UNIVERSITY OF CALIFORNIA, BERKELEY

PHYSICS 137A

Quantum Mechanics

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Contents

Chapter 1

The Quantum Regime

1.1 The Limits of Theories

As physical theories are constructed to account for patterns that emerge from observation and experiment, it is not surprising that such theories are limited by the data that inspired them, and thus are subject to failure when extended into new regimes. We are familiar with historical examples. Newton observed a world that was Galilean invariant – velocities added, observers in different Galilean frames agree on their measurements of space and time separations of events, thus $x_1 - x_2 = x'_1 - x'_2$ and $t_1 - t_2 = t'_1 - t'_2$, so that events simultaneous in one observer's frame are also simultaneous in another's. Yet these properties were aspects of a theory constructed to account for measurements for which the dynamics were governed by the condition

$$\frac{v^2}{c^2} \ll 1$$

Einstein's special theory of relativity did not replace classical mechanics, but rather incorporated it – the invariant separation among events changed to $c^2(t_1 - t_2)^2 - (x_1 - x_2)^2 =$ constant, but in the limit where velocities small, the classical results are all recovered and valid apart from corrections of order v^2/c^2. Classical mechanics is an *effective theory*, fully consistent with special relativity provided measurements are restricted to the effective theory's range of validity, $v \ll c$. If this condition is fulfilled, one can use the simpler classical theory, with confidence that the predictions made will be valid with small errors controlled by v^2/c^2. This is our first encounter with the *correspondence principle.*

In physics, one expects to discover the simplest theories – the most "effective" theories – first. We discovered classical mechanics first because it is the theory of falling apples, planetary motion, and sailing ships. Only when we started probing higher velocities were the limitations of the theory recognized – motivating the creation of an extended theory, special relativity.

Effective theory is one of the most powerful and pervasive concepts in modern physics. Physics can often be viewed as a tower of effective theories, with each successive layer more complete and more predictive, valid over a wider range of parameters. When we analyze an experiment, we use the effective theory lowest in this tower that is adequate for our needs. The theory will be simpler when the physics we study is accurately encoded in a smaller set of parameters. If you are dealing with a non-relativistic mechanics problem, you can of course choose to use special relativity in your analysis – but you will need to work *much* harder and you will learn no new information.

Once you have completed your analysis, the information you obtain can be "ported up" to the more general effective theories that reside above: this is the process of "matching" one effective theory to another.

In subatomic physics today the last experimentally validated member of this tower is the Standard Model (SM) – decades of experiments have established its validity, in some cases to precisions exceeding a part in a billion. But we also know there is something more – massive neutrinos, dark matter, and dark energy provided rather direct evidence of this. There is enormous effort underway to learn more about such phenomena, so that we will have a bit more guidance from experiments about the next effective theory in the tower. This theory will not replace SM, but rather incorporate it in a generalization that accounts for the new phenomena discovered.

Just as special relativity emerged when experiments began to probe higher velocities, *quantum mechanics* emerged when experiments started to probe atomic scales. The classical mechanics in use was not only nonrelativistic, but also deterministic. Knowledge of the initial conditions (e.g. positions and velocities) and interactions among objects allow one to compute the future evolution of the system. In principle this can be done to arbitrary accuracy, as the theory places no limits on the precision with which those initial conditions can be determined, or the classical equations solved.

This aspect of classical mechanics again reflects the limited range of the data informing the theory. A second scale that further restricts the applicability of classical physics and thus the boundary beyond which a more general, quantum description must be used, is defined in terms of Planck's reduced constant $\hbar$.

$$\begin{aligned} \Delta E \Delta t &\gg \hbar = 6.58 \times 10^{-16} \text{eV s} \\ \Delta E \Delta x &\gg \hbar c = 197.3 \text{ eV nm} \end{aligned} \tag{1.1}$$

If one were to ask, is quantum mechanics relevant to a squash ball confined to a squash court, the second expression in Equation 1.1 above tells us it is only if we are interested in changes of the squash ball's energy of about one part in 10^{70}. We are welcome to calculate the future trajectory of a squash ball using quantum mechanics, but we'll need about 10^{70} states in our calculations. The mistakes we make in treating squash ball dynamics using deterministic classical mechanics are *extraordinarily* small. Newton gave us the right effective theory for this purpose.

But $\hbar$ tells us where the determinism of the classical theory will fail us, and from the numbers above, the failures will begin with atomic physics, and continue as we probe the nuclear and particle scales. The hydrogen atom has the size (Bohr radius) a_0 of about an angstrom, or ~ 0.053 nm – and its electron is bound by $E_b \sim 13.6$ eV. How these parameters relate to the expressions above we will determine later, but we observe $E_b a_0 \sim 1$. The product is certainly not large on the $\Delta E \Delta x$ scale defined above.

1.1.1 Why did Quantum Mechanics emerge when it did?

It is the usual answer: Because experiment started telling us our prevailing theories were not up to the task of understanding the emerging subatomic world. It is helpful to look back to those early times to recognize what an interesting but confusing time it was.

Photoabsorption lines

In the early 1800s photoabsorption lines in the solar spectrum – a signature of the discrete transitions between atomic levels – were observed, but there was no theory context for their interpretation. By the middle of the century, specific spectral lines were understood to be associated with specific elements, and lines seen in the laboratory were correlated with some seen in the solar spectrum. Late in the century, the work of Balmer and Rydberg revealed the regularity of the hydrogen spectrum, with $1/\lambda$, where λ is the wavelength, related to integer differences in quantities $1/n_i^2$, where n_i is an integer.

Why were the spectral lines unexpected? Classically accelerating charges radiate, but their spectra produced are continuous. Even if someone brilliant in the 19th century had managed to come up with a quasi-modern description of atoms, she would have been hard-pressed to explain why electrons are confined to orbits of definite energy, the origin of the discrete spectral lines.

The Electron's Discovery

The first necessary steps in understanding spectra came with J.J. Thompson's discovery of the electron in 1897, followed by Rutherford's discovery through alpha-particle scattering of a dense nuclear core within atoms. Rutherford correctly concluded that the nuclear mass was a multiple of the hydrogen (proton) mass. In 1911, Rutherford proposed that the atom consisted of a central positive charge surrounded by orbiting negatively charged electrons. As discussed below, the conceptual difficulties presented by the instability of such a system in classical physics led to Bohr's early quantum mechanical theory of the atom. About a decade later – 1926 – a much more complete and self-consistent theory of wave mechanics emerged when Schroedinger introduced his equation, the focus of much of this book.

Radioactivities

Concurrent with these discoveries, radioactivities associated with nuclear decays were studied by Roentgen, Becquerel, and Marie and Pierre Curie. These included x-rays, β rays (energetic electrons produced in the weak process of β decay), and nuclear fission via α (the He nucleus) emission.

The Neutron

A correct theoretical interpretation of either the structure of atoms or the radiation coming from atoms would have been nearly impossible at the turn of the last century, as some particles participating in these reactions had not even been discovered. In 1916 Chadwick studied the continuous spectrum of electrons omitted in β decay. Rather than being pleased that a spectrum (not lines) was observed, he realized a continuous spectra contradicts energy conservation if the radioactive decay released definite energy. To avoid this, Chadwick speculated that some unobserved radiation was also coming out (preserving energy conservation). In 1930, Pauli proposed this radiation was a new, spin-1/2, light elementary particle he called the neutron, which we now call the neutrino. In 1932 Chadwick discovered the "real" neutron, of nearly the same mass as the proton, which quickly resolved enormous confusion over the varying masses, charges, and angular momentum/statistics of nuclei. It is remarkable we have had a basic understanding of the constituents of the atom – the neutron, proton, and electron – for less than a century.

Quantum mechanics is the theory that grew out of our need to understand atoms – their structure, stability, and radiation, as well as other phenomena we will discuss later. Along with special relativity, these two revolutions rocked physics early in the last century.

Further, the need to reconcile special relativity and quantum mechanics was also recognized in the 1920s. Heisenberg, Born, and Jordan took the first step in developing a conceptually autonomous and logically consistent formulation of quantum mechanics via *matrix mechanics*. One year later, Schroedinger introduced his *wave mechanics*, and another year later, Dirac proposed a relativistic equation for the electron, the Dirac equation. In 1933, in an extraordinary step, Fermi combined the new particles into a remarkably modern theory of β decay

$$n \rightarrow p + e^- + \bar{\nu}_e$$

His paper was actually rejected from the Physical Review for being too speculative. His theory involved the spontaneous production of new particles – the electron and neutrino are not constituents of a nucleus, but instead are produced spontaneously from the vacuum. Fermi's guess for the form of the interaction mediating beta decay was based on analogies with the Coulomb interaction of electromagnetism, though Fermi somehow recognized that there should be no electric field – the interaction occurred between all four particles at a point. He later incorporated into his theory aspects of special relativity – charges viewed in a moving frame produce currents. Four years later Gamow and Teller argued that a second interaction contributed to beta decay, involving the spins of the particles, and to account for experiment this second interaction must be of comparable strength to Fermi's interaction. Remarkably, by this point an effective theory equivalent at low energies to the SM with its vector and axial interactions was being formulated – including the capacity to account for phenomena like parity violation that would not be discovered for another 20 years. This quantum mechanics, relativity, and particle production by fields were being cobbled together in these early times. The SM, a field theory, was formulated in the 1960s, treating electromagnetism and the weak interaction as aspects of one theory, with the final step in validating the basic structure of the SM coming with the recent discovery of the Higgs Boson in 2012.

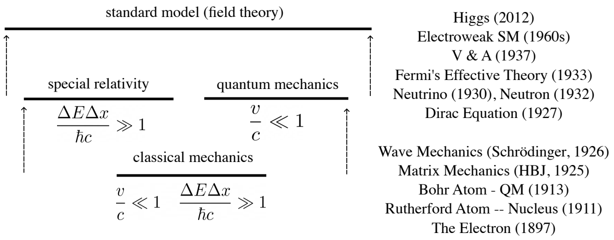


Figure 1.1: Summary of the developments leading up to and beyond wave mechanics and the Schroedinger equation

1.1.2 The Utility of Quantum Mechanics

Quantum Mechanics (QM) emerged from studies of physics at the atomic and nuclear scales, and remains the effective theory of choice for an enormous range of phenomena in materials and condensed matter, atomic physics, and nuclear physics. Such systems are typically nonrelativistic. In an atom, while the interior $1s$ orbital does become increasingly relativistic with increasing nuclear charge (scaling as Z^2), still the Coulomb $1s$ energy is less than a tenth of the electron rest mass, provided $Z < 60$. The quasiparticles of nuclear physics – bound states of quarks and gluons which we call nucleons – typically have $\frac{v^2}{c^2} \sim \frac{1}{100}$ throughout the table of nuclei. (The lack of variation is because, unlike the Coulomb interaction, the strong interaction is actually repulsive at short range, so nucleons keep their distance from one another, whether they are in deuterium or in uranium.) Yet these systems are far, far from the classical deterministic limit: a wave description and all the associated interference effects are essential to the physics. Consequently, QM is the effective theory of choice.

Second, there is a huge "buzz" surrounding QM today, sometimes termed the *second quantum revolution.* The first quantum revolution was acknowledged through a series of Nobel Prizes over the last thirty years recognizing the development of tools for *manipulating atoms* and other quantum matter, including the laser, the maser, quantum electronics, atom traps, optical tweezers, laser cooling, ultra-fast laser pulses, optical frequency combs, and atom interferometers. I recently had the luck of being able to attend a lecture on non-local quantum entanglement given by John Clauser, who won the Nobel Prize in 2022 for his work on entanglement. The first revolution allowed physicists and others to build computers and other devices based on classical concepts like a bit – information stored as a series of 0s or 1s – while achieving new milestones in speed and storage because devices could be packed ever more densely on silicon chips.

The second revolution – quantum information and computation – envisions new devices that employ quantum mechanics directly in the manipulation and processing of information. If one envisions the two possibilities encoded in a bit as a point either at the north or south poles of a unit sphere, what's known as the *Bloch Sphere*, its quantum mechanical analog – a qubit consisting of two interfering states carrying arbitrary phases – covers the entire surface of that sphere, vastly increasing the information that is stored and potentially read out on interrogation. Quantum mechanics is fun because it stretches your mind – the rules of the subatomic world contradict so many of those of our macroscopic one – but also prepares us for future steps, should we encounter the quantum information/computing bug.

Chapter 2

Early QM – Quantization & Wave-Particle Duality

Here we will go through early developments that helped define attributes of the theory that Schrödinger would later capture in his wave equation. These observations were in addition to some already mentioned, such as the regular but discrete patterns of lines in photoabsorption or photoemission processes of atoms.

2.1 The Stefan-Boltzmann Law

2.1.1 Rayleigh-Jeans

A black body consists of a cavity in which electromagnetic standing waves in the cavity interior have reached thermal equilibrium with the cavity walls. The walls are perfect absorbers, absorbing all incident radiation regardless of frequency, and perfect emitters, radiating energy isotropically in a spectrum we discuss below. Physics has some remarkable examples of black bodies, with the cosmic microwave background left over from the Big Bang one of the most spectacular, as the spectral deviation from a perfect black body is on the order of one part in a million (and extremely interesting from the perspective of what they tell us about the structure of the infant universe). One can envision probing the radiation by making a pin-prick in the cavity to monitor the radiation.

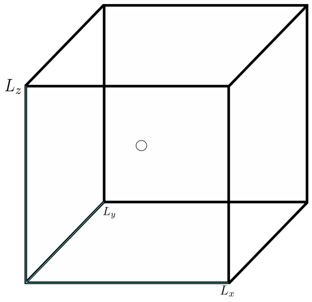


Figure 2.1: A cubic cavity with walls held at temperature T, and with a volume L^3. The walls perfectly absorb all incident energy, then readmit that radiation, maintaining an equilibrium between the contained radiation and the walls characteristic of T

The Stefan-Boltzmann Law was deduced experimentally in the late 19th century: the power P radiated per unit surface area A of a black body (of course, summed over all wavelengths) is

$$P/A = \sigma T^4$$

where $\sigma \sim 5.6703 \times 10^{-8}$ Watts$/m^2K^4$. This law nicely reproduces observations on systems that range from heated filament in the laboratory to the surface of stars. Rayleigh and Jeans attempted to derive this law – and thus obtain an expression for the Stefan-Boltzmann constant σ – from first principles, by explicitly summing over the electromagnetic standing waves in a box. This requires one to calculate the number of standing electromagnetic modes in the box of volume L^3. Electromagnetic waves satisfy Laplace's equation which in Cartesian coordinates is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+k^2\psi=0$$

One writes $k^2=k_x^2+k_y^2+k_z^2$ and separates the equation into a product of solutions in the x, y, z directions, each of which must vanish at the boundaries at 0 and L. The solutions are

$$\psi[n_x,n_y,n_z]=N\sin\left(\frac{\pi n_x}{L}x\right)\sin\left(\frac{\pi n_y}{L}y\right)\sin\left(\frac{\pi n_z}{L}z\right)$$

$$k^2=\frac{\pi^2}{L^2}(n_x^2+n_y^2+n_z^2)$$

where (n_x, n_y, n_z) are positive integers. We want to count how many modes (n_x, n_y, n_z) there are, and we can do that by switching to spherical coordinates and integrating over k, while assuming a large volume. Taking into account that $k_i/(\pi/L)=n_i$, in the large volume limit we have

$$N(k)dk=\frac{1}{8}\times 2\times\frac{4\pi k^2\,dk}{(\pi/L)^3}=\frac{Vk^2\,dk}{\pi^2}$$

where of course, $V=L^3$. The factor of $\frac{1}{8}$ is needed as we only want the fraction of the sphere where all $n_i>0$, and the factor of 2 is needed because each standing wave supports both transverse electric and transverse magnetic projections. One can use a classical Boltzmann distribution to calculate the average energy per cavity mode. One finds

$$\bar{E}=\frac{\int_0^\infty Ee^{-E/k_BT}\,dE}{\int_0^\infty e^{-E/k_BT}\,dE}=k_BT$$

The denominator is to account for normalization. This result applies separately to the light quanta of the same frequency in a black body cavity. We can then fold this with the expression for the number of standing wave modes, derived above, to get the energy density,

$$\frac{E}{V}=k_BT\int\frac{k^2\,dk}{\pi^2}=k_BT\int\frac{8\pi\nu^2\,d\nu}{c^3}=k_BT\int\frac{8\pi\,d\lambda}{\lambda^4}$$

where we have used the relationship between wave number, frequency, and wavelength $k=\frac{2\pi\nu}{c}=\frac{2\pi}{\lambda}$ to write equivalent formulas.

This result neither reproduces observation nor the Stefan-Boltzmann law. The calculation is not self-consistent, as the integrals diverge for large k or large ν, alternatively small λ.

2.1.2 Planck's Revision

In 1900 Planck revised the Boltzmann result for the energy per mode by replacing the classical Boltzmann integral over energy-weighted modes by a discrete sum corresponding to energy quantized as $E=nh\nu$, $n=0,1,2,\cdots$, where h is a new physical constant. This modifies the energy/mode calculation in the following way:

$$\begin{aligned}\bar{E}&=\frac{\sum_{n=0}^\infty nh\nu e^{-nh\nu/k_BT}}{\sum_{n=0}^\infty e^{-nh\nu/k_BT}}\\&=-\frac{1}{\sum_{n=0}^\infty e^{-nh\nu/k_BT}}\frac{d}{d\frac{1}{k_BT}}\sum_{n=0}^\infty e^{-nh\nu/k_BT}\end{aligned}$$

As the sum remaining is geometric, it can be done. A bit of algebra yields

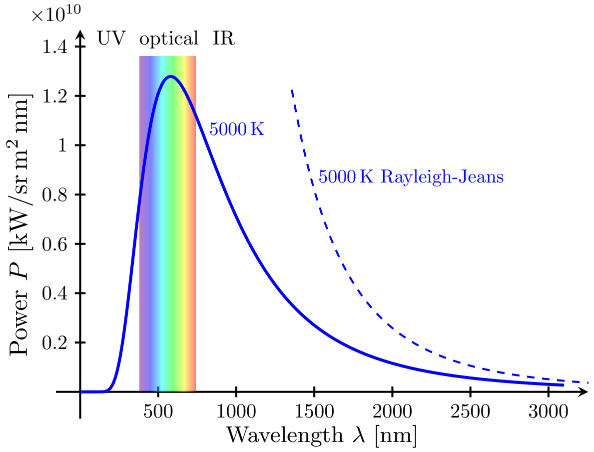
$$\bar{E}=\frac{h\nu}{e^{h\nu/k_BT}-1}$$

and thus Planck obtained (in frequency form)

$$\frac{E}{V}=\int_0^\infty\rho_E(\nu)\,d\nu$$

$$\rho_E(\nu)=\frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_BT}-1}\rightarrow\begin{cases}k_BT\frac{8\pi\nu^2}{c^3} & \frac{h\nu}{k_BT}\ll 1\\ \frac{8\pi h}{c^3}e^{-h\nu/k_BT}\nu^3 & \frac{h\nu}{k_BT}\gg 1\end{cases}$$

The Rayleigh-Jeans (classical) result is obtained for small frequencies, so we recognize $h\to 0$ as the classical limit of Planck's black-body formula. But for high frequencies the energy density as a function of frequency is now well-behaved, diminishing exponentially, very unlike the classical case. Below I plot a comparison between Rayleigh-Jeans and Planck's derivation as a function of wavelength.



Rayleigh-Jeans' prediction diverges as the wavelength of light becomes small which goes against energy conservation. Planck's revision, however, viewing light as discrete packets of energy known as *quanta*, recovers the Stefan-Boltzmann law and is well-behaved.

2.2 The Photoelectric Effect

At about the same period when the issues with black body radiation were confusing physicist, experimentalists were examining the emission of electrons from a metal surface when UV light was focused on the surface.

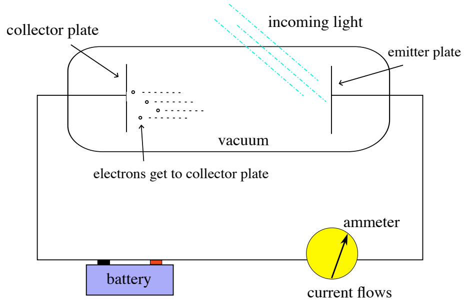


Figure 2.2: Basics of a photoelectric effect experimental setup

Results from such experiments produced the following phenomenology:

1. The number but not the energy of the photoelectrons depends on the light intensity;
2. Photoelectrons appear as soon as the light is turned on (within few nanoseconds), even when the light intensity is low;
3. Photoelectron energy depends on the frequency of light, with a faint blue light (higher frequency) producing more energetic electrons than an intense red light (lower frequency). If the frequency of light is too low, no emission is seen.

These results are unexpected in the classical picture of light as a wave. And at the time these experiments were done, there were many verifications of the wave nature of light. In particular, energy *from a wave* would be absorbed across the metal surface, so that to knock out an electron, one would have to wait until the area immediately around the electron had absorbed enough energy to make that possible. If the frequency of the 'wave' light were increased, with all other parameters kept fixed, the necessary period might shorten, but when the threshold for emission is reached, the electrons emitted would be similar in energy to those produced with lower frequency light.

Einstein in 1909 resolved this problem by proposing a wave-particle duality – that light sometimes acts as a wave, and other times as a photon. Following up on Planck, Einstein argued that the photoelectric effect observations were consistent with a ballistic process in which individual quanta of light of energy $h\nu$

were responsible for knocking out individual electrons from the metal. Energy conservation then yields

$$h\nu = KE_e + h\nu_0 \tag{2.1}$$

Here $h\nu_0$ is the energy required to remove an electron from the metal – the work function, which is a property of the specific metal being used – and consequently no photoelectrons are produced if the frequency of light $v < v_0$ In this picture, provided $\nu > \nu_0$, photoelectrons are expected immediately on illumination, as each photon has the ability to dislodge an electron. If the frequency of the light is increased, the energy of the photoelectron increases linearly. If the frequency is held fixed but the intensity is doubled, the photon flux and the number of photoelectron-producing collisions doubles.

This explanation is simple, yet seemed to contradict years of study of light ways interfering and undergoing diffraction – a wave phenomena. Thus the intellectual leap was the hypothesis of the wave-particle duality of light – that different aspects of light could be manifested in different experimental settings.

2.3 de Broglie & the Bohr atom

By the early 1900s, Rutherford had established that atoms had a dense nuclear core and many experiments had been done observing the absorption and emission of visible and other light from simple atoms, including hydrogen. As the binding energy in hydrogen (neglecting fine structure) is $-13.6\, eV/n^2$, where the principle quantum number takes on integer values $n = 1, 2, 3, \cdots$, the emission lines correspond to energies

$$E_{n_i} - E_{n_f} = 13.6\, eV \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right),\ n_f < n_i$$

The quantum number corresponds to the orbit an electron follows. The emission lines correspond to specific wavelengths of emitted radiation as a result of an electron falling from a higher energy level (higher quantum number n_i) to a lower energy level (lower quantum number n_f). Various "series" had been identified

Balmer 1885 (visible): $\Delta E = 13.6\, eV \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right)$

Lyman 1906 - 14 (UV): $\Delta E = 13.6\, eV \left(\frac{1}{1^2} - \frac{1}{n_i^2} \right)$

Paschen 1908 (IR): $\Delta E = 13.6\, eV \left(\frac{1}{3^2} - \frac{1}{n_i^2} \right)$

While Rutherford had proposed a model of atoms as electrons orbiting and bound to a nucleus, Bohr attempted to relate this idea to the emerging notion of quantization in a 1913 model. He recognized that the phenomenology above could be reproduced by a classical model of electrons in circular orbits about the nucleus, where

$$|\vec{v} \times \vec{p}| = mvr = \frac{nh}{2\pi} = n\hbar$$

where we have introduced the reduced Planck's constant $\hbar$ – which everyone calls "h bar." This is the constant we will be using in quantum mechanics *much* more often. If one accepts Bohr's hypothesis as a constraint and computes the energies, indeed one reproduces the emission results above.

The model also got two important matters right:

1. Atomic systems can exist only in certain stationary or quantized states, each characterized by a definite energy;
2. Transitions between such states can occur via emission or absorption of radiation with energy $\Delta E = h\nu$, in agreement with how both Planck and Einstein treated radiation.

But there as many unanswered questions as answered ones:

1. Why are the stationary states stationary? Since a classical electron in circular motion radiates, the electron should lose energy, spiraling into the nucleus;

2. From our modern perspective of quantum mechanics, a classical orbit with a definite radius violates the uncertainty principle

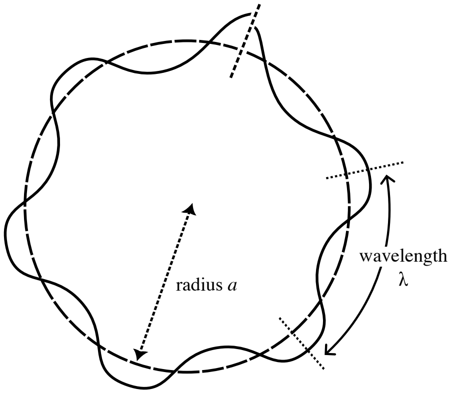


Figure 2.3: de Broglie proposed that atomic orbits correspond to an integer number of de Broglie wavelengths. The figure shows a slight mismatch at the top which means that the radius should be adjusted to remove this discontinuity.

In his 1924 thesis, de Broglie offered a possible explanation of the Bohr atom that anticipated the quantum mechanics revolution about to overtake physics. The details of how his suggestion supported the Bohr atom is not critical – the idea behind it is. Noting that Einstein and Planck had treated electromagnetic waves as particles, de Broglie suggested that perhaps *particles* (the electron in this case) sometimes behave as *waves*. This is quantum mechanics. For a photon,

$$p_\gamma = \frac{h\nu}{c} = \frac{h}{\lambda}$$

so perhaps a massive particle satisfies the same relationship:

$$p_e = m_e v = \frac{h}{\lambda} \quad \Rightarrow \quad \lambda = \frac{h}{m_e v} \tag{2.2}$$

Where λ in this case, is the particle's de Broglie wavelength. Yes, particles have a wavelength.

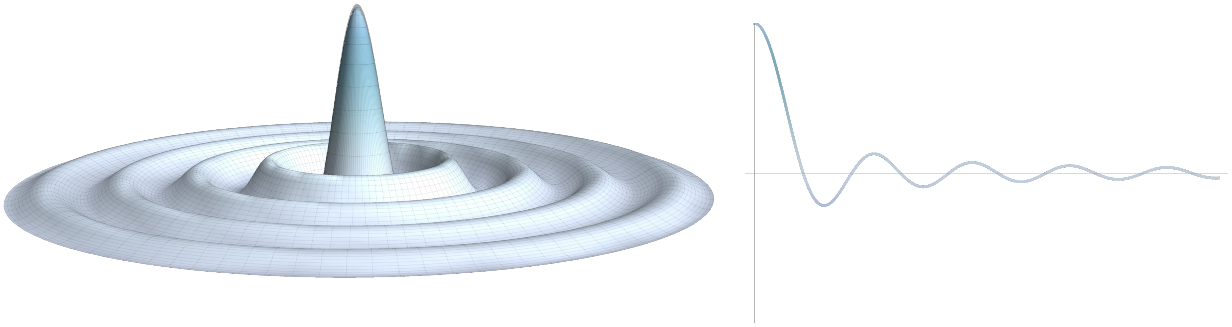
If one calculates the de Broglie wavelength of an electron moving at $v/c \sim 0.01$, one finds $\lambda \sim 2$ angstroms – so about the circumference of an atom.

De Broglie was able to account for the Bohr model by assuming that electronic orbits in hydrogen correspond to an integer number of de Broglie wavelengths.

Chapter 3

Derivation of Schrödinger's Equation, Correspondence, Superposition, & Wave Packets

3.1 The Classical Wave Equation



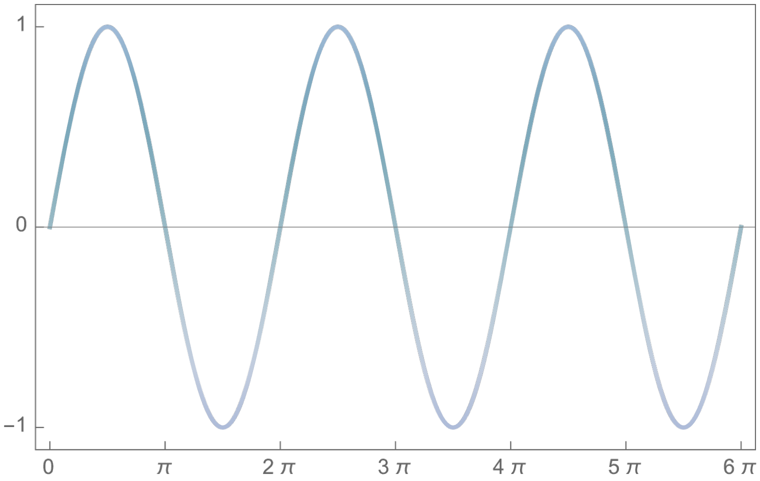
(a) $A_0 \frac{\sin r}{r}$ (b) 1D cut

Figure 3.1: Example of a very intuitive wave phenomena, but mathematically a slightly complicated one. The one-dimensional cut of this wave shows the oscillation is damped.

