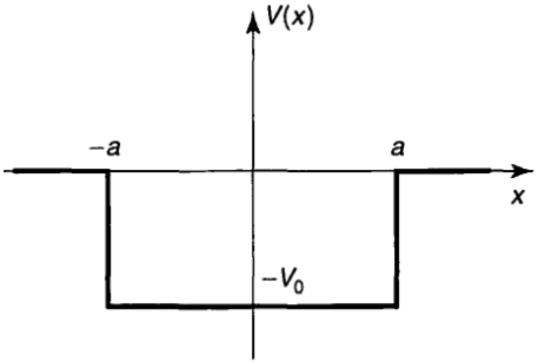


Figure 2.6: The finite square well potential

- First, consider the case of $E < 0$ (bound state).
- Three regions: $x \leq -a$, $-a < x < a$, $x \geq a$.
- For the region $x < -a$, the TISE is

  $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \text{ or } \frac{d^2\psi}{dx^2} = \kappa^2\psi,$$

  where $\kappa = \sqrt{-\frac{2mE}{\hbar^2}}$ is real and positive. The solution is

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

  where the term with coefficient A is dropped so that the function does not blow up in the limit $x \to -\infty$.
- For the region $-a < x < a$

  $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi, \text{ or } \frac{d^2\psi}{dx^2} = -l^2\psi,$$

  where $l = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$.
- We would further assume $-V_0 < E$ so that $l > 0$ and real (can you recall why such an assumption is necessary?). With this assumption, the general solution to the TISE in this region is

  $$\psi(x) = C\sin(lx) + D\cos(lx).$$

- For the region $x \geq a$, similar argument as that for the region $x \leq -a$ leads to

  $$\psi(x) = F\exp(-\kappa x)$$

  so that the stationary state does not blows up when $x \to \infty$.

- Note that since the potential is an **even function**, i.e., $V(x) = V(-x)$, we can prove that the solution $\psi(x)$ can always be taken to be either even (i.e., $\psi(x) = \psi(-x)$) or odd (i.e., $\psi(x) = -\psi(-x)$). Can you prove this statement?

- We will now proceed by assuming the solution $\psi(x)$ an even function. For the sake of completeness, we must also repeat the following analysis by taking the solution as an odd function (this case will be covered later).

- Using such parity argument saves us some efforts in obtaining the solution. Specifically, we need only to impose boundary conditions at one side of $x = 0$ (say at $x = x_0$). What happen to $\psi(x)$ and $\frac{d\psi}{dx}$ at the opposite site $x = -x_0$ can be easily inferred from $\psi(x = x_0)$, using the parity property of $\psi(-x_0) = \pm\psi(x_0)$. But more importantly, it allows us to treat the two solutions of opposite parity separately (hence the working is less messy).

- In general, the existence of parity in the potential is good for us as it helps to provide some information about the properties of the solutions even before we solve the problem. This information also will help to ease the working of obtainting the solutions.

- Assume $\psi(x)$ an even function,

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, \text{ for } x \leq -a, \\ D\cos(lx), \text{ for } -a < x < +a, \\ \psi(-x), \text{ for } x \geq a \end{cases}$$

- Boundary conditions (1) $\psi(x)$ continuous; (2) $\frac{d\psi}{dx}$ continuous.

- Look at the point $x = a$: Boundary condition (1) at this point requires

$$Fe^{-\kappa a} = D\cos la$$

- Boundary condition (2) requires

$$-\kappa Fe^{-\kappa a} = -lD\sin la$$

- Taking the ratio of both gives

$$\kappa = l\tan(la)$$

- This formula (a result of imposing the boundary conditions upon the solution of $\psi(x)$) gives rise to quantisation of allowed energies, as shows below:

- Let $z \equiv la$ and $z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}$.
- $\kappa = l\tan(la)$, rewritten in terms of z, z_0, is a transcendental function (i.e., function without an analytical solution). It needs to be solve numerically.

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

Exercise: Show this.

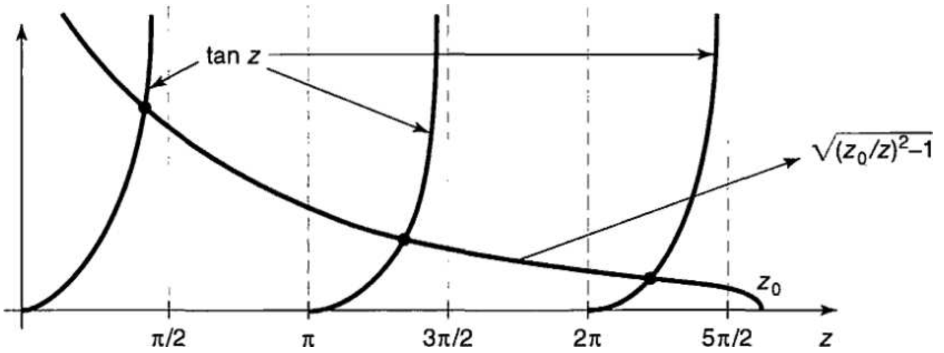


Figure 2.7: Graphical solution to $\tan z = \sqrt{(z_0/z)^2 - 1}$, for $z_0 = 8$ (*even states*).

- The values of z for the intersections in the curves (i.e., numerical values on the horizontal axis, let's call it $z_1, z_2, z_3, \cdots$) shown in Figure 2.6 gives the allowed energies.
- These z_n are to be determined numerically for a given set of $\{V_0, a\}$. The allowed energies in terms of z_n are

$$E_n = z_n^2 \frac{\hbar^2}{2ma^2} - V_0.$$

- For wide, deep well, $z_0 \gg 1$ because $V_0 \gg 1$. As a result, the function $\sqrt{(z_0/z)^2 - 1)}$ is "higher" for larger z_0. For large z_0, the intersections would be slightly lower than $n\pi/2$. Hence $z_n \approx \frac{n\pi}{2}$, so that

$$E_n \approx \frac{n^2\pi^2\hbar^2}{2m(2a)^2} - V_0.$$

- Figure 2.8 illustrate the numerical behavior of the transcendental equation generated using Mathematica code. The code can be downloaded at

  http://www2.fizik.usm.my/tlyoon/teaching/ZCT205_1112/finitesw.nb

- For shallow, narrow well, z_0 is tiny. Note that z_0 is the value where the curve $\sqrt{(z_0/z)^2 - 1}$ cuts the horizontal axis. The $\tan z$ curves are fixed. As z_0 gets smaller and smaller, it passes through $n\pi/2$ from higher n towards $z_0 = 0$. Once it pass through $z = \pi/2$, as long as $0 < z_0 < \pi/2$, there is always one bound state (correspond to a intersection value $z \approx \epsilon$), where ϵ a tiny but non-zero positive number. The sole bound state energy in this limit is

$$E = \frac{\hbar^2 \epsilon^2}{2ma^2} - V_0.$$

- The green coloured curve of the last graphs, with $V_0 = 1$ in Figure 2.8 illustrates such situation.

  Exercise: Show this. Hint: for tiny ϵ, $\tan \epsilon \approx \epsilon$.

  Exercise: Obtain the normalisation constants F, D.

- The above analysis is valid to the even parity solution of $\psi(x)$. It should also be repeated for odd parity solution of $\psi(x)$ to obtain a different set of bound states and energies. To do so, essentially, simply replace the $\cos(lx)$ function by a $\sin(lx)$ and go through the similar procedure of imposing boundary conditions. Odd solution takes the form

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, \text{ for } x \le -a, \\ C\sin(lx), \text{ for } -a < x < +a, \\ \psi(-x), \text{ for } x \ge a. \end{cases}$$

  Exercise: Work out the allowed energies for the odd parity case.

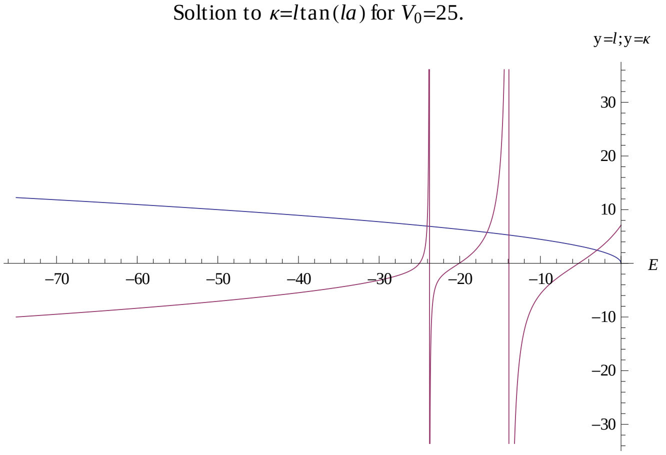
Figure 2.8: Numerical solutions for the transcendental obtained using Mathematica using various values of V_0

Solution to equation $\kappa = l\tan(la)$ for $V_0 = 25$ for even-parity solution. Note that there are only three solutions for this choice of V_0.

$$\kappa = \sqrt{-\frac{2\,m\,E}{\hbar^2}}\ ,\ l = \sqrt{\frac{2\,m\,(E - V_0)}{\hbar^2}}$$

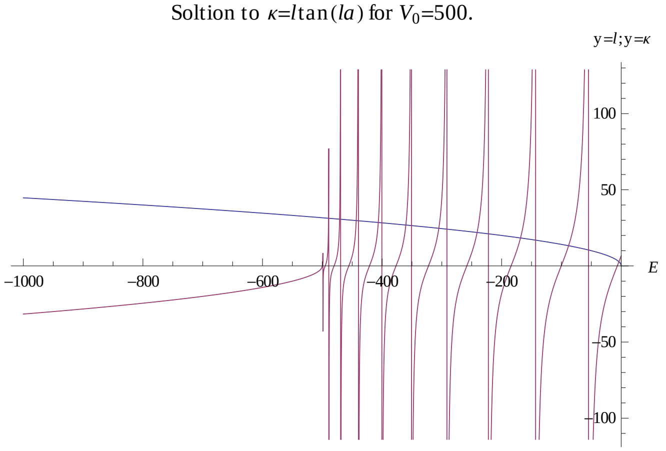
```
In[38]:= hbar = 1; V0 = 25.0; m = 1; a = 1.0;
         l[ee_] := Sqrt[2 m (ee + V0)] / hbar;
         k[ee_] := Sqrt[-2 m ee] / hbar;
         fl[ee_] := l[ee] * Tan[a * l[ee]];
         Plot[{k[ee], fl[ee]}, {ee, 0, -3 V0}, AxesLabel → {"E", "y=l;y=κ"}, PlotLabel →
           "Soltion to  κ=ltan(la)  for V₀="<> ToString[V0]]
```

Out[42]=



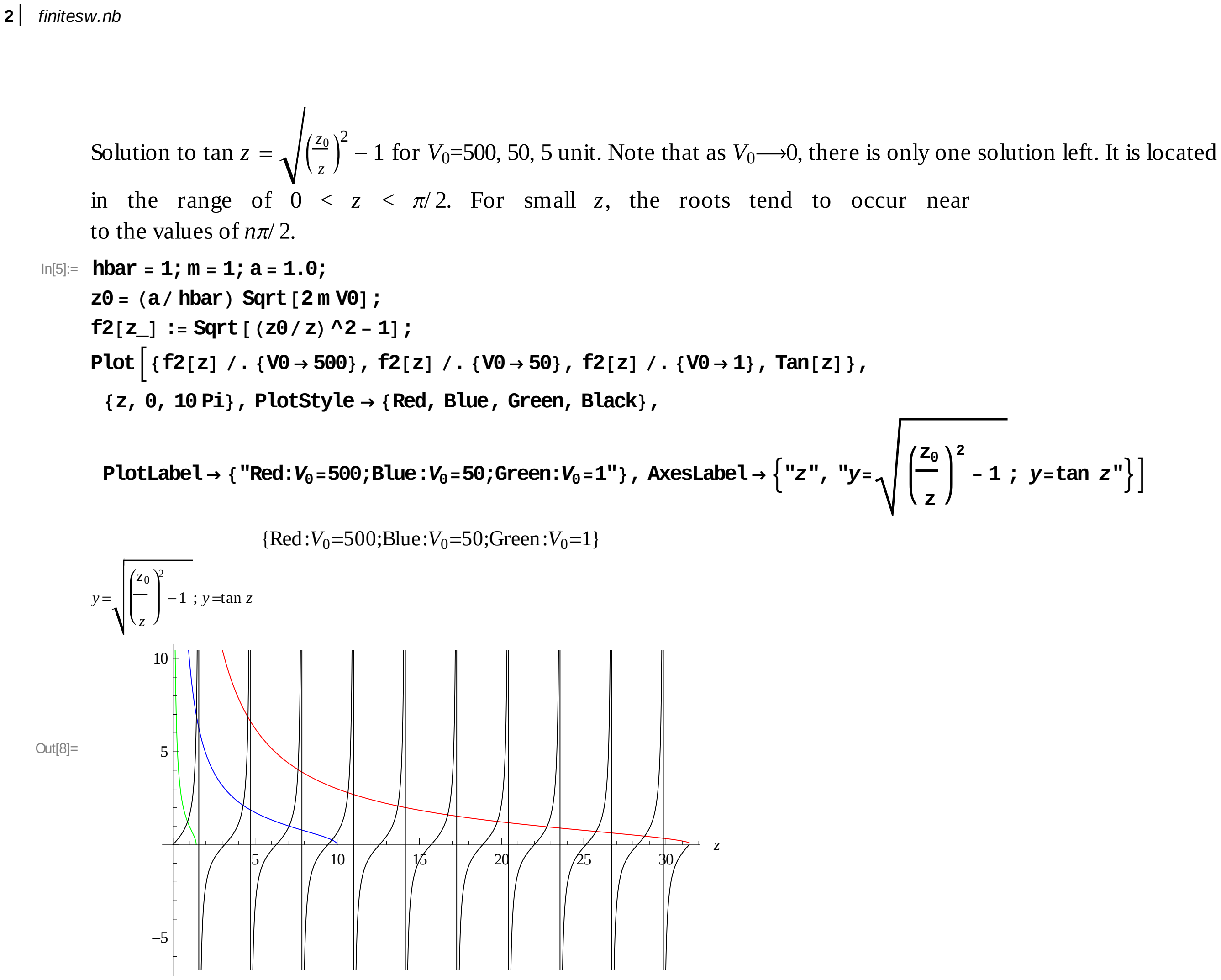
```
In[43]:= hbar = 1; V0 = 500.0; m = 1; a = 1.0;
         l[ee_] := Sqrt[2 m (ee + V0)] / hbar;
         k[ee_] := Sqrt[-2 m ee] / hbar;
         fl[ee_] := l[ee] * Tan[a * l[ee]];
         Plot[{k[ee], fl[ee]}, {ee, 0, -2 V0}, AxesLabel → {"E", "y=l;y=κ"}, PlotLabel →
           "Soltion to  κ=ltan(la)  for V₀="<> ToString[V0]]
```

Out[47]=



Solution to equation $\kappa = l\tan(la)$ for $V_0 = 500$ for even - parity solution.Note that there are 11 solutions for this choice of V_0.

Figure 2.9: Numerical solutions for the transcendental obtained using Mathematica using various values of V_0 (cont.)



Solution to tan $z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$ for V_0=500, 50, 5 unit. Note that as $V_0 \longrightarrow 0$, there is only one solution left. It is located in the range of $0 < z < \pi/2$. For small z, the roots tend to occur near to the values of $n\pi/2$.

In[5]:=

```
hbar = 1; m = 1; a = 1.0;
z0 = (a / hbar) Sqrt[2 m V0];
f2[z_] := Sqrt[(z0 / z)^2 - 1];
Plot[{f2[z] /. {V0 → 500}, f2[z] /. {V0 → 50}, f2[z] /. {V0 → 1}, Tan[z]},
 {z, 0, 10 Pi}, PlotStyle → {Red, Blue, Green, Black},
 PlotLabel → {"Red:V0=500;Blue:V0=50;Green:V0=1"}, AxesLabel → {"z", "y=Sqrt[(z0/z)^2 - 1] ; y=tan z"}]
```

Out[8]=

We have shown the bound state solutions. Next we are going to solve for the scattering state solutions for the finite square well, where $E > 0$. We consider a particle incident upon the potential from the left, and there is no particle incident or reflected from the right.

- For $x \leq -a$,

  $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \text{ or } \frac{d^2\psi}{dx^2} = -k^2\psi,$$

  where $k = \sqrt{\frac{2mE}{\hbar^2}}$ is real and positive. This is a second order differential equation encountered in classical simple harmonic motion (there you have a t instead of x) with a solution of the form (which you should be familiar with)

  $$\psi(x) = Ae^{ikx} + Be^{-ikx}.$$

  The first term in the RHS represent a traveling wave to the right (this is the incident particle), whereas the second a traveling wave to the left (this is the reflected particle upon bouncing on the boundary at $x = -a$). A is the amplitude of the incident wave; B the amplitude of the reflected wave.

- For $-a < x < a$,

  $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E + V_0)\psi, \text{ or } \frac{d^2\psi}{dx^2} = -l^2\psi,$$

  $l = \sqrt{\frac{2m}{\hbar^2}(E + V_0)}$, real and positive; The solution is

  $$\psi(x) = C\sin(lx) + D\cos(lx).$$

  This represents a sort of standing wave that is established in the potential well.