Since the propagation of the wave is radial and the amplitude decreases as the radius increases, the simplest stationary wave function reads:

$$A(r) = A_0 \frac{\sin r}{r}$$

where $A(r)$ is the displacement of the water at position r and A_0 indicates the amplitude at $r = 0$. A mathematically much simpler wave equation is the sine wave displayed below:



The wave function of the sinusoidal wave above is given by

$$A(x,t) = A_0 \sin(kx - \omega t) \tag{3.1}$$

where $A_0 = 1$ and $k = 1$, $\omega t = 0$. Here k is the wave number and ω is the angular frequency. Note that the two parameters together describe the *phase velocity* of the wave:

$$v = \frac{\omega}{k} \tag{3.2}$$

By taking the second derivative of Equation 3.1 with respect to x and it and using Equation 3.2:

$$\frac{\partial^2 A(x,t)}{\partial x^2} = -k^2 A_0 \sin(kx - \omega t)$$
$$\frac{\partial^2 A(x,t)}{\partial t^2} = -\omega^2 A_0 \sin(kx - \omega t)$$

Therefore,

$$\frac{\partial^2 A(x,t)}{\partial t^2} = \frac{\omega^2}{k^2}\frac{\partial^2 A(x,t)}{\partial x^2} = v^2 \frac{\partial^2 A(x,t)}{\partial x^2} \tag{3.3}$$

Equation 3.3 is the wave differential equation in classical mechanics. All parameters in the equation are real and physical. For the three dimensional problem this equation is given in the form of the Laplacian Operator ∇^2 :

$$\frac{\partial^2 A(\vec{r},t)}{\partial t^2} = v^2 \nabla^2 A(\vec{r},t) \tag{3.4}$$

Note that, since the cosine function can also describe this wave, it is possible to generalize this function via Euler's formula:

$$A(x,t) = A_0 e^{i(kx-\omega t)} \tag{3.5}$$

3.2 Schrödinger's Equation

Now that we are equipped with the classical definition of a wave, we can imbue Equation 3.5 with our knowledge of Energy and de Broglie's wavelength.

We now know the energy of electromagnetic waves is carried out by quanta (packets of energy) known as photons. Each photon carries with it an energy given by Equation 2.1:

$$E = h\nu = \hbar\omega \qquad \hbar = h/2\pi \tag{3.6}$$

We also know each photon is characterized by its de Broglie wavelength given by Equation 2.2

$$\lambda = \frac{h}{p} \tag{3.7}$$

By using Equation 3.7, and the relation between the wave number and wavelength $k = \frac{2\pi}{\lambda}$, we obtain

$$k = 2\pi \frac{p}{h} = \frac{p}{\hbar}$$

And with the help of Equation 3.6, we can recast the original classical wave Equation 3.5 into the form

$$\Psi(x,t) = \Psi_0 e^{i(px-Et)/\hbar} \tag{3.8}$$

where we have replaced the displacement $A(x,t)$ with $\Psi(x,t)$ along with the amplitude to indicate it is a quantum wave function.

Now, since we are talking about a non-relativistic free particle described by a plane wave, the total energy of the particle is just its kinetic energy, $E = p^2/2m$. By using this fact and taking the first derivative of Equation 3.8 with respect to t, as well as the second derivative with respect to x, we obtain

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} \tag{3.9}$$

which is the wave equation for a free particle of mass m. Since the right hand side of Equation 3.9 corresponds to the kinetic energy KE, we may generalize this equation to describe a particle moving under the influence of a potential energy V. In the three dimensional coordinate system we get

$$i\hbar = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r})\Psi(\vec{r},t) \tag{3.10}$$

where we have used the fact that the total energy $E = KE + V$. Equation 3.10 is the Schrödinger Equation in its general form. In one dimension, Schrödinger's Equation takes the form

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

This completes the derivation of the Schrödinger Equation. It is not rigorous by any means, however I feel it provides an intuition behind Schrödinger's Equation that many Quantum Mechanics textbooks/courses skim over.

3.3 The Correspondence Principle

The first chapter stressed that conceptional progress in physics is usually a process where an existing theory is not replaced by, but is instead subsumed into a more general theory that extends the scope and range of validity of the original theory. That is, Quantum Mechanics should not *replace* classical mechanics, but instead should include it within its wider scope.

This concept is incorporated in quantum mechanics via the *correspondence principle.* It states that classical mechanics emerges as a limit of quantum mechanics for large quantum numbers. For example, the bound states of a hydrogen atom have energies of -13.6 eV/n^2. Thus n can be increased without limit, and this process ultimately produces bound orbits with binding energies that approach zero, and with radii that steadily increase, scaling as n^2. Hydrogen (and other atoms) in such highly excited bound states are called *Rydbergatoms* . Their electron orbits approach the classical limit – the electron moves in a Keplerian orbit. This can be shown explicitly.

Another aspect of the correspondence principle is that the classical limit can also be obtained by altering quantum mechanics by taking the limit $\hbar \to 0$. In classical mechanics when one throws a ball from point x at time t_x that is caught by a receiver at point y at time t_y, the ball follows a precise path which we can calculate from Newton's laws. The path minimizes the action – the difference between the kinetic energy and potential energy, integrated along the time coordinate of the classical path,

$$S = \oint_{t_x}^{t_y} [KE - V]\, dt.$$

If you sample any path other than the one given by Newton's Laws, the action along the path will be higher. Note that the action carries the same units as Planck's constant h – energy × time.

There is formulation of quantum mechanics, equivalent to the one we will use in this class, in terms of paths. It provides a very intuitive picture of the relationship of quantum mechanics and classical mechanics. In quantum mechanics you are allowed to propagate from x to y by many paths – but the further a path deviates from the classical path, the less probable it is. One pays a "penalty" for increasing the action via a path other than the classical path – the bigger the increase in the action, the stiffer the penalty. Now to convert action to a number – something that could possibly lead to a probability – one needs a unit. h is that unit. The classical path remains the best path, but there are many many others that, though each may be somewhat less probable than the classical path, will contribute. The larger the deviation of the action from its classical path, the bigger the penalty one pays in units of h, and thus the less probable the path. So the difference between classical mechanics and quantum mechanics is that the former has a single defined path, while in the latter many, many paths are allowed, 'fuzzying' (that's probably not a word!) out the classical path – but not too much because of the heavy penalty one pays for taking a distant path. Classical mechanics is recovered by taking $h \to 0$. All penalties become infinite, so only the classical path is allowed. This is a beautiful way to think about Planck's constant, though is a little 'hand-wavy.'

The penalty one pays actually arises from the *interference* among paths. If we represent the action by S, the weighting of a path is

$$e^{iS/\hbar}$$

so that a large excess in the action causes rapid fluctuations with respect to the classical path and its nearest neighbors, leading to destructive interference among paths. In contrast, paths near the classical path have slowly varying relative phases, and thus tend to cohere. If one drives $\hbar \to 0$ constructive interference among paths only occurs for paths increasingly near the classical one. At $\hbar = 0$ one converges to the classical path. I think this gives one a much deeper feel for the physics of Planck's constant – how it governs the deviations from classical mechanics – and helps one visualize how the classical limit is achieved as $\hbar \to 0$. In summary,

Correspondence Principle

Quantum Mechanics becomes Classical as

$$n \to \infty \quad \text{or as} \quad \hbar \to 0.$$

3.4 The Principle of Superposition & Wave Packets

Any theory that would generalize classical mechanics should be required the reproduce classical mechanics in appropriate limits. The accumulation of phenomena in the early years of the 20th century indicating that light could behave as a particle and that particles could behave as waves, led us to a path where particles with definite positions and momenta gave way to a description in terms of waves and wave packets. Therefore, before we introduce the wave equation, we should remind ourselves of some of the properties achievable through waves.

Familiar wave equations are those for sound in air or waves in water, which in 1D take the form

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

We can look for solutions of this equation in the form of an oscillation wave.

$$\psi(x,t) = \phi(x)e^{i\omega t} \quad \Rightarrow \quad \frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\omega^2}{c^2}\phi(x)$$

and we find

$$\phi(x) = e^{ikx} \quad \text{where} \quad c^2k^2 = \omega^2$$

so that

$$\psi(x,t) = e^{i(kx-\omega t)} \quad \text{with} \quad k(\omega) = \pm\frac{w}{c}$$

This is the solution we found for Equation 3.5. These plane wave solutions are extended, covering the entire range of x. An important property of this equation is that it is linear in ψ. This leads to the principle of superposition:

Principle of Superposition

If $\psi_1(\vec{x},t)$ and $\psi_2(\vec{x},t)$ satisfy the wave equation, so does $\psi_1(\vec{x},t) + \psi_2(\vec{x},t),t)$.

This property allows one to build *wave packets*, as you would get by throwing a stone into the middle of a quiet pond. Such a localized wave can be made from superpositions of the extended plan waves derived above. An example is given below.

It would be very difficult to envision a successful theory of Quantum Mechanics that lacked this property. The correspondence principle requires us to be able to create localized particles, and we know how to build localized wave packets from waves via Fourier Analysis:

$$\psi(x,t=0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \phi(k)e^{ikx}\,dk$$

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

For example, let

$$\psi(x,t=0) = e^{-x^2/a^2}$$

Then,

$$\psi(x,t=0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-a^2k^2/4}e^{ikx}\,dk$$

We can easily build a Gaussian wave packet out of plane waves, but the equivalent infinite sum of plane waves would not be a solution of our quantum mechanical wave equation unless the superposition principle holds.

3.4.1 Wave Packets & Uncertainty Relationships

The simple Gaussian example shown above illustrates another important property of wave packets. There is a size scale associated with our coordinate-space wave packet, with $\Delta x \sim a$. But we see the smaller a – the more localized in x – the broader the range of contributing momentum-space (k) waves. That is,

$$e^{-a^2k^2/4} = e^{-k^2/(2/a)^2} \quad \Rightarrow \quad \Delta k = \frac{2}{a}$$

Consequently $\Delta x \Delta k \sim 1$. A property of wave packets is the more they are *localized* in coordinate (x) space, the more they *delocalize* in momentum space. Thus as a wave theory, we would expect quantum mechanics to have an *uncertainty principle* that prevents us from simultaneously having particle locations and momenta. As the de Broglie relation (Equation 2.2) gives us $p = \frac{h}{\lambda} = \frac{h}{2\pi}k$ so that $\Delta k = \Delta p/\hbar$, it is not surprising that Quantum Mechanics has an uncertainty principle relating the product of coordinate and momentum uncertainties to $\hbar$. Its precise form is

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

We will do a more precise and rigorous derivation of *Heisenberg's Uncertainty Principle* utilizing the Cauchy-Schwarz Inequality in the near future.

3.5 Back to Schrödinger

In 1D, Schrödinger's Equation takes the form

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

with the external potential $V(x)$ unspecified. As we saw, this equation is a fairly gentle variation of the sound/water wave equation we discussed, with a couple interesting differences.

So what does this equation mean? Staring at the LHS, the potential is clear, while the derivative term can be rewritten in a way that clarifies units

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2c^2}{2mc^2}\frac{\partial^2}{\partial x^2}$$

As $(\hbar c)^2$ has units of (Energy-Distance)^2, mc^2 is an energy, and $\frac{\partial^2}{\partial x^2}$ has units of (distance)$^{-2}$, the first term on the LHS is an energy, and by the "what else can it be" argument, must be the kinetic energy. Classically this is $p^2/2m$. But $p^2/2m + V = E$, so on the RHS, the differential operator must be generating E. The requirement that Schrödinger's Equation with its differential operator corresponds with energy conservation allows us to identify the equations differential operators with a classical view.

We define the momentum operator $\hat{p}$

$$\hat{p} \equiv \frac{\hbar}{i}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x} \tag{3.12}$$

And the energy operator $\hat{E}$

$$\hat{E} \equiv i\hbar\frac{\partial}{\partial t} \tag{3.13}$$

Therefore, we can rewrite Schrödinger's Equation using these operators as follows:

$$\begin{gathered}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)\\ \left[\frac{\hat{p}^2}{2m} + V(x)\right]\Psi(x,t) = \hat{E}\Psi(x,t)\end{gathered}$$

We indicate that $\hat{p}$ and $\hat{E}$ are Quantum Mechanical operators by giving them "hats." They are differential operators that act on the wave function.

One of the most important differences between the QM wave equation and the wave equation for sound/water, is that the latter is quadratic in its space and time differential operators, while the Schrödinger Equation is quadratic in space but *linear in time*. The time-linearity of the Schrödinger Equation is a reflection of the non-relativistic relationship between a particles momentum and its energy – a consequence of building theory beyond classical mechanics that extends to our reach and beyond the atomic scale, but shares with the nonrelativistic restrictions associated with classical mechanics. The linear-in-time nature of the Schrödinger Equation naturally leads to complex wave functions. As measurements involve *real* quantities, the connection between wave functions and observables requires discussion – the topic of next chapter.

I will quickly also note that our plane-wave solution of the Schrödinger Equation has a characteristic wavelength. The length of a wave corresponds to the distance required to change the phase by 2π, at a fixed time t. That is,

$$2\pi = \frac{p\Delta x}{\hbar} \equiv \frac{p\lambda}{\hbar}$$

Thus,

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

That is precisely de Broglie's wavelength!

Chapter 4

Properties of the Wave Function

4.1 Interpretation of Ψ

Given that we can solve Schrödinger's equation to generate a wave function $\Psi(x,t)$, the most natural first question to ask is "What is Ψ?". As the wave function for a particle is generally complex, Ψ cannot be associated with measurements. Instead, in the case of a wave function spread over a range of possible coordinates x, we identify the product of $\Psi(x,t)$ with its complex conjugate, $\Psi^*(x,t)$, as the *position probability density.*

$$P(x,t) = \text{ position probability density } = \Psi^*(x,t)\Psi(x,t) = |\Psi(x,t)|^2$$

Therefore,

$$dP(x,t) \equiv |\Psi(x,t)|^2 \, dx$$

is the probability of finding the particle in a region dx around x if the measurement is made at time t.

Generally this is the provided definition for what $\Psi(x,t)$ is – the function that when multiplied by its complex conjugate produces the position probability density of the particle it represents. Later however, when we encounter Dirac notation, we will learn of a much more intuitive and rigorous definition for Ψ. But for now, position probability density works.

Now since $|\Psi(x,t)|^2$ is a probability density, it follows that the integral of $|\Psi(x,t)|^2$ over all x must be 1 – the particle has to exist somewhere! Therefore, we require the *normalization condition* of the wave function:

$$\int_\Omega |\Psi(x,t)|^2 \, dx = 1 \tag{4.1}$$

where the integral extends over the domain Ω, where the wave function is defined. If we are discussing a free particle, it may be all of space, $-\infty < x < \infty$. Or perhaps if we consider a particle confined within a potential well with infinitely high walls where the width of the well is a – a problem we consider *very* soon, then the relevant boundaries of the integral may be $-a/2 < x < a/2$. Regardless of the situation, the particle has to exist somewhere, so we must require the normalization condition for all particles.

Of course, wave functions $\Psi(x,t)$ we obtain from solving Schrodinger's Equation have in general some arbitrary normalization. In that case we quantum mechanics have to fix that situation. If when we compute

$$\int_D |\Psi(x,t)|^2 \, dx = N$$

Then we form the normalized wave function $\Psi_N(x,t)$

$$\Psi_N(x,t) \equiv \frac{1}{\sqrt{N}} \Psi(x,t) \tag{4.2}$$

The wave function we use is the normalized one, $\Psi_N(x,t)$. But wait! suppose I normalize some way function at time $t = 0$. How do I know it *stays* normalized as time passes and $\Psi(x,t)$ evolves? Luckily, Schrödinger's Equation has the remarkable property that it *preserves* the normalization of the wave function. If this wasn't true, building a working theory of Quantum Mechanics would be a nightmare (at least, more of a nightmare). Because of how important this normalization-preservation fact is, I provide a proof, which utilizes the Schrödinger equation. We start by expanding the following time derivative:

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\Psi(x,t)|^2 \, dx. \tag{4.3}$$

By the product rule,

$$\frac{\partial}{\partial t} |\Psi(x,t)|^2 = \frac{\partial}{\partial t} [\Psi^*(x,t)\Psi(t)] = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi. \tag{4.4}$$

Now the Schrödinger equation states

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi, \tag{4.5}$$

and hence also (taking the complex conjugate of Equation 4.5,

$$\frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^*. \tag{4.6}$$

Therefore, substituting in Equation 4.5 and Equation 4.6 into Equation 4.4,

$$\frac{\partial}{\partial t} |\Psi|^2 = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) = \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]. \tag{4.7}$$

The integral in Equation 4.3 can now be evaluated explicitly:

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

And since $\Psi(x,t) \to 0$ as $x \to \pm\infty$ – otherwise the wave function would not be normalizable – it follows that

$$\frac{d}{dt}\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = 0. \tag{4.8}$$

Therefore, the integral is independent of time – if Ψ is normalized at $t = 0$, it *stays* normalized for all future time.

4.2 Expected Value & Variance

As $|\Psi(x,t)|^2$ represents a probability distribution, we can determine properties of this distribution by evaluating various moments of the outcome variable. The simplest would be the zeroth moment, defined here as the unweighted moment, which just checks that

$$\langle 1 \rangle \equiv \int_\Omega 1|\Psi(x,t)|^2 \, dx = 1$$

The next is the first moment – called the expected value (basically the mean) –

$$\langle x \rangle \equiv \int_\Omega x|\Psi(x,t)|^2 \, dx \tag{4.9}$$

If one measured the position x of a particle with an identical wave function $\Psi(x,t)$, and recorded its value an infinite amount of times. The average of the recorded measurements is the mean, or expected value. Therefore, $\langle x \rangle$ is the most-likely x to come as an outcome of measuring $\Psi(x,t)$. This intuitively makes sense if you think of Equation 4.9 as an infinite discrete sum $\langle x \rangle = \sum_N x_N |\Psi(x,t)|^2$. We multiply each possible outcome x_N by the likelihood of this outcome $|\Psi(x,t)|^2$, and afterward sum up all our values, producing a 'weighted average,' or the mean/expected value.

The second moment of most interest is the variance. The second moment about the mean

$$\langle x - \langle x \rangle \rangle^2 \equiv \int_\Omega (x - \langle x \rangle)^2 |\Psi(x,t)|^2 \, dx$$

And since $\langle x \rangle$ is just a number,

$$\langle x - \langle x \rangle \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 \geq 0$$

So knowledge of the first and second moments

$$\langle x \rangle = \int_\Omega x|\Psi(x,t)|^2 \, dx \qquad \langle x^2 \rangle \int_\Omega x^2|\Psi(x,t)|^2 \, dx$$

allows one to calculate the variance. The standard deviation

$$\sigma \equiv \sqrt{\langle x - \langle x \rangle \rangle^2}$$

For distributions approximately Gaussian, the probability that an outcome will be within 1σ of the mean is about 2/3rds.

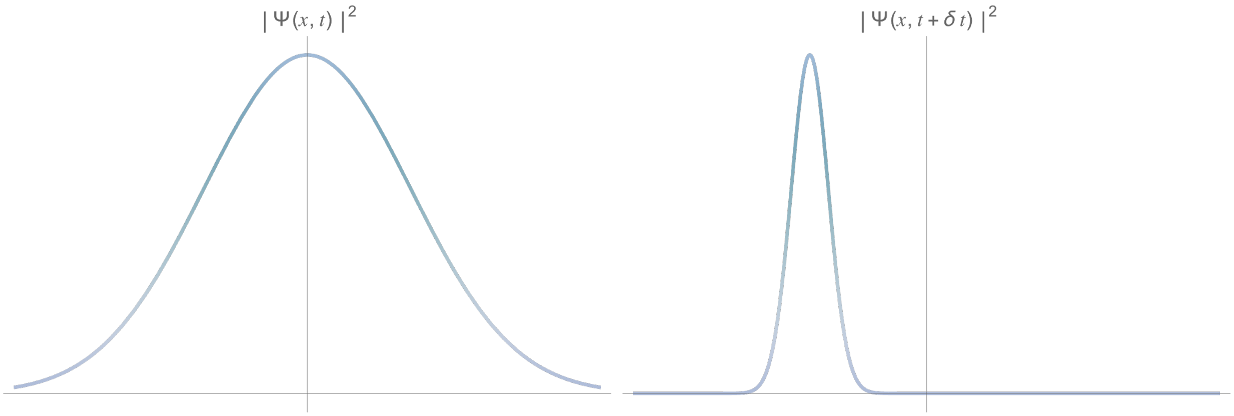
4.3 Measurement & Collapse of Ψ

A pitcher threw a fastball, and the hitter land off. The ball was caught by the catcher. But the umpire said nothing. Finally the batter said, “Well what was it, a ball or a strike?” The umpire replied “It ain’t nothing til I call it.” This is a pretty good description of the relationship of wave functions to measurement.

The position of an electron may be described by a probability $|\Psi(x,t)|^2$ that is nonzero over some range in x, but when a measurement is done, the electron’s location will be found to be some definite outcome x_1. If a million measurement experiments were prepared, all with the same identical initial conditions, each would likely yield a definite value on making a measurement producing $\{x_1, x_2, \cdots, x_{1000000}\}$. The individual experiments likely yield different results, but Quantum Mechanics tells us that if we look at the *distribution* of measurements, it will match $|\Psi(x,t)|^2$. This is known as the Copenhagen interpretation of Quantum Mechanics – $|\Psi(x,t)|^2$ predicts the probabilities of all possible outcomes x_i, but does not tell us the specific value x_i that emerges from a specific measurement.

This implies something interesting about measurement – it impacts the wave function. If one makes a measurement producing the result x_1 at some time t, then repeats the measurement immediately afterwards, at some time $t + \delta t$, then the same outcome $x_2 \sim x_1$ (within some small δx) will be obtained. The first measurement impacted the wave function, *collapsing* it, greatly narrowing the possibilities.

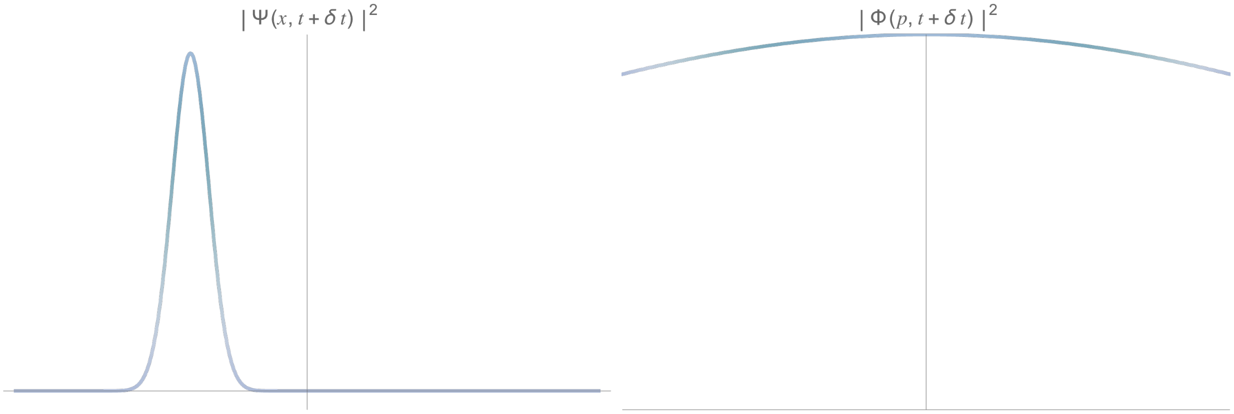
This intuitively makes sense. If we measure a particles position and get some value x_i, and if we immediately perform another measurement within some δt, the particle could not have moved *that much* from its initial position x_i in such a small δt. This means the position probability density becomes more narrow and localized around $x \sim x_i$. How narrow the $|\Psi(x, t + \delta t)|^2$ becomes after measurement depends on how precisely the measurement was done. We have also already mentioned the uncertainty principle, the notion that the better one defines x, the broader the spread in p. So this new, more localized, wave packet, very narrow in x, will contain, as a result of the measurement, many high-momentum components – a really wide spread of the ‘momentum probability density’.



(a) Initial $|\Psi(x,t)|^2$

(b) $|\Psi(x,t+\delta t)|^2$ after measuring $x \sim -x_i$

Figure 4.1: Performing a measurement collapses the wave function. Here, we consider that a measurement produces a value $x \sim -x_i$ for the particle. As a result the final position probability density is very narrow around $x = -x_i$.



(a) $|\Psi(x,t+\delta t)|^2$

(b) $|\Phi(p,t+\delta t)|^2$

Figure 4.2: A narrow $|\Psi(x,t)|^2$ (a) implies a very spread $|\Phi(p,t)|^2$ (b). Since coordinate-space wave packets and momentum-space packets are inverse Fourier transforms of one another, $\Psi(x,t)$ and $\Phi(p,t)$ are inverse F.T's of one another. Note from this moment on Ψ refers to coordinate-space and Φ refers to momentum-space.

Therefore, since a narrower coordinate-space wave packet contains many high-momentum and therefore high-velocity momentum-space wave packets, the particle moves *very* fast after an initial measurement. This means that the *narrower* $|\Psi(x,t)|^2$, after measurement, the *faster* $|\Psi(x,t)|^2$ *will spread.*

The more precise the measurement of x_1, the larger the spread in momentum-space components – and the faster $|\Psi(x,t)|^2$ will spread. Thus if you do not make the second measurement immediately, but wait some significant time, you likely will not get an x_2 very near x_1.

This is not classical mechanics, but a new theory guided by intuitive rules, and they are easy for us to embrace. The ideas are quite beautiful. We have not yet actually solved any Quantum Mechanics problems up to this point, but that is fine. If you are beginning to ***intuitively understand*** how the subatomic world works, that intuition will guide you as you begin to solve problems. Quantum Mechanics makes sense!

4.4 Expectation values of Operators

In our discussion of probability distributions and moments – means and standard deviations – we emphasized their importance in characterizing distribution functions, but the discussion directly above about measurement now takes us beyond the math, into the physics. If the outcome of our experiment is a particle's position, and if we repeat the experiment with identical initial conditions a thousand times, then we have already shown how the mean of those position outcomes relate to the wave function

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

In fact, we can rewrite this statement in a slightly different way that corresponds better to the concept of measurement,

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

It may seem like semantics at this point, but think of $\hat{x}$ as an operator that *interrogates* the wave function (the process of taking a measurement), and x as the *outcome* of the interrogation (the experimental result).

The momentum operator provides another example of the distinction drawn above – interrogation vs. outcome. We deduced the momentum operator from our discussion of the Schrödinger equation in Equation 3.12. Therefore,

$$\langle \hat{p}\rangle \equiv \int_{-\infty}^{\infty} \Psi^*(x,t)\,\hat{p}\,\Psi(x,t)\,dx = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t)\,dx \tag{4.10}$$

Here we can write out the needed interrogation operator for our coordinate-space wave function, but we can't actually evaluate the outcome if we do not have an explicit form for our wave function. But if someone tells you that $\Psi(x,t)$ is a normalized plane wave confined to a 1D "volume" of length L, then you can carry out the interrogation to obtain the outcome

$$\Psi(x,t) = \frac{1}{\sqrt{L}}e^{i(p_0x-E_0t)/\hbar} \text{ where } E_0 = E_0(p) = p_0^2/2m \quad \Rightarrow$$

$$\int_{-L/2}^{L/2} \psi^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t)\,dx = \int_{-L/2}^{L/2} \Psi^*(x,t)\,p_0\,\Psi(x,t)\,dx = p_0\int_{-L/2}^{L/2} |\Psi(x,t)|^2\,dx = p_0$$

I should stress that p_0 is just a number in the work above – a parameter defining the wave function.

4.4.1 Time Evolution of Operator Expectation Values

Consider an operator $\hat{x}$ or $\hat{p}$ that itself does not depend on time, but where the wave function it acts on *is* evolving in time. This would be the case, for example, of a wave packet moving with some velocity. Operator expectation values would then evolve in time because of the wave function changing. Following the same steps we employed to demonstrate that normalizations do not evolve in time, we get

$$
\begin{aligned}
\frac{d\langle\hat{x}\rangle}{dt} &= \frac{i\hbar}{2m}\int_{-\infty}^{\infty} x\frac{\partial}{\partial x}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t)\right]dx \\
&= -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t)\right]dx \\
&= -\frac{i\hbar}{m}\int_{-\infty}^{\infty}\Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t)\,dx = \frac{1}{m}\int_{-\infty}^{\infty}\Psi^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t)\,dx
\end{aligned}
$$

where we integrated by parts to get the second step, assuming that the wave packet vanishes at the boundaries; and then integrated by parts again in the third line. Thus we find

$$
\frac{d\langle\hat{x}\rangle}{di} = \frac{\langle\hat{p}\rangle}{m} \equiv \langle\hat{v}\rangle
$$

One can repeat the steps above starting with $\frac{d\langle\hat{p}\rangle}{dt}$ to find

$$
\frac{d\langle\hat{p}\rangle}{dt} = \langle-\frac{\partial V}{\partial x}\rangle
$$

which we recognize as Newton's second law. These two results constitute

Ehrenfest's Theorem

An example of the correspondence principle – expectation values obey the corresponding classical laws of motion.

4.4.2 The Uncertainty Principle

If you have taken linear algebra, you may have seen the Cauchy-Schwarz Inequality. If $\vec{u}$ and $\vec{v}$ are two vectors in some vector space, then

$$
\vec{u}\cdot\vec{u}\vec{v}\cdot\vec{v} \geq |\vec{u}\cdot\vec{v}|^2
$$

For functions there is an analogous Cauchy-Schwarz Identity

$$
\int |f(x)|^2\,dx \int |g(x)|^2\,dx \geq \left|\int f^*(x)g(x)\,dx\right|^2
$$

We make the following definitions:

$$(\sigma_x)^2 \equiv \langle(\hat{x}-\langle\hat{x}\rangle)^2\rangle = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2 \qquad (\sigma_p)^2 \equiv \langle(\hat{p}-\langle\hat{p}\rangle)^2\rangle = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2$$

and the following substitutions into the Cauchy-Schwarz Identity

$$f(x) \to (\hat{x}-\langle\hat{x}\rangle)\Psi(x,t) \quad \text{and} \quad g(x) \to (\hat{p}-\langle\hat{p}\rangle)\Psi(x,t)$$

The LHS is seen to be

$$(\sigma_x)^2(\sigma_y)^2$$

while the RHS can be manipulated into the form

$$\begin{aligned}
&\frac{1}{4}\left|\int \psi^*(x,t)[(\hat{x}-\langle\hat{x}\rangle)(\hat{p}-\langle\hat{p}\rangle) - (\hat{p}-\langle\hat{p}\rangle)(\hat{x}-\langle\hat{x}\rangle)]\Psi(x,t)\,dx\right|^2 \\
+&\frac{1}{4}\left|\int \psi^*(x,t)[(\hat{x}-\langle\hat{x}\rangle)(\hat{p}-\langle\hat{p}\rangle) + (\hat{p}-\langle\hat{p}\rangle)(\hat{x}-\langle\hat{x}\rangle)]\Psi(x,t)\,dx\right|^2 \\
\geq&\frac{1}{4}\left|\int \psi^*(x,t)[(\hat{x}-\langle\hat{x}\rangle)(\hat{p}-\langle\hat{p}\rangle) - (\hat{p}-\langle\hat{p}\rangle)(\hat{x}-\langle\hat{x}\rangle)]\Psi(x,t)\,dx\right|^2
\end{aligned}$$

as we have the sum of two positive definite terms. Now by direct evaluation you can show

$$[(\hat{x}-\langle\hat{x}\rangle)(\hat{p}-\langle\hat{p}\rangle) - (\hat{p}-\langle\hat{p}\rangle)(\hat{x}-\langle\hat{x}\rangle)] = i\hbar$$

Thus we obtain

$$(\sigma_x)^2(\sigma_p)^2 \geq \frac{\hbar^2}{4}$$

So we retrieve the uncertainty principle

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

This uncertainty relation also has an analog in *energy* and *time*. We consider the kinetic energy for an arbitrary wave packet

$$\Delta E = \Delta\frac{p^2}{2m} = \frac{p}{m}\Delta p$$

Hence, an uncertainty in momentum implies an uncertainty in energy. Now consider a measurement of the time it takes for the wave packet to pass a monitor that we setup to measure its passage. However, since the width of the packet is uncertain by Δx, there must be a corresponding uncertainty in the time measurement,

$$\Delta t = \frac{\Delta x}{v} = \frac{m}{p}\Delta x \geq \frac{m}{p}\frac{h}{2\Delta p} = \frac{h}{2}\frac{1}{\Delta E}$$

Therefore, rearranging yields

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Chapter 5

Stationary States & the "Prime Directive"

We are one step away from finally beginning to *solve* quantum mechanical problems using the Schrödinger Equation. The final step – understanding *stationary states*.

5.1 Stationary States

We begin with the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \Psi(x,t) \tag{5.1}$$

The V here could, in principle, be a function of both x and t. For example, an electron in a cycling uniform magnetic field whose strength is being adjusted by an experimentalist. Here we assume this is not the case: V is assumed to be time-independent, so $V = V(x)$. We then look for a solution of the form

$$\Psi(x,t) = \psi(x) e^{-iEt/\hbar} \tag{5.2}$$

The $e^{-iEt/\hbar}$ factor results from solving Equation 5.1 via separation of variables. More specifically, the method of searching for a solution in the form $\Psi(x,t) = X(x)T(t)$ and separating Equation 5.1 into two different ordinary differential equations in x and t. The resultant t solution is $e^{-iEt/\hbar}$, and is **always** the same for any time-dependent wave-function solution. Hence in practice, Equation 5.2 is used, where $\psi(x) = X(x)$ – the solution of the time-*independent* Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) \equiv \hat{H}(x)\psi(x) = E\psi(x) \tag{5.3}$$

Note that Equation 5.3, the time-independent Schrödinger equation is an *eigenvalue equation*, with ordinary derivatives as $\psi(x)$ just depends on x. That is, we have reduced the problem to just solving an ordinary differential equation in x. In general when we solve this equation, including boundary conditions having to do with how a particle may be confined, there will exist solutions only for specific energy eigenvalues E_i. That is, our solutions are $\{\psi_i(x)\}$, with energy eigenvalues $\{E_i\}$. These solutions are called *stationary states.*

The name comes from the fact that

$$|\Psi_i(x,t)|^2 = |\psi_i(x)|^2$$

as the energy-phase $e^{-iEt/\hbar}$ cancels out. Thus for such states the probability of finding the particle in a region δx is stationary – it does not evolve in time. These states are also states of definite energy – (the energy-time uncertainty principle!), given by the energy eigenvalue E_i corresponding to its state $\psi_i(x)$. A system in a stationary state *stays in that state*, forever. Only such states can have a precise energy.

I will now show that these stationary states actually form a complete *orthonormal basis* for the time-independent Schrödinger equation. In other words, the final time-independent wave function $\Psi(x,t)$, can actually be defined as a linear combination of stationary states $\psi_i(x)$ with their corresponding energy-phase factor $e^{-iE_it/\hbar}$ tacked on.

5.1.1 Stationary States as an Orthonormal Basis

In the very near future we will do several calculations where we find all the states of the time-dependent Schrödinger equation – the first being the *infinite square well.* Most examples will be problems where a particle occupies some region of space and where the "outcome" of a measurement could be a specific particle location x_i. As there are an infinite number of outcomes, it should not be surprising that the number of stationary states is also infinite. These (properly normalized) states $\{\psi_i\}$ with energies $\{E_i\}$ are solutions of the time-independent Schrödinger equation for a given potential $V(s)$. I show below that they form an orthonormal basis. We first show that any two stationary-state wave functions belonging to different energies are orthogonal – which requires us to define "orthogonality" for wave functions.

We have the two stationary state wave function solutions ψ_1 and ψ_2 that solve

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_1(x) \equiv \hat{H}(x)\psi_1(x) = E_1\psi_1(x) \tag{5.4}$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_2(x) \equiv \hat{H}(x)\psi_2(x) = E_2\psi_2(x) \tag{5.5}$$

Multiplying the first equation 5.4 on both sides by $\psi_2^*(x)$ and the second equation 5.5 by $\psi_1^*(x)$,

$$\psi_2^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_1(x) = E_1\psi_2^*(x)\psi_1(x) \tag{5.6}$$

$$\psi_1^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_2(x) = E_2\psi_1^*(x)\psi_2(x) \tag{5.7}$$

Taking the conjugate of the second equation 5.7,

$$\psi_1(x)\left[-\frac{\hbar^2}{2m}+V(x)\right]\psi_2^*(x) = E_2\psi_1(x)\psi_2^*(x) \tag{5.8}$$

Subtracting Equation 5.6 and Equation 5.8 and integrating over all x,

$$\int_{-\infty}^{\infty}\left[\psi_2^*\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_1(x)-\psi_1(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_2^*(x)\right]dx = (E_1-E_2)\int_{-\infty}^{\infty}\psi_1(x)\psi_2^*(x)\,dx$$

Notice that the second term on the right can be partially integrated twice to get

$$\psi_1(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_2^*(x)\,dx = \psi_2^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_1(x)\,dx$$

which is identical to the first term. So we find

$$0 = (E_1-E_2)\int_{-\infty}^{\infty}\psi_1(x)\psi_2^*(x)\,dx \Rightarrow \int_{-\infty}^{\infty}\psi_1(x)\psi_2^*(x)\,dx = 0 \quad \text{if } E_1 \neq E_2 \tag{5.9}$$

The vanishing integral above is what is meant by the orthogonality of two functions. But there was an exception noted above – our conclusion of orthogonality depended on the absence of degeneracy, that $E_1 \neq E_2$. What if this is not the case? We know the solution from our experience with ordinary vectors: Gram-Schmidt. If we have two normalized vectors $\vec{u}$ and $\vec{v}$ that are linearly independent but not orthogonal, we can form a new orthonormal basis by defining

$$\vec{u_1} \equiv \vec{u} \quad \vec{u_2} = \vec{v} - \vec{u}\cdot\vec{v}\,\vec{u} \quad \text{ so that } \vec{u_1}\cdot\vec{u_2} = \vec{u}\cdot\vec{v} - \vec{u}\cdot\vec{v} = 0$$

then normalizing $\vec{u_2}$. We can do the same if we have two normalized functions $\psi_1(x)$ and $\psi_2(x)$ that are not orthogonal, with the same energy eigenvalue E.

$$\psi_1(x) \rightarrow \psi_1(x) \quad \psi_2(x) \rightarrow \psi_2(x) - \psi_1(x)\int_{-\infty}^{\infty}\psi_1^*(x)\psi_2(x)\,dx \equiv \psi_2'(x)$$

Then

$$\int_{-\infty}^{\infty} \psi_1^*(x)\psi_2'(x)\,dx = \int_{-\infty}^{\infty} \psi_1^*(x)\psi_2(x) - \int_{-\infty}^{\infty} \psi_1^*(x)\psi_1(x) \int_{-\infty}^{\infty} \psi_1^*(x)\psi_2(x)\,dx = 0$$

So if we normalize $\psi_2'(x)$ we then have two orthogonal basis functions $\psi_1(x), \psi_2'(x)$, and by the principle of superposition, $\psi_2'(x)$ is also a solution of the time-independent Schrödinger equation with energy eigenvalue E.

In practice the tedious Gram-Schmidt process is almost never needed: degeneracies usually arise for a reason known to the quantum mechanic, and she chooses wave function labels that reflect the physics. As we will discuss later, this amounts to finding operators other than $\hat{H}$ that commute with $\hat{H}$. If we find such an operator, we can label our eigenstates by the quantum numbers of both $\hat{H}$ (energy) and this other operator. These other labels distinguish the degenerate state, and guarantee their orthogonality.

This past derivation was heavy in content; before moving on, you should be fully clear on how orthogonality is defined and how stationary states of different energies are orthogonal.

5.1.2 Stationary States Form a Complete Basis

The basis just formed above, $\{E_i, \psi_i(x), I = 1, \cdots, \infty\}$ is a *complete orthonormal basis* for the time-independent Schrödinger equation. I'll not provide a general proof, but we will encounter bases that soon you will recognize as complete, such as the Fourier series.

Normalized stationary-state solutions form an orthonormal basis:

$$\boxed{\int_{-\infty}^{\infty} \psi_i^*(x)\psi_i(x) = 1 \qquad \int_{-\infty}^{\infty} \psi_j^*(x)\psi_i(x)\,dx = 0,\ i \neq j}$$

Consequently any general function in the space can be expanded in terms of the basis of stationary states, with coefficients that follow from the orthogonality condition.

Expansion of time-independent arbitrary wave function $\Psi(x)$ in terms of stationary states

$$\Psi(x) = \sum_{i=1}^{\infty} c_i\psi_i(x) \qquad c_i = \int_{-\infty}^{\infty} \psi_i^*(x)\Psi(x)\,dx \tag{5.10}$$

5.2 The "Prime Directive"

If you were going to choose to understand any one portion of this book – choose this one. We finally come to a result so important that we can dub it, in homage to Star Trek, the *prime directive*.

Suppose some experimentalist has started up some experiment at time t_0 that is governed by quantum mechanics – perhaps some interesting wave packet $\Psi(x, t_0)$ that is arbitrary, not corresponding to any one of the stationary states. This wave packet might describe the possible position outcomes for a particle, should we interrogate it at time t_0. The wave function would be normalized – $\int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 \, dx = 1$.

Because the stationary states form a complete set, we know

$$\Psi(x, t_0) = \sum_i c_i \psi_i(x) \tag{5.11}$$

But the wave packet is normalized and the stationary states are an orthonormal set. So

$$1 = \int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 \, dx = \sum_{j=1}^{\infty} \sum_{i=1}^{\infty} c_j^* c_i \int_{-\infty}^{\infty} \psi_j^*(x) \psi_i(x) \, dx = \sum_{j=1}^{\infty} \sum_{i=1}^{\infty} c_j^* c_i \delta_{ji} = \sum_{i=1}^{\infty} |c_i|^2$$

Do not get confused by all the math above, I just substitute in Equation 5.11 to ultimately show that $|c_i|^2$ is the initial probability of being in the ith stationary state. To simplify notation let's set our clock to start at $t_0 = 0$. Then consider the wave function

$$\Psi(x, t) = \sum_i c_i \psi_i(x) e^{-iE_i t/\hbar}, t > 0$$

Plugging this into the time-dependent Schrödinger equation (superposition principle) yields

$$\sum_i E_i c_i \psi_i(x) e^{-iE_i t/\hbar} = \sum_i E_i c_i \psi_i(x) e^{-iE_i t \hbar}$$

So we have a solution! Consequently we have what you might call the *prime directive* of quantum mechanics:

The Prime Directive

The prime directive: Let $\{\psi_i(x)\}$ and $\{E_i\}$ denote the complete set of stationary-state solutions and eigenvalues, that is

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi_i(x) = E_i \psi_i(x)$$

Given a wave packet at $t = 0, \Psi(x, t = 0) = \sum_i c_i \psi_i(x)$, then the solution of the full time-dependent Schrödinger equation is

$$\Psi(x, t) = \sum_i c_i \psi_i(x) e^{-iE_i t/\hbar} \tag{5.12}$$

This is such a powerful result. It implies that apart from the special case of a pure stationary state, the stationary components of wave functions propagate with different phases, interfering in a time-dependent way. Thus the probability at some point x, $|\Psi(x, t)|^2$, is not fixed – not stationary – but instead varies in time. But it also states the probabilities $|c_i|^2$ do not evolve in time – all of the weird quantum physics comes from time-varying interference.

Hence, according to our *prime directive*, to solve for the time dependent wave function of any particle or wave packet, we should

1. Find the stationary state and their eigenvalues via the time-independent Schrödinger Equation 5.3
2. Solve for the c_i's using an initial starting wave packet via Equation 5.10
3. Solve for the full time-dependent $\Psi(x, t)$ by summing over Equation 5.12

So now we roll up our sleeves and start doing quantum mechanics.

Chapter 6

Solving the Time-Independent Schrödinger Equation

We will now implement the prime directive for several different potentials, the first of which is the infinite square well.

6.1 The Infinite Square Well

A particle of mass m is confined to a region of width a, $-a/2 < x < a/2$, by the potential

$$V(x) = \begin{cases} 0 & |x| < a/2 \\ \infty & \text{otherwise} \end{cases}$$

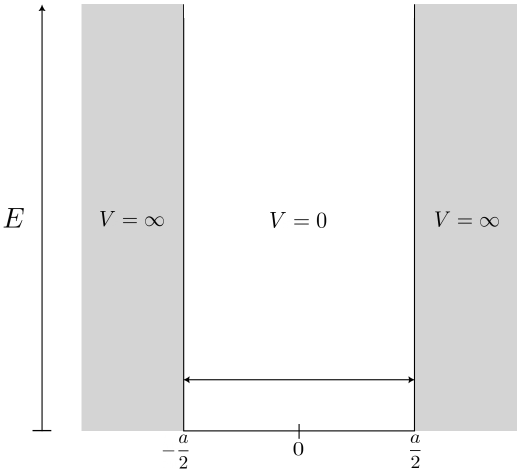


Figure 6.1: The Infinite Square Well

Aligning ourselves with the prime directive, we look for solutions of Schrödinger equation of the form

$$\Psi(x,t) = \sum_i \psi(x) e^{-iE_i t/\hbar} \qquad \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_i(x) = E_i\psi_i(x)$$

The solution outside the well is $\psi_i(x) = 0$. This will be demonstrated later in the chapter by solving the finite square well, then taking the infinite well limit. But intuitively it makes sense, since as the outside potential is infinite, the wave function can not penetrate past the boundary at all.

Inside the well we solve

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_i(x) = E_i\psi_i(x) \quad \Rightarrow \quad \frac{d^2}{dx^2}\psi_i(x) = -k_i^2\psi_i(x)$$

where $k_i = \frac{\sqrt{2mE_i}}{\hbar}$. This differential equation has the general solution (verify) of

$$\psi_i(x) = A\sin k_i x + B\cos k_i x$$

We now deal with the boundary conditions. The wave functions must vanish at $|x| = a/2$, as it vanishes for all $|x| > \frac{a}{2}$, and the wave function must also be continuous. This requires

$$\lim_{x\to\pm a}\psi_i(x) = 0$$

Substituting in for $\psi_i(x)$, and evaluating the limit, we get

$$A\sin\frac{k_i a}{2} + B\cos\frac{k_i a}{2} = 0 \tag{6.1}$$

$$A\sin\left(-\frac{k_i a}{2}\right) + B\cos\left(-\frac{k_i a}{2}\right) = -A\sin\frac{k_i a}{2} + B\cos\frac{k_i a}{2} = 0 \tag{6.2}$$

Adding and subtracting Equations 6.1 and 6.2,

$$A\sin\frac{k_i a}{2} + B\cos\frac{k_i a}{2} + \left(-A\sin\frac{k_i a}{2} + B\cos\frac{k_i a}{2}\right) \quad \Rightarrow \quad B\cos\frac{k_i a}{2} = 0 \tag{6.3}$$

$$A\sin\frac{k_i a}{2} + B\cos\frac{k_i a}{2} - \left(-A\sin\frac{k_i a}{2} + B\cos\frac{k_i a}{2}\right) \quad \Rightarrow \quad A\sin\frac{k_i a}{2} = 0 \tag{6.4}$$

Therefore we yield two sets of solutions,

$$\psi_n(x) = \begin{cases} B\cos k_n x & k_n = \{\frac{\pi}{a}, \frac{3\pi}{a}, \cdots\} = \frac{\pi n}{a},\ n = 1,3,5,\cdots & \text{even parity} \\ A\sin k_n x & k_n = \{\frac{2\pi}{a}, \frac{4\pi}{a}, \cdots\} = \frac{\pi n}{a},\ n = 2,4,6,\cdots & \text{odd parity} \end{cases} \tag{6.5}$$

We replace i with n, the quantum number that "labels" our solutions. The even parity solutions for odd n occur when the stationary state wave function is symmetric about the origin. The odd parity solutions are antisymmetric. Now, knowing that

$$k_n = \frac{\sqrt{2mE_n}}{\hbar} \Rightarrow E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2ma^2}$$

We get the allowed energy eigenvalues that correspond to the stationary states labeled with quantum number n. Now we move onto normalization to determine the coefficients A and B. Using Equation 4.1,

$$\int_{-a/2}^{a/2} |\psi_{i,\text{even parity}}(x)|^2\,dx = \int_{-a/2}^{a/2} B^2 \cos^2 \frac{\pi n x}{a}\,dx = B^2 \frac{a}{2} = 1 \quad \Rightarrow \quad B = \sqrt{\frac{2}{a}} \tag{6.6}$$

$$\int_{-a/2}^{a/2} |\psi_{i,\text{ odd parity}}(x)|^2\,dx = \int_{-a/2}^{a/2} A^2 \sin^2 \frac{\pi n x}{a}\,dx = A^2 \frac{a}{2} = 1 \quad \Rightarrow \quad A = \sqrt{\frac{2}{a}} \tag{6.7}$$

Therefore, our normalized stationary state solutions,

Infinite Square Well Stationary States

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos \frac{\pi n x}{a},\ n = 1, 3, 5, \cdots & \text{even parity} \\ \sqrt{\frac{2}{a}} \sin \frac{\pi n x}{a},\ n = 2, 4, 6, \cdots & \text{odd parity} \end{cases}$$

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

I plot the first four stationary state solutions along with their defined energies in Figure 6.2.

6.1.1 Various Comments about the Solutions

1. There are an infinite number of allowed energy eigenvalues and eigenfunctions labeled by the discrete quantum number index n. This is a consequence of the boundary condition that $\psi(x)$ vanish at $|x| < a/2$, limiting solutions to integer and half-integer wavelengths.

2. The basis is orthonormal as

   $$\int_{-a/2}^{a/2} \psi_n'^*(x)\psi_n(x)\,dx = \delta_n' n$$

   can be readily verified.

3. The basis is complete for any function $\Psi(x)$ satisfying the boundary condition $\Psi(a/2) = \Psi(-a/2) = 0$ and defined on the interval $[-a/2, a/2]$. Any function satisfying these conditions can be expanded in

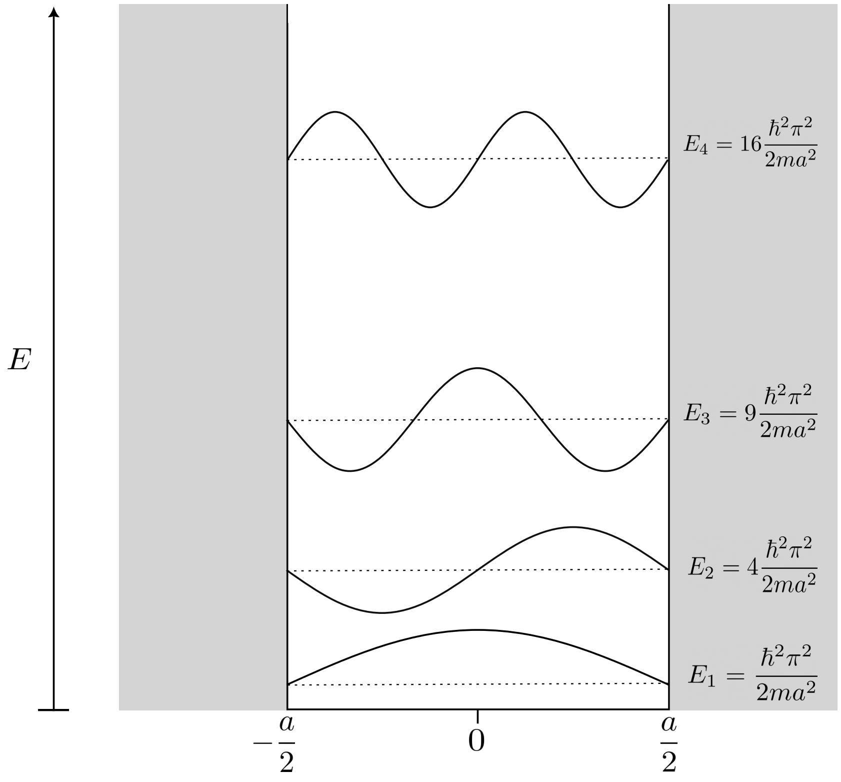


Figure 6.2: Infinite Square Well Stationary States

this basis. Those of you familiar with Fourier Series may have noticed that the odd basis functions

$$\sqrt{\frac{2}{a}}\sin\left(\frac{\pi n x}{a}\right),\ n = 2,4,6,\cdots \ \text{ which can be written as } \sqrt{\frac{2}{a}}\sin\left(\frac{\pi n' x}{a/2}\right),\ n' = 1,2,3,\cdots$$

are the standard odd functions of a Fourier Series, while the even basis functions

$$\sqrt{\frac{2}{a}}\cos\frac{\pi n x}{a},\ n = 1,3,5,\cdots \ \text{which can be written as } \sqrt{\frac{2}{a}}\cos\left(\frac{\pi(n'-\frac{1}{2})x}{a/2}\right),\ n' = 1,2,3,\cdots$$

have been shifted in index, and the constant term ($n' = 0$) is absent. These modifications reflect restrictions imposed on the basis by our use of specific boundary conditions.

4. These wave functions have $n-1$ interior zeroes – coordinates at which the probability to find the trapped particle vanishes.

5. The eigenfunctions have alternating definite parity – even or odd – a consequence of the reflection symmetry of the potential.

6.1.2 Wave Function Curvature

Within the well interior the particle propagates as a free particle – a particle in the absence of any confining potential. One can understand the physics of our well solutions from the correlation between wave function curvature and momentum. The momentum operator *measures* curvature, and our energy is quadratic in p. This can be made explicit by evaluating the expectation value of $\langle p^2 \rangle$ between the stationary states

$$\langle \hat{p}^2 \rangle = \frac{\hbar^2 \pi^2 n^2}{a^2} \qquad \text{so that} \qquad \frac{1}{2m} \langle \hat{p}^2 \rangle = \langle \hat{H} \rangle$$

For a fixed number of nodes, doubling a will half the curvature. Therefore, energies depend *inversely* on a^2. Conversely doubling the number of nodes doubles the curvature. Consequently energies scale as n^2.

The square well is exceptional in that it confines all wave functions in the same way. This leads to the steep n^2 dependence of energy eigenvalues. In a finite well – a future exercise – where the boundaries are not infinitely strong – the wave functions at higher excitation energies *penetrate* into the classically-forbidden region of the potential, reducing the curvature and thus producing energies that increase less steeply than n^2. This is known as ***quantum tunneling***. In the harmonic oscillator – another future exercise – the widening r^2 potential leads to a spectrum that is evenly spaced, with eigenvalues rising with n.

6.1.3 Example Problem – The Prime Directive

We calculated the stationary states for the infinite square well above. But what is the full, time-dependent normalized wave function? How do you find the $c_i's$ in Equation 5.12?.

To determine these, we have to have an additional boundary condition, namely the wave function value at some time t, call it $t = 0$.

Example A particle in an infinite square well has the initial wave function shown in Figure 6.3.

$$\Psi(x,0) = \begin{cases} Ax(a-x) & 0 \le x \le a \\ 0 & x > 0 \end{cases} \tag{6.8}$$

for some constant A. Find $\Psi(x,t)$.

First we must determine A using the normalization condition. If $\Psi(x,0)$ is normalized, $\Psi(x,t)$ will stay normalized.

$$\int_0^a |\Psi(x,0)|^2 \, dx = |A|^2 \int_0^a x^2 (a-x)^2 \, dx = |A|^2 \int_0^a (a^2 x^2 - 2ax^3 + x^4) \, dx \tag{6.9}$$

$$= |A|^2 \left(a^2 \frac{x^3}{3} - 2a \frac{x^4}{4} + \frac{x^5}{5} \right) \Bigg|_0^a = |A|^2 \left(\frac{a^5}{3} - \frac{2a^5}{4} + \frac{a^5}{5} \right) = |A|^2 \frac{a^5}{30} = 1 \tag{6.10}$$

$$\Rightarrow |A| = \sqrt{\frac{30}{a^5}} \tag{6.11}$$

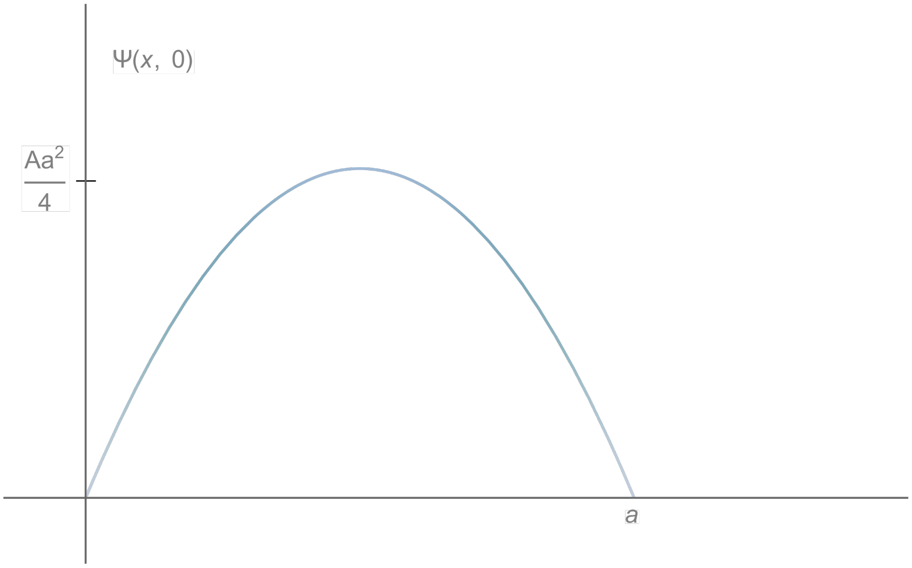


Figure 6.3: $\Psi(x, 0)$

Now we can determine the coefficients c_n using Equation 5.12.

$$\begin{aligned}
\Psi(x,0) &= \sum_{n=1}^{\infty} c_n \psi_n(x) \\
c_n &= \int \psi_n(x) \Psi(x,0)\, dx \\
&= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a} x\right) \sqrt{\frac{30}{a^5}} x(a-x)\, dx \\
&= \frac{2\sqrt{15}}{a^3} \left[a \int_0^a x \sin\left(\frac{n\pi}{a} x\right)\, dx - \int_0^a x^2 \sin\left(\frac{n\pi}{a} x\right)\, dx \right] \\
&= \frac{2\sqrt{15}}{a^3} \left[a \left[\left(\frac{a}{n\pi}\right)^2 \sin\left(\frac{n\pi}{a} x\right) - \frac{ax}{n\pi} \cos\left(\frac{n\pi}{a} x\right) \right]_0^a - \left[2 \left(\frac{a}{n\pi}\right)^2 x \sin\left(\frac{n\pi}{a} x\right) - \frac{(n\pi x a)^2 - 2}{(n\pi a)^3} \cos\left(\frac{n\pi}{a} x\right) \right]_0^a \right] \\
&= \frac{2\sqrt{15}}{a^3} \left[-\frac{a^3}{n\pi} \cos(n\pi) + a^3 \frac{(n\pi)^2 - 2}{(n\pi)^3} \cos(n\pi) + a^3 \frac{2}{(n\pi)^3} \cos(0) \right] \\
&= \frac{4\sqrt{15}}{(n\pi)^3} [\cos(0) - \cos(n\pi)] \\
&= \begin{cases} 0 & \text{if } n \text{ even} \\ \frac{8\sqrt{15}}{(n\pi)^3} & \text{if } n \text{ odd} \end{cases}
\end{aligned}$$

So now we can form our time-dependent wave function using the prime directive by putting everything together. We get

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \tag{6.12}$$

$$\Psi(x,t) = \sqrt{\frac{30}{a}} \left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5,\cdots} \frac{1}{n^3} \sin\left(\frac{n\pi x}{a}\right) e^{-in^2\pi^2\hbar t/2ma^2} \tag{6.13}$$

Notice the solution only contains the $\sin\left(\frac{n\pi x}{a}\right)$ component. This is because the square well in this problem is defined from $0 < x < a$ and not reflection symmetric around the origin. The final solution in Equation 6.13 describes how the wave function changes as a function of time, provided the particle is in a square well.