- For $x \geq a$,

  $$\psi(x) = Fe^{ikx} + Ge^{-ikx}.$$

  Ge^{-ikx} represents a traveling wave coming from the right. In our problem under consideration, there is no boundary to the right of the potential (hence no reflected wave from such a boundary) or any source of wave coming from the right. As such, this term is dropped, so that

  $$\psi(x) = Fe^{ikx}, \ \ x \geq a.$$

- Imposing boundary condition (BC) #1 at $x = -a$ gives

$$Ae^{-ika} + Be^{ika} = C\sin(-la) + D\cos(-la) = -C\sin(la) + D\cos(la) \quad (2.27)$$

- Imposing boundary condition (BC) #2 at $x = -a$ gives

$$ik\left[Ae^{-ika} - Be^{ika}\right] = l\left[C\cos(la) + D\sin(la)\right] \quad (2.28)$$

- Imposing boundary condition (BC) #1 at $x = a$ gives

$$Fe^{ika} = C\sin(la) + D\cos(la) \quad (2.29)$$

- Imposing boundary condition (BC) #2 at $x = a$ gives

$$ikFe^{ika} = l\left[C\cos(la) - D\sin(la)\right] \quad (2.30)$$

- The BC results in a total of 4 algebraic equations with 5 unknowns (A, B, C, D, F). Choose any four of these to be expressed in terms of the remaining one. We choose to express B, C, D, F in terms of A.

$$B = i\frac{\sin(2la)}{2kl}(l^2 - k^2)F, \quad (2.31)$$

$$F = \frac{e^{-2ika}A}{\cos(2la) - i\frac{(k^2+l^2)}{2kl}\sin(2la)}, \quad (2.32)$$

Exercise: Derive Eq. (2.31), Eq. (2.32). Hint: Use Eqs. (2.30), (2.29) to solve for C and D in terms of F, and then plug them into Eqs. (2.27), (2.28).

- The probability of finding the particle at a specific location is given by $|\Psi|^2$, so the relative probability that an incident particle (with an incident amplitude

A) will be reflected back (the reflected wave has an amplitude of B) is

$$R = \frac{|B|^2}{|A|^2}$$

This is the **reflection coefficient**, a quantity of relevance only in region to the left of $x = -a$. It tells you the fraction of the incoming number that will bounce back.

- Likewise, to the right of $x > a$ we can define the **transmission coefficient**,

$$T = \frac{|F|^2}{|A|^2}$$

which tells you how much of the incident number has transmitted through the potential to come out to the other side.

- To conserve probability, $T + R = 1$.
- The transmission coefficients can be shown to be

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

Exercise: Show this.

- The well become "transparent" to the incident wave (i.e., $T = 1$) if the energy E is set to some discrete values such that the argument in the $\sin^2$ terms vanishes, i.e.,

$$\frac{2a}{\hbar}\sqrt{2m(E + V_0)} = n\pi,$$

or

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2m(2a)^2} - V_0.$$

- Notice that this is exactly the same set of discrete energies as that of an infinite square well.
- This phenomena is known as **Ramsauer-Townsend effect**. This is an example of resonance phenomena. See Figure 2.19.

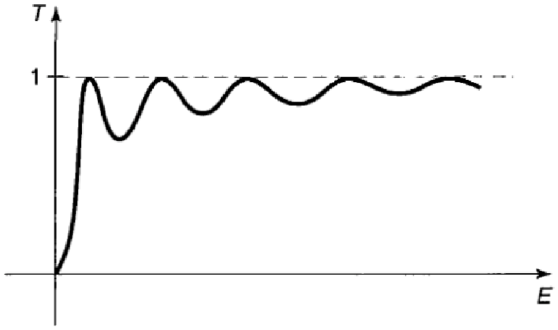


FIGURE 2.19: Transmission coefficient as a function of energy

- There are two more very common forms of potential in standard QM textbooks, i.e. rectangular potential barrier and the step potential. These are offered as your home works in the problem sets for chapter 2.

2.7 Problem Set

ZCA 205 Quantum Mechanics
Problem set for Chapter 2

*****Problem 2.1** Prove the following three theorems:

(a) For normalizable solutions, the separation constant E must be *real*. *Hint:* Write E (in Equation 2.7) as $E_0 + i\Gamma$ (with E_0 and Γ real), and show that if Equation 1.20 is to hold for all t, Γ must be zero.

(b) The time-independent wave function $\psi(x)$ can always be taken to be *real* (unlike $\Psi(x, t)$, which is necessarily complex). This doesn't mean that every solution to the time-independent Schrödinger equation *is* real; what it says is that if you've got one that is *not*, it can always be expressed as a linear combination of solutions (with the same energy) that *are*. So you *might as well* stick to ψ's that are real. *Hint:* If $\psi(x)$ satisfies Equation 2.5, for a given E, so too does its complex conjugate, and hence also the real linear combinations $(\psi + \psi^*)$ and $i(\psi - \psi^*)$.

(c) If $V(x)$ is an **even function** (that is, $V(-x) = V(x)$) then $\psi(x)$ can always be taken to be either even or odd. *Hint:* If $\psi(x)$ satisfies Equation 2.5, for a given E, so too does $\psi(-x)$, and hence also the even and odd linear combinations $\psi(x) \pm \psi(-x)$.

Problem 2.2 Show that E must exceed the minimum value of $V(x)$, for every normalizable solution to the time-independent Schrödinger equation. What is the classical analog to this statement? *Hint:* Rewrite Equation 2.5 in the form

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi;$$

if $E < V_{\min}$, then ψ and its second derivative always have the *same sign*—argue that such a function cannot be normalized.

Problem 2.5 A particle in the infinite square well has as its initial wave function an even mixture of the first two stationary states:

$$\Psi(x, 0) = A[\psi_1(x) + \psi_2(x)].$$

(a) Normalize $\Psi(x, 0)$. (That is, find A. This is very easy, if you exploit the orthonormality of ψ_1 and ψ_2. Recall that, having normalized Ψ at $t = 0$, you can rest assured that it *stays* normalized—if you doubt this, check it explicitly after doing part (b).)

(b) Find $\Psi(x, t)$ and $|\Psi(x, t)|^2$. Express the latter as a sinusoidal function of time, as in Example 2.1. To simplify the result, let $\omega \equiv \pi^2\hbar/2ma^2$.

(c) Compute $\langle x \rangle$. Notice that it oscillates in time. What is the angular frequency of the oscillation? What is the amplitude of the oscillation? (If your amplitude is greater than $a/2$, go directly to jail.)

(d) Compute $\langle p \rangle$. (As Peter Lorre would say, "Do it ze *kveek* vay, Johnny!")

(e) If you measured the energy of this particle, what values might you get, and what is the probability of getting each of them? Find the expectation value of H. How does it compare with E_1 and E_2?

Problem 2.7 A particle in the infinite square well has the initial wave function[1]

$$\Psi(x, 0) = \begin{cases} Ax, & 0 \le x \le a/2, \\ A(a - x), & a/2 \le x \le a. \end{cases}$$

(a) Sketch $\Psi(x, 0)$, and determine the constant A.

(b) Find $\Psi(x, t)$.

(c) What is the probability that a measurement of the energy would yield the value E_1?

(d) Find the expectation value of the energy.

Problem 2.8 A particle of mass m in the infinite square well (of width a) starts out in the left half of the well, and is (at $t = 0$) equally likely to be found at any point in that region.

(a) What is its initial wave function, $\Psi(x, 0)$? (Assume it is real. Don't forget to normalize it.)

(b) What is the probability that a measurement of the energy would yield the value $\pi^2\hbar^2/2ma^2$?

1. Derive Eq. 2.80 in Griffiths, page 53.

Problem 2.15 In the ground state of the harmonic oscillator, what is the probability (correct to three significant digits) of finding the particle outside the classically allowed region? *Hint:* Classically, the energy of an oscillator is $E = (1/2)ka^2 = (1/2)m\omega^2a^2$, where a is the amplitude. So the "classically allowed region" for an oscillator of energy E extends from $-\sqrt{2E/m\omega^2}$ to $+\sqrt{2E/m\omega^2}$. Look in a math table under "Normal Distribution" or "Error Function" for the numerical value of the integral.

2. Find the probability current $J = \frac{i\hbar}{2m}\left(\Psi\frac{\partial\Psi^*}{\partial x} - \Psi^*\frac{\partial\Psi}{\partial x}\right)$ for the free particle wave function $\Psi_k(x,t) = Ae^{i(kx - \frac{\hbar k^2}{2m}t)}$.

Problem 2.21 A free particle has the initial wave function

$$\Psi(x,0) = Ae^{-a|x|},$$

where A and a are positive real constants.

(a) Normalize $\Psi(x,0)$.

(b) Find $\phi(k)$.

(c) Construct $\Psi(x,t)$, in the form of an integral.

(d) Discuss the limiting cases (a very large, and a very small).

3. Analyze the odd bound state wave functions for the finite square well. Derive the transcendental equation for the allowed energies, and solve it graphically. Examine the two limiting cases. Is there always an odd bound state?

****Problem 2.33** Determine the transmission coefficient for a rectangular *barrier* (same as Equation 2.145, only with $V(x) = +V_0 > 0$ in the region $-a < x < a$). Treat separately the three cases $E < V_0$, $E = V_0$, and $E > V_0$ (note that the wave function inside the barrier is different in the three cases). *Partial answer:* For $E < V_0$,[42]

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

∗**Problem 2.34** Consider the "step" potential:

$$V(x) = \begin{cases} 0, & \text{if } x \le 0, \\ V_0, & \text{if } x > 0. \end{cases}$$

(a) Calculate the reflection coefficient, for the case $E < V_0$, and comment on the answer.

(b) Calculate the reflection coefficient for the case $E > V_0$.

(c) For a potential such as this, which does not go back to zero to the right of the barrier, the transmission coefficient is *not* simply $|F|^2/|A|^2$ (with A the incident amplitude and F the transmitted amplitude), because the transmitted wave travels at a different *speed*. Show that

$$T = \sqrt{\frac{E - V_0}{E}} \frac{|F|^2}{|A|^2}, \qquad [2.172]$$

for $E > V_0$. *Hint:* You can figure it out using Equation 2.98, or—more elegantly, but less informatively—from the probability current (Problem 2.19). What is T, for $E < V_0$?

(d) For $E > V_0$, calculate the transmission coefficient for the step potential, and check that $T + R = 1$.

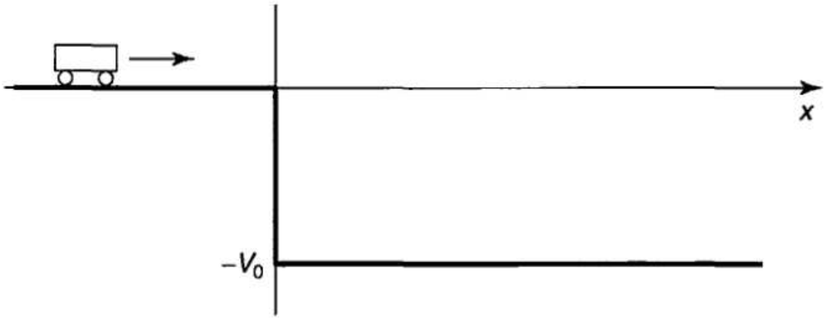


FIGURE 2.20: Scattering from a "cliff" (Problem 2.35).

Chapter 3

Formalism

3.1 Hilbert Space

- So far we have studied a few quantum systems. Now we would like to put them into a coherent formalism.

- Note that in the few systems studied so far, we dealed with two kinds of mathematical constructs: *wavefunctions* and *operators*.

- In these systems, the state of a system is represented by its wave function, wherease observables are represented by operators.

- Mathematically, the wave functions satisfy the defining conditions for abstract **vectors**.

- Operator acts on these vectors as **linear transformation**.

- Now, you will need to recall the linear algebra learned in ZCA 110 (vector space, linear transformation, basis, etc.)

- Consider an N-dimensional space in which a vector $|\alpha\rangle$ lives. The vector is represented by the N-tuple of its components, $\{a_n\}$ with respect to a specified orthornomal basis:

- $|\alpha\rangle = |a_1, a_2, \cdots, a_N\rangle$.

- The **inner product**, $\langle\alpha|\beta\rangle$, of two vectors

$$\langle\alpha|\beta\rangle = a_1^* b_1 + a_2^* b_2 + \cdots + a_N^* b_N.$$

- Linear transformation, T, is represented by **matrices** (with respect to the specified basis). It acts on a vector to produce another vector

$$|\beta\rangle = \mathbf{T}|\alpha\rangle \Rightarrow \mathbf{b} = \mathbf{Ta} = \begin{pmatrix} t_{11} & t_{12} & \cdots & t_{1N} \\ t_{21} & t_{22} & \cdots & t_{2N} \\ \vdots & \vdots & & \vdots \\ t_{N1} & t_{N2} & \cdots & t_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N. \end{pmatrix}$$

- In QM, the "vectors" are actually functions. The algebra obey by vectors (e.g. inner product, transformation) also applies to functions.

- Remember in ZCA 110 we studied vector space. There we learned that the collection of all vectors constitute a vector space.

- In fact, the collection of all functions of x also constitute a vector space. You can safely take the symbol $|\alpha\rangle$ mentioned above as referring to a function f without lost of generality.

- In many ways a function is mathematical not different from a vector. A N-dimensional vector has N components:

  $$|\alpha\rangle = |a_1, a_2, \cdots a_N\rangle$$

  where these components are defined with respect to a specific basis set,

  $$\{|\hat{e}\rangle\}.$$

  The dimensionality of the vector space for the collections of these vectors is N.

- In comparison to a finite dimensional vector, a function can be understood as a "vector" with infinite number of components. The dimensionality of the vector space for functions is infinite.

- As an example, a function $f(x)$ can be expanded into a Taylor series containing infinite terms,

  $$f(x) = \sum_{n=0}^{n=\infty} \frac{f^{(n)}(0)}{n!} x^n = \sum_{n=0}^{n=\infty} a_n x^n.$$

  The components are $\{a_n\} = \{\frac{f^{(n)}(0)}{n!}\}$, and the basis set is $\{x^n\}$, $n = 0, 1, 2, 3, \cdots$.

- One can alternatively expand the function in other basis, such as in Fourier series:

  $$f(x) = \sum_{n=0}^{n=\infty} a_n \cos(n\pi x) + b_n \sin(n\pi x).$$

The components are $\{a_n\}$ and $\{b_n\}$. The basis set is $\{\sin n\pi x\}$, $\{\cos n\pi x\}$, $n = 0, 1, 2, 3, \cdots$.

- The choice of basis set is arbitrary. This is similar to the fact that a finite dimensional vector can be expressed in many basis set of choice.
- However, some bases are more preferred than another. For example we usually prefer bases that are orthogonal and is normalised to 1, such as the Fourier bases.
- In QM, the physical state represented by a wave function must be *normalised*:

$$\int |\Psi|^2 dx = 1.$$

- The collection of all **square integrable functions** on a specified interval

$$f(x) \text{ such that } \int |f(x)|^2 dx < \infty,$$

constitute a smaller vector space called **Hilbert space**.

- **Wave functions live in Hilbert space.**
- For two functions in a Hilbert space, the inner product of two functions, defined as

$$\langle f|g\rangle \equiv \int_a^b f(x)^* g(x) dx,$$

is guaranteed to exist. This can be proven on the basis that all functions in Hilbert space is square-integrable.

- In particular, note the property

$$\langle g|f\rangle = \langle f|g\rangle^*.$$

"permuting the order in the inner product amounts to complex conjugating it."

- $$\langle f|f\rangle = \int_a^b |f(x)|^2 dx$$

is real and non-negative.

- **Schwarz inequality**: For f, g that are both square-integrable,

$$\left| \int_a^b f(x)^* g(x) dx \right| \leq \sqrt{\int_a^b |f(x)|^2 dx \int_a^b |g(x)|^2 dx},$$

  or equivalently, in short hand notation,

$$|\langle f|g\rangle|^2 \leq \langle f|f\rangle\langle g|g\rangle.$$

- The only function whose inner product with itself vanishes is 0, i.e.,

$$\langle f|f\rangle = 0 \Rightarrow f(x) = 0$$

- Two functions are said to be orthogonal if

$$\langle g|f\rangle = 0.$$

- A set of functions, $\{f_n\}$, is orthornomal if they are normalised and mutually orthornomal:

$$\langle f_n|f_m\rangle = \delta_{mn}.$$

- A set of functions is complete if any other function (in Hilbert space) can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x).$$

- If the functions $\{f_n(x)\}$ are orthornomal, the coefficients can be "projected out" by Fourier's trick:

$$c_n = \langle f_n|f\rangle$$

- How to make sense of all these definition?
- Make contact with Chapter 2 - the stationary states for the infinite square well constitute a complete orthonomal set on the inverval $(0, a)$;
- The stationary states for the harmonic oscillator are a complete set on the interval $(-\infty, +\infty)$.

Notes on vector space

A **vector space** consists of a set of **vectors** ($|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle, \dots$), together with a set of **scalars** (a, b, c, …),[1] which is **closed**[2] under two operations: vector addition and scalar multiplication.

- **Vector Addition**

  The "sum" of any two vectors is another vector:

  $$|\alpha\rangle + |\beta\rangle = |\gamma\rangle. \qquad [A.1]$$

  Vector addition is **commutative**:

  $$|\alpha\rangle + |\beta\rangle = |\beta\rangle + |\alpha\rangle, \qquad [A.2]$$

  and **associative**:

  $$|\alpha\rangle + (|\beta\rangle + |\gamma\rangle) = (|\alpha\rangle + |\beta\rangle) + |\gamma\rangle. \qquad [A.3]$$

  There exists a **zero** (or **null**) **vector**,[3] $|0\rangle$, with the property that

  $$|\alpha\rangle + |0\rangle = |\alpha\rangle, \qquad [A.4]$$

  for every vector $|\alpha\rangle$. And for every vector $|\alpha\rangle$ there is an associated **inverse vector** ($|-\alpha\rangle$),[4] such that

  $$|\alpha\rangle + |-\alpha\rangle = |0\rangle. \qquad [A.5]$$

- **Scalar Multiplication**

  The "product" of any scalar with any vector is another vector:

  $$a|\alpha\rangle = |\gamma\rangle. \qquad [A.6]$$

  Scalar multiplication is **distributive** with respect to vector addition:

  $$a(|\alpha\rangle + |\beta\rangle) = a|\alpha\rangle + a|\beta\rangle, \qquad [A.7]$$

  and with respect to scalar addition:

  $$(a + b)|\alpha\rangle = a|\alpha\rangle + b|\alpha\rangle. \qquad [A.8]$$

  It is also **associative** with respect to the ordinary multiplication of scalars:

  $$a(b|\alpha\rangle) = (ab)|\alpha\rangle. \qquad [A.9]$$

  Multiplication by the scalars 0 and 1 has the effect you would expect:

  $$0|\alpha\rangle = |0\rangle; \quad 1|\alpha\rangle = |\alpha\rangle. \qquad [A.10]$$

  Evidently $|-\alpha\rangle = (-1)|\alpha\rangle$ (which we write more simply as $-|\alpha\rangle$).

There's a lot less here than meets the eye—all I have done is to write down in abstract language the familiar rules for manipulating vectors. The virtue of such abstraction is that we will be able to apply our knowledge and intuition about the behavior of ordinary vectors to other systems that happen to share the same formal properties.

3.2 Observables

3.2.1 Hermitian Operator

- The expectation value of an observable $Q(x,p)$ in QM is expressed in terms of inner-product
$$\langle Q\rangle = \int \Psi^* \hat{Q}\Psi dx = \langle \Psi|\hat{Q}\Psi\rangle.$$
- The observable has to be a real number, and it is the average of many measurement:
$$\langle Q\rangle = \langle Q\rangle^*.$$
- Since $\langle f|g\rangle^* = \langle g|f\rangle$ according to the definition of the inner-product, $\langle Q\rangle = \langle Q\rangle^*$ leads to
$$\langle \Psi|\hat{Q}\Psi\rangle = \langle \hat{Q}\Psi|\Psi\rangle$$
for all wave function Ψ. You can see this easily by identifying $f \equiv \hat{Q}\Psi, g \equiv \Psi$.
- The operators representing observable in QM, $\hat{Q}$, has the property that
$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle \text{ for all } f(x), g(x).$$
Such operators are called Hermitian.
- The Hermitian operator $\hat{Q}$ can either act on the first member or the second in the inner product, with the same result.
- Hermitian operator arise naturally in QM because their expectation values are real.
- Definition: Hermitian conjugate (or adjoint) of an operator $\hat{Q}$ is the operator $\hat{Q}^\dagger$ such that
$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}^\dagger f|g\rangle$$
for all f and g.
- You can try to find out what is $p^\dagger$ and $x^\dagger$ based on this definition. It turns out that $\hat{p}^\dagger = \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$, and $\hat{x}^\dagger = \hat{x}$.
- In general, a Hermitian operator is equal to its conjugate, i.e.,
$$\hat{Q}^\dagger = \hat{Q}.$$

- Example: Take $\hat{Q} \equiv \hat{p} = \frac{\hbar}{i}\frac{d}{dx}$, the momentum operator.

  $$\langle f|\hat{p}g\rangle = \int_{-\infty}^{\infty} f^* \frac{\hbar}{i}\frac{dg}{dx} dx = \cdots = \langle \hat{p}f|g\rangle.$$

  This can be shown by integration by parts, and the requirement that the functions $f(x), g(x)$ behave properly, i.e., they approaches to zero when $x \to \infty$. In QM, all wave functions obey this requirement.

  Exercise: Show this.

Observables in QM are represented by Hermitian operators $\hat{Q}$

3.2.2 Determinate States

- An determinate state for an observable Q is one in which every measurement of Q is certain to return the same value (call it q).

- Example: Stationary states are determinate state of the Hamiltonian (which is the observable energy), i.e., a measurement of the total energy on a particle in the stationary state Ψ_n is certain to yield the corresponding allowed energy E_n. Mathematically, such a situation is described by the statment $\sigma_E = 0$.

- Hence, the variance of Q in a determinate state is zero.

  $$\sigma^2 = \langle(\hat{Q} - \langle Q\rangle)^2\rangle = \langle\Psi|(\hat{Q} - q)^2\Psi\rangle = \langle(\hat{Q} - q)\Psi|(\hat{Q} - q)\Psi\rangle = 0.$$

- Since the only function whose inner product with itself vanishes is 0, so

  $$\hat{Q}\Psi = q\Psi$$

- This is the **eigenvalue equation** for the operator $\hat{Q}$; Ψ is an **eigenfunction** of $\hat{Q}$, and q is the corresponding **eigenvalue**. Thus

  $$\boxed{\textbf{Determinate states are eigenfunctions of } \hat{Q}}$$

- The collection of all the eigenvalues of an operator is called its **spectrum**.

- Example: determinate states of the total energy are eigenfunctions of the Hamiltonian:

  $$\hat{H}\psi_n = E_n\psi.$$

  The spectrum are the set of discrete eigenenergies $\{E_n\}$.

- Sometimes two or more linearly independent eigenfunctions share the same eigenvalue. In that case the spectrum is said to be **degenerate**. For example, in certain quantum states of an atom characterised by quantum number (l, m), two distinct eigenfunctions $\psi_{m_1,l_1}, \psi_{m_2,l_2}$ may share the same eigenenergy. In this case the energy spectrum is said to be degenerate for the states $\psi_{m_1,l_1}, \psi_{m_2,l_2}$.

- Eigenfunctions and eigenvalues can be considered as intrinsic parts of an operator. In other words, given a Hermitian operator $\hat{Q}$ in QM, there always exist a set of eigenfunctions and the corresponding eigenvalues. Our task is to find out what are the engenfunctions and the corresponding eigenevalues of that operator.

- Example: Consider the operator

  $$\hat{Q} \equiv i\frac{d}{d\phi},$$

  where ϕ is the usual polar coordinate in 2D. Is $\hat{Q}$ hermitian? Find its eigenfunctions and eigenvalues.

Solution: Here we are working with functions $f(\phi)$ on the *finite* interval $0 \leq \phi \leq 2\pi$, and stipulate that

$$f(\phi + 2\pi) = f(\phi). \qquad [3.26]$$

since ϕ and $\phi + 2\pi$ describe the same physical point. Using integration by parts,

$$\langle f|\hat{Q} g\rangle = \int_0^{2\pi} f^* \left(i\frac{dg}{d\phi}\right) d\phi = if^*g\Big|_0^{2\pi} - \int_0^{2\pi} i\left(\frac{df^*}{d\phi}\right) g\, d\phi = \langle \hat{Q} f|g\rangle,$$

so $\hat{Q}$ *is* hermitian (this time the boundary term disappears by virtue of Equation 3.26).

The eigenvalue equation,

$$i\frac{d}{d\phi} f(\phi) = qf(\phi), \qquad [3.27]$$

has the general solution

$$f(\phi) = Ae^{-iq\phi}. \qquad [3.28]$$

Equation 3.26 restricts the possible values of the q:

$$e^{-iq2\pi} = 1 \quad \Rightarrow \quad q = 0, \pm 1, \pm 2, \ldots \qquad [3.29]$$

The spectrum of this operator is the set of all integers, and it is nondegenerate.

- As an example of a non determinate observable, consider the stationary state $n = 1$ of a particle in an infinite well. The position of the particle in such a stationary state is non determinate. Every measurement on an ensemble of identically prepared state will yield a different measured value for x. Mathematically, such a situation is described by the statment $\sigma_x \neq 0$.

- If a given state is determinate for an observable A in general does not mean the same state is determinate for other observable B. In the example given above, stationary state $n = 1$ of a particle in an infinite well is determinate state for the energy observable but not for the position observable.

3.3 Eigenfunctions of a Hermitian Operator

- Two categories of Hermitian operators: those with discrete eigenvalues and those with continuous eigenvalues.

- Eigenfunctions with discrete eigenvalues are normalisable and lie in Hilbert space. They represents physically realisable states.

- Eigenfunctions with continuous eigenvalues are not normalisable, hence do not represents physically realisable states.

- Hermitian operator with discrete eigenvalues: e.g., Hamiltonian for harmonic oscillator, Hamiltonian for infinite square well, etc.

- Hermitian operator with continuous eigenvalues: e.g., Hamiltonian for free particle.

- Hamiltonian for finite square well has both.

- Renormalisable eigenfunctions of a Hermitian operator have three important mathematical properties: (1) Their eigenvalues are real, and (2) eigenfunctions belonging to distinct eigenvalues are orthogonal. (3) The eigenfunctions of an observable operator are complete: Any function in Hilbert space can be expressed as linear combination of them. The statement (3) is taken as an axiom of QM.

- (1) is mathematically expressed as: $\hat{Q}f = qf$, then $q = q^*$.

- (2) is mathematically expressed as: $\hat{Q}g = q'g, \hat{Q}f = qf$. If $q \neq q'$, then $\langle f|g\rangle = 0$.

- That explains why in the harmonic oscillator or in the infinite square well, the stationary states are orthogonal: because they are all eigenfunctions of the Hamiltonian of distinct eigenvalues.

- Orthonormality of eigenstates are very useful as it allows Fourier's trick to be used in quantum mechanical calculations to kill off orthogonal terms.

- For eigenfunctions that are degenerate, it is in principle possible to construct orthogonal eigenfunctions within each degenerate subspace through **Gram-Schmidt orthogonalisation procedure**. This allow the originally degenerate eigenfunctions to be re-expressed in terms of eigenfunctions that are orthogonal, thus restoring orthogonality even in the present of degeneracy.

- As an example, $f(x) = e^{-x}, g(x) = e^x$ are two degenerate eigenfunctions of the operator d^2/dx^2 with eigenvalue 1. One can construct linear combinations from $f(x), g(x)$ such as $z_1(x) = \alpha f(x) + \beta g(x), z_2(x) = \alpha f(x) - \beta g(x)$, where α, β satisfy $\langle z_1|z_2\rangle = 0$, $\langle z_1|z_1\rangle = \langle z_2|z_2\rangle = 1$ on (-1,1). $z_1(x)$ and $z_2(x)$ are now two orthogonal functions with a common eigenvalue 1.

3.3.1 Continuous Spectra

- For eigenfunctions with continuous spectra, reality, orthogonality and completeness still hold but the proof are not so straight forward (we will not show it). We will show these properties through examples.

- **Example**: Find the eigenvalues and eigenfunctions of the momentum operator for a free particle, $\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$. *Note: momentum of a free particle is a continuous observable.*

- Let $f_p(x)$ and p be the eigenfunction and eigenvalue for $\hat{p}$, so that $\hat{p}f_p(x) = pf_p(x)$.

- The general solution is $f_p(x) = Ae^{ipx/\hbar}$.

- This is not square-integrable for a generic value (complex in general) of p, as

$$\int_{-\infty}^{\infty} {f^*}_{p'}(x)f_p(x)dx = |A|^2\int_{-\infty}^{\infty} e^{i(p-p'^*)x/\hbar}dx$$

  does not converge - the momentum operator has no eigenfunctions in Hilbert space.

- However, if we restrict only to **real** eigenvalues, then we obtain "orthornomalilty" in the continuous sense, i.e.,

$$\int_{-\infty}^{\infty} {f^*}_{p'}(x)f_p(x)dx = |A|^2\int_{-\infty}^{\infty} e^{i(p-p')x/\hbar}dx = |A|^2 2\pi\hbar\delta(p'-p).$$

  Show that the Dirac delta function can be expressed in the integral form as given by:

$$\int_{-\infty}^{\infty} e^{i(p'-p)y}dy = 2\pi\delta(p'-p). \tag{3.1}$$

  Solution:

  Using Plancherels theorem, we express the Dirac delta function in terms of its Fourier transform $F(k)$,

$$\delta(x) = \frac{1}{\sqrt{2\pi}}\int F(k)e^{ikx}dk. \tag{3.2}$$

$$F(k) = \frac{1}{\sqrt{2\pi}}\int \delta(x)e^{-ikx}dx. \tag{3.3}$$

But $F(k)$ in Eq. (3.3) is

$$F(k) = \frac{1}{\sqrt{2\pi}} \int \delta(x) e^{-ikx} dx = \frac{1}{\sqrt{2\pi}}$$

That means Eq. (3.2) can be expressed as

$$\delta(x) = \frac{1}{\sqrt{2\pi}} \int F(k) e^{ikx} dk = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk,$$

which is straight forwardly generalised to

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} dk,$$

which is just an equivalent form of Eq. (3.1).

- Choosing $A = \frac{1}{\sqrt{2\pi\hbar}}$,
$$\langle f_p | f_{p'} \rangle = \delta(p' - p).$$
- This is orthornomalilty for the continuous case. We call this "**Dirac orthornomalilty**". The Dirac delta function now plays the role of Kronecker delta function as in the discrete case.
- The eigenfunctions with continuous, real eigenvalues are complete in the sense that the any square-integrable function $f(x)$ can be written as an integral of the form
$$f(x) = \int c(p) f_p(x) dp = \frac{1}{\sqrt{2\pi\hbar}} \int c(p) e^{ipx/\hbar} dp.$$
- The coefficients $c(p)$ appeared in the expansion of $f(x)$ can be obtained using Fourier's trick (thanks to the orthogonality of the eigenfunctions f_p):

$$\begin{aligned}
\langle f_{p'} | f \rangle &= \int_{-\infty}^{\infty} f_{p'}^*(x) f(x) dx = \int_{-\infty}^{\infty} f_{p'}^*(x) \left\{ \int_{-\infty}^{\infty} c(p) f_p(x) dp \right\} dx \\
&= \int_{-\infty}^{\infty} c(p) \left\{ \int_{-\infty}^{\infty} f_{p'}^*(x) f_p(x) dx \right\} dp = \int_{-\infty}^{\infty} c(p) \delta(p' - p) dp = c(p').
\end{aligned}$$

- **Example**: Find the eigenvalues and eigenfunctions of the position operator. Note: position is a continuous observable.

  Solution: Let $g_y(x)$ be the eigenfunction and y be the eigenvalue.

  $$\hat{x} g_y(x) = y g_y(x).$$

  The eigenfunction turns out to be

  $$g_y(x) = A\delta(y - x),$$

  with $A = 1$ for normalisation.

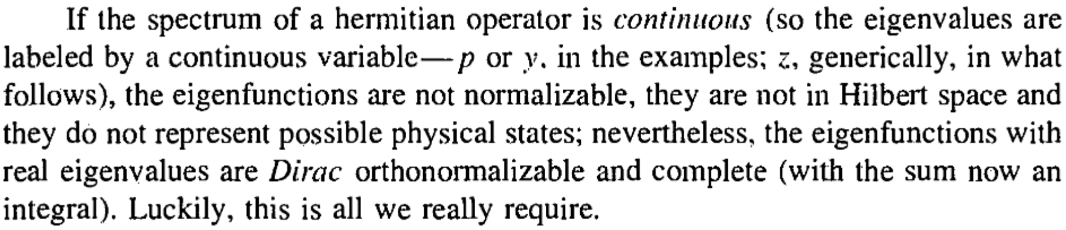
- The eigenvalue y has to be real (else $g_y(x)$ is not square-integrable).
- $g_y(x)$ is orthonormal in the sense that $\langle g_{y'} | g_y \rangle = \delta(y - y')$.
- $g_y(x)$ is complete:

  $$f(x) = \int_{-\infty}^{\infty} c(y) g_y(x) dy$$

  .

- The coefficient $c(x)$ in the expansion can be easily obtained via Fourier's trick:

  $$f(x) = \int_{-\infty}^{\infty} c(y) g_y(x) dy = \cdots = \int_{-\infty}^{\infty} c(y)\delta(x - y) dy = c(x).$$



If the spectrum of a hermitian operator is *continuous* (so the eigenvalues are labeled by a continuous variable—p or y, in the examples; z, generically, in what follows), the eigenfunctions are not normalizable, they are not in Hilbert space and they do not represent possible physical states; nevertheless, the eigenfunctions with real eigenvalues are *Dirac* orthonormalizable and complete (with the sum now an integral). Luckily, this is all we really require.

3.4 Generalised Statistical Interpretation

- In QM, the results of any measurement is not deterministic but "spread out" according to a probability distribution. In this section we would learn how to calculate the possible results of any measurement.

- Generalised statistical interpretation: If you measure an observable $Q(x,p)$ on a particle in the state $\Psi(x,t)$, you are certain to get one of the eigenvalues of the hermitian operator $\hat{Q}(x,-i\hbar d/dx)$. If the spectrum is discrete, the probability of getting the particular eigenvalue q_n associated with the orthornomalised eigenfunction $f_n(x)$ is
$$|c_n|^2, \text{ where } c_n = \langle f_n|\Psi\rangle$$

- $|c_n|^2$ is the probability that a measurement of Q will yield the value q_n. $|c_n|^2$ can also be understood as the probability that the particle which is now in the state Ψ will be in the state f_n subsequent to a measurement of Q.

- If the spectrum is continuous, the real eigenvalues $q(z)$ and associated Dirac-orthonormalised eigenfunction $f_z(x)$, the probability of getting a result in the range dz is
$$|c(z)|^2 dz \text{ where } c(z) = \langle f_z|\Psi\rangle.$$

- Upon measurement, the function "collapses" to the corresponding eigenstate.