Now let us study this wave function, and its implications on observables. We first determine what the expectation value of the energy is.

$$\langle E \rangle = \int \Psi(x,t)^* \hat{H} \Psi(x,t)\, dx \tag{6.14}$$

$$= \int \Psi(x,t)^* E_n \Psi(x,t)\, dx \tag{6.15}$$

Performing the calculation, one will find

$$\langle E \rangle = \sum_n |c_n|^2 E_n$$

So we can think of $|c_n|^2$ as the probability to measure the energy eigenvalue E_n. Therefore,

$$\sum_m |c_n|^2 = 1$$

The c_n^2 can also be thought of as telling us the "amount" of Ψ_n that is in the *total* wave function. In the example above, we can see that the initial wave function closely resembles Ψ_1. If we look at c_1,

$$|c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 = 0.998555...$$

we see that it is very close to 1, indicating that the $n = 1$ state dominates.

The Infinite Square Well is the classic introductory quantum mechanics problem. Before moving on, ensure you understand every derivation in this section *completely.*

6.2 The Harmonic Oscillator

This next section is *very* important. In nature, literally everything is a harmonic oscillator. The harmonic oscillator stationary-state basis is arguably the most versatile and important in physics. Every field in physics includes key problems that require one to understand small-amplitude behavior that maps onto the harmonic oscillator.

The *quantum* 1D harmonic oscillator is to solve the Schrödinger equation for the potential shown in Figure 6.4

$$V(x) = \frac{1}{2}m\omega^2 x^2 \tag{6.16}$$

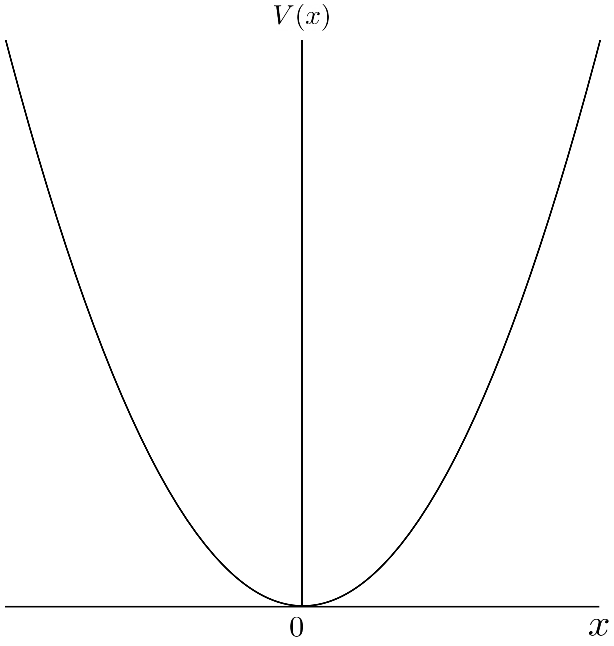


Figure 6.4: Quantum Harmonic Oscillator Potential

Therefore, by the prime directive, the time-independent Schrödinger equation reads

$$-\frac{h^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi \tag{6.17}$$

There are two methods to solve this problem. The first is the "brute force" attempt to solve the differential equation using power series. The second, according to Griffiths, is a "diabolically clever" technique using *ladder operators*. We will start with the ladder operator technique.

6.2.1 Ladder Operator Algebraic Technique

We rewrite Equation 6.17 utilizing the momentum operator:

$$\frac{1}{2m}\left[\hat{p}^2 + (m\omega w)^2\right]\psi = E\psi \tag{6.18}$$

where $\hat{p} \equiv -i\hbar\frac{d}{dx}$ is the momentum operator. We define the ladder operators as the following:

$$\hat{a}_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p} + m\omega x) \tag{6.19}$$

You might be wondering why the following operators are known as *ladder* operators – we'll get to that in a bit, but for now, let us determine the product $\hat{a}_-\hat{a}_+$.

$$\begin{aligned}\hat{a}_-\hat{a}_+ &= \frac{1}{2\hbar m\omega}(i\hat{p} + m\omega x)(-i\hat{p} + m\omega x) & (6.20)\\ &= \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega x)^2 - im\omega(x\hat{p} - \hat{p}x)\right] & (6.21)\end{aligned}$$

Note above, we do not combine the terms $(m\omega x)(-i\hat{p})$ and $(i\hat{p})(m\omega x)$. This is because in we are dealing with operators. Operators do not, in general, **commute** ($x\hat{p} \neq \hat{p}x$). So we have to separate the two. As a result, there is an extra term involving ($x\hat{p} - \hat{p}x$). We call this the **commutator** of x and $\hat{p}$. In general, the commutator of operators $\hat{A}$ and $\hat{B}$ is

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{6.22}$$

Using this notation,

$$\hat{a}_-\hat{a}_+ = \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega x)^2\right] - \frac{i}{2\hbar}[x, \hat{p}] \tag{6.23}$$

And so we need to figure out the commutator of x and $\hat{p}$. To do this, we employ an arbitrary "test" function f to see what the *effect* of the commutator is. At the end we can then throw away f to determine the value of the commutator. We have

$$\begin{aligned}[x, \hat{p}]f(x) &= \left[x(-i\hbar)\frac{d}{dx}f(x) - (-i\hbar)\frac{d}{dx}(xf)\right] & (6.24)\\ &= -i\hbar\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right) & (6.25)\\ &= i\hbar f(x) & (6.26)\end{aligned}$$

Therefore, $[x, \hat{p}] = i\hbar$. This formula is known as the **canonical commutation relation**. With this, Equation 6.23 becomes

$$\hat{a}_-\hat{a}_+ = \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2} \tag{6.27}$$

$$\Rightarrow \hat{H} = \hbar\omega\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\right) \tag{6.28}$$

Notice that the ordering of $\hat{a}_+$ and $\hat{a}_-$ is important here; the same argument with $\hat{a}_+$ on the left, yields

$$\hat{a}_+\hat{a}_- = \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2} \tag{6.29}$$

Therefore, another expression for the Hamiltonian can be derived by rearranging Equation 6.29.

$$\hat{H} = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right) \tag{6.30}$$

Then, in terms of $\hat{a}_\pm$, the Schrödinger equation for the harmonic oscillator can be written as

$$\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi \tag{6.31}$$

Now comes the pinnacle of the ladder operator method – the reason it is "diabolically clever."

Energy Eigenvalues of Ladder Operator

If ψ satisfies the Schrödinger equation with energy E (that is, $\hat{H}\psi = E\psi$), then $a_+\psi$ satisfies the Schrödinger equation with energy $(E + \hbar\omega)$ (that is, $\hat{H}(\hat{a}_+\psi) = (E + \hbar\omega)(\hat{a}_+\psi)$.

Because this is so important and may seem like it came out of the blue, I provide a proof.

$$\hat{H}(\hat{a}_+\psi) = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)(\hat{a}_+\psi) = \hbar\omega\left(\hat{a}_+\hat{a}_-\hat{a}_+ + \frac{1}{2}\hat{a}_+\right)\psi \tag{6.32}$$

$$= \hbar\omega\hat{a}_+\left(\hat{a}_-\hat{a}_+ + \frac{1}{2}\right)\psi = \hat{a}_+\left[\hbar\omega\left(\hat{a}_+\hat{a}_- + 1 + \frac{1}{2}\right)\psi\right] \tag{6.33}$$

$$= \hat{a}_+(\hat{H} + \hbar\omega)\psi = \hat{a}_+(E + \hbar\omega)\psi = (E + \hbar\omega)(\hat{a}_+\psi). \qquad \text{QED.} \tag{6.34}$$

Note that in the second line I replaced $\hat{a}_-\hat{a}_+$ by $(\hat{a}_+\hat{a}_- + 1)$. I can do this because (verify) $[\hat{a}_-, \hat{a}_+] = 1$. By the same procedure, $\hat{a}_-\psi$ is a solution as well, with energy eigenvalue $(E - \hbar\omega)$.

$$\begin{aligned} \hat{H}(\hat{a}_-\psi) &= \hbar\omega\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\right)(\hat{a}_-\psi) = \hbar\omega\hat{a}_-\left(\hat{a}_+\hat{a}_- - \frac{1}{2}\right)\psi & (6.35)\\ &= \hat{a}_-\left[\hbar\omega\left(\hat{a}_-\hat{a}_+ - 1 - \frac{1}{2}\right)\psi\right] = \hat{a}_-\left(\hat{H} - \hbar\omega\right)\psi = \hat{a}_-(E - \hbar\omega)\psi & (6.36)\\ &= (E - \hbar\omega)(\hat{a}_-\psi). & (6.37) \end{aligned}$$

This is why we call $\hat{a}_\pm$ ladder operators. If we could just find *one* solution, we can use $\hat{a}_\pm$ to "climb up and down" in energy, getting *all* the possible energy eigenvalues. Hence, we call $\hat{a}_+$ the **raising operator** and $\hat{a}_-$ the **lowering operator**.

Let us try to find the *lowest rung*, ψ_0, such that $\hat{a}_-\psi_0 = 0$. Therefore,

$$\frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{d}{dx} + m\omega x\right)\psi_0 = 0 \tag{6.38}$$

Rearranging gives

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}x\psi_0 \tag{6.39}$$

Implementing separation of variables,

$$\int\frac{1}{\psi_0}\,d\psi_0 = -\frac{m\omega}{\hbar}\int x\,dx \quad\Rightarrow\quad \ln\psi_0 = -\frac{m\omega}{2\hbar}x^2 + \text{const.} \tag{6.40}$$

Hence,

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2} \tag{6.41}$$

Normalizing,

$$1 = |A|^2\int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar}\,dx = |A|\sqrt{\frac{\pi\hbar}{m\omega}} \quad\Rightarrow\quad A^2 = \sqrt{m\omega/\pi\hbar} \tag{6.42}$$

Therefore, we get the final "lowest-rung" stationary state

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \tag{6.43}$$

To determine the energy of this state we plug it into the Schrödinger Equation 6.31 and exploit the fact that $\hat{a}_-\psi_0 = 0$.]

$$\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi_0 = E_0\psi_0 \tag{6.44}$$

$$\hbar\omega\left(\hat{a}_+(\hat{a}_-\psi_0) + \frac{1}{2}\psi_0\right) = E_0\psi_0 \tag{6.45}$$

$$\hbar\omega\left(0 + \frac{1}{2}\psi_0\right) = E_0\psi_0 \tag{6.46}$$

Therefore, $E_0 = \frac{1}{2}\hbar\omega$. We have secured the **ground state** of the quantum harmonic oscillator. We now can just apply $\hat{a}_+$ repeatedly to generate the excited states, increasing the energy by $\hbar\omega$ each step as we go along. Therefore, every stationary state, labeled by a quantum number n can be defined as follows:

$$\psi_n(x) = A_n(\hat{a}_+)^n\psi_0(x), \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{6.47}$$

where A_n is the normalization constant. You can get A_n algebraically, however, and the proof is laid out in Griffiths. It turns out that $A_n = \frac{1}{\sqrt{n!}}$. Thus,

$$\psi_n = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0 \tag{6.48}$$

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}}$$

6.2.2 Example – Expectation Value of V(x)

Example Find the expectation value of the potential energy in the nth stationary state of the harmonic oscillator.

$$\langle V\rangle = \langle\frac{1}{2}m\omega^2x^2\rangle = \frac{1}{2}m\omega^2\int_{-\infty}^{\infty}\psi_n^* x^2\psi_n\,dx$$

Expressing x and $\hat{p}$ in terms of the raising and lowering operators,

$$\boxed{x = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-); \qquad \hat{p} = i\frac{\hbar m\omega}{2}(\hat{a}_+ - \hat{a}_-)}$$

Therefore,

$$x^2 = \frac{\hbar}{2m\omega}\left[(\hat{a}_+^2 + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-^2\right]$$

Hence,

$$\langle V\rangle = \frac{\hbar\omega}{4}\int_{-\infty}^{\infty}\psi_n^*\left[(\hat{a}_+^2 + (\hat{a}_+\hat{a}_-) + (\hat{a}_-\hat{a}_+) + \hat{a}_-^2\right]\psi_n\, dx$$

But $\hat{a}_+^2\psi_n$ is (apart from normalization), just ψ_{n+2}, which is orthogonal to ψ_n and the same goes for $\hat{a}_-^2\psi_n \sim \psi_{n-2}$. So those terms drop out, and we are left with

$$\langle V\rangle = \frac{\hbar\omega}{4}\int_{-\infty}^{\infty}\psi_n^*\left[(\hat{a}_+\hat{a}_-) + (\hat{a}_-\hat{a}_+)\right]\psi_n\, dx$$

Now, without proof (but check Griffiths) I will use the following relations:

$$\hat{a}_+\hat{a}_-\psi_n = n\psi_n, \qquad \hat{a}_-\hat{a}_+\psi_n = (n+1)\psi_n$$

Therefore, we get the final result,

$$\langle V\rangle = \frac{\hbar\omega}{4}(n+n+1) = \frac{1}{2}\hbar\omega(n+\frac{1}{2}).$$

We see that the expectation value of the potential energy $V(x)$ is exactly *half* of the total energy $E = \left(n+\frac{1}{2}\right)\hbar\omega$. This is a beautiful fact of the harmonic oscillator and a reason as to why it shows up literally everywhere in physics.

6.2.3 Power Series Analytic Method

I will now show the second, 'brute-force' power series method to solve the Schrödinger equation for the harmonic oscillator,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi \tag{6.49}$$

and solve it directly. We first introduce a dimensionless variable ξ to make things cleaner, where

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x \tag{6.50}$$

Hence, the Schrödinger equation now reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi \tag{6.51}$$

where $K \equiv \frac{2E}{\hbar\omega}$. Our problem is to solve Equation 6.51 and in the process obtain the allowed values of K, and thus E. To begin with, we notice that at very large ξ, (very large x), ξ^2 completely dominates over the constant K, so in this circumstance,

$$\frac{d^2\psi}{d\xi^2} \approx \xi^2\psi \tag{6.52}$$

which has the approximate solution (verify)

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{\xi^2/2} \tag{6.53}$$

And since the B term blows up as $|x| \to \infty$, we get rid of it to ensure $\psi(\xi)$ is normalizable. The physically acceptable solutions are then

$$\psi(\xi) \to h(\xi)e^{\xi^2/2}, \qquad \text{at large } \xi \tag{6.54}$$

where we replaced the constant A with another function $h(\xi)$ in hopes that it has a simpler functional form that $\psi(xi)$ itself. Differentiating Equation 6.54,

$$\frac{d\psi}{d\xi} = \left(\frac{dh}{d\xi} - \xi h\right) e^{\xi^2/2} \tag{6.55}$$

$$\frac{d^2\psi}{d\xi^2} = \left(\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (\xi^2 - 1)h\right) e^{-\xi^2/2} \tag{6.56}$$

And therefore, equating Equation 6.51 and Equation 6.56 transforms the Schrödinger equation into

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K - 1)h = 0 \tag{6.57}$$

And here is where we utilize power series. We search for solutions to Equation 6.57 in the form of a power series in ξ.

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j \xi^j \tag{6.58}$$

Differentiating the power series term by term to determine $\frac{dh}{d\xi}$ and $\frac{d^2h}{d\xi^2}$,

$$\frac{dh}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + \qquad \cdots = \sum_{j=0} j a_j \xi^{j-1} \tag{6.59}$$

$$\frac{d^2h}{d\xi^2} = 2a_2 + 2\cdot 3a_3\xi + 3\cdot 4a_4\xi^2 + \qquad \cdots = \sum_{j=0}^{\infty}(j+1)(j+2)a_{j+2}\xi^j \tag{6.60}$$

Putting all these equations into Equation 6.57, we find

$$\sum_{j=0}^{\infty}[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j]\xi^j = 0 \tag{6.61}$$

It follows that the coefficient of *each power* of ξ must vanish (since the whole thing equals 0). In other words

$$(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j = 0$$

Rearranging gives us a recurrence relation,

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)}a_j \tag{6.62}$$

Starting with a_0, we can generate all the even-numbered coefficients. Starting with a_1, we can generate all the odd-numbered coefficients. Therefore, we can write $h(\xi)$ as

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi) \tag{6.63}$$

where

$$h_{\text{even}} = a_0 + a_2\xi^2 + a_4\xi^4 \tag{6.64}$$

$$h_{\text{odd}} = a_1\xi + a_3\xi^3 + a_5\xi^5 \tag{6.65}$$

For very large j, the recursion formula becomes approximately,

$$a_{j+2} \approx \frac{2}{j} a_j$$

with the solution

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

for some constant C. This yields (for very large ξ),

$$h(\xi) \approx C \sum \frac{1}{(j/2)!} \xi^j \approx C \sum \frac{1}{j!} \xi^{2j} \approx C e^{\xi^2}$$

However, something seems wrong. If $h \sim e^{+\xi^2}$, then $\psi(\xi) = h(\xi) e^{-\xi^2/2} \sim e^{+\xi^2/2}$ – which blows up for large ξ, (and hence for large x). There is only one way to resolve this. For normalizable solutions, **the series must terminate at some j**. There must occur some "highest j ". (call it $j_{\max}$, such that the recursion formula spits out $a_{j_{\max}+2} = 0$, which will make every coefficient afterwards also 0. Therefore, for physically acceptable solutions, Equation 6.62 requires

$$K = 2 j_{\max} + 1$$

for some positive integer $j_{\max}$. And since $K = \frac{2E}{\hbar\omega}$, we recover the energy equation for a harmonic oscillator

$$E_j = \left(j + \frac{1}{2}\right) \hbar\omega, \qquad \text{for } j = 0, 1, 2, \ldots \tag{6.66}$$

We recover, by a completely different method, the fundamental quantization condition we algebraically uncovered in Equation 6.47.

For the allowed values of K, the recursion formula reads

$$a_{j+2} = \frac{-2(j_{\max} - j)}{(j+1)(j+2)} a_j \tag{6.67}$$

If $j_{\max} = 0$, there exists only one term in the series, $h_0(\xi) = a_0$. And hence

$$\psi_0(\xi) = a_0 e^{-\xi^2/2} \qquad \text{if } j_{\max} = 0$$

which, apart from normalization is equivalent to Equation 6.43. For $j_{\max} = 1$, we take $a_0 = 0$, and Equation 6.67 with $j = 1$ yields $a_3 = 0$, so

$$h_1(\xi) = a_1\xi \quad \Rightarrow \quad \psi_1(\xi)a_1\xi e^{-\xi^2/2} \tag{6.68}$$

For $j_{\max} = 2$, $j = 0$ yields $a_2 = -2a_0$, and $j = 2$ gives $a_4 = 0$, so

$$h_2(\xi) = a_0\left(1 - 2\xi^2\right) \quad \Rightarrow \quad \psi_2(\xi) = a_0(1 - 2\xi^2)e^{-\xi^2/2} \tag{6.69}$$

and so on. The polynomials for $h(\xi)$ that are generated are known as **Hermite Polynomials**. There are actually two different forms of Hermite Polynomials – the "physicist's" and the "probabilist's," that are related. Obviously, the type us superior physicists use are the physicist's Hermite Polynomials. By convention, the arbitrary multiplicative factor is chosen so that the coefficient of the highest power of ξ is $2^{j_{\max}}$. Then, the normalized stationary states for the harmonic oscillator are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \tag{6.70}$$

where we use $j_{\max} = n$ to label the quantum number of each state. These are identical of course to the ones we obtained algebraically in Equation 6.48. I plot the solutions $\psi_n(x)$ in Figure 6.5 below.

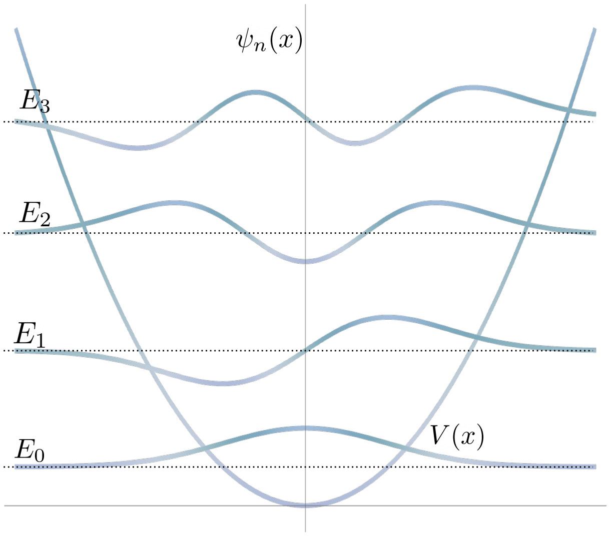


Figure 6.5: Stationary State Wave Functions for 1D Harmonic Oscillator

Note the energies are evenly spaced as $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$. We can afterwards determine $\Psi(x,t)$ via the prime directive using Equation 5.12.

6.3 The Free Particle

We have previously (in studying the infinite square well) considered a particle that could propagate freely in the region $-a/2 < x < a/2$, but was confined at the boundaries by an infinitely strong potential. The solutions of the time-independent Schrödinger equation were states of definite energy. We described these states as sin and cos functions – standing waves with fixed nodes, formed by combining left-moving with right-moving amplitudes. These states were normalizable and provided a complete orthonormal basis for describing the propagation of any wave packet $\Psi(x,t)$.

Here we consider a similarly free propagating particle, but one not confined by any potential. Instead the particle is free – able to move over the region $-\infty < x < \infty$. Here however, we will choose to describe the waves as plane waves in the form e^{ikx} rather than with sin and cos. These states, as you shall soon see, are not normalizable and are thus not true stationary states, yet they are still of use as they form a basis for expanding physical states – wave packets – that *are* normalizable physical states.

As the particle is free ($V(x) = 0$) for all $-\infty < x < \infty$, the Schrödinger equation for the time-independent stationary states is the following:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{6.71}$$

In terms of the wave number

$$k = \frac{\sqrt{2mE}}{\hbar} \qquad \Rightarrow \qquad \frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

And therefore the general time-independent solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{6.72}$$

And the full time-dependent solution is therefore, via the prime directive,

$$\Psi(x,t) = Ae^{ikx - iEt/\hbar} + Be^{-ikx-iEt/\hbar} \quad k \text{ positive} \tag{6.73}$$

If we allow k to run over both positive and negative values, then $k = \pm\frac{\sqrt{2mE}}{\hbar}$, and this simplifies the time-dependent solution into

$$\Psi(x,t) = Ae^{ikx-iEt/\hbar} = Ae^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} \quad k \text{ positive or negative} \tag{6.74}$$

We can identify the *velocity* of our solutions by jumping on the wave function – hanging onto a point of fixed phase – and measuring which way we travel. We take a positive step in time Δt and demand that the phase remain fixed

$$kx - \frac{\hbar k^2}{2m}t \to k(x+\Delta x) - \frac{\hbar k^2}{2m}(t+\Delta t) \Rightarrow k\Delta x - \frac{\hbar k^2}{2m}\Delta t = 0 \tag{6.75}$$

$$\Rightarrow \frac{\Delta x}{\Delta t} \equiv v = \frac{\hbar k}{2m} \tag{6.76}$$

Therefore, our solutions with positive k have a positive velocity (traveling to the right) while those with negative k have negative velocity (traveling to the left).

$$\begin{aligned} k &= +\frac{\sqrt{2mE}}{\hbar} > 0 \to \text{ traveling to the right } (+x) \\ k &= -\frac{\sqrt{2mE}}{\hbar} < 0 \to \text{ traveling to the left } \quad (-x) \end{aligned}$$

We can define the wavelength as a positive number

$$\lambda = \frac{2\pi}{|k|} \tag{6.77}$$

but include a sign in the de Broglie relationship for momentum,

$$p = \frac{2\pi\hbar}{\lambda} \to (2\pi\hbar)\left(\frac{k}{2\pi}\right) = \hbar k$$

so that momentum becomes a signed quantity (positive for waves moving to the right, negative for those moving to the left).

However, there is are two issues with our calculations. The first is regarding our calculated wave velocity. The velocity of the waves we calculated in Equation 6.76 is

$$v_{\text{quantum}} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}} \tag{6.78}$$

On the other hand, the *classical* speed of a free particle with energy E is given by $E = \frac{1}{2}mv^2$, so

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}} = 2v_{\text{quantum}} \tag{6.79}$$

We get a quantum mechanical wave function that travels at *half* the speed of what the particle *should*. The second issue is the fact that our calculated wave function *is not normalizable*.

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2\, dx = |A|^2 \int_{-\infty}^{\infty} \left(e^{-ikx+iEt/\hbar}\right)\left(e^{ikx-iEt/\hbar}\right) dx \quad \rightarrow \quad |A|^2(\infty) \tag{6.80}$$

Therefore, our solutions do not represent physically realizable states. A free particle can not exist in a stationary state – *there is no such thing as a free particle of definite energy.* But like I said previously, they still serve purpose. They play a *mathematical* role entirely dependent of their *physical* interpretation. The general solution to the time-dependent Schrödinger equation via the prime directive is still a linear combination of our stationary states. Only this time its an *integral* over the continuous variable k instead of a discrete sum over index n.

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i\left(kx - \frac{\hbar k^2}{2m}\right)}\, dk \tag{6.81}$$

The quantity $\frac{1}{\sqrt{2\pi}}$ is factored out for convenience.e This wave function *can* be normalized. But it carries a *range* of ks, and hence a range of energies and velocities. This is what we call a **wave packet**.

In a normal quantum mechanics problem, we are provided $\Psi(x,0)$ and asked to find $\Psi(x,t)$. For a free particle the solution takes the form of Equation 6.81. But how do we determine $\phi(k)$? so as to match the initial wave function

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

The answer, as you may have noticed given the form of Equation 6.81 is via Fourier/Inverse fourier Transform.

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

$F(k)$ is the *fourier transform* of $f(x)$, and likewise $f(x)$ is the *inverse fourier transform* of $F(k)$. These integrals exist if the initial wave packet $\Psi(x,0)$ is normalized. The solution for a free particle is Equation 6.81 with

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx}\, dx \tag{6.82}$$

Putting everything together,

Wave Packet → Wave Function

Given an arbitrary initial wave packet $\Psi(x,0)$.

For a discrete system (Harmonic Oscillator, Infinite Square Well, ...)

$$\Psi(x,0) = \sum_n c_n \psi_n(x) \qquad c_n = \int_\Omega \psi_n^*(x)\Psi(x,0)\,dx$$
$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$$

where $\psi_n(x)$ and E_n are the solutions to the discrete problem, and where the integration in x is over the region Ω where ψ_n is nonzero.

For a free particle, with its continuous plane-wave basis,

$$\Psi(x,0) = \int_{-\infty}^{\infty} \phi(k)\psi(k,x)\,dk \qquad \phi(k) = \int_{-\infty}^{\infty} \psi^*(k,x)\Psi(x,0)\,dx$$
$$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(k)\psi(k,x)e^{-iE(k)t/\hbar}\,dk$$

where $\psi(k,x) \equiv \sqrt{\frac{1}{2\pi}}e^{ikx}$ and $E(k) = \frac{\hbar^2 k^2}{2m}$.

6.3.1 Example Problem – Trapped Wave Packet

We start with a normalized wave packet that has been confined to a region of width $2a$,

$$\Psi(x,0) = \begin{cases} \frac{1}{\sqrt{2a}} & -a < x < a \\ 0 & |x| > a \end{cases} \tag{6.83}$$

Using Equation 6.82,

$$\phi(k) = \int_{-\infty}^{\infty} \left(\frac{1}{\sqrt{2\pi}}e^{-ikx}\right)\Psi(x,0)\,dx = \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2a}}\int_{-a}^{a} \cos kx\,dx = \frac{1}{\sqrt{\pi a}}\frac{\sin ak}{k}$$

Then finally, via the prime directive, or by using Equation 6.81,

$$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(k)\psi(k,x)e^{-iE(k)t/\hbar}\,dk = \int_{-\infty}^{\infty} \frac{1}{\sqrt{\pi a}}\frac{\sin ak}{k}\left(\frac{1}{\sqrt{2\pi}}e^{ikx}\right)e^{-i\hbar k^2 t/2m}\,dk \tag{6.84}$$

Below I plot the initial probability density function at $|\Psi(x,0)|^2$ along with the probability density function $|\Psi(x, ma^2/\hbar)|^2$, at a later time $t = ma^2/\hbar$ (the curve) in Figure 6.6. As you can see, the probability density function and the wave function itself begin to delocalize over time.

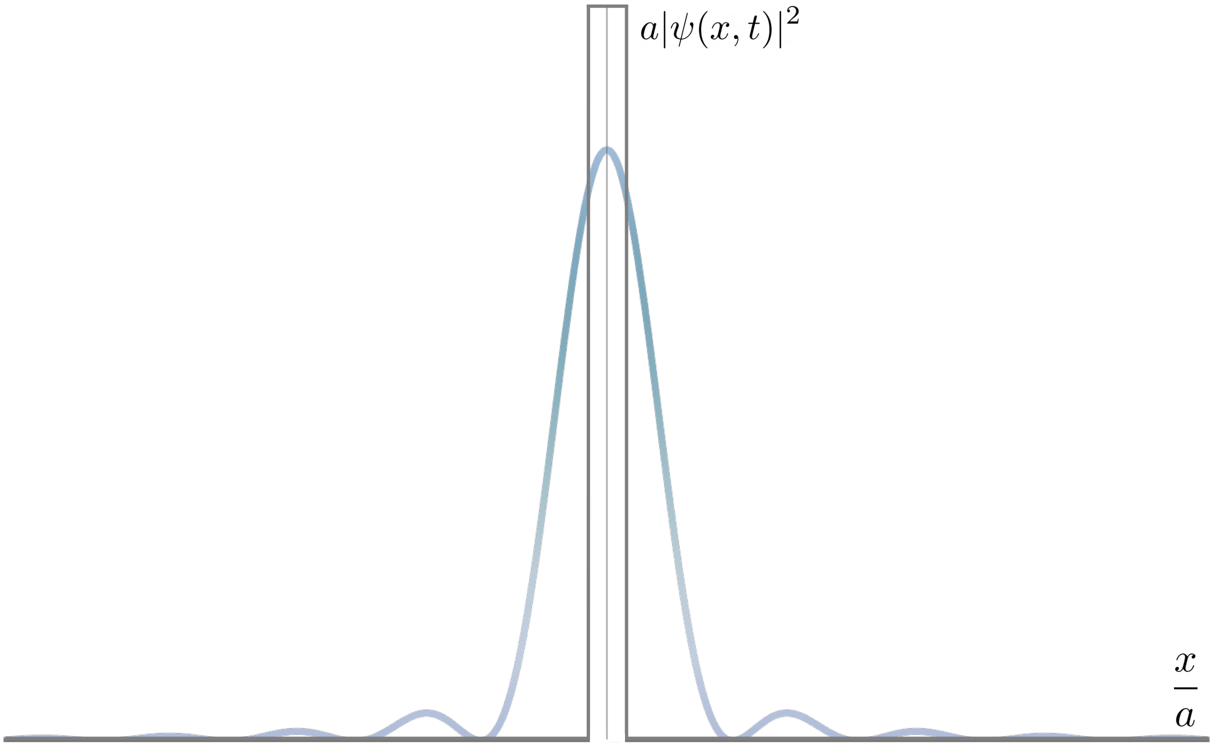


Figure 6.6: Plot of $|\Psi(x,0)|^2$ and $|\Psi(x, ma^2/\hbar)|^2$.

6.4 The Finite Square Well

We have previously solved problems involving *bound* stationary states (Infinite Square Well, Harmonic Oscillator) and where the basis consists entirely of plane waves (Free Particle). Here we tackle the first problem where free and bound states coexist. The *Finite Square Well* depicted in Figure 6.7 below.

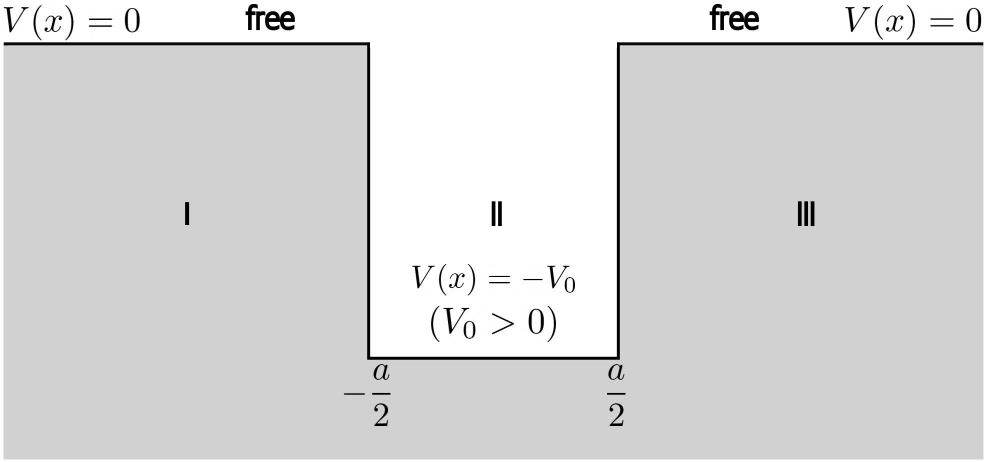


Figure 6.7: Finite Well Potential

6.4.1 Bound States

We seek solutions where $E < 0$. In region I the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) = -|E|\psi(x) \quad \Rightarrow \frac{d^2\psi(x)}{dx^2} = \kappa^2\psi(x); \qquad \kappa \equiv \frac{\sqrt{2m|E|}}{\hbar} > 0$$

The general solution is

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

However, the first term diverges as $x \to -\infty$. Therefore the solution in region I is

$$\text{Region I: } \psi_I(x) = Be^{\kappa x}, \quad x < -\frac{a}{2}$$

The same arguments lead to

$$\text{Region III: } \psi_{III}(x) = Ae^{-\kappa x}, \quad x > \frac{a}{2}$$

In region II we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - V_0\psi(x) = -|E|\psi(x) \quad \Rightarrow \quad \frac{d^2\psi(x)}{dx^2} = -k^2\psi(x); \qquad k \equiv \frac{\sqrt{2m(V_0 - |E|}}{\hbar}$$

We require $V_0 > |E|$ – the eigenvalue above the floor of the potential – as is the case classically. The general solution is

$$\text{Region II: } \psi_{II}(x) = C\cos kx + D\sin ks, \qquad -\frac{a}{2} < x < \frac{a}{2}$$

As the potential is mirror-symmetric, we can label the wave function by parity – whether even or odd around zero. In this way we can construct solutions corresponding to either the even or odd terms in region II.

Even Solution: Choosing the even-parity solution of region II,

$$\text{Region II: } \psi_{II}(x) = C\cos kx, \qquad -\frac{a}{2} < x < \frac{a}{2}$$

Second order differential equations require two constraints as initial conditions to solve. We can use the required continuity of the wave function across regions for both. The value and first derivative of the wave function at the boundary between regions must match to guarantee continuity. Thus at the boundary of II and III,

$$\left. C\cos kx = Ae^{-\kappa x} \right|_{x=a/2} \quad \Rightarrow \quad C\cos\frac{ka}{2} = Ae^{-\frac{\kappa a}{2}} \tag{6.85}$$

$$\left. -Ck\sin kx = -\kappa Ae^{-\kappa x} \right|_{x=a/2} \quad \Rightarrow \quad -Ck\sin\frac{ka}{2} = -A\kappa e^{-\frac{\kappa a}{2}} \tag{6.86}$$

These yield two constraints:

$$A = Ce^{\frac{\kappa a}{2}}\cos\left(\frac{ka}{2}\right) \qquad k\tan\left(\frac{ka}{2}\right) = \kappa,$$

the second of which, the eigenvalue condition, is obtained by taking the ratio of the two equations. The same matching at the boundary of I and II yields

$$C\cos\left(-\frac{ka}{2}\right) = Be^{-\frac{ka}{2}} \quad \text{and} \quad -Ck\sin\left(-\frac{ka}{2}\right) = B\kappa e^{-\frac{-\kappa a}{2}} \tag{6.87}$$

$$C\cos\left(\frac{ka}{2}\right) = Be^{-\frac{ka}{2}} \quad \text{and} \quad Ck\sin\left(\frac{ka}{2}\right) = B\kappa e^{-\frac{\kappa a}{2}} \tag{6.88}$$

These yield the same eigenvalue constraints as above with an additional condition,

$$B = Ce^{\frac{\kappa a}{2}}\cos\left(\frac{ka}{2}\right)$$

The matching at the second boundary was unnecessary – we could have just used the fact that the wave function is even under parity to get the same constraint. We finally obtain

Even Solution

$$\psi(x) = \begin{cases} Ce^{\frac{\kappa a}{2}} \cos\left(\frac{ka}{2}\right) e^{\kappa x} & x < -\frac{a}{2} \\ C \cos kx & -\frac{a}{2} < x < \frac{a}{2} \\ Ce^{\frac{\kappa a}{2}} \cos\left(\frac{ka}{2}\right) e^{-\kappa x} & x > \frac{a}{2} \end{cases}$$

$$\text{eigenvalue condition: } k \tan\left(\frac{ka}{2}\right) = \kappa$$

The remaining work is to solve for the allowed eigenvalues, and find C by requiring the solution to be normalized. This will be shown after deriving the odd-parity solution.

Odd Solution: Choosing the odd-parity solution of region II,

$$\text{Region II: } \psi_{II}(x) = D \sin kx, \qquad -\frac{a}{2} < x < \frac{a}{2}$$

We match the solutions at the boundary of II and III,

$$D \sin kx = Ae^{-\kappa x}\Big|_{x=a/2} \quad \Rightarrow \quad D \sin \frac{ka}{2} = Ae^{-\frac{\kappa a}{2}} \tag{6.89}$$

$$Dk \cos kx = -\kappa Ae^{-\kappa x}\Big|_{x=a/2} \quad \Rightarrow \quad Dk \cos \frac{ka}{2} = -A\kappa e^{-\frac{\kappa a}{2}} \tag{6.90}$$

These yield two constraints,

$$A = De^{\frac{\kappa a}{2}} \sin\left(\frac{ka}{2}\right) \qquad k \cot\left(\frac{ka}{2}\right) = -\kappa.$$

The same matching at the boundary of I and II yields

$$D \sin\left(-\frac{ka}{2}\right) = Be^{-\frac{ka}{2}} \quad \text{and} \quad Dk \cos\left(-\frac{ka}{2}\right) = B\kappa e^{-\frac{\kappa a}{2}} \quad \Rightarrow \tag{6.91}$$

$$-D \sin\left(\frac{ka}{2}\right) = Be^{-\frac{ka}{2}} \quad \text{and} \quad Dk \cos\left(\frac{ka}{2}\right) = B\kappa e^{-\frac{\kappa a}{2}} \tag{6.92}$$

These yield the same eigenvalue constraints as above with the additional condition

$$-B = A = De^{\frac{\kappa a}{2}} \cos\left(\frac{ka}{2}\right)$$

which makes sense as the solution in region I is the odd-mirror of the solution in region II. Therefore we obtain

Odd Solution

$$\psi(x) = \begin{cases} -De^{\frac{\kappa a}{2}}\sin\left(\frac{ka}{2}\right)e^{\kappa x} & x < -\frac{a}{2} \\ D\sin ks & -\frac{a}{2} < x < \frac{a}{2} \\ De^{\frac{\kappa a}{2}}\sin\left(\frac{ka}{2}\right)e^{-\kappa x} & x > \frac{a}{2} \end{cases}$$

$$\text{eigenvalue condition: } k\cot\left(\frac{ka}{2}\right) = -\kappa$$

Even Solution

$$\psi(x) = \begin{cases} Ce^{\frac{\kappa a}{2}}\cos(\frac{ka}{2})e^{\kappa x} & x < -\frac{a}{2} \\ C\cos kx & -\frac{a}{2} < x < \frac{a}{2} \\ Ce^{\frac{\kappa a}{2}}\cos(\frac{ka}{2})e^{-\kappa x} & x > \frac{a}{2} \end{cases}$$

$$\text{eigenvalue condition: } k\tan\left(\frac{ka}{2}\right) = \kappa$$

The kinematic variables are

$$k = \frac{\sqrt{2m(V_0 - |E|}}{\hbar} \qquad \kappa = \frac{\sqrt{2m|E|}}{\hbar}$$

Now all that is left is to calculate the eigenvalues of the bound states, then normalize.

6.4.2 Counting Eigenvalues

The allowed bound-state energies are obtained by solving the eigenvalue conditions

$$k\tan\left(\frac{ka}{2}\right) = \kappa \quad \text{and} \quad k\cot\left(\frac{ka}{2}\right) = -\kappa$$

for the even and odd cases, respectively, subject to the constraint

$$k^2 + \kappa^2 = \frac{2mV_0}{\hbar^2} \quad \Rightarrow \quad \kappa^2 = \frac{2mV_0}{\hbar^2} - k^2$$

Multiplying the top equations by $a/2$ and the bottom equations by $(a/2)^2$, we can re-express them in a simpler form:

> $$z \equiv \frac{ka}{2} = \frac{a\sqrt{2m(V_0 - |E|)}}{2\hbar} \qquad z_0 \equiv \frac{a}{2\hbar}\sqrt{2mV_0} \quad \text{so } \frac{\kappa a}{2} = \sqrt{z_0^2 - z^2}$$
>
> $$\text{even eigenvalues: } \tan z = \frac{1}{z}\sqrt{z_0^2 - z^2} = \sqrt{\frac{z_0^2}{z^2} - 1}$$
>
> $$\text{odd eigenvalues: } \cot z = -\frac{1}{z}\sqrt{z_0^2 - z^2} = -\sqrt{\frac{z_0^2}{z^2} - 1}$$

z_0 is a unit-less number derived by the potential we are given – the parameters V_0 and a.
Before we draw graphs to visualize this in Figure 6.8, consider the process of gradually increasing V_0, which allows more and more states to be captured in the potential well. When does a new state enter? When $|E| \sim 0 \Rightarrow \kappa = 0 \Rightarrow z \sim z_0$. This means

$$\text{even: } \tan z \sim \tan z_0 = 0 \quad \Rightarrow \quad z_0 = n\frac{\pi}{2}, n = 0, 2, 4, \ldots \quad \Rightarrow \quad a^2 V_0 = n^2\pi^2\frac{\hbar^2}{2m}, n = 0, 2, 4, \ldots$$

Therefore if

$$(n+2)^2\pi^2\frac{\hbar^2}{2m} > a^2V_0 > n^2\pi^2\frac{\hbar^2}{2m},\ n = 0, 2, 4, \ldots \qquad \text{there are } \frac{n}{2} + 1 \text{ even bound states}$$

Note that there is always at least one bound state that persists even as $V_0 \to 0$.
For the odd-parity states,

$$\text{odd: } \cot z \sim \cot z_0 = 0 \quad \Rightarrow \quad z_0 = n\frac{\pi}{2}, n = 1, 3, 5, \ldots \quad \Rightarrow \quad a^2 V_0 = n^2\pi^2\frac{\hbar^2}{2m}, n = 1, 3, 5, \ldots$$

Therefore if

$$(n+2)^2\pi^2\frac{\hbar^2}{2m} > a^2V_0 > n^2\pi^2\frac{\hbar^2}{2m}, n = 1, 3, 5, \cdots \qquad \text{there are } \frac{n+1}{2} \text{ odd bound states}$$

Putting these two results together:

Number of Energy Eigenstates

For a finite well of width a and depth V_0, if

$$(n+1)^2\pi^2\frac{\hbar^2}{2m} > a^2V_0 > n^2\pi^2\frac{\hbar^2}{2m}, n = 0, 1, 2, \ldots$$

there are $n + 1$ bound states. The equivalent condition on z_0 is

$$(n+1)\frac{\pi}{2} > z_0 > n\frac{\pi}{2} \tag{6.93}$$

6.4.3 Finding Eigenvalues

Our eigenvalue equations are

$$\tan z = \sqrt{\frac{z_0^2}{z^2} - 1} \qquad \cot z = -\sqrt{\frac{z_0^2}{z^2} - 1}$$

which we must solve as a function of z_0. We do so by plotting the left and right-handed sides, for a series of z_0^2 and finding the intersections. This is shown in Figure 6.8 for the cases of $z_0 = \pi/4$ and $z_0 = 3\pi/4$. The pattern of solutions follows the discussion above. One can also use Mathematica or MATLAB to get accurate results.

Consistency with the Infinite Square Well: In our calculation we can take $V_0 \to \infty$ or equivalently $z_0 \to \infty$. Then our even eigenvalue equation becomes

$$\tan z = \tan\frac{ka}{2} = \frac{1}{z}\sqrt{z_0^2 - z^2} \to \infty \quad \Rightarrow \quad \frac{k_n a}{2} = \frac{n\pi}{2}, \quad n = 1, 3, 5, \ldots$$

and our odd equation becomes

$$-\cot z = -\cot\frac{ka}{2} = \frac{1}{z}\sqrt{z_0^2 - z^2} \to \infty \quad \Rightarrow \quad \frac{k_n a}{2} = \frac{n\pi}{2}, \quad n = 2, 4, 6, \ldots$$

Thus

$$k_n a = n\pi, \quad n = 1, 2, 3, \ldots \quad \Rightarrow \quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad n = 1, 2, 3, \ldots$$

which is the same result as before.

6.4.4 Finding Bound Stationary States Example

We consider a specific case where

$$z_0 = \frac{\pi}{20}$$

Let's first determine how many bound states this potential can hold. Referring to our eigenvalue condition on z_0 from Equation 6.93,

$$(n+1)\frac{\pi}{2} > \frac{\pi}{20} > n\frac{\pi}{2}$$

The only n that satisfies this equation is $n = 0$. Therefore this potential will have only a single, even-parity bound state. This choice leads to

$$z_0 \equiv \frac{a}{2\hbar}\sqrt{2mV_0} \quad \Rightarrow \quad V_0 = \left(\frac{\pi}{20}\right)^2 \frac{2\hbar^2}{ma^2}$$

This is a very weak potential, one that supports a barely-bound state. We can compute the wave number and wavelength of the wave function inside the well,

$$k = \frac{\sqrt{2m(V_0 - |E|)}}{\hbar} < \frac{\sqrt{2mV_0}}{\hbar} = \frac{\pi}{10}\frac{1}{a} \quad \Rightarrow \lambda = \frac{2\pi}{k} > 20a$$

The wave length is *much* longer than the width of the well. We will return to this fact soon when we study *quantum tunneling*. Solving our even eigenvalue equation yields

$$z \equiv \frac{ka}{2} = 0.1551918$$

But from our earlier formulae,

$$\frac{\kappa a}{2} = \sqrt{z_0^2 - \left(\frac{ka}{2}\right)^2} = 0.02428 \quad \text{and} \quad |E| = \left(\frac{\kappa a}{2}\right)^2 \frac{2\hbar^2}{ma^2} = \left(\frac{\kappa a}{2}\right)^2 V_0 \left(\frac{20}{\pi}\right) 2 = 0.02245V_0$$

This state is very near the top of the well – 98% of the well is below. The wave function is almost free! Only about 5% of the probability density is within the well – the rest is spread out in the classically forbidden region. We could make this solution less and less bound, forcing it to approach arbitrarily close to a free particle wave of the form

$$\frac{1}{2}\left[e^{ikx} + e^{-ikx}\right]$$

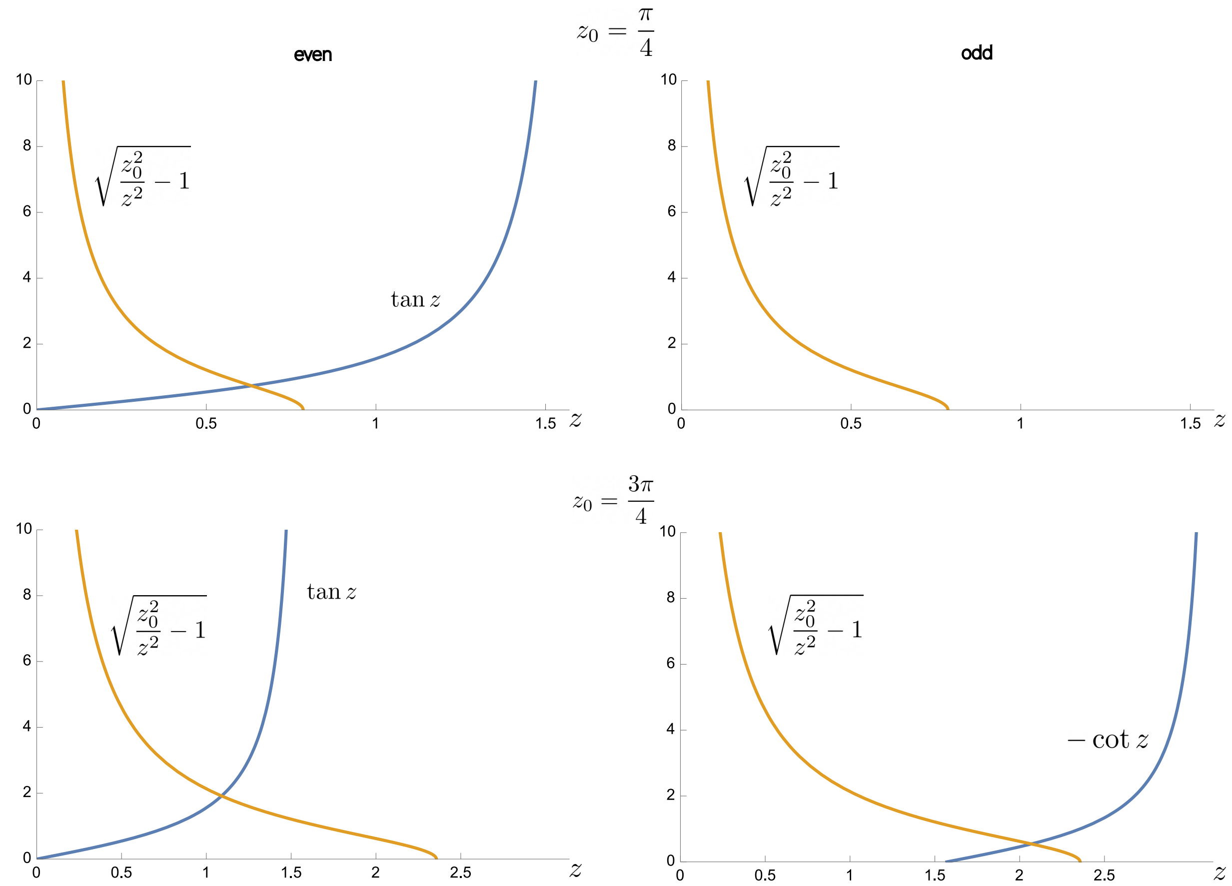


Figure 6.8: Finite Well even (left) and odd (right) parity plots to identify eigenvalues. For $z_0 = \pi/4$, one even solution is found. For $z_0 = 3\pi/4$, one even and one odd solution is found.

6.5 The Delta Function Potential

Here we define the delta function $\delta(x)$ as the limit

$$\delta(x-0) = \delta(x) \equiv \lim_{b\to 0} \frac{1}{|b|\sqrt{\pi}} e^{-(x/b)^2}$$

If we integrate the Gaussian over all x,

$$\int_{-\infty}^{\infty} e^{-(x/b)^2}\, dx = \sqrt{\pi}|b| \quad \text{so} \quad \int_{-\infty}^{\infty} \delta(x)\, dx = 1$$

Delta Function Definition and Properties

$$\delta(x) \equiv \lim_{b\to 0} \frac{1}{|b|\sqrt{\pi}} e^{-(x/b)^2} \qquad \int_{-\infty}^{\infty} f(x)\delta(x-\beta)\,dx = f(\beta) \qquad \delta(\beta x) = \frac{1}{|\beta|}\delta(x)$$

Delta Function Potential: Consider the case of a square well potential and a weakly bound state, where $\lambda \gg a$. Were we to consider the expectation value of $V(x)$ for this low-momentum state, we could approximate

$$\int_{-\infty}^{\infty} \psi^*(x)V(x)\psi(x)\,dx \sim \int_{-\infty}^{\infty} [\psi*(0) + x\psi'^*(0) + \cdots]V(x)[\psi(0) + x\psi'(0) + \cdots]\,dx \tag{6.94}$$

$$= \psi^*(0)\psi(0)\int_{-\infty}^{\infty} V(x)\,dx + (\psi'^*(0)\psi(0) + \psi^*(0)\psi'(0))\int_{-\infty}^{\infty} xV(x)\,dx + \cdots \tag{6.95}$$

For the limits of the well we get,

$$\psi^*(0)\psi(0)\int_{-a/2}^{a/2} (-V_0)\,dx + (\psi'^*(0)\psi(0) + \psi^*(0)\psi'(0))\int_{-a/2}^{a/2} x(-V_0)\,dx + \cdots \tag{6.96}$$

$$= -\psi^*(0)V_0 a\psi(0) + 0(\psi'^*(0)\psi(0) + \psi^*(0)\psi'(0)) + \cdots \tag{6.97}$$

$$= -V_0 a \int \psi^*(x)\delta(x)\psi(x)\,dx \tag{6.98}$$

where the second term vanishes because our potential is even. Therefore, our work above identifies

$$\int_{-\infty}^{\infty} \psi^*(x)V(x)\psi(x)\,dx \sim -aV_0 \int \psi^*(x)\delta(x)\psi(x)\,dx$$

These two potentials – $V(x)$ and $-aV_0\delta(x)$ would give us equivalent answers if we restrict our attention to low energies. For such low-momentum, long-wavelength states, this derivation suggests we can replace our square well interaction $V(x)$ with a simpler one:

$$V(x) \to V_\delta(x) \equiv -aV_0\delta(x)$$

This derivation showed that the delta function 'strength' in general is given by the integral

$$\int_{-a/2}^{a/2} V(x)\,dx$$

where $V(x)$ is the potential and a defines the region over which the unspecified potential is nonzero. We define $\alpha = aV_0$ to be the strength of the attractive finite well potential. The finite square well potential $V(x)$ and $V_\delta = \alpha\delta(x)$ should yield equivalent solutions of the Schrödinger equation that have wavelength $\lambda \gg a$.

But this also guarantees that we can take a similar limit of the square well potential itself, shrinking a and proportionally increasing V_0, since the proper delta function strength depends on the product $\alpha = aV_0$. This is nice because we have solved the square well, and can use those results for any a.

When counting the number of possible eigenstates in Equation 6.93, we found

$$\text{If } \pi^2\frac{\hbar^2}{2m} > a^2V_0 > 0, \text{ we have one even bound state}$$
$$\text{If } 4\pi^2\frac{\hbar^2}{2m} > a^2V_0 > \pi^2\frac{\hbar^2}{2m}, \text{ we have one even and one odd bound state}$$

In taking the delta function limit, we keep the product aV_0 constant. But the factor appearing above is $a^2V_0 = a\alpha$. Thus as we make a smaller, clearly at some point the second equation is unsatisfied. But the first states

$$a^2V_0 = \alpha a > 0$$

No matter how small we make a, keeping aV_0 fixed, this condition remains satisfied. We conclude

> An attractive delta function potential $V_\delta = -\alpha V_0\delta(x), \alpha > 0$, has exactly one even bound state, independent of the potential's strength α.

What is the strength of this bound state? The finite square well eigenvalue condition is

$$\frac{ka}{2}\tan\left(\frac{ka}{2}\right) = \frac{\kappa a}{2} \qquad k = \frac{\sqrt{2m(V_0 - |E|)}}{\hbar} \qquad \kappa = \frac{\sqrt{2m|E|}}{\hbar}$$

But as $a \to 0$,

$$\frac{ka}{2} = \sqrt{a}\frac{\sqrt{2ma(V_0 - |E|)}}{2\hbar} = \sqrt{a}\frac{\sqrt{2maV_0(1 - \frac{|E|}{V_0})}}{2\hbar} \to 0 \quad \text{so} \quad \frac{ka}{2}\tan\left(\frac{ka}{2}\right) \to \left(\frac{ka}{2}\right)^2$$

So our eigenvalue equation becomes

$$\frac{ka}{2}\tan\left(\frac{ka}{2}\right) = \frac{\kappa a}{2} \quad \Rightarrow \quad \left(\frac{ka}{2}\right)^2 = \frac{\kappa a}{2} \quad \text{exact as } a \to 0 \quad \Rightarrow \tag{6.99}$$

$$\frac{a}{4\hbar^2}2maV_0\left(1 - \frac{|E|}{V_0}\right) = \frac{a}{2\hbar}\sqrt{2m|E|} \quad \Rightarrow \quad \frac{m(aV_0)}{\hbar}\left(1 - \frac{|E|}{V_0}\right) = \sqrt{2m|E|} \tag{6.100}$$

$$\Rightarrow \quad \frac{m(aV_0)}{\hbar} = \sqrt{2m|E|} \quad \text{exact as } a \to 0 \tag{6.101}$$

Solving for $|E|$,

$$|E| = \frac{m(aV_0)^2}{2\hbar^2} = \frac{m\alpha^2}{2\hbar^2}$$

This result is also valid (for long wavelength ψ) for our finite well potential and a weakly bound state, but as noted, becomes *exact* when we take the delta function limit, keeping $\alpha = aV_0$ fixed. This makes sense, as in the limit *every* wave function is long compared to the delta function potential. In summary

> The bound state of a delta function potential $V_\delta = -\alpha\delta(x)$ has a binding energy of
>
> $$|E| = \frac{m\alpha^2}{2\hbar^2}$$

The other result we can derive concerns the derivative of the wave function at the delta function potential, or more correctly, the discontinuity of the derivative across the delta function. We saw in the case of the infinite square well that the derivative could be discontinuous at the interface with an infinite wall. (In all other cases, where there is no infinite potential, the wave function derivative must be continuous). Here the situation is not so clear, because the potential is going to infinity, but its width is going to zero...

Our finite square well solution left of the potential well is

$$\psi_L(x) = Ce^{\frac{\kappa a}{2}} \cos\frac{ka}{2} e^{\kappa x} \to Ce^{\kappa\left(x+\frac{a}{2}\right)}$$

And because we just showed in the delta function limit that $ka \sim \sqrt{a} \to 0$,

$$\psi'_L(x) = C\kappa e^{\kappa\left(x+\frac{a}{2}\right)} \to C\kappa \text{ as } x \to -\frac{a}{2}$$

And similarly on the right side,

$$\psi_R(x) \to Ce^{-\kappa\left(x-\frac{a}{2}\right)} \qquad \psi'_R(x) = -C\kappa e^{-\kappa\left(x-\frac{a}{2}\right)} \to -C\kappa \text{ as } x \to \frac{a}{2}$$

and as $\psi(x=0) = C$, one concludes

> The discontinuity of the derivative across $V_\delta = -\alpha\delta(x), \alpha > 0$ is
>
> $$\psi'_R(0) - \psi'_L(0) = -2\kappa\psi(0) = -2\frac{\sqrt{2m|E|}}{\hbar}\psi(0) = -\frac{2m\alpha}{\hbar^2}\psi(0). \qquad (6.102)$$
>
> The wave functions are continuous and $\frac{d\psi}{dx}$ is continuous except at points where the potential is infinite.