- The eigenfunctions of an observable operator are complete, e.g., the wave function can be expressed as a linear combination of them:
$$\Psi(x,0) = \sum_n c_n f_n(x).$$

- Since eigenfunctions are orthonormal, the coefficients can be projected out by Fourier's trick:
$$c_n = \langle f_n|\Psi\rangle = \int f_n(x)^* \Psi(x,0)dx.$$

- c_n tells you how much f_n is contained in Ψ. The probability a measurement will return a particular eigenvalue q_n is determined by the amount of f_n in Ψ, which is in turn given by $|c_n|^2$.

- Note that although we consider only the static case $t=0$, the argument can be generalised to dynamic case, $t>0$.

- Based on the interpretation for $|c_n|^2$ as mentioned above, the sum over of all possible outcome of a measurement got to be
$$\sum_n |c_n|^2 = 1.$$

- $\sum_n |c_n|^2 = 1$ can be easily derived from the normalisation of the wave function,
$$\langle\Psi|\Psi\rangle = 1.$$

- The expectation value of Q for a particle in a state Ψ is defined as
$$\langle Q\rangle = \langle\Psi|\hat{Q}\Psi\rangle.$$
It should be equal to the sum over all possible probability-weighted outcomes:
$$\langle Q\rangle = \sum_n q_n|c_n|^2$$
- We can prove $\langle Q\rangle = \sum_n q_n|c_n|^2$ from the definition $\langle Q\rangle = \langle\Psi|\hat{Q}\Psi\rangle$ (see chapter 2).
- The discussion above are for discrete spectrum. However the argument are easily generalise to the continuous case, for example, $\langle R\rangle = \int r(k)|\phi(k)|^2 dk$, where R represent a continuous variable, $|\phi(k)|^2 dk$ the probability density to find the continuous eigenvalue $r(k)$ to lie in the interval $[k, k+dk]$.

3.4.1 Checking consistency of the formalism on position measurement

- We will now show that the above discussion is consistent with the statistical interpretation for position measurement, that the probability a measurement will result in an specific eigenvalue y in the range $[y, y+dy]$ in a measurement is
$$|\Psi|^2 dy.$$
- In this case, the observable is x, observable operator $\hat{x}$, eigenfunction $g_y(x) = \delta(x-y)$ and eigenvalue y.
- In this case, $\hat{x}g_y(x) = yg_y(x)$.
- We wish to show that indeed $|c(y)|^2 dy$ is just equal to the probability $|\Psi|^2 dy$.
- $c(y) = \langle g_y|\Psi\rangle = \int_{-\infty}^{\infty}\delta(x-y)\Psi(x,t)dx = \Psi(y,t)$. That establish our consistency check, $|c(y)|^2 dy = |\Psi|^2 dy$.

3.4.2 Momentum measurement

- For the case of momentum, $\hat{p}f_p(x) = pf_p(x)$, $f_p(x) = (1/\sqrt{2\pi\hbar})\exp(ipx/\hbar)$, $\hat{p} = -i\hbar d/dx$.

- The coefficient $c(p)$ can be projected out from the wave function $\Psi(x,t)$ using Fourier's trick:
$$c(p) = \langle f_p|\Psi\rangle = \int_{-\infty}^{\infty} f_p^*(x)\Psi(x,t)dx.$$
- $\Phi(p,t) \equiv \langle f_p|\Psi\rangle$ is a very important quantity called **momentum space wave function**.
-
$$|\Phi(p,t)|^2 dp.$$
is the probability to obtain an eigenvalue p in the range dp in an momentum measurement.
- $\Phi(p,t)$ is in fact the Fourier transform conjugate of $\Psi(x,t)$. Both form a Fourier conjugate pair, i.e.,
$$\Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} \exp(-ipx/\hbar)\Psi(x,t)dx,$$
$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} \exp(ipx/\hbar)\Phi(p,t)dp.$$
- Nomenclature: $\Psi(x,t)$ is sometimes called "wave function in position space" or "wave function in position representation".
- $\Phi(p,t)$ is called "wave function in momentum space" or "wave function in momentum representation".
- Example. A particle of mass m is found in the delta function well $V(x) = -\alpha\delta(x)$. What is the probability that a measurement of its momentum would yield a value greater than $p_0 = m\alpha/\hbar$?
- Solution: The position wave function is given by $\Psi(x,t) = \frac{\sqrt{m\alpha}}{\hbar}\exp(-m\alpha|x|/\hbar^2)\exp(-iEt/\hbar)$, $E = -m\alpha^2/2\hbar^2$. The momentum space wave function is therefore
$$\begin{aligned}\Phi(p,t) &= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\exp(-ipx/\hbar)\Psi(x,t)dx \\ &= \frac{\sqrt{m\alpha}}{\hbar}\frac{\exp(-iEt/\hbar)}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\exp(-ipx/\hbar)\exp(-m\alpha|x|/\hbar^2)dx \\ &= \sqrt{\frac{2}{\pi}}\frac{p_0^{3/2}e^{-iEt/\hbar}}{p^2+p_0^2}.\end{aligned}$$
- The probability to measure the momentum to lie between p and $p \pm dp$ is
$$\mathrm{Prob}(p \pm dp) = |\Phi(p,t)|^2 dp = \frac{2}{\pi}\frac{p_0^3}{(p^2+p_0^2)^2}dp. \tag{3.4}$$

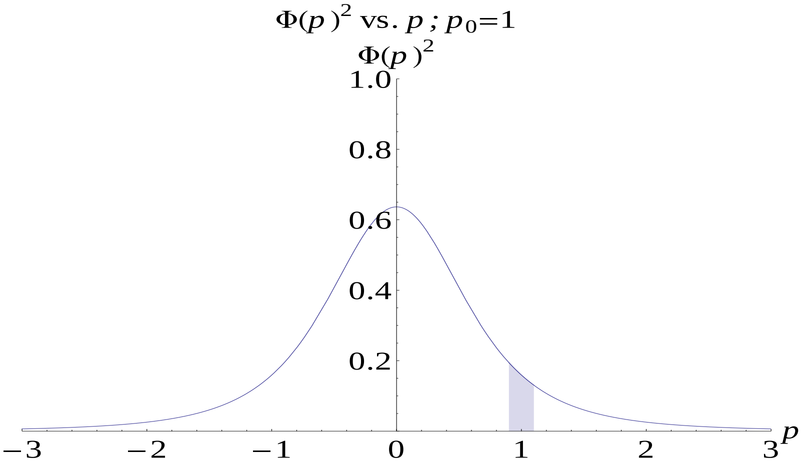


Figure 3.1: Shaded area showing probability to find particle with momentum lying in $p_0 \pm dp$.

- The probability to measure the momentum p to lie above p_0 is simply

$$\begin{aligned}\text{Prob}(p > p_0) &= \int_{p_0}^{\infty} |\Phi(p,t)|^2 dp = \frac{2}{\pi}\int_{p_0}^{\infty} \frac{p_0^3}{(p^2+p_0^2)^2} dp \\ &= \frac{2}{\pi}\left[\frac{pp_0}{p^2+p_0^2} + \tan^{-1}\left(\frac{p}{p_0}\right)\right]\Bigg|_{p_0}^{\infty} = \frac{1}{4} - \frac{1}{2\pi} \qquad (3.5)\end{aligned}$$

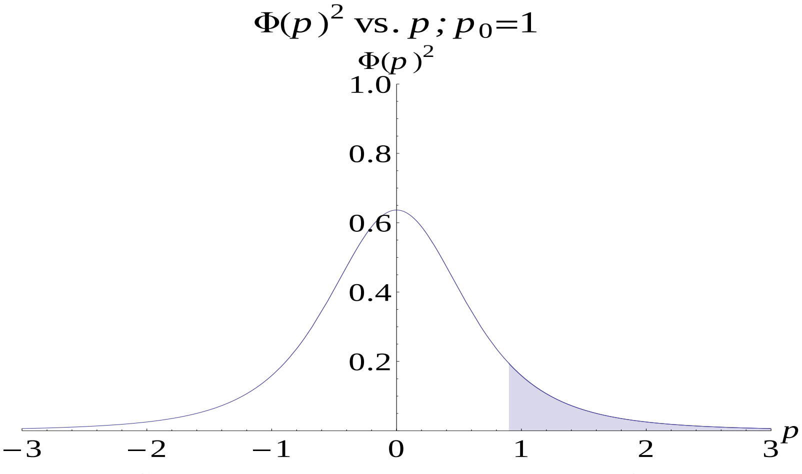


Figure 3.2: Shaded area showing probability to find particle with momentum larger than p_0.

3.5 The Uncertainty Principle

3.5.1 Proof of Generalised Uncertainty Principle

- For any observable A, the variance is

  $$\sigma_A^2 = \langle (\hat{A} - \langle A \rangle)\Psi | (\hat{A} - \langle A \rangle)\Psi \rangle = \langle f | f \rangle,$$

  where $f = (\hat{A} - \langle A \rangle)\Psi$.

- Like wise, for *other* observable B, (e.g., A is position, B is momentum)

  $$\sigma_B^2 = \langle (\hat{B} - \langle B \rangle)\Psi | (\hat{B} - \langle B \rangle)\Psi \rangle = \langle g | g \rangle,$$

  where $g = (\hat{B} - \langle B \rangle)\Psi$

- Due to Schwarz inequality,

  $$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2, \tag{3.6}$$

  where $z \equiv \langle f | g \rangle$ (a complex number).

- The square of the amplitude of a complex number is less than the sum of the squares of both of its real and complex parts, i.e.,

  $$|z|^2 = (\operatorname{Im} z)^2 + (\operatorname{Re} z)^2 \geq (\operatorname{Im} z)^2 = \left[\frac{1}{2i}(z - z^*) \right]^2. \tag{3.7}$$

- In terms of f and g, Eq. 3.7 reads

  $$|\langle f | g \rangle|^2 \geq \left[\frac{1}{2i}(\langle f | g \rangle - \langle f | g \rangle^*) \right]^2 = \left[\frac{1}{2i}(\langle f | g \rangle - \langle g | f \rangle) \right]^2 \tag{3.8}$$

- Furthermore, one can show that $z = \langle f | g \rangle = \cdots \langle \hat{A}\hat{B} \rangle - \langle A \rangle \langle B \rangle$

- Similarly, $z^* = \langle g | f \rangle = \cdots \langle \hat{B}\hat{A} \rangle - \langle B \rangle \langle A \rangle$.

- $$z - z^* = \langle f | g \rangle - \langle g | f \rangle = \langle \hat{A}\hat{B} \rangle - \langle \hat{B}\hat{A} \rangle = \langle [\hat{A}, \hat{B}] \rangle, \tag{3.9}$$

  where

  $$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}.$$

- Putting everything together (i.e., combining Eqs. 3.9, 3.8 and 3.6),
$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle\right)^2$$
This is the generalised uncertainty principle.

- The commutator relation for the pairs of operators $\hat{x}, \hat{p}$ is known as **cononical commutation relation**. It is taken as the *axiom of* the theory and everything in QM stems from it:
$$[\hat{x},\hat{p}] = i\hbar$$

- Plug in the canonical commutation relation into the generalised uncertainty principle,
$$\sigma_x^2\sigma_p^2 \geq \left(\frac{1}{2i}i\hbar\right)^2 = (\hbar/2)^2,$$
or
$$\sigma_x\sigma_p \geq \hbar/2.$$

- We just recovered Heisenberg's uncertainty principle from a more general consideration.

- There is an "uncertainty principle" for every pair of observable whose operators do not commute - **incompatible observables**.

- Incompatible observables do not have shared eigenfunctions.

- Example: there is no eigenfunction of position that is also an eigenfunction of momentum, because these operators are incompatible, i.e.
$$\hat{p}f(x) = pf(x), \hat{x}g(x) = xg(x) \Rightarrow f(x) \neq g(x)$$
because
$$[\hat{p},\hat{x}] = -i\hbar \neq 0.$$

- There is no eigenfunction of position that is also an eigenfunction of momentum.

- This is due to the fact that two noncommuting matrices cannot be simultaneously diagonalised by the same similarity transformation.

- Similarity transformation: $V_aAU_a^\dagger = D_a = \text{dia}\{a_1, a_2, \cdots, a_n\}$, $V_bBU_b^\dagger = D_b = \text{dia}\{b_1, b_2, \cdots, b_n\}$.

- If $[A,B] \neq 0 \Rightarrow \{U_a, V_a\} \neq \{U_b, V_b\}$.

- In contrast, *compatible* (commuting) variables do admit complete sets of simultaneous eigenfunctions.

- Example: Hamiltonian $\mathcal{H}$, magnitude of angular momentum $\hat{L}$ and the z-component of angular momentum $\hat{L}_z$ do share a common eigenfunction: $\hat{L}^2 f(x) = \ell(\ell+1)\hbar^2 f(x), \hat{L}_z f(x) = \hbar m_\ell f(x)$, $\mathcal{H}f(x) = Ef(x)$.

- The uncertainty principle is a consequence of the statistical interpretation of the wave function.

- When a sharp position is measured, the wave function is collapsed into a spike which carries a broad range of wave lengths (hence momentum) in its Fourier decomposition. That corresponds to the momentum being not sharply defined.

- On the other hand, if the momentum is now measured to a share value (i.e. the wavelength being sharply defined, and there is no spread in it), the particle no longer has the position you got in the first measurement. The measurement of momentum will destroy the previous position of the particle.

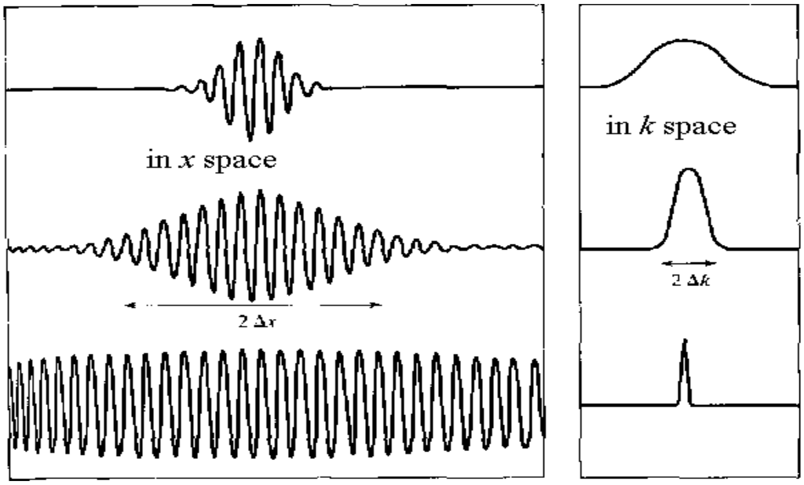


Figure 3.3: A narrow wave packet (small Δx) corresponds to a large spread of wavelengths (large Δp). A wide wave packet (large Δx) corresponds to a small spread of wavelengths (small Δ_p).

- Only if the wave function were simultaneously an eigenstate of both observables would it be possible to make the second measurement without disturbing the state of the particle.

- Other than $\sigma_x\sigma_p$, other very important results obtained from the generalised uncertainty principle include $\sigma_H\sigma_x$ and $\sigma_H\sigma_p$. The following exercises are meant to illustrate these results.

  Exercise: Show that $[H,x] = -\frac{i\hbar p}{2m}$. Hence, show that $\sigma_H\sigma_x \geq \frac{\hbar|\langle p\rangle|}{2}$. *Hint*: You need the relation

$$[AB,C] = A[B,C] + [A,C]B$$

  Exercise: Show that $[H,p] = i\hbar\frac{d}{dx}V(x)$. Hence, show that $\sigma_H\sigma_p \geq \frac{\hbar}{2}\langle\frac{dV(x)}{dx}\rangle$. *Hint*: You need the relation

$$[f(x),p] = i\hbar\frac{df(x)}{dx}.$$

3.5.2 The Minimum-Uncertainty Wave Packet

- A revision:
  Schwarz inequality for standard deviations of two operators A, B, i.e., $\sigma_A^2\sigma_B^2 \geq |\langle f|g\rangle|^2$, where $f = \hat{A} - \langle A\rangle\Psi$, $g = \hat{B} - \langle B\rangle\Psi$.

- $z = \langle f|g\rangle$ a complex number in general.

- We wish to know what is the minimum uncertainty limit - i.e., when the inequality becomes an equality for the incompatible pair $\{x,p\}$.

- The inequality becomes an equality when

1. $g(x) = cf(x)$ where c a complex number, and
2. z contains only imaginary part.

- In this limit, $\langle f|g\rangle = c\langle f|f\rangle$, so that $\mathrm{Re}\langle f|g\rangle = \mathrm{Re}(c\langle f|f\rangle) = 0$.
- Since $\langle f|f\rangle$ must be real, $\mathrm{Re}(c\langle f|f\rangle) = 0$ means c is purely imaginary, $c = ia$, a a real number.
- Hence we found that in this limit,

$$g(x) = iaf(x).$$

- Now, take $A \equiv \hat{x}$, $B \equiv \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$,

$$f = \left(\hat{A} - \langle A\rangle\right)\Psi = \left(\hat{x} - \langle x\rangle\right)\Psi,$$

$$g = \left(\hat{B} - \langle B\rangle\right)\Psi = \left(\frac{\hbar}{i}\frac{\partial}{\partial x} - \langle p\rangle\right)\Psi,$$

- Slot these two into $g(x) = iaf(x)$, we obtain

$$\left(\frac{\hbar}{i}\frac{d}{dx} - \langle p\rangle\right)\Psi = ia(x - \langle x\rangle)\Psi.$$

- The general solution is a gaussian (bell shaped function)

$$\Psi(x) = Ae^{-a(x-\langle x\rangle)^2/2\hbar}e^{i\langle p\rangle x\hbar}.$$

- This corresponds to the minimum-uncertainty wave packet.

3.5.3 The Energy-Time Uncertainty Principle

- We will derive the energy-time uncertainty principle in this subsection

$$\Delta E\Delta t \geq \hbar/2.$$

- Note that unlike other dynamical variables such as p, x, E, time t is an independent variable of which the dynamical quantities are functions.
- Δt is *not* the standard deviatioin of a collection of time measurements; it is the *time it takes the system to change substantially.*

- We wish to quantify how fast the system is changing. To this end, we calculate the time derivative of the expectation value of some observable, $Q(x, p, t)$:

$$\frac{d}{dt}\langle Q\rangle = \frac{d}{dt}\langle\Psi|\hat{Q}\Psi\rangle = \langle\frac{\partial\Psi}{\partial t}|\hat{Q}\Psi\rangle + \langle\Psi|\frac{\partial\hat{Q}}{\partial t}\Psi\rangle + \langle\Psi|\hat{Q}\frac{\partial\Psi}{\partial t}\rangle.$$

- Combine it with the Shroedinger equation

$$\frac{\partial\Psi}{\partial t} = \frac{1}{i\hbar}\hat{H}\Psi,$$

$$\begin{aligned}\frac{d}{dt}\langle Q\rangle &= -\frac{1}{i\hbar}\langle\hat{H}\Psi|\hat{Q}\Psi\rangle + \frac{1}{i\hbar}\langle\Psi|\hat{Q}\hat{H}\Psi\rangle + \langle\frac{\partial\hat{Q}}{\partial t}\rangle \\ &= \frac{i}{\hbar}\langle[\hat{H},\hat{Q}]\rangle + \langle\frac{\partial\hat{Q}}{\partial t}\rangle. \qquad (3.10)\end{aligned}$$

The last line is due to the fact that $\hat{H}$ is a Hermitian, $\langle\Psi|\hat{Q}\hat{H}\Psi\rangle = \langle\hat{Q}\Psi|\hat{H}\Psi\rangle$.

- Typically, $\hat{Q}$ does not depend on time explicitly, hence we could approximate

$$\langle\frac{\partial\hat{Q}}{\partial t}\rangle = 0.$$

- Ignoring the $\langle\frac{\partial\hat{Q}}{\partial t}\rangle$ term, we now has an equation telling use how the expectation value of Q evolves in time.
- The evolution is determined by the commutator of the operator Q with the Hamiltonian.
- Furthermore, if $\hat{Q}$ and $\hat{H}$ commute, i.e., $[\hat{Q},\hat{H}] = 0$, the expectation of Q is a constant in time. Q is an conserved quantity in the sense that its expectation value is not changing with time.
- Two very important results of Eq. (3.10) are $\frac{d}{dt}\langle p\rangle$ and $\frac{d}{dt}\langle x\rangle$.

  Exercise: Show that $\frac{d}{dt}\langle p\rangle = -\langle\frac{dV(x)}{dx}\rangle$.

  Exercise: Show that $\frac{d}{dt}\langle x\rangle = \frac{1}{m}\langle p\rangle$.

- Now recall the earlier result on generalised uncertainty principle for two operators A, B:
$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle\right)^2.$$
- Let $A \rightarrow H, B \rightarrow Q$,
$$\sigma_H^2\sigma_Q^2 \geq \left(\frac{1}{2i}\langle[\hat{H},\hat{Q}]\rangle\right)^2 = \left(\frac{1}{2i}\frac{\hbar}{i}\frac{d}{dt}\langle Q\rangle\right)^2 = \left(\frac{\hbar}{2}\right)^2\left(\frac{d\langle Q\rangle}{dt}\right)^2$$
$$\sigma_H\sigma_Q \geq \left(\frac{\hbar}{2}\right)\left|\frac{d\langle Q\rangle}{dt}\right|.$$
- Define $\Delta E \equiv \sigma_H, \Delta t \equiv \frac{\sigma_Q}{|d\langle Q\rangle/dt|}$, we then obtain
$$\Delta E\Delta t \geq \frac{\hbar}{2}.$$
- Notice that in the definition of Δt as in
$$\sigma_Q = \left|\frac{d\langle Q\rangle}{dt}\right|\Delta t,$$
Δt represents the *the amount of time it takes the expectation value of Q to change by one standard deviation.*
- Δt depends on what observable (Q) you are looking at. Different Q has a different rate of change in time $\frac{d\langle Q\rangle}{dt}$.
- If any observable changes rapidly, i.e., $\Delta t \ll 1$, the "uncertainty" (ΔE) must be large.

Example 3.5
A stationary state has definite energy, so $\Delta E = 0$, $\Delta t \rightarrow \infty$. But for a mixture of two stationary states, we could show that the product of ΔE and Δt obey the uncertainty bound.

Consider a linear combination of two stationary states,
$$\Psi(x,t) = a\psi_1(x)e^{-iE_1t/\hbar} + b\psi_2(x)e^{-iE_2t/\hbar},$$
where $a, b, \psi(x), \psi(x)$ are real.
$$|\Psi(x,t)|^2 = a^2\psi_1(x)^2 + b^2\psi_2(x)^2 + 2ab\psi_1(x)\psi_2(x)\cos\left(\frac{E_2-E_1}{\hbar}t\right).$$

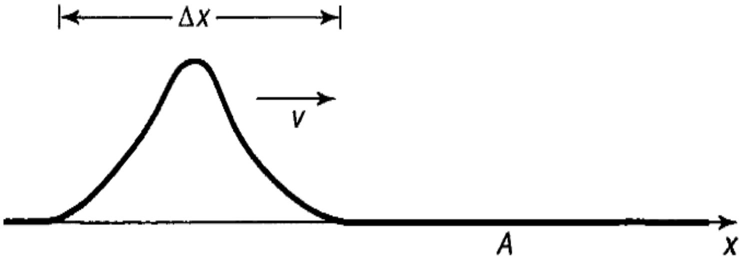
The period of oscillation is $\tau = 2\pi\hbar/(E_2 - E_1)$.
Roughly speaking, $\Delta E = E_2 - E_1$ and $\Delta t = \tau$, so

$$\Delta E \Delta t = 2\pi\hbar \geq \hbar/2.$$

Example 3.6
How long does it take a free-particle wave packet to pass by a particular point? Qualitatively, $\Delta t = \Delta x/v = m\Delta x/p$. But $E = p^2/2m$, so $\Delta E = p\Delta p/m$. Therefore,

$$\Delta E \Delta t = \frac{p\Delta p}{m}\frac{m\Delta x}{p} = \Delta x \Delta p,$$

which is $\geq \hbar/2$ by the position-momentum uncertainty principle.

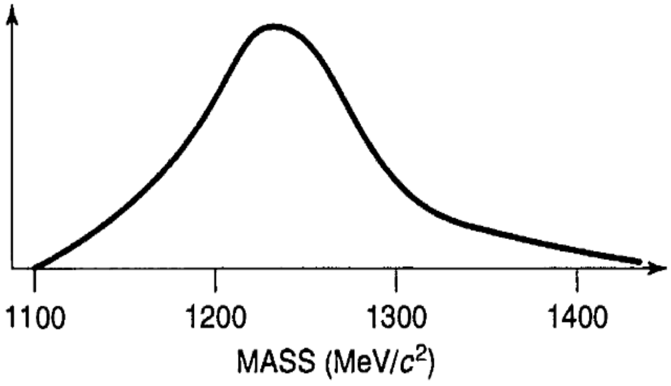


A free particle wave packet approaches the point A (Example 3.6).

Example 3.7
The Δ particle last about 10^{-23} seconds, before spontaneously disintegrating. If you make a histogram of all measurements of its mass, you get a kind of bell-shaped curve centered at 1232 MeV/c^2, with a width of about 120 MeV/c^2. Why does the rest energy mc^2 sometimes come out higher that 1232, and sometimes lower? Is this experimental error? No, for

$$\Delta E \Delta t = \left(\frac{120}{2}\text{MeV}\right)(10^{-23}\text{sec}) = 6 \times 10^{-22}\text{MeV sec},$$

whereas $\hbar/2 = 3 \times 10^{-22}$ MeV sec. So the spread in m is about as small as the uncertainty principle allows – a particle with so short of lifetime just does not have a very well defined mass.



Histogram of measurements of the Δ mass (Example 3.7).

In the previous examples, Δt takes on a variety of specific meaning. In Example 3.5, it's a period oscillation. In Example 3.6, it's the time it takes a particle to pass a point; in Example 3.7 it's the lifetime of an unstable particle. In these examples, Δt is the time it takes for the system to undergo "substantial" change.

3.6 Problem Set

ZCA 205 Quantum Mechanics
Problem set for Chapter 3

1. Suppose $\hat{Q}$ is hermitian, and α is a complex number. Under what condition (on α) is $\alpha\hat{Q}$ a hermitian?

2. Show that the position operator ($\hat{x} = x$) and the hamiltonian operator ($\hat{H} = -(\hbar^2/2m)^2/dx^2 + V(x)$) are hermitian.

Problem 3.5 The **hermitian conjugate** (or **adjoint**) of an operator $\hat{Q}$ is the operator $\hat{Q}^\dagger$ such that

$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}^\dagger f|g\rangle \quad \text{(for all } f \text{ and } g\text{).} \qquad [3.20]$$

(A hermitian operator, then, is equal to its hermitian conjugate: $\hat{Q} = \hat{Q}^\dagger$.)

(a) Find the hermitian conjugates of x, i, and d/dx.

(b) Construct the hermitian conjugate of the harmonic oscillator raising operator, a_+ (Equation 2.47).

(c) Show that $(\hat{Q}\hat{R})^\dagger = \hat{R}^\dagger\hat{Q}^\dagger$.

Problem 3.6 Consider the operator $\hat{Q} = d^2/d\phi^2$, where (as in Example 3.1) ϕ is the azimuthal angle in polar coordinates, and the functions are subject to Equation 3.26. Is $\hat{Q}$ hermitian? Find its eigenfunctions and eigenvalues. What is the spectrum of $\hat{Q}$? Is the spectrum degenerate?

3. Prove that for a renormalisable eigenfunctions of a Hermitian operator (i) Their eigenvalues are real, and (ii) eigenfunctions belonging to distinct eigenvalues are orthogonal.

Problem 3.8

(a) Check that the eigenvalues of the hermitian operator in Example 3.1 are real. Show that the eigenfunctions (for distinct eigenvalues) are orthogonal.

(b) Do the same for the operator in Problem 3.6.

Problem 3.10 Is the ground state of the infinite square well an eigenfunction of momentum? If so, what is its momentum? If not, *why* not?

4. Derive $\sum_n |c_n|^2 = 1$ from the normalisation condition of the wave function, $\langle\Psi|\Psi\rangle = 1$.

5. Prove $\langle Q\rangle = \sum_n q_n|c_n|^2$ from the definition $\langle Q\rangle = \langle\Psi|\hat{Q}\Psi\rangle$.

Problem 3.12 Show that

$$\langle x\rangle = \int \Phi^*\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}\right)\Phi\, dp. \qquad [3.57]$$

Hint: Notice that $x\exp(ipx/\hbar) = -i\hbar(d/dp)\exp(ipx/\hbar)$.

In momentum space, then, the position operator is $i\hbar\partial/\partial p$. More generally,

$$\langle Q(x, p)\rangle = \begin{cases} \displaystyle\int \Psi^*\hat{Q}\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\, dx, & \text{in position space;} \\ \displaystyle\int \Phi^*\hat{Q}\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}, p\right)\Phi\, dp, & \text{in momentum space.} \end{cases} \qquad [3.58]$$

In principle you can do all calculations in momentum space just as well (though not always as *easily*) as in position space.

6. (a) Prove the following commutator identity:

$$[AB, C] = A[B, C] + [A, C]B.$$

(b) Show that

$$[x^n, p] = i\hbar n x^{n-1}.$$

7. Show that for two operators $\hat{P}$ and $\hat{Q}$ that have a common eigenfunction f, then $[\hat{P}, \hat{Q}]f = 0$.

8. Solve
$$\left(\frac{\hbar}{i}\frac{d}{dx} - \langle p\rangle\right)\Psi = ia(x - \langle x\rangle)\Psi$$
for $\Psi(x)$. Note that $\langle x\rangle$ and $\langle p\rangle$ are *constant*.

9. Test the energy-time uncertainty principle for the wave function $\Psi(x,0) = A[\psi_1(x) + \psi_2(x)]$ as mentioned in in Problem 2.5 and the observable x, by calculating σ_H, σ_x, and $d\langle x\rangle/dt$ exactly.

10. Repeat the question above for another wave funciton as mentioned in Problem 2.43, $\Psi(x,0) = Ae^{-ax^2}e^{i\ell x}$, where ℓ is a real constant.

Chapter 4

Quantum Mechanics in Three Dimension

Acknowledgement: The content of this topic in this manuscript is mainly contributed by Dr. Myo Thaik.

4.1 Schroedinger Equation in Spherical Coordinates

- Generalising from one- to three-dimension, the potential energy V and the wave function Ψ are now functions of $\mathbf{r} = (x, y, z)$ and t, i.e., $V = V(\mathbf{r}, t)$, $\Psi = \Psi(\mathbf{r}, t)$.

- We will first solve the 3-D equation in terms of $V(\mathbf{r}) = V(r)$ without explicitly specifying the form of $V(\mathbf{r})$ except that it is assumed a central potential (a function depends only on just r (the distance from the origin) rather than on the angular positions.

- After that we will replace the generic central potential $V(r)$ by the hydrogen's central potential $V(r) \sim -\frac{1}{r^2}$. Since the angular parts are decoupled from the radial part, only the radial part of the solution to the TISE is tied to the form of $V(r)$, whereas the angular parts are independent of it.

- If the potential is independent of time, i.e., $V = V(\mathbf{r})$ only, there will be a complete sets of stationary states,

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_nt/\hbar}$$

where the spatial wavefunction $\psi_n(\mathbf{r})$ satisfy the TISE:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi.$$

- The general solution to the TDSE is

$$\Psi(\mathbf{r},t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n t/\hbar}$$

with the constant c_n determined by the initial wave function, $\Psi(x,0)$ in the usual way.

4.1.1 Separation of Variable

- Typically the potential is a function only of the distance from the origin. In that case it is natural to adopt spherical coordinates, (r,θ,ϕ).

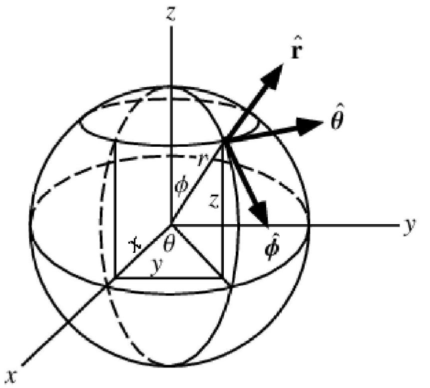


Figure 4.1: Spherical coordinates

- Here we will assume $V = V(r)$, i.e., V depends on r only.
- In spherical coordinates the Laplacian ∇^2 takes the form

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

- In spherical coordinates, the TISE reads

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V(r)\psi = E\psi. \tag{4.1}$$

- We begin by looking for solutions that are separable into products:

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

- $$\frac{\partial\psi}{\partial r} = Y\frac{dR}{dr}; \quad \frac{\partial\psi}{\partial\theta} = R\frac{\partial Y}{\partial\theta}, \quad \frac{\partial^2\psi}{\partial\phi^2} = R\frac{\partial^2 Y}{\partial\phi^2}.$$

- Put these back into Eq.(4.1),

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right] + V(r)RY = ERY. \tag{4.2}$$

- Dividing by RY and multiplying by $-2mr^2/\hbar^2$:

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

- The term in the first square bracket depends only on r, whereas the remainder depends only on θ and ϕ; accordingly, each must be a constant.

- For reasons that will appear in due course, this “separation constant” can be written in the form $\ell(\ell+1)$:

- $$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(\mathbf{r})-E) = \ell(\ell+1) \tag{4.3}$$

  This is known as the **Radial equation**.

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

  This is known as the **angular equation**.

- The separation constant ℓ is known as the **azimuthal quantum number**.

4.1.2 The angular Equation

- This equation determines the dependence of ψ on θ and ϕ:
- Multiply by $Y \sin^2\theta$, it becomes

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

- Again apply a separation of variable method: Plug $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ into the angular equation, we find

$$\left\{\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta\right\} + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = 0$$

- The first term is a function of θ only, and the second is a function only of ϕ, so each must be a constant. This time the separation constant is denoted as m^2.
-

$$\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2, \quad (\theta \text{ equation })$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2, \quad (\phi \text{ equation })$$

- The ϕ equation is easy:

$$\Phi(\phi) = e^{im\phi} + e^{-im\phi}. \tag{4.4}$$

  m is known as **magnetic quantum number**. If we allow m to take both positive or negative values, $e^{im\phi}$ will also cover the domain of $e^{-im\phi}$, hence we drop the second term in the solution so that Eq. (4.4) can be just compactly represented by

$$\Phi(\phi) = e^{im\phi}.$$

  The arbitrary constant that should appear in the solution is absorbed into Θ.