6.5.1 Wave Function Solution

Now

$$\kappa = \frac{\sqrt{2m|E|}}{\hbar} = \frac{m\alpha}{\hbar^2}$$

Our wave function normalization condition is

$$\int_{-\infty}^{0} |C|^2 e^{2\kappa x}\,dx + \int_{0}^{\infty} |C|^2 e^{-2\kappa x}\,dx = \frac{|C|^2}{\kappa} \quad \Rightarrow \quad C = \sqrt{\kappa} = \frac{\sqrt{m\alpha}}{\hbar}$$

Putting everything together, we have a universal bound state solution for an attractive delta function potential:

Delta Function Potential Solution

$$V_\delta(x) = -\alpha\delta(x), \alpha > 0$$

$$|E| = \frac{m\alpha^2}{2\hbar^2} \quad \kappa = \frac{m\alpha}{\hbar^2}$$

$$\psi(x) = \begin{cases} \sqrt{\kappa}e^{\kappa x}, & x < 0 \\ \sqrt{\kappa}e^{-\kappa x}, & x > 0 \end{cases} \quad \psi'(x) = \begin{cases} \kappa^{3/2}e^{\kappa x}, & x < 0 \\ -\kappa^{3/2}e^{-\kappa x}, & x > 0 \end{cases}$$

6.6 Review and Outlook

Let's review what we have done so far

1. We have studied bound states of the infinite square well, the harmonic oscillator, and the finite square well. In the last, the bound states were the states defined by $E < 0$.

2. In these problems we sought the stationary states, the solutions of the time-independent Schrödinger equation. This required us to solve eigenvalue equations – finding solutions only at certain energies. Consequently the energies were discrete. The eigenvalue conditions were somewhat different in detail, but conceptually similar:

   - For the infinite square well, the wave functions were required to vanish at the infinite potential wall.
   - For the bound states of the finite square well, we required continuity of the wave function and its derivative at the finite wall boundary. The eigenvalue equation came from this formula

$$\left.\frac{\psi'(x)}{\psi(x)}\right|_{x=-\frac{a}{2}-\epsilon} \leftrightarrow \left.\frac{\psi'(x)}{\psi(x)}\right|_{x=-\frac{a}{2}+\epsilon}$$

- For the harmonic oscillator, the eigenvalue equation comes from demanding that the wave function not increase at large r to maintain normalize ability. At certain energies this proved possible, yielding wave functions that die off as a Gaussian $e^{-\xi^2/2}$, times finite Hermite polynomials in ξ.

3. The resulting stationary states are normalizable and labeled by a discrete index n. Thus the stationary states are physical states we can prepare in a laboratory.

4. We also introduced free-particle states. These stationary states were labeled by a continuous index k, extended over all space, and were not normalizable. These states are still useful as a basis, but a single stationary state is not a candidate for a real physical state. We can not envision ever preparing such a state.

5. Our finite square well gave us another example of free but distorted states – states with $E > 0$ that extend over all space. These wave functions near the well get distorted by the well.

6. In all cases, the (complete set) stationary states can be used to expand any wave packet presented to us – a physical state. Under subsequent time evolution, the expansion coefficients remain, but each accumulates a distinct phase governed by the stationary state energy. Thus we obtain general solutions of the time-dependent Schrödinger equation. This is the prescription we call the *prime directive.* Note that for the finite well the complete basis requires both bound and continuum states.

This is amazing progress. However, there are a number of phenomena we know about classically which we can examine in quantum mechanics, as well as some phenomena with no classical analog. Phenomena without any classical analog often involve free ($E > 0$) but interacting states that encounter potential wells or hills, generating phenomena like reflection and transmission, or particle *spin* – which we will get to later. The next chapter deals with understanding reflection and transmission, the main concepts behind *quantum tunneling.* Afterwards we begin studying QM less tightly connected to wave functions.

6.7 Transmission and Reflection

6.7.1 Scattering off V_δ

We can utilize a simple delta function potential – either a well or a barrier – to scatter. As we have learned, this will give us a very accurate representation of scattering of much more complicated potentials, provided the deBroglie wavelength of the incident particle is significantly larger than the width of the barrier.

Consider scattering for a delta function potential at $x = 0$. $E > 0$ and the time-independent Schrödinger equation for $x < 0$ is

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \qquad k = \frac{\sqrt{2mE}}{\hbar} \qquad \Rightarrow \qquad \psi(x) = Ae^{ikx} + Be^{-ikx}$$

Likewise for $x > 0$,

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

Continuity at $x = 0$ requires

$$A + B = F + G$$

And we can compute the derivative on either side of the delta function,

$$\left.\frac{d\psi}{dx}\right|_R = ik(F - G) \tag{6.103}$$

$$\left.\frac{d\psi}{dx}\right|_L = ik(A - B) \tag{6.104}$$

So for an attractive well, combining both continuity conditions and our calculated derivative discontinuity across the delta potential from Equation 6.102,

$$V_\delta = -\alpha\delta(x) \quad \Rightarrow \quad ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}\psi(0) = -\frac{2m\alpha}{\hbar^2}(A + B) \tag{6.105}$$

$$\Rightarrow\ F - G = A(1 + 2i\beta) - B(1 - 2i\beta) \qquad \beta \equiv \frac{m\alpha}{\hbar^2 k} = \frac{\alpha}{\hbar}\sqrt{\frac{m}{2E}} \quad \beta^2 = \frac{m\alpha^2}{2\hbar^2 E} \tag{6.106}$$

There are two constraints and four unknowns – A, B, F, G, so to get a solution we need more information. Normalization is of no help, as these are free-particle non-normalizable states.

Recall that when we convert to time-dependent solutions, per the prime directive, a phase $e^{-iEt/\hbar}$ is added. When that is done, one sees

1. e^{ikx} generates a wave traveling with positive velocity (traveling to the right): it would be associated with a wave packet component $e^{i(kx-\omega t)}$ that travels to the right.

2. e^{-ikx} generates a wave with negative velocity (travels to the left).

So suppose we wish to describe the scattering of a wave packet coming in from the left, off our potential. Part of the wave will be reflected, moving back to the left. Some of it will be transmitted, going to the right, through the potential. But there is no wave to generate at positive x that is moving to the left. So if we set our initial conditions to reflect the experiment just described, we should require

$$G = 0$$

The experiment described is depicted in Figure 6.9 below.

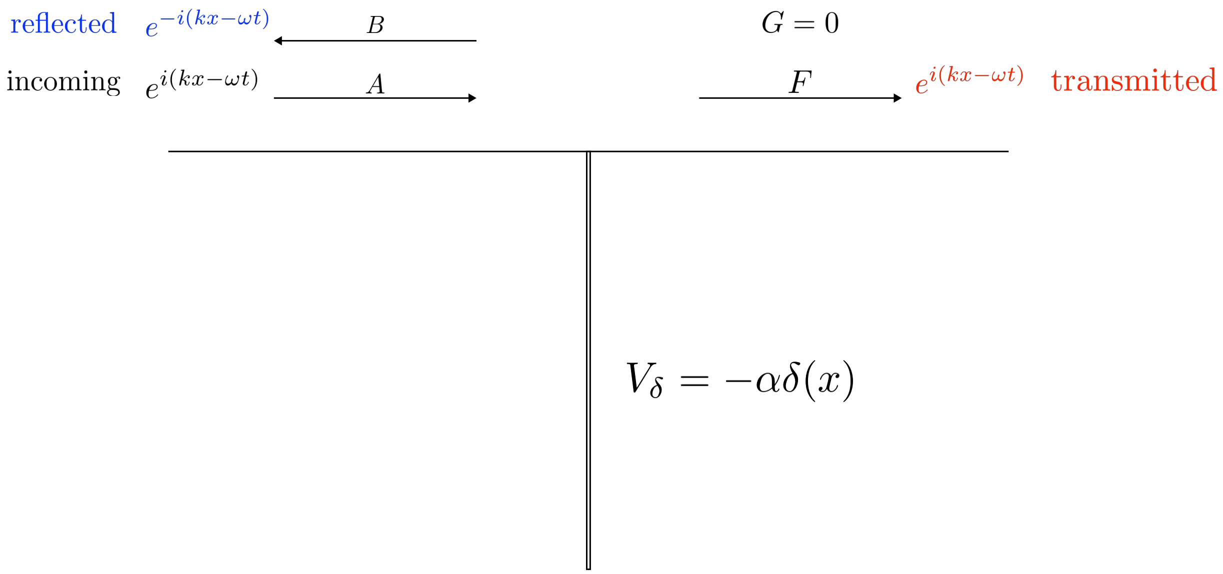


Figure 6.9: Scattering by a beam incident on a delta function potential from the left

A then corresponds to the amplitude of the incident wave coming in from the left. We can then solve our two equations to find

$$B = \frac{i\beta}{1-i\beta}A \qquad F = \frac{1}{1-i\beta}A \tag{6.107}$$

which should be interpreted as the amplitude of the reflected and transmitted wave, respectively. The probability of reflection is then

$$R = \frac{|B|^2}{|A|^2} \equiv \frac{|\text{Amplitude}_{\text{reflected}}|^2}{|\text{Amplitude}_{\text{incoming}}|^2} = \frac{\beta^2}{1+\beta^2} \tag{6.108}$$

Similarly, the probability of transmission is

$$T = \frac{|F|^2}{|A|^2} \equiv \frac{|\text{Amplitude}_{\text{transmitted}}|^2}{|\text{Amplitude}_{\text{incoming}}|^2} = \frac{1}{1+\beta^2} \tag{6.109}$$

You can check that $R+T=1$. Plugging in our expression for β,

Transmission and Reflection Coefficients – Delta Potential

$$V_\delta = \pm\alpha\delta(x) \quad \Rightarrow \quad T = \frac{1}{1+\beta^2} \quad R = \frac{\beta^2}{1+\beta^2} \quad \beta^2 = \frac{m\alpha^2}{2\hbar^2 E} \tag{6.110}$$

Note that we allowed for the scattering to be off a well or a *barrier*, as we found that the answer does not depend on the sign of α. We see

1. As $E \to 0$, $T \to 0$, $R \to 1$. The wave is fully reflected.
2. As $E \to \infty$, $T \to 1$, $R \to 0$. The wave is fully transmitted.
3. As $\alpha \to \infty$, $T \to 0$, $R \to 1$. The wave is fully reflected.
4. As $\alpha \to 0$, $T \to 1$, $R \to 0$. The wave is fully transmitted.

All of this is as expected classically. However, our barrier is infinitely high for any finite α, and yet there is always some transmission for any nonzero E. This is quantum mechanical tunneling.

6.7.2 Scattering off a Square Well

There are additional unique phenomena that are not captured in the delta-potential well calculation just outlined, but do emerge from scattering off a realistic well of equivalent strength $\alpha = aV_0$. The situation is depicted in Figure 6.10 below.

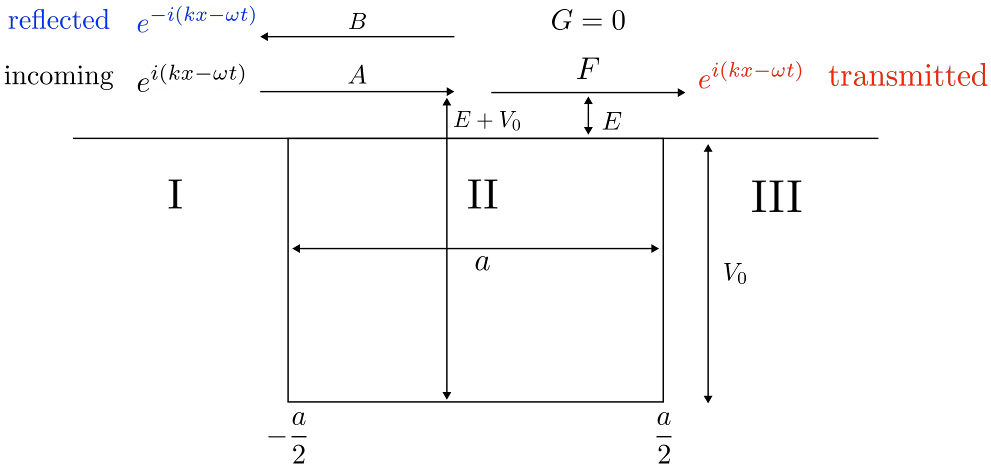


Figure 6.10: Scattering by a beam incident from the left on a well of depth V_0 and width a.

We will now repeat our previous calculations to see what new aspects arise from details of the well, beyond its net strength $\alpha \equiv aV_0$.

This is a slightly new problem for us as we are solving a problem involving the free states *above* the well, not bound states within. We define our kinematic variables in the usual way, remembering by assumption that $E > 0$,

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad l = \frac{\sqrt{2m(E+V_0)}}{\hbar}$$

Because of our experience above, we can speed things along by setting $G = 0$ as before. Only a transmitted wave is allowed in Region III.

I have previously stressed in earlier problems how much efficiency is gained by utilizing reflection symmetry. However now we require an asymmetric solution by setting $G = 0$. Consequently we have to deal with all three regions. The solutions in each region are

$$\psi(x) = \begin{cases} Fe^{ikx} & x > \frac{a}{2} \\ Ce^{ilx} + D^{-ilx} & -\frac{a}{2} < x < \frac{a}{2} \\ Ae^{ikx} + Be^{-ilx} & x < -\frac{a}{2} \end{cases}$$

We match solutions and their derivatives at the boundary of regions II and III ($x = \frac{a}{2}$). We yield

$$\begin{aligned} Fe^{ika/2} &= Ce^{ila/2} + De^{-ila/2} \\ ikFe^{ika/2} &= il\left(Ce^{ila/2} - D^{-ila/2}\right) \end{aligned}$$

As there are two constraints, F determines C and D. Doing (a lot of) the algebra,

$$C = F\left(\frac{l+k}{2l}\right)e^{i(k-l)\frac{a}{2}} \qquad D = F\left(\frac{l-k}{2l}\right)e^{i(k+l)\frac{a}{2}} \tag{6.111}$$

Now we need to match the boundary of regions I and II ($x = -\frac{a}{2}$). Let's first use the information above to write out the solutions in the two regions.

$$\psi(x) = \begin{cases} F\left(\frac{l+k}{2l}\right)e^{ika/2}e^{il(x-a/2)} + F\left(\frac{l-k}{2l}\right)e^{ika/2}e^{-il(x-a/2)} & -\frac{a}{2} < x < \frac{a}{2} \\ Ae^{ikx} + Be^{-ikx} & x < -\frac{a}{2} \end{cases}$$

The continuity of the wave function and its derivative yields

$$\begin{aligned} F\left(\frac{l+k}{2l}\right)e^{ika/2}e^{-ila} + F\left(\frac{l-k}{2l}\right)e^{ika/2}e^{ila} &= Ae^{-ika/2} + Be^{ika/2} \\ il\left[F\left(\frac{l+k}{2l}\right)e^{ika/2}e^{-ila} - F\left(\frac{l-k}{2l}\right)e^{ika/2}e^{ila}\right] &= ik\left[Ae^{-ika/2} - Be^{ika/2}\right] \end{aligned}$$

These two constraints can be used to eliminate A and B. Doing (again a lot of) algebra,

$$A = F\frac{e^{ika}}{4lk}\left[(l+k)^2 e^{-ila} - (l-k)^2 e^{ila}\right] \tag{6.112}$$

$$B = F\frac{(l+k)(l-k)}{4lk}\left[e^{ila} - e^{-ila}\right] \tag{6.113}$$

When all the dust clears, we have a solution in which only one unknown constant F remains. This is no problem since F will cancel when calculating the transmission and reflection ratios.

$$\psi(x) = \begin{cases} Fe^{ikx} & x > \frac{a}{2}, \\ F\frac{e^{ika/2}}{2l}\left[(l+k)e^{il(x-a/2)} + (l-k)e^{-il(x-a/2)}\right] & -\frac{a}{2} < x < \frac{a}{2}, \\ Fe^{ikx}\frac{1}{4lk}\left[(l+k)^2 e^{i(k-l)a} + (l-k)^2 e^{i(k+l)a}\right] + Fe^{-ikx}\frac{(l^2-k^2)}{4lk}2i\sin la & x < -\frac{a}{2}. \end{cases} \tag{6.114}$$

From this we identify

$$\text{transmitted wave :} \qquad Fe^{ikx} \qquad x > \frac{a}{2} \tag{6.115}$$

$$\text{incoming wave :} \qquad Fe^{ikx}\frac{1}{4lk}\left[(l+k)^2 e^{i(k-l)a} - (l-k)^2 e^{i(k+l)a}\right] \qquad x < -\frac{a}{2} \tag{6.116}$$

$$\text{reflected wave :} \qquad Fe^{-ikx}\frac{(l^2-k^2)}{4lk}2i\sin la \qquad x < -\frac{a}{2} \tag{6.117}$$

We can now calculate the ratios of reflection and transmission.

Transmission and Reflection Coefficients – Finite Well

$$R = \text{ Prob. of reflection } = \frac{|A_{\text{reflect}}|^2}{|A_{\text{incoming}}|^2} = \frac{4(l^2-k^2)\sin^2 la}{(4lk)^2 + 4(l^2-k^2)^2\sin^2 la} \tag{6.118}$$

$$= \frac{(l^2-k^2)\sin^2 la}{(2lk)^2 + (l^2-k^2)^2\sin^2 la} \tag{6.119}$$

$$T = \text{ Prob. of transm } = \frac{|A_{\text{transmission}}|^2}{|A_{\text{incoming}}|^2} = \frac{(4lk)^2}{(4lk)^2 + 4(l^2-k^2)^2\sin^2 la} \tag{6.120}$$

$$= \frac{(2lk)^2}{(2lk)^2 + (l^2-k^2)^2\sin^2 la} \tag{6.121}$$

6.7.3 Perfect Transmission

Physically we argued that $V_\delta = -\alpha\delta(x)$ should be effectively equivalent to a square well solution if the scattered particle's wavelength is very large relative to a. For the finite well our kinematic variable l

$$l = \frac{\sqrt{2m(E+V_0)}}{\hbar}$$

Thus, for a particle's wavelength λ_l to be much larger than a,

$$\lambda_l = \frac{2\pi}{l} \gg a \quad \Rightarrow \quad l \ll \frac{2\pi}{a}$$

Consequently, V_δ fails to capture an interesting aspect of real wells – the fact that $T \to 1$ when $\sin^3 la = 0$. This occurs at

$$la = n\pi, \; n = 1, 2, 3 \ldots$$

The physics of this effect is shown below in Figure 6.11, drawn for $la = 2\pi$.

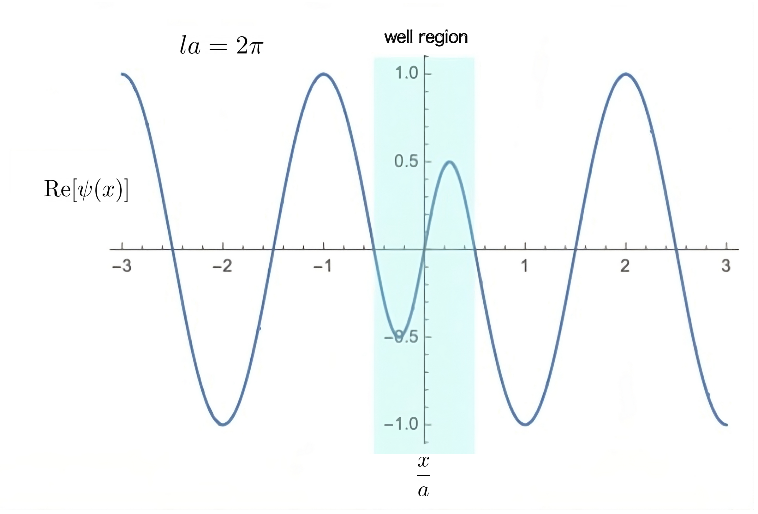


Figure 6.11: Perfect transmission, $la = 2\pi$

One sees that the wave function while in the well executes exactly a 2π phase change and consequently, since our wave functions and their derivatives are continuous, one could "cut out" the well from $-a/2$ to $a/2$ and patch the two exterior pieces together with no change in the wave function phase from scattering.

6.7.4 Comparing V_δ and the Square Well

A bit of algebra and the identification $\alpha = aV_0$ yields the following relations

$$ka = \frac{a\sqrt{2mE}}{\hbar} = \frac{a\sqrt{2mV_0}}{\hbar}\sqrt{\frac{E}{V_0}} \qquad la = \frac{a\sqrt{2mV_0}}{\hbar}\sqrt{1+\frac{E}{V_0}} \qquad \beta^2 = \frac{m\alpha^2}{2\hbar^2 E} = \frac{m\alpha^2 V_0}{2\hbar^2}\frac{V_0}{E}$$

We will consider the scattering off three wells of different strengths in the ratio of $\frac{1}{16}$: 1 : 16 : 256,

$$V_0 = \frac{\hbar^2}{32ma^2} \qquad V_0 = \frac{\hbar^2}{2ma^2} \qquad V_0 = \frac{8\hbar^2}{ma^2} \qquad V_0 = \frac{128\hbar^2}{ma^2}$$

which then yields

$$V_0 = \frac{\hbar^2}{32ma^2} \quad \Rightarrow \quad ka = \frac{1}{4}\sqrt{\frac{E}{V_0}} \qquad la = \frac{1}{4}\sqrt{1+\frac{E}{V_0}} \qquad \beta^2 = \frac{1}{64}\frac{V_0}{E} \tag{6.122}$$

$$V_0 = \frac{\hbar^2}{2ma^2} \quad \Rightarrow \quad ka = \sqrt{\frac{E}{V_0}} \qquad la = \sqrt{1+\frac{E}{V_0}} \qquad \beta^2 = \frac{1}{4}\frac{V_0}{E} \tag{6.123}$$

$$V_0 = \frac{8\hbar^2}{mas^2} \quad \Rightarrow \quad ka = 4\sqrt{\frac{E}{V_0}} \qquad la = 4\sqrt{1+\frac{E}{V_0}} \qquad \beta^2 = 4\frac{V_0}{E} \tag{6.124}$$

$$V_0 = \frac{128\hbar^2}{ma^2} \quad \Rightarrow \quad ka = 16\sqrt{\frac{E}{V_0}} \qquad la = 16\sqrt{1+\frac{E}{V_0}} \qquad \beta^2 = 64\frac{V_0}{E} \tag{6.125}$$

The progression increases the depth of the well while keeping fixed width. This identifies E/V_0 as the “control parameter” for the scattering.

Let’s analyze the λ/a ratios for particles at the top of the well ($E = V_0$) each of the four cases.

First Case: $V_0 = \frac{\hbar^2}{32ma^2}$

$$\text{at } E = V_0, \qquad \frac{\lambda_k}{a} = 8\pi \quad \frac{\lambda_l}{a} = 4\sqrt{2}\pi \quad \beta^2 = \frac{1}{64}$$

Second Case: $V_0 = \frac{\hbar^2}{2ma^2}$

$$\text{at } E = V_0, \qquad \frac{\lambda_k}{a} = 2\pi \quad \frac{\lambda_l}{a} = \sqrt{2}\pi \quad \beta^2 = \frac{1}{4}$$

Third Case: $V_0 = \frac{8\hbar^2}{ma^2}$

$$\text{at } E = V_0, \qquad \frac{\lambda_k}{a} = \frac{\pi}{2} \quad \frac{\lambda_l}{a} = \frac{\pi}{2\sqrt{2}} \quad \beta^2 = 4$$

Fourth Case: $V_0 = \frac{128\hbar^2}{ma^2}$

$$\text{at } E = V_0, \qquad \frac{\lambda_k}{a} = \frac{\pi}{8} \quad \frac{\lambda_l}{a} = \frac{\pi}{8\sqrt{2}} \quad \beta^2 = 64$$

In the first case, the wavelengths are very long compared to the well both in the exterior and interior. The potential is weak, and the delta function representation might work well up to fairly high energies. In the second case, wavelengths are on the order $2\pi a$ – the well’s shape should start to play a role at incident energies comparable to the well depth. And in the third case, the well can definitely be detected, and one suspects that the delta function representation will certainly have failed as E is increased toward V_0.

We can plot our transmission and reflection coefficients as a function of ka parameterized by V_0/E. Results are shown in Figure 6.12 as a function of E/V_0. We should expect that as $E/V_0 \to 1$, for higher V_0, the delta function and square well results to spread apart. The delta function results (orange) and square well results (blue) only agree at small ka (and la).

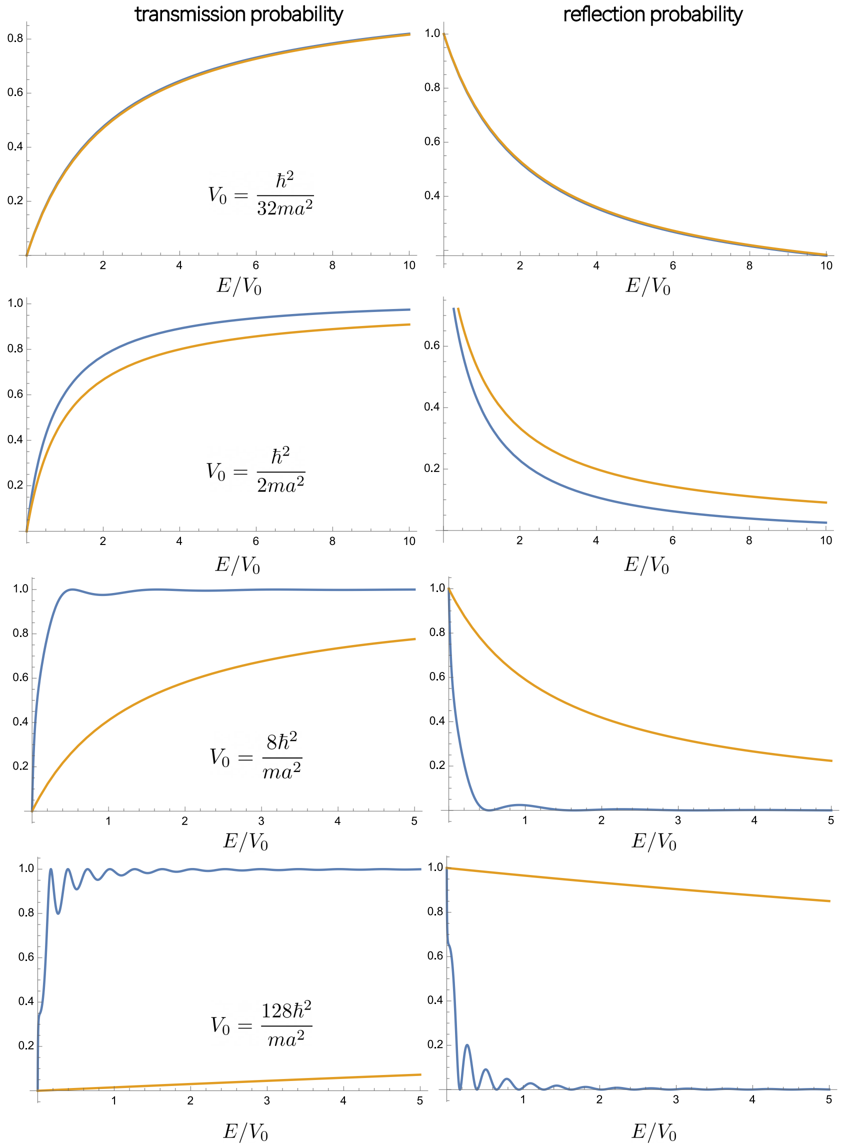


Figure 6.12: Transmission and Reflection Coefficients plotted for increasing V_0. Blue represents the square well potential and orange represents delta function potential of equivalent strength.

This concludes our introduction to the fundamental problems in Quantum Mechanics. By now, you should have a strong grasp of the methods used to solve the time-independent Schrödinger equation for basic potentials, providing a solid foundation for the material to come. It's not necessary to memorize every algebraic step or derivation for each potential discussed. Instead, focus on developing an intuitive sense of how these problems are approached and solved. What matters most is understanding the general procedure for solving these problems and truly comprehending the underlying principles of each derivation.

Next chapter presents ways of thinking of Quantum Mechanics less tightly connected to wave functions. We are diving directly into Quantum theory.

Chapter 7

Quantum Mechanics Formalism

We have so far focused on wave functions and their properties, developing some intuition about wave mechanics. A few curiosities may have struck you however. For example, we found in the harmonic oscillator that we could express the Hamiltonian (once we chose the right variables) in terms of a dimensionless operator

$$\frac{\hbar\omega}{2}\left(\hat{p}_\xi^2+\hat{\xi}^2\right) \quad \rightarrow \frac{\hbar\omega}{2}\left(\hat{p}_\xi^2+\xi^2\right)$$

Most textbooks, notably Griffiths, have the habit of indicating $\hat{p}$ is an operator, but dropping the "hat" on $\hat{x} \rightarrow x$. Why is this? At an even more basic level, the harmonic oscillator is manifestly symmetric in $\hat{p}$ and $\hat{x}$, yet our wave function formalism favored x. When we operate on our wave function with the $\hat{x}$ operator we just get back the value x. But when we act with $\hat{p}$, we have to take a derivative. Where did we lose the $p-x$ symmetry?

It has been lost because we choose a basis for representing our states – a position basis. We will now review some of what we know about vectors and their representations. Take the example of a vector $\vec{v}$ in 3D space. We are aware that this is a geometrical object, with a length and a direction, that exists independent of the basis we select to represent the vector. We will denote this abstract vector, without a specified basis, with the following notation of Dirac – $|\vec{v}\rangle$.

7.1 Dirac Notation

Suppose we have a vector in ordinary 3D space. That vector is a geometric object, consisting of a length and direction, independent on the basis we choose. We could choose to *represent* the vector in a specific basis. For example, the basis could be taken to be the three Cartesian unit vectors

$$\hat{e}_x,\ \hat{e}_y,\ \hat{e}_y \quad \Rightarrow \quad |\hat{e}_x\rangle,\ |\hat{e}_y\rangle,\ |\hat{e}_z\rangle$$

The bases we use satisfy two important conditions. The first requirement on our basis vectors is *orthonormality*,

$$\langle\hat{e}_i|\hat{e}_j\rangle = \langle i|j\rangle = \delta_{ij} \qquad \{i,j\} \in \{x,\ y,\ z\}$$

That is, our basis vectors are unit vectors orthogonal to one another. The second, implicit when we expand a vector $|\alpha\rangle$ in a basis, is *completeness.*

$$\sum_{i\in\{x,y,z\}} |\hat{e}_i\langle\hat{e}_i|\rangle \equiv \sum_i |i\rangle\langle i| = 1$$

We use this result when we represent a vector in terms of an orthonormal basis. Thus

$$|\vec{v}\rangle = \sum_i |\hat{e}_i\rangle\langle\hat{e}_i|\vec{v}\rangle = |\hat{e}_x\rangle v_x + |\hat{e}_y\rangle v_y + |\hat{e}_z\rangle v_z$$

These requirements involve both vectors, e.g., $|\alpha\rangle$, and adjoint vectors, $\langle\alpha|$, which I explain below.

One is free to choose any basis satisfying the conditions above, a freedom that can be used to simplify many problems. For example, if one is working in 3D and interested in a problem with spherical symmetry, an alternative basis that transforms more simply under rotations is the spherical basis:

$$|\hat{e}_1\rangle = -\frac{1}{\sqrt{2}}(|\hat{e}_x\rangle + i|\hat{e}_y\rangle) \qquad |\hat{e}_0\rangle = |\hat{e}_z\rangle \qquad |\hat{e}_{-1}\rangle = \frac{1}{\sqrt{2}}(|\hat{e}_x\rangle - i|\hat{e}_y\rangle)$$

Here the adjoint basis vectors are

$$\langle\hat{e}_1| = -\frac{1}{\sqrt{2}}(\langle\hat{e}_x| - i\langle\hat{e}_y| \qquad \langle\hat{e}_0| = \langle\hat{e}_z| \qquad \langle\hat{e}_{-1}| = \frac{1}{\sqrt{2}}(\langle\hat{e}_x| + i\langle\hat{e}_y|)$$

That is, $\langle\alpha|$ is the *conjugate transpose* of $|\alpha\rangle$. For this basis one can readily verify orthonormality and completeness. Consequently we can also represent a vector in 3D in a spherical basis

$$|\vec{v}\rangle = \sum_i |\hat{e}_i\rangle\langle\hat{e}_i|\vec{v}\rangle = |\hat{e}_{-1}\rangle v_{-1} + |\hat{e}_0\rangle v_0 + |\hat{e}_1\rangle v_1$$

The discussion above can be generalized beyond simple vectors in 3D, as we can represent any vector $|\alpha\rangle$ of finite dimension N similarly,

$$|\alpha\rangle = \sum_{i=1}^{N} |i\rangle\langle i|\alpha\rangle = \sum_{i=1}^{N} \alpha_i |i\rangle$$

in terms of a chosen N-dimensional set of unit basis vectors. Here $\langle i|\alpha\rangle$ is a scalar, the inner product defined below. The adjoint (conjugate transpose) of a vector is defined by

$$\langle\alpha| \equiv |\alpha\rangle^\dagger = \sum_{i=1}^{N} \langle\alpha|i\rangle\langle i\rangle = \sum_{i=1}^{N} \alpha_i^* \langle i\rangle$$

That is, the inner product satisfies

$$\langle i|\alpha\rangle^* = \langle\alpha|i\rangle.$$

We can think of $|\alpha\rangle$ represented in a basis as a column vector whose entries are the expansion coefficients in that basis

$$|\alpha\rangle = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{pmatrix}$$

Correspondingly, the adjoint vector can be viewed as a row matrix in that basis,

$$\langle\alpha| = (\alpha_1^*,\ \alpha_2^*,\ \cdots,\ \alpha_N^*)$$

7.2 Infinite Dimensional Representations and Wave Functions

On several occasions (infinite square well, harmonic oscillator) we have expanded initial wave packets over stationary states that were discrete (like above) but infinite dimensional (unlike above), obtaining an expression for the wave function that could be used with the prime directive to determine the time evolution of the wave packet.

$$\Psi(x,t=0) = \sum_{i=1}^{\infty} c_i\psi_i(x) \quad \text{where} \quad c_i = \int_\Omega \psi_i^*(y)\Psi(y,t=0)\,dy$$

where Ω is the relevant domain). Let's assume we have a problem like the harmonic oscillator where the wave functions extend over all space ($\Omega \equiv -\infty < x < \infty$). In this case,

$$\Psi(x,t=0) = \sum_{i=1}^{\infty} c_i\psi(x) \quad \text{where} \quad c_i \int_{-\infty}^{\infty} \psi_i^*(y)\Psi(y,t=0)\,dy$$

where $\psi_i(y)$ are the stationary state wave functions.

Can we extract this result from the more abstract Dirac-formulation described just above? Consider

$$|\Psi(t=0)\rangle = \sum_{i=1}^{\infty} |\psi_i\rangle\langle\psi_i|\Psi(t=0)\rangle \tag{7.1}$$

We introduce the complete set of normalized position states (postponing additional discussion until later). As position is a continuous quantum number,

$$1 = \sum_i |\hat{e}_i\rangle\langle\hat{e}_i| \quad \Rightarrow \quad 1 = \int_{-\infty}^{\infty} |y\rangle\langle y|\, dy$$

Consequently,

$$|\Psi(t=0)\rangle = \int_{-\infty}^{\infty} |y\rangle\langle y|\Psi(t=0)\rangle \tag{7.2}$$

Inserting this into Equation 7.1 then yields

$$|\Psi(t=0)\rangle = \sum_{i=1}^{\infty} |\psi_i\rangle \int_{-\infty}^{\infty} \langle\psi_i|y\rangle\langle y|\Psi(t=0)\rangle\, dy$$

Finally we take the scalar product with $\langle x|$,

$$\langle x|\Psi(t=0)\rangle = \sum_{i=1}^{\infty} \langle x|\psi_i\rangle \int_{-\infty}^{\infty} \langle\psi_i|y\rangle\langle y|\Psi(t=0)\rangle\, dy \tag{7.3}$$

Now if we define the wave function as the quantity

$$\Psi(x, t=0) = \langle x|\Psi(t=0)\rangle$$

and likewise with the other quantities appearing in Equations 7.2 and 7.3, those equations become

$$(7.2') \quad |\Psi(t=0)\rangle = \int_{-\infty}^{\infty} \Psi(y,t)|y\rangle\, dy \qquad (7.3') \quad |\Psi(x,t=0)\rangle = \sum_{i=1}^{\infty} \psi_i(x) \int_{-\infty}^{\infty} \psi_i^*(y)\Psi(y,t=0)\, dy$$

Equation 7.3' is just the expression we have been using up to this point, where we expand the initial wave packet in terms of stationary-state wave functions, prior to employing the prime directive. Equation 7.2' identifies the wave function $\psi(x)$ as the coefficients of the expansion of the state $|\psi\rangle$ in terms of the position basis functions $|x\rangle$. In other words, wave functions are expansion coefficients, analogous to the c_i that arose in the discrete case we described first.

The notion of expansions and wave functions lead to an interpretation of the wave function as a particular representation of a more basic and more object, abstract state – Dirac's "ket", which he denoted as $|\Psi\rangle$.

7.2.1 Summary

We now recognize wave functions are just a particular representation of a more fundamental quantity, the state vector $|\Psi\rangle$, that exists independent of the representation, just as an ordinary 3D vector exists independent of any coordinate basis. However, one always has the freedom to select a basis, to represent both state vectors and their adjoins. In Dirac's notation,

Dirac Notation

$$\text{Dirac's Ket: } |\Psi\rangle \quad \text{representation in a basis } i\text{: } |\Psi\rangle \equiv \sum_i |i\rangle\langle i|\Psi\rangle \equiv \sum_i |i\rangle c_i$$

$$\text{Dirac's Bra: } \langle\Psi| \quad \text{representation in a basis } i\text{: } \langle\Psi| \equiv \sum_i \langle\Psi|i\rangle\langle i| \equiv \sum_i \langle i|c_i^*$$

If the basis is described by a continuous index rather than a discrete one like i, the sum is replaced with an integral.

Up to this point we have repeatedly dealt with states of infinite dimension, representing them by taking an integral over the position eigenstates,

$$\sum_i |i\rangle\langle i| \equiv 1 \quad \Rightarrow \quad \int |x\rangle\langle x|\, dx = 1$$

We used the position eigenstate representation and an inner product defined over the vector space of functions,

$$\delta_{\beta a} = \langle\psi_\beta|\psi_\alpha\rangle \Rightarrow \int \langle\psi_\beta|x\rangle\langle x|\psi_\alpha\rangle\, dx = \int \langle x|\psi_\beta\rangle^* \langle x|\psi_\alpha\rangle\, dx = \int \psi_\beta^*(x)\psi_\alpha(x)\, dx$$

7.3 Continuous Spectra, Momentum, and Position Wave Functions

The *spectrum* of an operator is defined as the set of possible outcomes after measurement.

If the spectrum of a Hamiltonian, or any other quantum mechanical operator is continuous, the eigenfunctions are not normalizable – not part of the "Hilbert Space" we will describe soon. For example, in the infinite square well and harmonic oscillator, we found the resultant eigenfunctions / wave functions to be discrete in energy, following

$$\text{Infinite Square Well: } E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2} \qquad \text{Harmonic Oscillator: } E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

If you refer back to Figures 6.5 and 6.2 you will see the spectrum of the Hamiltonian is discrete – only certain wave functions are allowed at specific energies. Because the set of wave functions, the spectrum, is not continuous, the wave functions are normalizable.

7.3.1 Momentum-Position Symmetry

Now that we understand the Dirac formulation of Quantum mechanics, let's return to our question at the beginning of this chapter – why the momentum operator $\hat{p}$ requires a derivative, yet the position operator $\hat{x} \to x$ just returns x. I answered that the reason for this is our choice of representing our quantum states with the position basis – $\psi(x)$. Let's try to understand this more closely.

In the *position basis*, the position operator $\hat{x}$ acting on a position eigenstate $|x\rangle$ yields

$$\hat{x}|x\rangle = x|x\rangle$$

Because $p \leftrightarrow x$ are manifestly symmetric, in the *momentum basis*, the momentum operator $\hat{p}$ acting on a momentum eigenstate $|p\rangle$ yields

$$\hat{p}|p\rangle = p|p\rangle$$

However, in the position basis, from our Dirac formulation, this equation can also be written as

$$\hat{p}\langle x|p\rangle = p\langle x|p\rangle$$

Here, $\langle x|p\rangle$ is the wave function of the momentum eigenstate $|p\rangle$, in the position basis. Substituting in the momentum operator $\hat{p} = -i\hbar\frac{d}{dx}$ into the above equation,

$$-i\hbar\frac{d}{dx}\langle x|p\rangle = p\langle x|p\rangle$$

This is a first-order differential equation. We separate the variables,

$$\frac{d}{dx}\langle x|p\rangle = \frac{ip}{\hbar}\langle x|p\rangle \tag{7.4}$$

$$\frac{1}{\langle x|p\rangle}\frac{d}{dx}\langle x|p\rangle = \frac{ip}{\hbar} \tag{7.5}$$

Integrating,

$$\int \frac{1}{\langle x|p\rangle}\frac{d\langle x|p\rangle}{dx}\,dx = \int \frac{ip}{\hbar}\,dx$$

Finally,

$$\ln\langle x|p\rangle = \frac{ipx}{\hbar} + C \tag{7.6}$$

$$\langle x|p\rangle = Ae^{\frac{ipx}{\hbar}} \tag{7.7}$$

The expression $\langle x|p\rangle = Ae^{ipx/\hbar}$ thus represents the wave function of the momentum eigenstate in the position basis. To solve for A, we normalize,

$$\langle p'|p\rangle = \int_{-\infty}^{\infty} \langle p'|x\rangle\langle x|p\rangle\, dx = A^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar}\, dx = |A^2|2\pi\hbar\delta(p-p')$$

Therefore to allow $\langle p'|p\rangle = \delta(p'-p)$, i.e. satisfying orthonormality (both orthogonality and normalization), $A = \frac{1}{\sqrt{2\pi\hbar}}$. Thus

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} \qquad \text{then} \qquad \langle p'|p\rangle = \delta(p'-p)$$

Griffiths calls this *Dirac-Delta Orthonormality.* These wave functions form a complete basis that can expand any normalizable state vector. We note

$$\int_{-\infty}^{\infty} |p\rangle\langle p|\, dp = \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} |x\rangle\langle x|p\rangle\langle p|x'\rangle\langle x'|\, dx' = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} |x\rangle\langle x'|e^{ip(x-x')/\hbar}\, dx' \tag{7.8}$$

$$= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} |x\rangle\langle x'|\delta(x-x')\, dx' = \int_{-\infty}^{\infty} |x\rangle\langle x|\, dx = 1 \tag{7.9}$$

Thus we can use these momentum eigenstates just as we use the position eigenstates. Given a state vector $|\alpha\rangle$, we can insert a complete set to determine

$$|\alpha\rangle = \int_{-\infty}^{\infty} |p\rangle\langle p|\alpha\rangle\, dp = \int_{-\infty}^{\infty} |p\rangle\psi_\alpha(p)$$

Then taking the inner product with $\langle x|$,

$$\psi_\alpha(x) \equiv \langle x|\alpha\rangle = \int_{-\infty}^{\infty} \langle x|p\rangle\langle p|\alpha\rangle\, dp = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} e^{ipx/\hbar}\psi_\alpha(p)\, dp$$

And conversely,

$$\psi_\alpha(p) = \langle p|\alpha\rangle = \int_{-\infty}^{\infty} \langle p|x\rangle\langle x|\alpha\rangle\, dx = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} e^{-ipx/\hbar}\psi_\alpha(x)\, dx$$

The momentum wave function is the Fourier transform of the position wave function! Hence the symmetry.

This raises a question we have not yet answered – what is the *wave function* of a position state? That is, we have a position ket $|x_0\rangle$ with

$$\hat{x}|x_0\rangle = x_0|x_0\rangle$$

So inserting a complete set of position states,

$$|x_0\rangle = \int_{-\infty}^{\infty} |x\rangle\langle x|x_0\rangle\, dx \equiv \int_{-\infty}^{\infty} |x\rangle \psi_{x_0}(x)\, dx \quad \Rightarrow \quad \psi_{x_0} = \delta(x - x_0)$$

7.3.2 Example Problem – Schrödinger equation to the wave equation

We have learned that the Schrödinger equation wave functions that we have focused on thus far of are a particular representation – in position space – of a *more fundamental* equation that can be written out in terms of an abstract state vector and operators acting on it. Let's try to go from the abstract equation to the wave equation. We start with an elementary Hamiltonian energy eigenvalue equation:

$$\left[-\frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})\right] |\alpha\rangle = E|\alpha\rangle$$

We take the inner product with $\langle x|$,

$$\langle x| \left[-\frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})\right] |\alpha\rangle = E\langle x|\alpha\rangle = E\psi_\alpha(x)$$

So far so good, we have the wave function on the right. Now

$$\langle x|\hat{V}(x)|\alpha\rangle = \int_{-\infty}^{\infty} \langle x|\hat{V}(\hat{x})|x'\rangle\langle x'|\alpha\rangle\, dx' = \int_{-\infty}^{\infty} V(\hat{x'})\langle x|x'\rangle\langle x'|\alpha\rangle\, dx' = \int_{-\infty}^{\infty} V(x')\delta(x - x')\psi_\alpha(x')\, dx' = V(x)\psi_\alpha(x)$$

In the next section, where we discuss *Hermitian* operators, we will be able to obtain the same result more efficiently. $\hat{V}$ is Hermitian, and such operators can be moved from the ket to the bra in the following way,

$$\langle x|\hat{V}(\hat{x})|\alpha\rangle = \langle \hat{V}(\hat{x})x|\alpha\rangle = V(x)\langle x|\alpha\rangle = V(x)\psi_\alpha(x)$$

obtaining the same result as above. And for $\hat{p}^2$,

$$\langle x|\hat{p}^2|\alpha\rangle = \int_{-\infty}^{\infty} \langle x|\hat{p}^2|p\rangle\langle p|\alpha\rangle\, dp = \int_{-\infty}^{\infty} p^2\langle x|p\rangle\langle p|\alpha\rangle\, dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} p^2 e^{-ipx/\hbar}\langle p|\alpha\rangle\, dp \tag{7.10}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \left(-\hbar^2 \frac{d^2}{dx^2}\right) e^{ipx/\hbar}\langle p|\alpha\rangle\, dp = \int_{-\infty}^{\infty} \left(-\hbar^2 \frac{d^2}{dx^2}\right) \langle x|p\rangle\langle p|\alpha\rangle\, dp = \left(-\hbar^2 \frac{d^2}{dx^2}\right) \langle x|\alpha\rangle \tag{7.11}$$

$$= \left(-\hbar^2 \frac{d^2}{dx^2}\right) \psi_\alpha(x) \tag{7.12}$$

Putting the pieces together, we get our familiar position-space wave function equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_\alpha(x) = E\psi_\alpha(x)$$

7.4 Hilbert Spaces, Hermitian Operators

Here, we review the properties of vector spaces and scalar products, connecting them to function spaces and integration. These concepts allow us to extract scalars – representing amplitudes and observables – from our infinite-dimensional vectors (functions).

7.4.1 Hilbert Spaces

The Hilbert spaces in which quantum mechanical state vectors and operators reside are vector spaces to which an inner product has been added, one with specific properties connecting to our quantum mechanical requirements that $|\psi(x)|^2$ be normalizable.

Inner Product Spaces

Inner product spaces are vector spaces with an inner product defined on them. The inner product of two vectors $|\alpha\rangle$ and $|\beta\rangle$ is a mapping from these vectors to a scalar in the scalar field of the vector space, $\langle u|v\rangle = a$. In our applications this is a complex scalar. The inner product (or scalar product) has the following properties:

1. $\langle\gamma|\alpha+\beta\rangle = \langle\gamma|\alpha\rangle + \langle\gamma|\beta\rangle$
2. $\langle\beta|a\alpha\rangle = a\langle\beta|\alpha\rangle$
3. $\langle\alpha|\alpha\rangle \geq 0$
4. $\langle\alpha|\beta\rangle^* = \langle\beta|\alpha\rangle$

Note that

$$\langle\alpha+\beta|\gamma\rangle = \langle\gamma|\alpha+\beta\rangle^* = \langle\gamma|\alpha\rangle^* + \langle\gamma|\beta\rangle^* = \langle\alpha|\gamma\rangle + \langle\beta|\gamma\rangle$$
$$\langle a\alpha|\beta\rangle = \langle\beta|a\alpha\rangle^* = (a\langle\beta|\alpha\rangle)^* = a^*\langle\alpha|\beta\rangle$$
$$|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle$$

The last result, the triangle inequality, is familiar from ordinary vectors in geometry,

$$|\vec{a}\cdot\vec{b}| = |ab\cos\theta| \leq ab \quad \Rightarrow |\langle a|b\rangle|^2 \leq \langle a|a\rangle\langle b|b\rangle$$

The triangle inequality takes the form of the Schwarz inequality the infinite-dimensional vector spaces use in quantum mechanics

$$|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \to \left|\int_a^b \psi_2^*(x)\psi_1(x)\,dx\right|^2 \leq \int_a^b |\psi_1(x)|^2\,dx \int_a^b |\psi_2(x)|^2\,dx$$

The normalizable stationary states we have derived form complete basis in an infinite dimensional complex vector space with these properties. Such spaces are called *Hilbert spaces.* Specifically, our vector space of states includes only those whose wave functions are *square integrable.* Thus this choice of functions (our vectors describing physical states) along with the complex numbers (our scalar field) and the inner product defined as above, constitutes our Hilbert space.

7.4.2 Observables as expectations of Hermitian operators

We want to define the properties of operators whose expectation values correspond to possible quantum mechanical measurements. We note operators with their "hats" $\hat{Q}$. Operators act on states to produce new states:

$$\hat{Q}|\alpha\rangle = |\hat{Q}\alpha\rangle \equiv |\beta\rangle$$

Here an operator $\hat{Q}$ acts on a state $|\alpha\rangle$ to produce a new state $|\hat{Q}\alpha\rangle$. If we want we can give this new state a different name – we call it $|\beta\rangle$.

We have discussed how abstract states can be represented in a basis that we select, by using completeness of this basis, $\sum_i |i\rangle\langle i| = 1$

$$|\alpha\rangle = \sum_i |i\rangle\langle i|\alpha\rangle \equiv \sum_i |i\rangle\alpha_i \quad \text{e.g.} \quad |\alpha\rangle = \int |x\rangle\langle x|\alpha\rangle\,dx \equiv \int |x\rangle\psi_\alpha(x)\,dx \tag{7.13}$$

The coefficients of the basis vectors $|i\rangle$ in the expansion are numbers generated from the inner product for our vector space – $\langle i|\alpha\rangle$. If the basis we adopt is the position eigenstates, then $\langle|\alpha\rangle = \psi_\alpha(x)$, the wave function value at that x.

In exactly the same way, we can pick a basis in which to represent operators

$$\hat{Q} = \sum_i\sum_j |i\rangle\langle i|\hat{Q}|j\rangle\langle j| \equiv \sum_i\sum_j |i\rangle\langle j|Q_{ij}$$

The $Q_{ij} \equiv \langle i|\hat{Q}|j\rangle$ are just numbers generated from taking the inner product of vectors

$$Q_{ij} = \langle i|\hat{Q}|j\rangle = \langle i|\hat{Q}j\rangle$$

and are the expansion coefficients of our operator $\hat{Q}$ in terms of the basis operators $|i\rangle\langle j|$, exactly in the way that $\alpha_i \equiv \langle i|\alpha\rangle$ in Equation 7.13 are the expansion coefficients of the state vector $|\alpha\rangle$ in terms of the basis vectors $|i\rangle$. The quantity $\langle i|\hat{Q}|j\rangle$ is called the *matrix element* of $\hat{Q}$ in the basis introduced above.

Frequently in quantum mechanics we are asked to solve an eigenvalue/eigenvector problem,

$$\hat{Q}|\alpha\rangle = Q_\alpha|\alpha\rangle \quad \text{e.g.} \quad \hat{H}_{SE}|\alpha\rangle = \left[\frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})\right]|\alpha\rangle = E_\alpha|\alpha\rangle \tag{7.14}$$

Up to this point, $\hat{Q}$ has been our Schrödinger Hamiltonian $\hat{H}_{SE}$ for which we were asked to find the eigen-energies and eigenvector wave functions. We generally did this working in a specific representation – the position basis. But as we noted with the harmonic oscillator, underlying this is the abstract, basis-independent form of the Schrödinger equation of Equation 7.14.

While we solved the harmonic oscillator in its abstract form, via raising and lowering operators, in all other cases we solved the eigenvalue/eigenfunction problems using a basis. Let's go through the steps of representing the operator Equation 7.14 above in terms of a basis. Since this reduces an abstract problem into one that involves only numbers, we can solve using differential equations, or a computer. We assume a finite Hilbert space of dimension N to make visualization easier.

$$\hat{Q}|\alpha\rangle = Q_\alpha|\alpha\rangle \;\Rightarrow \tag{7.15}$$

$$\sum_i\sum_j |i\rangle\langle i|\hat{Q}|j\rangle\langle j|\alpha\rangle = Q_\alpha\sum_k |k\rangle\langle k|\alpha\rangle \;\Rightarrow \tag{7.16}$$

$$\sum_i\sum_j \langle m|i\rangle\langle i|\hat{Q}|j\rangle\langle j|\alpha\rangle = Q_\alpha\sum_k \langle m|k\rangle\langle k|\alpha\rangle \;\Rightarrow \tag{7.17}$$

$$\sum_j \langle m|\hat{Q}|j\rangle\langle j|\alpha\rangle = Q_\alpha\langle m|\alpha\rangle \tag{7.18}$$

In the third line above we took the inner product with a specific adjoint basis state $\langle m|, m \in \{1, 2, \ldots, N\}$ so we have N choices for that state. Everything appearing in these equations is a number. We can write out these N equations

$$\begin{pmatrix} Q_{11} & Q_{12} & \cdots Q_{1N} & \\ Q_{21} & Q_{22} & \cdots & Q_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ Q_{N1} & Q_{N2} & \cdots & Q_{NN} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{pmatrix} = Q_\alpha \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \alpha_N \end{pmatrix}$$

This is the familiar matrix form of an eigenvalue problem.

In other cases, we are simply acting on a state with an operator, not necessarily looking for the operator's eigenvalues. We represented this abstractly by

$$\hat{Q}|\alpha\rangle = |\hat{Q}\alpha\rangle \equiv |\beta\rangle$$

The new vector generated, $|\beta\rangle$ in general would not be proportional to $|\alpha\rangle$. If we now adopt a representation, this becomes

$$\sum_i \sum_j |i\rangle\langle i|\hat{Q}|j\rangle\langle j|\alpha\rangle = \sum_k |k\rangle\langle k|\beta\rangle$$

and taking the inner product with $\langle m|, m \in \{1, 2, \ldots, N\}$ yields N equations of the form

$$\sum_j \langle m|\hat{Q}|j\rangle\langle j|\alpha\rangle = \langle m|\beta\rangle \tag{7.19}$$

The matrix/vector form of this is

$$\hat{Q}|\alpha\rangle \leftrightarrow \begin{pmatrix} Q_{11} & Q_{12} & \cdots & Q_{1N} \\ Q_{21} & Q_{22} & \cdots & Q_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ Q_{N1} & Q_{N2} & \cdots & Q_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_N \end{pmatrix} \leftrightarrow |\hat{Q}\alpha\rangle \quad \text{where} \quad b_i = \sum_{j=1}^{N} Q_{ij} a_j$$

Infinite Dimensional Spaces

Although we used a finite-dimensional vector space to illustrate the operator algebra, the results extend to the infinite dimensional case. For example, if we specialize Equation 7.18 to the Hamiltonian and use the position basis,

$$\sum_j \langle m|\hat{Q}|j\rangle\langle j|\alpha\rangle = Q_\alpha\langle m|\alpha\rangle \Rightarrow \int \langle x| \left[\frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})\right] |x'\rangle\psi_\alpha(x') = E_\alpha\psi_\alpha(x) \tag{7.20}$$

Now we showed previously that

$$\langle x|\hat{V}(\hat{x})|x'\rangle = V(x')\delta(x - x')$$

while

$$\begin{aligned}
\langle x|\hat{p}^2|x'\rangle &= \int_{-\infty}^{\infty} \langle x|\hat{p}^2|p\rangle\langle p|x'\rangle\, dp = \int_{-\infty}^{\infty} p^2\langle x|p\rangle\langle p|x'\rangle\, dp = \int_{-\infty}^{\infty} p^2 \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}\langle p|x'\rangle\, dp && (7.21)\\
&= -\hbar^2 \frac{d^2}{dx^2} \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}\langle p|x'\rangle\, dp = -\hbar^2 \frac{d^2}{dx^2} \int_{-\infty}^{\infty} \langle x|p\rangle\langle p|x'\rangle\, dp = -\hbar^2 \frac{d^2}{dx^2}\langle x|x'\rangle && (7.22)\\
&= -\hbar^2 \frac{d^2}{dx^2}\delta(x - x') && (7.23)
\end{aligned}$$

Plugging in these two results into Equation 7.20 and using the delta function to do the integral over x' yields the familiar result:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_\alpha(x) = E_\alpha \psi_\alpha(x)$$

Adjoint of matrices and Hermitian Operators

The adjoint of a matrix is obtained by taking is transpose, then complex conjugating. So in a representation,

$$[\hat{Q}^\dagger]_{ij} = [\hat{Q}]^*_{ji} = Q^*_{ji}$$

A vector $|\alpha\rangle$ in a representation is just a matrix with one column, with components $[|\alpha\rangle]_{i1}$. So the adjoint vector $\langle\alpha|$ has components of

$$[\langle\alpha|]_{1i} \leftrightarrow \langle\alpha|i\rangle = \langle i|\alpha\rangle^* = a_i^* \leftrightarrow [|\alpha\rangle]^*_{i1}$$

That is, vectors and their adjoints in a representation are related by

$$|\alpha\rangle : \qquad \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} \leftrightarrow (a_1^*,\ a_2^* \ldots,\ a_N^*) \qquad : \langle\alpha|$$

Now if we take the conjugate of Equation 7.18,

$$\sum_{j=1}^{N} Q^*_{mj} a^*_j = b^*_m \quad \sum_{j=1}^{N} [\langle\alpha|]_{1j} [Q^\dagger]_{jm} = [\langle\beta|]_{1m}$$

So we see

$$[\hat{Q}|\alpha\rangle]^\dagger = |\hat{Q}\alpha\rangle^\dagger = \langle\hat{Q}\alpha| = \langle a|Q^\dagger$$

In quantum mechanics the expectation of a measurement should be real, as it must correspond to an observable. Thus we should require

$$\langle\alpha|\hat{Q}|\alpha\rangle = \langle\alpha|\hat{Q}|\alpha\rangle^* \quad \Leftrightarrow \quad \langle\alpha|\hat{Q}|\alpha\rangle = \langle\alpha|\hat{Q}^\dagger|\alpha\rangle \quad \Leftrightarrow \quad \langle\alpha|\hat{Q}\alpha\rangle = \langle\hat{Q}\alpha|\alpha\rangle$$

In a representation, Hermitian operators correspond to matrices for which $[\hat{Q}^\dagger]_{ij} = [\hat{Q}]_{ij}$ – the matrix is equal to its adjoint. Operators that satisfy the above conditions for all $|\alpha\rangle$ are called Hermitian.