- The continuity boundary condition imposed on $\Phi(\phi)$ reads

$$\Phi(\phi + n2\pi) = \Phi(\phi)$$

  or

$$\exp(2\pi i m) = 1.$$

- From this it follows that m must be an integer:

$$m = 0, \pm 1, \pm 2, \cdots .$$

- For the θ equation, the solution is not so simple. The solution is a special function known as **associated Legendre function**,

$$\Theta(\theta) = A P_\ell^m(\cos\theta),$$

where

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

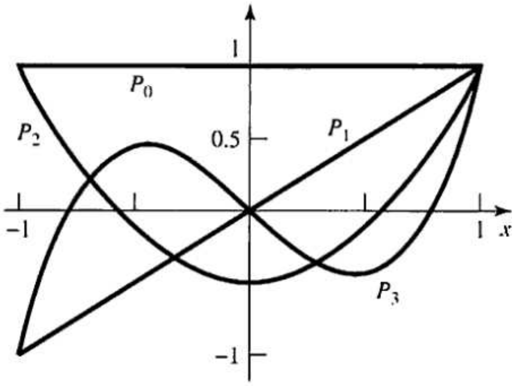
and $P_\ell(x)$ is the ℓth **Legendre polynomial**, defined by the **Rodrigues formula**:

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

TABLE 4.1: The first few Legendre polynomials, $P_l(x)$: (a) functional form, (b) graphs.

$$P_0 = 1$$
$$P_1 = x$$
$$P_2 = \tfrac{1}{2}(3x^2 - 1)$$
$$P_3 = \tfrac{1}{2}(5x^3 - 3x)$$
$$P_4 = \tfrac{1}{8}(35x^4 - 30x^2 + 3)$$
$$P_5 = \tfrac{1}{8}(63x^5 - 70x^3 + 15x)$$

(a)



(b)

- Notice that $P_\ell^m(x) = P_\ell^{-m}(x)$.

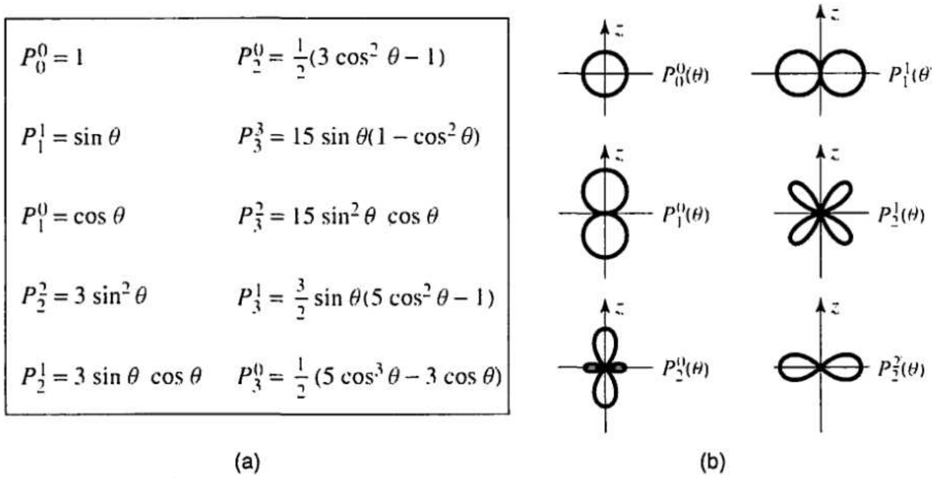
- From the Rodrigues formula that defines the Legendre polynomial, ℓ must be a non-negative integer (e.g., $(\frac{d}{dx})^\ell$ make no sense if ℓ is negative or a fractional number).

- From the definition of the associated Legendre function, since $P_\ell(x)$ is a polynomial of order ℓ, $(\frac{d}{dx})^{|m|} P_\ell(x)$ vanish if $|m| > \ell$ (can you see this?) In other words, $P_\ell^{|m|}(x)$ is non-zero only if

$$|m| \le \ell \Rightarrow m = 0, \pm 1, \pm 2, \cdots, \pm \ell$$

for a given ℓ (non-negative integer).

TABLE 4.2: Some associated Legendre functions, $P_l^m(\cos\theta)$: (a) functional form, (b) graphs of $r = P_l^m(\cos\theta)$ (in these plots r tells you the magnitude of the function ir the direction θ; each figure should be rotated about the z-axis).



$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1-\cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\,\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\,\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

(a) (b)

- Notice that for a given ℓ, there are $2\ell+1$ values of allowed m.

- The θ equation is a second order differential equation which should admit two different solutions. The associated Legendre functions are only one of these. The other solution,

  $$\Theta(\theta) = A\ln[\tan(\theta/2)],$$

  is discarded because it is physically unacceptable (they blow up when $\theta \to 0$ or π).

  Exercise: Derive the first 3 non-zero Legendre polynomial based on the Rodrigues formula.

Exercise: Derive the associated Legendre function $P_2^0(x)$, $P_2^1(x)$, $P_2^2(x)$ based on $P_2(x)$ that your have derived in previous exercise.

- The angular solutions are hence compactly expressed in terms of

$$Y \equiv Y(\theta,\phi) = \Phi(\phi)\cdot\Theta(\theta) \equiv \Phi(\phi)\cdot AP_\ell^m(\theta)$$

- A is the normalisation associated with the angular solutions $Y(\theta,\phi)$.
- Next we would like to discuss the normalisation of Y. This is to be carried out in spherical coordinates.
- The volume element in spherical coordinates is (see Fig 4.2)

$$dV = d^3\mathbf{r} = r^2\sin\theta dr d\theta d\phi$$

so that the normalisation condition becomes

$$\int_{\text{all space}} |\psi|^2 r^2 \sin\theta dr d\theta d\phi = \int_0^\infty R^2 r^2 dr \int_{\phi=0}^{\phi=2\pi}\int_{\theta=0}^{\theta=\pi} |Y(\theta,\phi)|^2 \sin\theta d\theta d\phi = 1$$

- It is convenient to normalise Y and R separately:

$$\int_0^\infty R^2 r^2 dr = 1,$$

$$\int_{\phi=0}^{\phi=2\pi}\int_{\theta=0}^{\theta=\pi} |Y|(\theta,\phi)|^2 \sin\theta d\theta d\phi = 1.$$

- The normalised angular wavefunctions are called spherical harmonics:

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

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

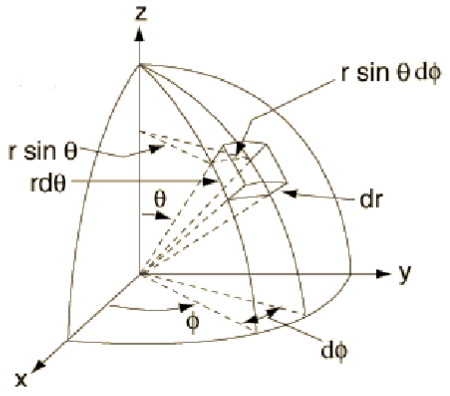
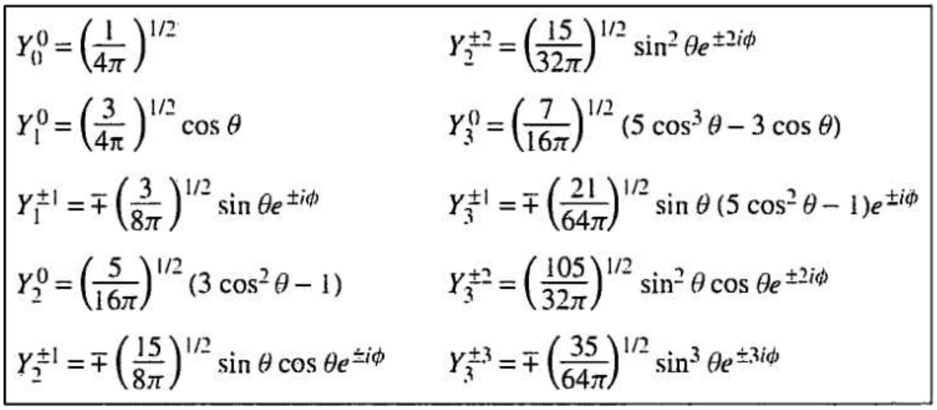


Figure 4.2: Volume element in spherical coordinates.



$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1) e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

Figure 4.3: The first few spherical harmonics, $Y_\ell^m(\cos\theta, \phi)$.

- The spherical harmonics are automatically orthogonal,

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

Exercise (Problem 4.3): Check that the spherical harmonics Y_0^0, Y_2^1 are normalised and orthogonal.

4.1.3 The radial Equation

- Now let's turn to the radial equation, Eq.(4.3).
- Let $u(r) \equiv rR(r)$ so that $R = u(r)/r$

$$\frac{dR}{dr} = \frac{r\frac{du}{dr} - u}{r^2} \longrightarrow r^2\frac{dR}{dr} = r\frac{du}{dr} - u$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = r\frac{d^2u}{dr^2} + \cancel{\frac{du}{dr}} - \cancel{\frac{du}{dr}} = r\frac{d^2u}{dr^2}$$

so that the radial equation now reads

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

Multiply it by $-\frac{\hbar^2}{2mr}$ and rearranging, the radial equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]u = Eu \tag{4.5}$$

- The square bracket term represent an effective potential

$$V_{eff} = V(r) + \frac{\hbar^2}{2mr^2}\ell(\ell+1)$$

which is the original potential $V(r)$ modified by a ℓ-dependent centrifugal term $\frac{\hbar^2}{2mr^2}\ell(\ell+1)$.

- The normalisation condition for the radial function, in terms of $u(r)$ is

$$\int_0^\infty R^2r^2dr = \int_0^\infty u(r)^2dr = 1.$$

4.1.4 Infinite Spherical Well

- Consider an especially simple case of spherical potential:

$$V(\mathbf{r}) = \begin{cases} 0, & \text{if } r \leq a \\ \infty, & \text{if } r > a. \end{cases}$$

- What is its wavefunction and the allowed energy?

- The wavefunction is $\Psi(\mathbf{r},t) = R(r)Y_\ell^m(\theta,\phi)e^{-iEt/\hbar}$, where the angular solution is the same as solved in previous subsection. Recall that the angular solution is independent of the form of the potential as long as it is spherical (i.e., angular-independent).

- We will use the machinery developed in previous subsection to solve for $R(r)$.
- Let $R(r) = u(r)/r$, the radial part of TISE in inside the well is given as Eq.(4.5), rearrange it into the convenient form

$$\frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2\right] u, \tag{4.6}$$

where $k \equiv \sqrt{\frac{2mE}{\hbar^2}}$

Exercise: Show this.

- The solution is not so trivial. It is given by the linear combination of **spherical Bessel function** of order ℓ, $j_\ell(x)$ and **spherical Neumann function** of order ℓ,

$$u(r) = Arj_\ell(kr) + Brn_\ell(kr),$$

$$\begin{aligned} j_\ell(x) &= (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x}, \\ n_\ell(x) &= -(-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x}. \end{aligned} \tag{4.7}$$

These are the generating functions for Bessel and Neumann functions.

TABLE 4.4: The first few spherical Bessel and Neumann functions, $j_n(x)$ and $n_l(x)$; asymptotic forms for small x.

$j_0 = \dfrac{\sin x}{x}$	$n_0 = -\dfrac{\cos x}{x}$
$j_1 = \dfrac{\sin x}{x^2} - \dfrac{\cos x}{x}$	$n_1 = -\dfrac{\cos x}{x^2} - \dfrac{\sin x}{x}$
$j_2 = \left(\dfrac{3}{x^3} - \dfrac{1}{x}\right) \sin x - \dfrac{3}{x^2} \cos x$	$n_2 = -\left(\dfrac{3}{x^3} - \dfrac{1}{x}\right) \cos x - \dfrac{3}{x^2} \sin x$
$j_l \to \dfrac{2^l l!}{(2l+1)!} x^l,$	$n_l \to -\dfrac{(2l)!}{2^l l!} \dfrac{1}{x^{l+1}}, \quad \text{for } x \ll 1.$

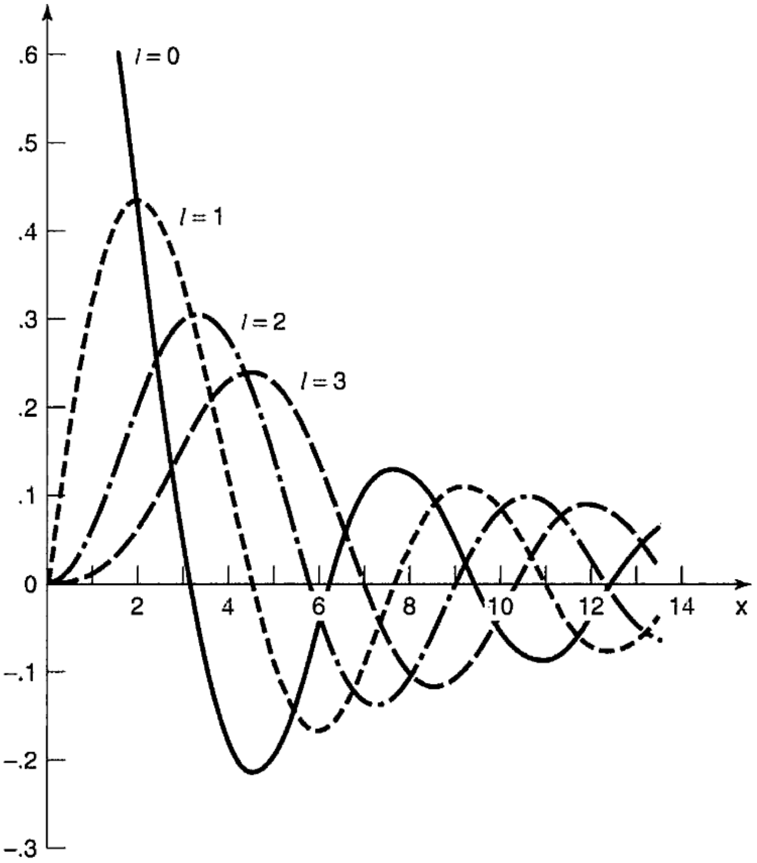


FIGURE 4.2: Graphs of the first four spherical Bessel functions.

Exercise: Derive $n_0(x)$, $n_1(x)$, $j_0(x)$, $j_1(x)$. Do you think the Neumann function a physically acceptable solution? Explain.

- Due to the reason you have explained in the *Exercise* above, the radial solution takes the form
$$R(r) = Aj_\ell(kr).$$
- Based on the definitions of the generating functions for Bessel and Neumann functions, Eq.(4.7), ℓ must be a non-zero integer, $\ell = 0, 1, 2, \cdots$.
- Now impose the boundary condition $R(r = a) = 0$:
$$R(r = a) = Aj_\ell(ka) = 0 \Rightarrow j_\ell(ka) = 0,$$
- ka is a zero of the ℓth-order spherical Bessel function, which values has no closed form (they have to be solved numerically).
- Note that the Bessel functions are oscillatory (see Figure 4.2). For a given ℓ, there are many zeros correspond to that particular $j_\ell(x)$ (zeros in this case refers to the values of x in $j_\ell(x)$ for which $j_\ell(x) = 0$.)
- Say, for a fixed ℓ, the zeros are labeled $\beta_{n\ell}$, where $n = 1, 2, 3, \cdots$. $\beta_{n\ell}$ are discrete values labeled by a set of two non-negative integers $\{n, \ell\}$. They are the "nth zero of the ℓ spherical Bessel function." (note: $n = 0$ is forbidden by the virtual of the Heisenberg uncertainty principle.)
- Hence we arrive at the quantisation of energy:
$$k = k_{n\ell} = \beta_{n\ell}/a \Leftrightarrow E = E_{n\ell} = \frac{\hbar^2}{2ma}\beta_{nl}.$$

- The stationary wavefunction are

$$\psi(\mathbf{r}) = \psi_{nlm}(r,\theta,\phi) = A_{nl} j_\ell(\frac{r\beta_{n\ell}}{a}) Y_\ell^m(\theta,\phi).$$

- Notice that each stationary state $\phi_{n,\ell,m}(r,\theta,\phi)$ is indexed by a set of three quantum numbers, $\{n,\ell,m\}$. That is, when you want to specify a particular stationary state, you have to specify the set of these three quantum numbers (or else it is not a qualified specification).

- Compare the above situation to the 1-D stationary states encountered so far. There only one quantum number is required; here we have got three instead.

- Notice that the normalisation constant for the radial function $A_{n\ell}$ is labeled by two quantum numbers, $\{n,\ell\}$. They are to be determined by normalisation,

$$\int_0^\infty A_{n\ell}^2 j_\ell(\frac{r\beta_{n\ell}}{a})^2 r^2 dr = 1$$

  which turns out to be quite complicated. We are not going to derive their explicit form anyway, except to note that they have to be evaluated for different set for each set of $\{n,\ell\}$.

- Another important feature to take notice is that: The energy is dependent on both quantum number n and ℓ. For a given set of $\{n,\ell\}$, the energy is given by $E_{n\ell}$. However, there are actually $2\ell+1$ (= number of allowed values of m) stationary states that carry the same energy.

- We say: Each energy level $E_{n\ell}$ is $(2\ell+1)$-fold degenerate, since there are $(2\ell+1)$ different values of m for each value of ℓ.

- For example, there are there stationary states that have the same energy $E_{n=1,\ell=1}$, i.e., $\psi_{n=1,\ell=1,m=-1}, \psi_{n=1,\ell=1,m=0}, \psi_{n=1,\ell=1,m=+1}$.

Exercise: What is the solutions and allowed energies for $\ell = 0$?

Answers:

For $\ell = 0$, the allowed values for n is $n = 1, 2, 3, \cdots$; and the allowed value for m is m=0.

The allowed energies are $E_{\ell=0,n} = \frac{\hbar^2}{2ma^2}\beta_{n0}, \;\; n = 1, 2, 3, \cdots$

The solutions are $\psi_{n,\ell=0,m=0}, \;\; n = 1, 2, 3, \cdots$

4.2 The Hydrogen Atom

-

- Coulomb potential is a special case of central potential:

  $$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

  where r is the distance between the electron and the nuclease.

- We assume $M_{\text{proton}} \gg m_e$.

- Plug into the radial equation

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

- To solve the equation means we wish to determine (1) $u(r)$ hence $R(r) = ru(r)$, and (2) the allowed energies E.

4.2.1 The radial wave equation

- Define $\kappa = \frac{\sqrt{-2mE}}{\hbar}$. For bound states, E is negative, so κ is real.

- The radial equation is cast into the form

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

- The equation is further simplified in terms of a new variable $\rho \equiv \kappa r$ and a constant $\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$, so that

  $$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u. \tag{4.8}$$

  Exercise: Show this.

- We then examine the limiting behavior of the solutions in order to guess the form of the solution as a products of the solutions in these limits. Doing so allow us to “peel off” the divergent parts out of the general solution so that a physically acceptable solution (that without infinities) could result. The whole idea is very similar in spirit to the method used when solving the QHO. The following is how we do this:

- Taking the limiting case $\rho \to \infty$, Eq.(4.8) becomes

  $$\frac{d^2u}{d\rho^2} = u,$$

  with the solution $u(\rho) = Ae^{-\rho} + Be^{\rho}$. In order for the solution to remain finite when $\rho \to \infty$, B has to be set to 0.

- In short, the solution must behave like $u(\rho) \sim Ae^{-\rho}$ when $\rho \to \infty$.

- Taking the limiting case $\rho \to 0$, Eq.(4.8) becomes

  $$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u. \tag{4.9}$$

  with the general solution $u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$.

  Exercise: Check this.

  In order for the solution to remain finite when $\rho \to 0$, D has to be set to 0.

- In short, the solution must behave like $u(\rho) \sim C\rho^{\ell+1}$ when $\rho \to 0$.

- In the intermediate region, we assume the general solution to take on the form

  $$u(\rho) = \rho^{\ell+1}e^{-\rho}\upsilon(\rho)$$

  (note: υ is pronounced as "upsilon".)

- Slotting this ansatz into Eq.(4.8), we arrive at (after some algebra)

  $$\rho\frac{d^2\upsilon}{d\rho^2} + 2(\ell+1-\rho)\frac{d\upsilon}{d\rho} + [\rho_0 - 2(\ell+1)]\,\upsilon = 0. \tag{4.10}$$

- We seek the solution $\upsilon(\rho)$ in terms of the power series

  $$\upsilon(\rho) = \sum_{j=0}^{\infty} c_j\rho^j.$$

- Twice differentiating the power series term by term, and plugging the result back into Eq.(4.10), we have

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j - 2\sum_{j=0}^{\infty} jc_j\rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} c_j\rho^j = 0.$$

- Equating the coefficients of like powers yields the recurrent formula

$$c_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} c_j. \tag{4.11}$$

- Based on the recurrent formula, starting from c_0, all the subsequent $c_{j=1}, c_{j=2}, \cdots$ can be derived. In other words, we can expressed all $c_j, j > 1$ in terms of c_0, an overall constant which would be fixed by normalisation.

- Now let's investigate c_j in the $j \to \infty$ limit:

$$c_{j+1} \approx \frac{2}{j+1} c_j.$$

- Suppose for a moment this relation is exact (instead of being just an approximation), the solution to $c_{j+1} \approx \frac{2}{j+1} c_j$ can be expressed as

$$c_j \approx \frac{2^j}{j!} c_0,$$

so that the power series now read

$$\upsilon(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho} \Rightarrow u(\rho) = c_0 \rho^{\ell+1} e^{\rho} \overset{\rho \to \infty}{\longrightarrow} \infty.$$

- What that means is: if we allow the power series to sum up to $j \to \infty$ terms, the solution $u(\rho)$ in the limit $\rho \to \infty$ will blow up (this is bad).

- To avoid this from happening, the only way is to terminate the power series at certain maximal integer, $j_{\max}$ such that $c_j = 0$ for all $j > j_{\max}$.

- Such a requirement when is translated into the recurrent relation Eq.(4.11), reads

$$2(j_{\max} + \ell + 1) = \rho_0.$$

- Defining the so-called **principle quantum number**

$$n \equiv j_{\max} + \ell + 1, \tag{4.12}$$

which is obviously a non-negative integer, we have

$$2n = \rho_0 \Rightarrow E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^2}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

- The allowed energies are

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

- Known as **Bohr formula**.
- The Bohr radius is defined as $a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}$ m.
- E_1 (= -13.6 eV) is the ground state energy (the lowest allowed energy)
- In terms of Bohr radius, $\rho = \rho_n = \frac{r}{an}$.
- Hence, $\psi_{n,\ell,m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$, $R_{n\ell}(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}\upsilon(\rho)$, $\upsilon(\rho)$ a polynomial of degree $j_{\text{max}} = n - \ell - 1$ in $\rho = \frac{r}{na}$, whose coefficients are determined by the recursion formula Eq.(4.11).
- Ground state corresponds to the state with lowest energy. This occurs for $n = 1$. Since $n = j_{max} + \ell + 1$, $\ell = 0$. Since $|m| \le \ell$, $m = 0$. In short, the three quantum numbers that label the ground state is $\{n, \ell, m\} = \{1, 0, 0\}$.

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

$$R_{10}(r) = \frac{c_0}{a}e^{-r/a}, Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

- Normalisation: $\int_{r=0}^{\infty} R_{10}^2 r^2 dr = 1 \Rightarrow c_0 = 2/\sqrt{a}$, so that

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

- The first excited state corresponds to ether

$$n = 2, \ell = 1, m = -1, 0, 1,$$

or

$$n = 2, \ell = 0, m = 0.$$

$$\rho_2 = \frac{r}{2a}.$$

- For $\ell = 1$ ($j_{max} + \ell = n - 1 = 1$)

$$R_{21}(r) = \left(\frac{1}{r}{\rho_2}^2 e^{-\rho_2}\right)\sum_{j=0}^{j=j_{max}=0} c_j\rho_2^j = \left(\frac{r}{4a^2}e^{\frac{-r}{2a}}\right)(c_0\rho_2^0) = \frac{c_0}{4a^2}re^{-\frac{r}{2a}}$$

- For $\ell = 0$ $(j_{max} + \ell = n - 1 = 1 \Rightarrow j_{max} = 1)$

$$R_{20}(r) = \left(\frac{1}{r}{\rho_2}^2 e^{-\rho_2}\right) \sum_{j=0}^{j=j_{max}=1} c_j \rho_2^j = \left(\frac{r}{4a^2} e^{\frac{-r}{2a}}\right)(c_0\rho_2^0 + c_1\rho_2^1) = \cdots = \frac{c_0}{2a}(1 - \frac{r}{2a})e^{-r/2a}.$$

- For arbitrary n, $\ell = 0, 1, 2, \cdots, n-1$, and for each ℓ there are $2\ell + 1$ possible values of m.
- The total degeneracy of the energy level E_n is $\sum_{\ell=0}^{n-1}(2\ell + 1) = n^2$.
- For example, in the previous example of the first excited state, there are a total of 4 states $\{n = 2, \ell = 1, m = 1\}$, $\{n = 2, \ell = 1, m = 0\}$, $\{n = 2, \ell = 1, m = -1\}$, $\{n = 2, \ell = 0, m = 0\}$ all share the ssame energy level E_2. These are degeneracy states.
- The polynomial $v(\rho)$ (which is indexed by ℓ, n), apart from an overall normalisation constant, is known as **associated Laguerre polynomial**,

$$v(\rho) = L^{2\ell+1}_{n-\ell-1}(2\rho), \tag{4.13}$$

where

$$L^q_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x).$$

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

is known as the qth **Laguerre polynomial**.

TABLE 4.5: The first few Laguerre polynomials, $L_q(x)$.

$L_0 = 1$

$L_1 = -x + 1$

$L_2 = x^2 - 4x + 2$

$L_3 = -x^3 + 9x^2 - 18x + 6$

$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$

$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$

$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$

TABLE 4.6: Some associated Laguerre polynomials, $L^p_{q-p}(x)$.

$L^0_0 = 1$	$L^2_0 = 2$
$L^0_1 = -x + 1$	$L^2_1 = -6x + 18$
$L^0_2 = x^2 - 4x + 2$	$L^2_2 = 12x^2 - 96x + 144$
$L^1_0 = 1$	$L^3_0 = 6$
$L^1_1 = -2x + 4$	$L^3_1 = -24x + 96$
$L^1_2 = 3x^2 - 18x + 18$	$L^3_2 = 60x^2 - 600x + 1200$

- The normalised hydrogen wave functions are

$$\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^{\ell} \left[L^{2\ell+1}_{n-\ell-1}(2r/na)\right] Y^m_\ell(\theta, \phi).$$

- Note that despite the wave function depends on three quantum numbers, the energy levels depend only on n – this is a peculiarity of the Coulomb potential (c.f., in the spherical well, the energies depend on both n, ℓ).

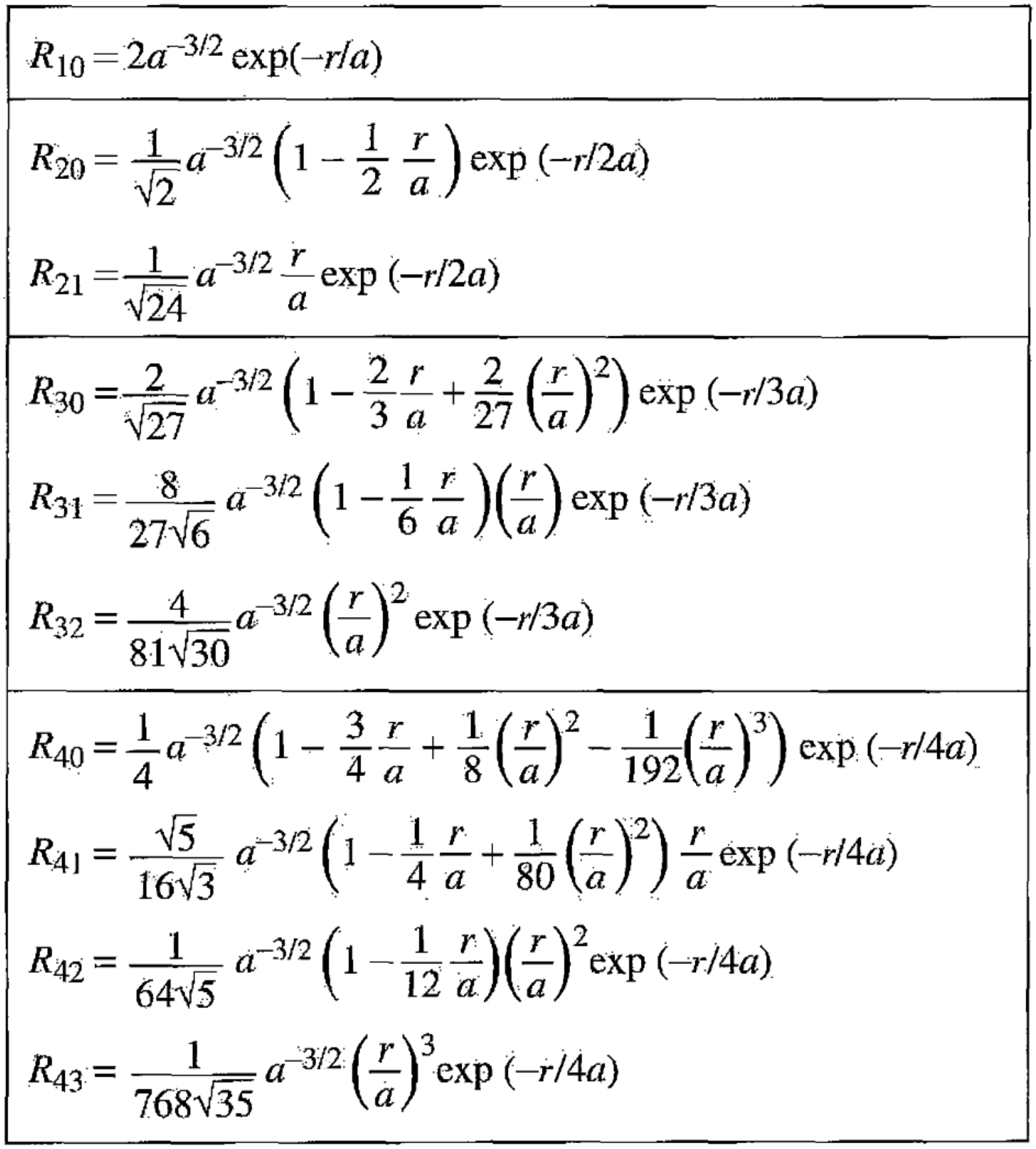
- The wave functions are mutually orthogonal:

$$\int \psi^*_{n'\ell'm'}\psi_{n\ell m}r^2\sin\theta dr d\phi = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}.$$

  The orthogonality is due to the spherical harmonics (the $\delta_{\ell,\ell'}$ and $\delta_{m,m'}$ terms) as well as from the radial functions (the $\delta_{n,n'}$ term).

- The $\delta_{n,n'}$ term arises due to the fact that ψ_n and $\psi_{n'}$ are eigenfunctions of H with distinct eigenvalues.

TABLE 4.7: The first few radial wave functions for hydrogen, $R_{nl}(r)$.



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

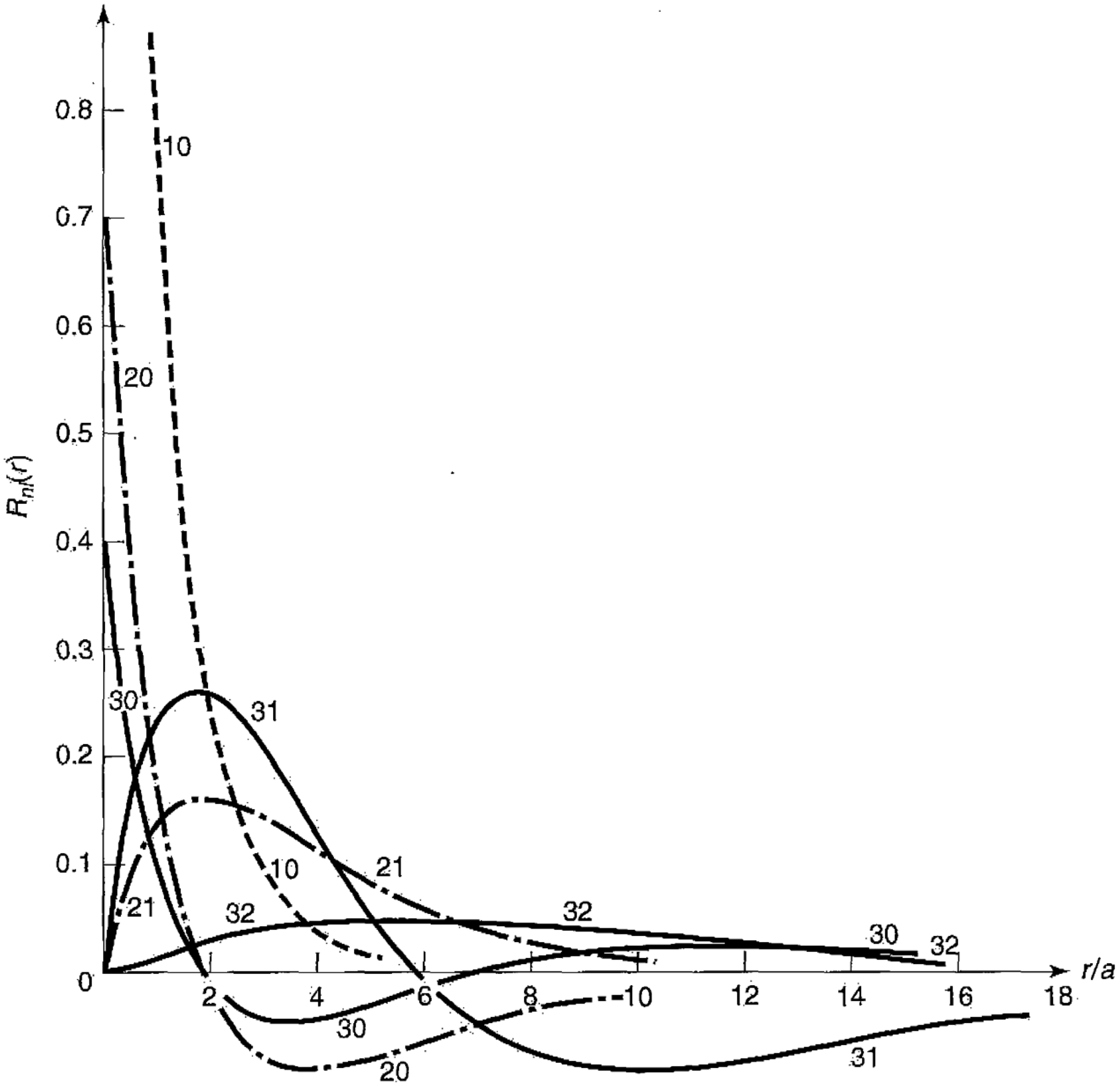


FIGURE 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

- The density plot of hydrogen for a specific n, ℓ, m, $|\psi_{n,\ell,m}|^2$ can be visualised using coloured density plot,

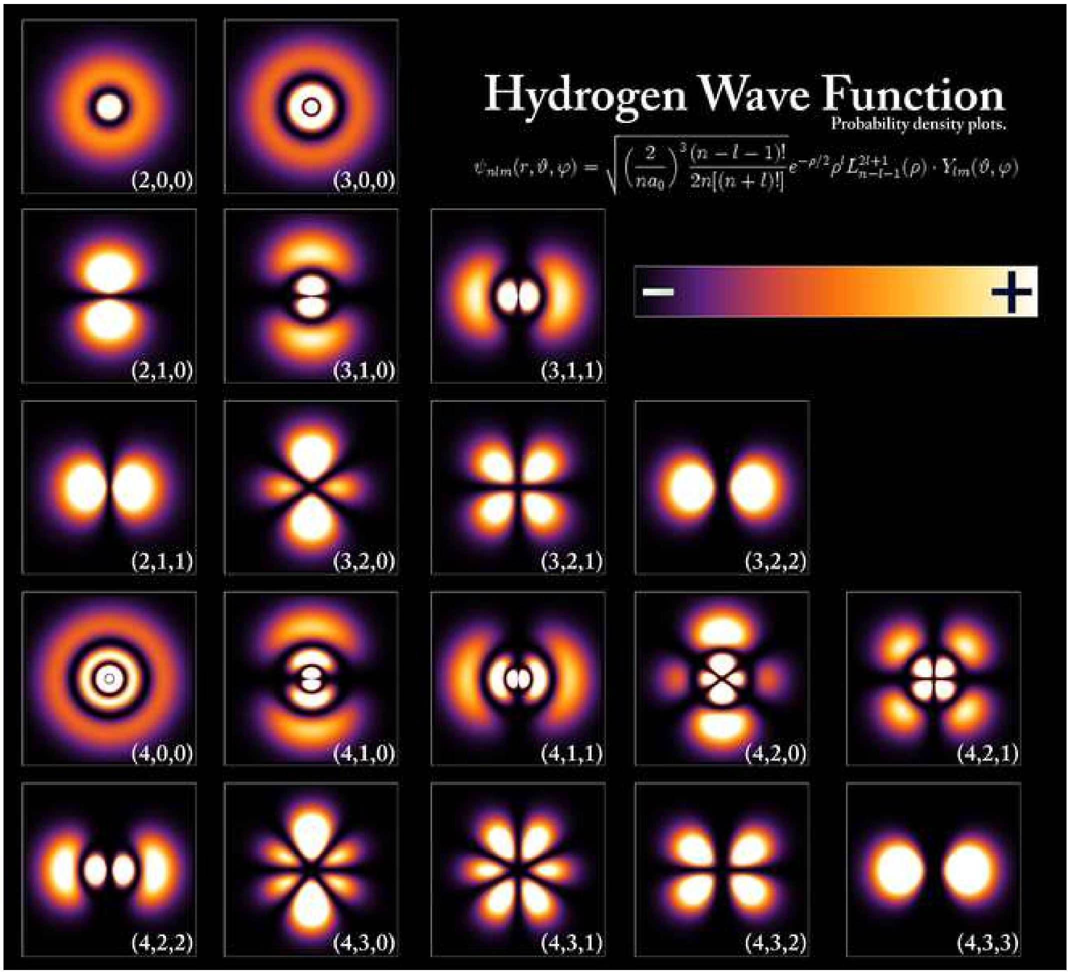


Figure 4.4: Figure adopted from http://en.wikipedia.org/wiki/File:Hydrogen_Density_Plots.png.

- Go to the online physlets (by Prentice-Hall) to generate your own density plot: http://webphysics.davidson.edu/faculty/dmb/hydrogen/intro_hyd.html

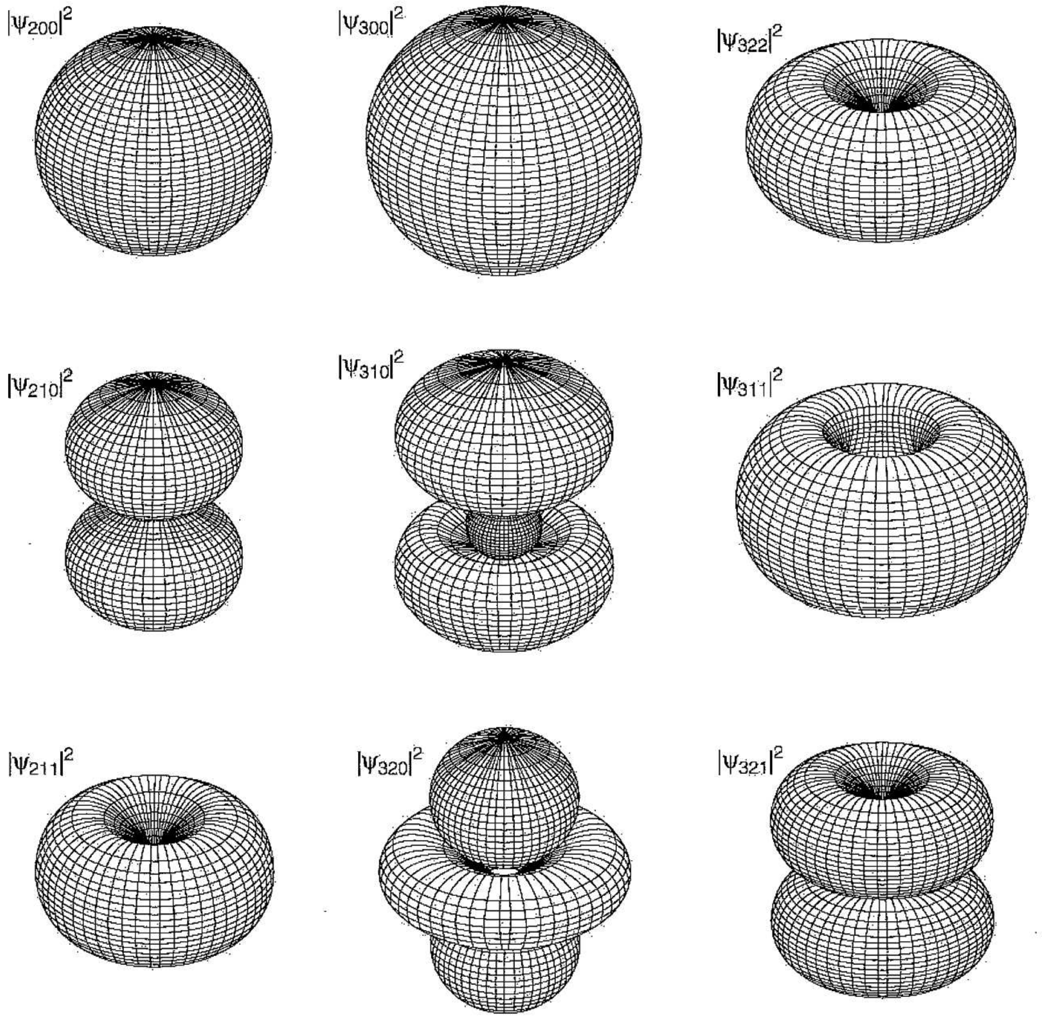


Figure 4.5: Surfaces of constant $|\psi|^2$ for the first few hydrogen wave functions. The are obtained by rotating surfaces of constant $|\psi|^2$ (of the density plots) about the vertical axis. Figures adopted from *The picture book of quantum mechanics, Springer*, New York (2001).

- Observe that for the 3D plot in Fig.4.5:
  - For all cases with $\ell = 0$, the wavefunctions are spherically symmetric.
  - For all cases with $\ell \neq 0$, the wavefunctions are only cylindrical symmetric.

Exercise:
What is the most probably value of r in the ground state of the hydrogen?

Solution
The most probably value of r is the value in r where the probability density to find the electron, $P(r)$, is the largest. If $r = r'$ is the value where the probability density is the largest, then, $\frac{dP(r)}{dr}|_{r=r'} = 0$.

By definition, $p(r) = P(r)dr$ is the probablity to find the electron in the interval $\pm\Delta r$ located at r. $P(r)$ is the probability density of the electron at r.

The probability to find the electron in a volume element dV located at $\{r, \theta, \phi\}$ is

$$p(r, \theta, \phi) = \psi^*_{n,\ell,m}\psi_{n,\ell,m}dV = \psi^*_{n,\ell,m}\psi_{n,\ell,m}r^2 dr \sin\theta d\theta d\phi$$

Integrating over all angular contibution results in a factor of 4π,

$$p(r) = \int_{\phi=0}^{\phi=2\pi}\int_{\theta=0}^{\theta=\pi} \psi^*_{n,\ell,m}\psi_{n,\ell,m}r^2 dr \sin\theta d\theta d\phi = 4\pi r^2 R^2_{n,\ell}(r)dr$$

For ground state, $n = 1, \ell = 0$, $R_{n=1,\ell=0} = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$.

$$p(r) = 4\pi r^2 R^2_{n,\ell}(r)dr = P(r)dr$$

$$P(r) = 4\pi r^2 R^2_{n,\ell}(r) = 4\pi r^2 \frac{1}{\pi a^3}e^{-2r/a}$$

Optimising $P(r)$ with respect to r, $\frac{dP(r)}{dr}|_{r=r'} = 0$, gives r' as $r' = a$.

Exercise:

- Find $\langle r\rangle$ and $\langle r^2\rangle$ for an electron in the ground state of hydrogen atom.

  Solution

- $\langle \hat{Q} \rangle = \int\int\int \psi^*_{n,\ell,m} \hat{Q} \psi_{n,\ell,m} r^2 dr \sin\theta d\theta d\phi$. Here $\hat{Q} = r$ and $\hat{Q} = r^2$, $\psi_{n,\ell,m} = \psi_{1,0,0} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$.

  For $\hat{Q} = r$,

  $$\langle \hat{r} \rangle = \int\int\int \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r^2 dr \sin\theta d\theta d\phi = 4\pi \frac{1}{\pi a^3} \int_0^\infty e^{-2r/a} r^3 dr = \frac{3a}{2}.$$

  For $\hat{Q} = r^2$,

  $$\langle \hat{r}^2 \rangle = \int\int\int \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r^2 \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r^2 dr \sin\theta d\theta d\phi = 4\pi \frac{1}{\pi a^3} \int_0^\infty e^{-2r/a} r^4 dr = 3a^2$$

4.2.2 The Spectrum of Hydrogen

- If in the beginning, a hydrogen atom is in a given stationary state $\{n, \ell, m\}$, it would stay there forever (including the state $n > 1$).

- However, upon perturbation (which in practice is constantly present), the electron may undergo a **transition** to some other stationary state – either by absorbing ("excitation", e.g., when being irradiated by electromagnetic wave or bombarded by other atoms) or giving off energy ("de-excitation", usually in the form of electromagnetic radiation).

- Let us now recall the Bohr hydrogen model (remember ZCT 104?). The Bohr's hydrogen atom is what we called *the old quantum theory* - an ad hoc model combining quantisation of angular moment postulate, Planck's postulate, and classical mechanics. The Bohr's atom is not a quantum mechanical treatment of hydrogen atom.

- In the Bohr's model, the energy difference in such a transition (from initial to final states) is given by

  $$\Delta E = E_f - E_i = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right).$$

- Planck formula relates the energy of a photon E_γ to its frequency ν via

  $$E_\gamma = h\nu = \frac{hc}{\lambda}$$

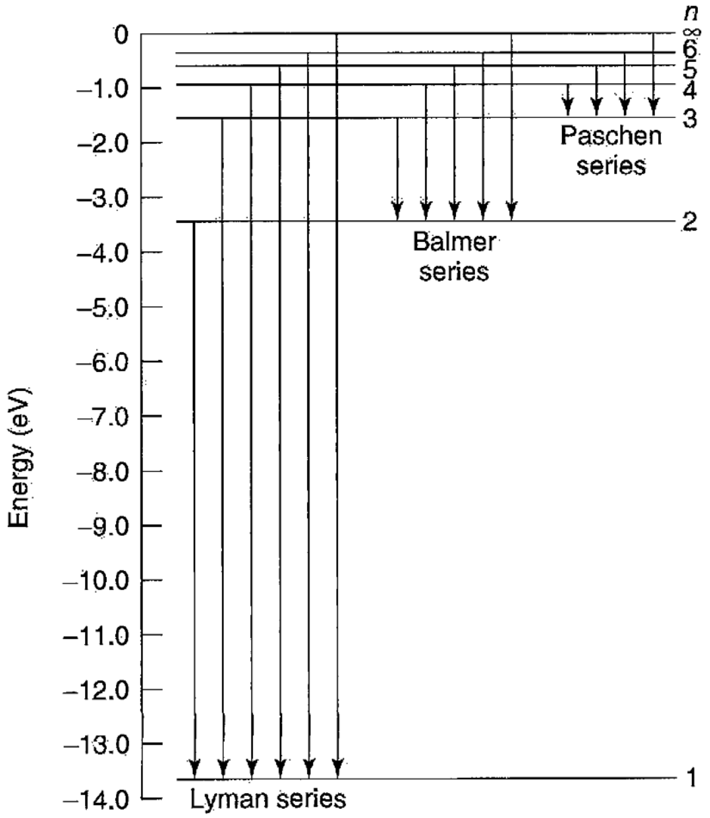
  (λ is the wavelength and c the speed of light).

so that

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),$$

where R is the **Rydberg constant**,

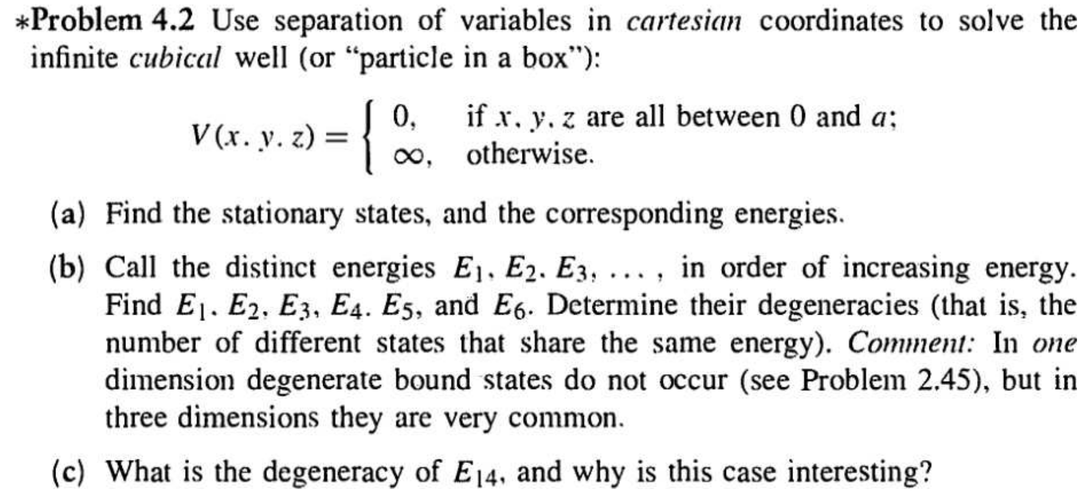
$$R = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = 1.097 \times 10^7 \text{ m}^{-1}.$$



IGURE 4.7: Energy levels and transitions in the spectrum of hydrogen.

4.3 Problem Set

ZCA 205 Quantum Mechanics
Problem set for Chapter 4



∗Problem 4.2 Use separation of variables in *cartesian* coordinates to solve the infinite *cubical* well (or "particle in a box"):

$$V(x, y, z) = \begin{cases} 0, & \text{if } x, y, z \text{ are all between 0 and } a; \\ \infty, & \text{otherwise.} \end{cases}$$

(a) Find the stationary states, and the corresponding energies.

(b) Call the distinct energies $E_1, E_2, E_3, \ldots,$ in order of increasing energy. Find $E_1, E_2, E_3, E_4, E_5,$ and E_6. Determine their degeneracies (that is, the number of different states that share the same energy). *Comment:* In *one* dimension degenerate bound states do not occur (see Problem 2.45), but in three dimensions they are very common.

(c) What is the degeneracy of E_{14}, and why is this case interesting?

1. Check that $Arj_\ell(kr)$ satisfy the radial equation for the case $\ell = 1$ in the infinite spherical well.
2. Work out the radial wave functions R_{32} using the recursion formula, Eq.(4.11). Don't bother to normalise it.
3. Referring to Table 4.7 for the radial function, normalise R_{21} and construct $\psi_{211}, \psi_{210}, \psi_{21-1}$.
4. Based on the definition of the associated Laguerre polynomial and the definition of Eq.(4.13), find $v(\rho)$ for the case $n = 5, \ell = 2$.
5. What is the expectation value $\langle r \rangle$ for an electron in the ground state of hydrogen? Express your answer in unit of Bohr radius.
6. A hydrogen atom starts out in the following linear combination of the stationary states $n = 2, \ell = 1, m = 1$ and $n = 2, \ell = 1, m = -1$:

$$\Psi(\mathbf{r}, 0) = 1\sqrt{2}\left(\psi_{211} + \psi_{21-1}\right).$$

   (a) Construct $\Psi(\mathbf{r}, t)$. Simplify it as much as you can.

(b) Find the expectation value of the potential energy, $\langle V \rangle$. (Does it depend on t?) Give both the formula and the actual number, in eV.

Note: A linear combination of stationary states itself is not a stationary states.

Bibliography

[1] D. Griffiths **Introduction to Quantum Mechanics second edition** Pearson, 2005.