Hermitian Operators

$$\hat{Q} = \hat{Q}^\dagger$$

Observables are represented by Hermitian operators – real, possible measurements: $\langle\alpha|\hat{Q}\alpha\rangle = \langle\hat{Q}\alpha|\alpha\rangle$

For example, the momentum operator is Hermitian, which we show via partial integration,

$$\langle\psi|\hat{p}\psi\rangle = \int \langle\psi|x\rangle\langle x|\hat{p}\psi\rangle\,dx = \int \psi^*(x)\frac{\hbar}{i}\frac{d}{dx}\psi(x)\,dx = \int \left[-\frac{\hbar}{i}\frac{d}{dx}\psi^*(x)\right]\psi(x)\,dx \tag{7.24}$$

$$= \int \left[\frac{\hbar}{i}\frac{d}{dx}\psi(x)\right]^* \psi(x)\,dx = \int [\langle x|\hat{p}\psi\rangle]^*\langle x|\Psi\rangle\,dx = \int \langle\hat{p}\psi|x\rangle\langle x|\Psi\rangle\,dx = \langle\hat{p}\psi|\psi\rangle \tag{7.25}$$

But the operator $\frac{d}{dx}$ would not be.

7.4.3 Determinate States of Hermitian Operators

The Hamiltonians we have studied thus far have stationary states of definite energy. If you measure the energy of a stationary state you always get back the same value. $|\alpha\rangle$ is said to be a determinate state of an operator $\hat{Q}$ if every measurement

$$\langle\alpha|\hat{Q}|\alpha\rangle = Q$$

returns the same value Q. In this case,

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

But this can only be if

$$\hat{Q}\alpha = Q|\alpha\rangle$$

Determinate states of an operator $\hat{Q}$ are eigenfunctions of $\hat{Q}$. This means the eigenvalue Q can be used as a wave function label! – we'll get to that later.

The eigenvalue Q of a Hermitian operator is a real number – I will distinguish operators from their eigenvalues by denoting the former with a hat, $\hat{Q}$. Thus the stationary states $|\alpha_i\rangle$ of the Hamiltonians we have considered

$$\hat{H}|\alpha_i\rangle = E_i|\alpha_i\rangle$$

are the determinate states of $\hat{H}$. The collection of all eigenvalues of an operator $\hat{Q}$ is the *spectrum* of $\hat{Q}$. States with the same eigenvalue are said to be *degenerate*.

7.4.4 Discrete Spectra

We consider a Hermitian operator with a discrete spectrum – the eigenvalues correspond to eigenfunctions that are normalizable and thus proper states. We note

> The eigenvalues of the normalizable eigenfunctions of a Hermitian operator are *real* and eigenfunctions belonging to distinct eigenvalues are *orthogonal*.

The eigenvalues are real because

$$Q_\alpha = \langle\alpha|\hat{Q}\alpha\rangle = \langle\hat{Q}\alpha|\alpha\rangle = \left[|\hat{Q}\alpha\rangle\right]^\dagger|\alpha\rangle = [Q_\alpha|\alpha\rangle]^\dagger|\alpha\rangle = Q_\alpha^*\langle\alpha|\alpha\rangle = Q_\alpha^*$$

Eigenfunctions belonging to distinct eigenvalues are orthogonal because, if $\hat{Q}|\alpha\rangle = Q_\alpha|\alpha\rangle$ and $\hat{Q}|\beta\rangle = Q_\beta|\beta\rangle$, with $Q_\alpha \neq Q_\beta$, then

$$Q_\beta\langle\alpha|\beta\rangle = \langle\alpha|\hat{Q}\beta\rangle = \langle\hat{Q}\alpha|\beta\rangle = Q_\alpha\langle\alpha|\beta\rangle \quad\Rightarrow\quad (Q\beta - Q_\alpha)\langle\alpha|\beta\rangle = 0 \quad\Rightarrow\quad \langle\alpha|\beta\rangle = 0$$

If a subset of eigenfunctions are degenerate, we have previously described how these states can be *made* ortogonal/orthonormal via Gram-Schmidt. Thus we can assume that the eigenfunctions of a Hermitian operator form an orthonormal basis.

A third property of the eigenfunctions of a Hermitian operator is

> The eigenfunctions of an operator for any observable are complete. Any state in the Hilbert space can be expanded in terms of this basis.

We have generally used the eigenstates of the Hamiltonian $\hat{H}$ as our basis, expanding initial wave packets in terms of these stationary states, then exploiting the prime directive to determine the time evolution of the wave packet. While this is a special basis because of the prime directive, we certainly have the freedom to use as a basis the eigenfunctions of other operators.

7.4.5 Projection Operators

We have previously expressed the completeness of our Hilbert space, for simplicity assumed discrete here, by the identity

$$I = \sum_{i=1}^{\infty}|i\rangle\langle i|$$

The projection operator onto the state i is defined by

$$\hat{P}_i = |i\rangle\langle i| \quad \textit{so equivalently} \quad I = \sum_{i=1}^{\infty} \hat{P}_i$$

Projection operators have the following properties, which follow immediately from the assumed orthonormality of the basis,

$$\hat{P}_i\hat{P}_j = \delta_{ij}\hat{P}_j \quad \text{so in particular} \quad \hat{P}_i\hat{P}_i = \hat{P}_i$$

Projection operators in quantum mechanics are connected with measurement, and thus are very useful. For example, if a measurement is done on a wave packet formed as a sum over many stationary states, there may be many possible outcomes of that measurement. However, a specific measurement will yield one result. The act of measurement is often said to "collapse" the wave function. To be specific, suppose a measurement is done on a system described by a wave packet to determine the energy. Assuming the stationary states are non-degenerate, the result obtained will correspond to the energy of one of the stationary states i. The measurement will thus have collapsed the wave packet to that state. The state of the system immediately after measurement will then be given by the projection operator $\hat{P}_i$ acting on the original wave packet (up to normalization, which in this case would be adjusted to one).

In the case of measurement, the basis you use and thus the projection operator employed depends on what one measures – energy, position, momentum, spin, etc. But each such observable corresponds to a Hermitian operator for which there is a complete set of eigenfunctions, as noted above. The appropriate projection operator thus should use the basis appropriate to the measurement. If the operator is not the Hamiltonian, measurement will again collapse the wave function, but the projection will generally not be to a single stationary state.

7.4.6 Generalized Statistical Interpretation of Measurements

We can generalize early discussions about operators and measurements to include any Hermitian operator, which all correspond to possible observables. The normalizable eigenfunctions of a Hermitian operator $\hat{Q}$ are real and the normalized eigenfunctions form an orthonormal basis. Consequently for any Hermitian operator with a discrete spectrum,

$$\langle\alpha|\hat{Q}|\alpha\rangle = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\langle\alpha|i\rangle\langle i|\hat{Q}|j\rangle\langle j|\alpha\rangle = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\langle\alpha|i\rangle Q_j\langle i|j\rangle\langle j|\alpha\rangle = \sum_{i=1}^{\infty} Q_i|\langle i|\alpha\rangle|^2 \equiv \sum_{i=1}^{\infty} Q_i|c_i^{\alpha}|^2$$

Here it is understood that $|\alpha\rangle$ is the state of a system at some time of measurement t, and that the sum is over all discrete eigenstates of $\hat{Q}$ which here is taken to be infinite, but could also very well be finite.

The Quantum Mechanical interpretation is that if a series of identical experiments are done, with $|\alpha\rangle$ prepared identically each time, then the possible outcomes Q_i will be found with probability $|\langle i|\alpha\rangle|^2 = |c_i^{\alpha}|^2$. This is a probability because

$$1 = \langle\alpha|\alpha\rangle = \sum_{i=1}^{\infty}\langle\alpha|i\rangle\langle i|\alpha\rangle = \sum_{i=1}^{\infty}|c_i^{\alpha}|^2$$

Thus any outcome Q_i is possible in a given measurement – that is, any outcome for which the amplitude $\langle i|\alpha\rangle$ is nonzero. Only the expectation – the average of the outcomes after many repetitions of an identical experiment – is certain in Quantum Mechanics,

$$\langle\hat{Q}\rangle = \sum_{i=1}^{\infty} Q_i |c_i^\alpha|^2$$

This interpretation generalizes to the continuous case

$$\langle\alpha|\hat{Q}|\alpha\rangle = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} \langle\alpha|z\rangle\langle z|\hat{Q}(\hat{z}')|z'\rangle\langle z'|\alpha\rangle\, dz' = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} \langle\alpha|z\rangle Q(z')\langle z|z'\rangle\langle z'|\alpha\rangle\, dz' \tag{7.26}$$

$$= \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} \langle\alpha|z\rangle Q(z')\delta(z-z')\langle z'|\alpha\rangle\, dz' = \int_{-\infty}^{\infty} Q(z)|\langle z|\alpha\rangle|^2\, dz \tag{7.27}$$

where z represents the appropriate continuous eigenspectrum, for example, x if we are finding the expectation values for some potential $\hat{V}(\hat{x})$ or p if we were evaluating the operator $-\frac{\hbar^2}{2m}\hat{p}^2$. So we can summarize

> A Hermitian $\hat{Q}$ has a discrete spectrum and eigenstates
>
> $$\{Q_i, |i\rangle\} \Rightarrow \langle\alpha|\hat{Q}|\alpha\rangle = \sum_{i=1}^{\infty} Q_i|c_i^\alpha|^2$$
>
> $$\text{Probability of outcome} \quad Q_i = |c_i^\alpha|^2 = |\langle i|\alpha\rangle|^2.$$
>
> A Hermitian $\hat{Q}$ has a continuous spectrum and eigenstates
>
> $$\{Q(z), |z\rangle\} \Rightarrow \langle\alpha|\hat{Q}|\alpha\rangle = \int_{-\infty}^{\infty} Q(z)|\langle z|\alpha\rangle|^2\, dz$$
>
> $$\text{Probability of outcome} \quad dQ(z) = |\langle z|\alpha\rangle|^2\, dz$$

Here we define $dQ(z)$ via a Taylor series expansion. If z_0 is the middle of the region δz,

$$\text{outcome between } Q(z_0+\delta z/2) \text{ and } Q(z_0-\delta z/2) \text{ has the probability } |\langle z_0|\alpha\rangle|^2\delta z$$

$$\text{outcome between } Q(z_0) \pm \frac{1}{2}\left.\frac{dQ(z)}{dz}\right|_{z_0} dz \text{ has the probability } |\langle z_0|\alpha\rangle|^2\, dz$$

7.4.7 Simultaneous Measurements & Commuting Operators

Now we come to a key point that will influence much of the rest of this book, as we move onto problems in 3D with more degrees of freedom.

Suppose we have two Hermitian operators $\hat{A}$ and $\hat{B}$ with a common, complete set of eigenvectors. That is,

$$\hat{A}\psi_{A_i,B_i} = A_i\psi_{A_i\,B_i} \qquad \hat{B}\psi_{A_i\,B_i} = B_i\psi_{A_i\,B_i}$$

Let's first pause here to explain the notation. I've assumed a basis exists that can be enumerated by i, with each basis state carrying to quantum numbers A_i and B_i that are the eigenvalues obtained when the operators $\hat{A}$ and $\hat{B}$ act on the basis state. One can view (A_i, B_i) as the index of the various basis states – one has to specify two basis state eigenvalues to identify the basis state. Our basis states are simultaneously eigenvectors of both $\hat{A}$ and $\hat{B}$.

It follows that

$$\hat{A}[\hat{B}\psi_{A_i\,B_i}] = \hat{A}[B_i\psi_{A_i\,B_i}] = A_iB_i\psi_{A_i\,B_i} \tag{7.28}$$

$$\hat{B}[\hat{A}\psi_{A_i\,B_i}] = \hat{B}[A_i\psi_{A_i\,B_i}] = A_iB_i\psi_{A_i\,B_i} \tag{7.29}$$

Thus $(\hat{A}\hat{B} - \hat{B}\hat{A})\psi_{A_i\,B_i} = 0$ for every state in the Hilbert space. We conclude

> If two observables are simultaneously measurable,
>
> $$[\hat{A}, \hat{B}] = 0$$
>
> Conversely one can show if $[\hat{A}, \hat{B}] = 0$, a common set of eigenfunctions for the operators can be found.

7.4.8 Generalized Uncertainty Principle

Most Hermitian do not commute ($[\hat{A}, \hat{B}] = 0 \to \hat{A}\hat{B} = \hat{B}\hat{A}$). If $\hat{A} = \hat{p}$ and $\hat{B} = \hat{x}$, then working in position space,

$$[\hat{A}, \hat{B}]\psi(x) = \left[\frac{\hbar}{i}\frac{d}{dx}x - x\frac{\hbar}{i}\frac{d}{dx}\right]\psi(x) = \frac{\hbar}{i}\psi(x) \quad [\hat{A}, \hat{B}] = \frac{\hbar}{i}$$

So one can not label states simultaneously by their position and momentum.

If $\hat{A}$ and $\hat{B}$ are Hermitian, then their product can be written as the sum of two Hermitian operators,

$$\hat{A}\hat{B} = \frac{1}{2}\left[(\hat{A}\hat{B} + \hat{B}\hat{A}) + i\left(\frac{1}{i}[\hat{A}, \hat{B}]\right)\right] \equiv \frac{1}{2}\left[\hat{H}_1 + i\hat{H}_2\right]$$

as

$$\hat{H}_1^\dagger \equiv \left(\hat{A}\hat{B} + \hat{B}\hat{A}\right)^\dagger = \hat{B}\hat{A} + \hat{A}\hat{B} = \hat{H}_1$$

$$\hat{H}_2^\dagger \equiv \left(\frac{1}{i}[\hat{A}, \hat{B}]\right)^\dagger = -\frac{1}{i}(\hat{A}\hat{B} - \hat{B}\hat{A})^\dagger = -\frac{1}{i}(\hat{B}\hat{A} - \hat{A}\hat{B}) = \hat{H}_2$$

We have previously defined uncertainty for a (Hermitian) operator $\hat{A}$ in terms of the variance

$$\langle(\Delta\hat{A})^2\rangle \equiv \langle\psi|(\hat{A}-\langle\hat{A}\rangle)^2|\psi\rangle = \langle\Delta\hat{A}\psi\rangle \equiv \langle f|f\rangle$$

so also

$$\langle(\Delta\hat{B})^2\rangle \equiv \langle\Delta\hat{B}\psi|\Delta\hat{B}\psi\rangle \equiv \langle g|g\rangle$$

Previously we have used various forms of the Schwarz inequality, which comes from

$$\int (\langle g|g\rangle f(x) - \langle g|f\rangle g(x))^*(\langle g|g\rangle f(x) - \langle g|f\rangle g(x))\, dx \geq 0 \tag{7.30}$$

$$\Rightarrow [\langle g|g\rangle^2\langle f|f\rangle - \langle g|g\rangle\langle f|g\rangle\langle g|f\rangle - \langle g|g\rangle\langle g|f\rangle^*\langle g|f\rangle + \langle g|f\rangle^*\langle g|f\rangle\langle g|g\rangle] \geq 0 \tag{7.31}$$

$$\Rightarrow \langle g|g\rangle\langle f|f\rangle \geq |\langle f|g\rangle|^2 \tag{7.32}$$

So applying this to the f and g defined above,

$$\langle\Delta\hat{A}\psi|\Delta\hat{A}\psi\rangle\langle\Delta\hat{B}\psi|\Delta\hat{B}\psi\rangle \geq \left|\langle\Delta\hat{A}\psi|\Delta\hat{B}\psi\rangle\right|^2 \tag{7.33}$$

$$\Rightarrow \langle\psi|(\Delta\hat{A})^2|\psi\rangle\langle\psi|(\Delta\hat{B})^2|\psi\rangle \geq \left|\langle\psi|\Delta\hat{A}\Delta\hat{B}|\psi\rangle\right|^2 \tag{7.34}$$

Now we utilize our theorem above,

$$\Delta\hat{A}\Delta\hat{B} = \frac{1}{2}\left[(\Delta\hat{A}\Delta\hat{B} + \Delta\hat{B}\Delta\hat{A}) + i\left(\frac{1}{i}[\Delta\hat{A},\Delta\hat{B}]\right)\right] \equiv \frac{1}{2}\left[\hat{H}_1 + i\hat{H}_2\right]$$

So applying this to the RHS above and remembering expectation values of Hermitian operators are real numbers (observables),

$$\left|\langle\psi|\Delta\hat{A}\Delta\hat{B}|\psi\rangle\right|^2 = \left|\langle\psi|\frac{1}{2}\left[\hat{H}_1 + i\hat{H}_2\right]|\psi\rangle\right|^2 = \langle\psi|\frac{1}{2}\hat{H}_1|\psi\rangle^2 + \langle\psi|\frac{1}{2}\hat{H}_2|\psi\rangle^2 \geq \langle\psi|\frac{1}{2}\hat{H}_2|\psi\rangle^2$$

Thus we obtain the generalized uncertainty principle:

Generalized Uncertainty Principle

$$\langle(\Delta\hat{A})^2\rangle\langle(\Delta\hat{B})^2\rangle \;\geq\; \langle\frac{1}{2i}\left[\Delta\hat{A},\Delta\hat{B}\right]\rangle^2 = \langle\frac{1}{2i}\left[\hat{A},\hat{B}\right]\rangle^2$$

$$\text{or}\quad \sigma_A\sigma_B \;\geq\; \left|\langle\frac{1}{2i}\left[\hat{A},\hat{B}\right]\rangle\right|$$

Consequently if $\left[\hat{A},\hat{B}\right]$ commute, then it is possible that $\sigma_A^2\sigma_B^2 = 0$, in which case we could find a basis in which the state has *definite* eigenvalues A and B. But if $\left[\hat{A},\hat{B}\right] \neq 0$, like position and momentum, we can not label wave functions by the eigenvalues of both operators. These observables are incompatible in this sense, and we can not construct a complete set of common eigenfunctions. It follows

> There is an uncertainty principle for every pair of observables whose operators do not commute.

It is enormously helpful to identify *maximal sets of commuting operators* such as $\hat{H},\hat{P},\hat{\vec{L}}^2,\hat{L}_z,\ldots$. Once identified, they provide instructions for identifying complete orthonormal bases that simply our mechanics. Such bases break up the Hilbert space into blocks that can often be treated separately.

But we also learn that uncertainties are inherent in Quantum Mechanics when we ask multiple questions of systems. It is not just $\hat{x}$ and $\hat{p}$ that can not be determined simultaneously with unlimited precision, but most observables.

7.4.9 Energy-Time Uncertainty Principle

We consider the time variation of the expectation of observable $\hat{Q}$

$$\frac{d}{dt}\langle\psi|\psi\rangle = \langle\frac{\partial\psi}{\partial t}|\hat{Q}|\psi\rangle + \langle\psi|\frac{d\hat{Q}}{dt}|\psi\rangle + \langle\psi|\hat{Q}|\frac{\partial\psi}{\partial t}$$

where we allow for $\hat{Q}$ itself having explicit time dependence. Now if $|\psi\rangle$ is a solution of the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \quad\Rightarrow \frac{\partial}{\partial t}|\psi\rangle = -\frac{i}{\hbar}\hat{H}|\psi\rangle$$

This yields

Generalized Ehrenfest Theorem

$$\frac{d}{dt}\langle\psi|\hat{Q}|\psi\rangle = \frac{i}{\hbar}\langle\psi|[\hat{H},\hat{Q}]|\psi\rangle + \langle\psi|\frac{\partial\hat{Q}}{\partial t}|\psi\rangle$$

Thus for operators that have no explicit dependence on time, the rate of change of the expectation value of an operator is determined by the commutator of $\hat{Q}$ with $\hat{H}$. If $\hat{Q}$ commutes with $\hat{H}$, its expectation value is constant in time.

We can obtain a related result from the generalized uncertainty principle by the substitutions $\hat{A} \to \hat{H}$ and $\hat{B} \to \hat{Q}$, yielding in a case for an operator that has no explicit time dependence

$$\sigma_H^2 \sigma_Q^2 \ \geq\ \langle\psi|\frac{1}{2i}\left[\hat{H},\hat{Q}\right]|\psi\rangle^2 = \left[-\frac{\hbar}{2}\frac{d}{dt}\langle\psi|\hat{Q}|\psi\rangle\right]^2 \quad \Rightarrow \quad \sigma_H \sigma_Q \ \geq\ \frac{\hbar}{2}\left|\frac{d}{dt}\langle\psi|\hat{Q}|\psi\rangle\right|$$

If we abbreviate the expectation value of the Hamiltonian, $\langle\psi|\hat{H}|\psi\rangle$ as $\bar{E}$,

$$\sigma_H^2 = \langle\psi|(\hat{H}-\bar{E})^2|\psi\rangle = \sum_{i,j}\langle\psi|E_j\rangle\langle E_j|(\hat{H}-\bar{E})^2|E_i\rangle\langle E_i|\psi\rangle = \sum_i |c_i|^2(E_i-\bar{E})^2 \equiv (\Delta E)^2$$

Given a time t_0 of a measurement, we can also define a time interval Δt where the expectation value of $\hat{Q}$ will change by one standard deviation,

$$\sigma_Q = \left|\frac{d\langle\psi|\hat{Q}|\psi\rangle}{dt_0}\right|\Delta t_Q$$

Plugging these into our result above, we obtain

Energy-Time Uncertainty Principle

$$\Delta E \Delta t_Q \ \geq\ \frac{\hbar}{2}$$

where

$$\Delta E = \sqrt{\langle|\hat{H}^2|\psi\rangle - \langle\psi|\hat{H}|\psi\rangle^2} \qquad \sigma_Q = \left|\frac{d\langle\psi|\hat{Q}|\psi\rangle}{dt_0}\right|\Delta t_Q$$

Thus if a wave packet is a stationary state, $\Delta E \to 0$, requiring $\left|\frac{d\langle\psi|\hat{Q}|\psi\rangle}{dt_0}\right|\Delta t_Q \to 0$. Thus any observable that is itself not explicitly dependent on time will not vary.

Chapter 8

Quantum Mechanics beyond 1D

So far we have studied quantum mechanical problems that are either finite, or involving functions in only one-dimension, described by the coordinate x. Our experience with 1D prepares us to solve a huge variety of 3D problems, many of which can be reduced to effectively 1D properties by exploiting symmetries like rotational invariance.

8.1 Schrödinger's Equation in 3D

The generalization of the Schrödinger equation

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

for 3D is obtained by the replacement

$$\hat{H} = \frac{1}{2m}\hat{p}_x^2 + \hat{V}(\hat{x}) \to \frac{1}{2m}\hat{\vec{p}}^2 + \hat{V}(\hat{x},\hat{y},\hat{z}) = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + \hat{V}(\hat{x},\hat{y},\hat{z})$$

The operators $\hat{p}_x,\ \hat{p}_y,\ \hat{p}_z^2$ in position space are just the natural generalization of the 1D case,

$$\hat{p}_x \to \frac{1}{i}\frac{\partial}{\partial x} \quad \hat{p}_y \to \frac{\hbar}{i}\frac{\partial}{\partial y} \quad \hat{p}_z \to \frac{\hbar}{i}\frac{\partial}{\partial z}$$

This can be expressed more compactly as the replacement

$$\hat{p}_x \to \hat{\vec{p}} = \frac{\hbar}{i}\left(\hat{e}_x\frac{\partial}{\partial x}, \hat{e}_y\frac{\partial}{\partial y}, \hat{e}_z\frac{\partial}{\partial z}\right) = \frac{\hbar}{i}\nabla$$

Here $\hat{e}_x,\ \hat{e}_y,\ \hat{e}_z$ are the unit vectors along someone's favorite coordinate system, while ∇ expresses the same thing, without reference to a coordinate system. Thus the Schrödinger equation can be written compactly as

3D Schrödinger's Equation

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

with $r = (x, y, z)$ with our usual assumption that V is not explicitly time dependent, and with the Laplacian defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

8.1.1 Normalization and the Prime Directive

We require that our wave functions in 3D represent a probability distribution and thus require that

$$\int |\Psi|^2\, d^3r = \int |\Psi|^2\, dxdydz = \int |\Psi|^2 r^2\, drd\Omega = 1, \qquad \text{where } d\Omega = \sin\theta\, d\theta d\phi$$

Our strategy for solving problems in 3D will continue to be based on finding the stationary states so we can implement the prime directive.

$$\Psi(\vec{r},t) \to \psi_n(\vec{r})e^{-iE_nt/\hbar} \qquad \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi_n(\vec{r}) = E_n\psi_n(\vec{r})$$

Given a wave packet $\Psi(\vec{r},0)$, the prime directive generates a solution of the Schrödinger equation with this initial condition

$$|\Psi(t)\rangle = \sum_n |\psi_n\rangle\langle\psi_n|\Psi(0)\rangle e^{-iE_nt/\hbar}$$

which in position space becomes

$$\langle\vec{r},\psi(t)\rangle = \sum_n \langle\vec{r}|\psi_n\rangle\langle\psi_n|\Psi(0)\rangle e^{-iE_nt/\hbar} \quad \Rightarrow \quad \Psi(\vec{r},t) = \sum_n \psi_n(\vec{r})\langle\psi_n|\Psi(0)\rangle e^{-iE_nt/\hbar}$$

8.2 Infinite Cubical Box

An interesting first problem is the infinite cubical box, the analog of the 1D infinite square well, where

$$V(x,y,z) = \begin{cases} 0 & \frac{a}{2} < x,\, y,\, z < \frac{a}{2} \\ \infty & \text{otherwise} \end{cases}$$

The time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi(x,y,z)=E\psi(x,y,z)$$

We write it in this form because the box is Cartesian, so the boundary conditions will be easier to implement if we exploit that symmetry. We look for a separable solution $\psi_{n_x,n_y,n_z}=\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$. Substituting this in, the dividing by $\psi_{n_x}\psi_{n_y}\psi_{n_z}(z)$ yields

$$\frac{1}{\psi_{n_x}}\frac{d^2\psi_{n_x}}{d^2x^2}+\frac{1}{\psi_{n_y}}\frac{d^2\psi_{n_y}}{dy^2}+\frac{1}{\psi_{n_z}}\frac{d^2\psi_{n_z}}{dz^2}=-\frac{2m}{\hbar^2}E_{n_x,n_y,n_z}$$

Since each term on the left is independent and can be varied separately from the others, while the term on the right is constant, it must be that each term on the left is constant, that is,

$$\frac{1}{\psi_{n_x}}\frac{d^2\psi_{n_x}}{dx^2}=-k_{n_x}^2 \qquad \frac{1}{\psi_{n_y}}\frac{d^2\psi_{n_y}}{dy^2}=-k_{n_y}^2 \qquad \frac{1}{\psi_{n_z}}\frac{d^2\psi_{n_z}}{dz^2}=-k_{n_z}^2 \qquad E=\frac{\hbar^2}{2m}\left(k_{n_x}^2+k_{n_y}^2+k_{n_z}^2\right)$$

But these are three 1D problems for which we know the solutions from our 1D infinite square well.

$$\psi_n(\xi)=\begin{cases}\sqrt{\frac{2}{a}}\cos\frac{\pi n\xi}{a} & n=1,3,5,\ldots \text{ even}\\ \sqrt{\frac{2}{a}}\sin\frac{\pi n\xi}{a} & n=2,4,6,\ldots \text{ odd}\end{cases} \qquad \xi\in\{x,\,y,\,z\}$$

$$k_n^2=\frac{n^2\pi^2}{a^2}$$

Consequently,

$$\psi_{n_x,n_y,n_z}(x,y,z)=\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) \qquad E_{n_x,n_y,n_z}=\frac{\hbar^2\pi^2}{2ma^2}(n_x^2+n_y^2+n_z^2)$$

Thus to enumerate all the states and their energies, we need to enumerate all ordered triplets (n_x,n_y,n_z). So there are many more possible states in 3D! Note that (1, 1, 2) is distinct from (1, 2, 1) – the orthonormality condition is given below.

One sees that this solution in 3D is labeled by quantum numbers from *three commuting Hermitian operators* corresponding to three observables that can be measured simultaneously,

$$\hat{p}_x=\hbar\hat{k}_x \qquad \hat{p}_y=\hbar\hat{k}_y \qquad \hat{p}_z=\hbar\hat{k}_z$$

This is an important theme in all of the 3D problems we do – finding a maximal set of independent but commuting operators whose eigenvalues then act as the wave function labels, or quantum numbers. We showed previously that given two commuting Hermitian operators, a basis exists in which the basis states are simultaneously eigenfunctions of both operators. Note that in this case considered above, $\hat{H}$ is not an independent operator, as E is determined if one knows p_x, p_y, p_z. This contrasts with the 1D case, where wave functions typically carry one label, which in most cases is the energy eigenvalue.

A couple of observations

1. The solution is properly normalized

$$\int |\psi_{n_x,n_y,n_z}(x,y,z)|^2 \, d\vec{r} = \left[|\psi_{n_x}(x)|^2 \, dx\right] \left[\int |\psi_{n_y}(y)|^2\right] \left[\int |\psi_{n_z}(z)|^2\right] = 1$$

2. The solutions are orthonormal

$$\int \psi^*_{n'_x,n'_y,n'_z}(x,y,z)\psi_{n_x,n_y,n_z}(x,y,z)\, d\vec{r} =$$

$$\left[\psi^*_{n'_x}(x)\psi_{n_x}(x)\right] \left[\psi^*_{n'_y}(y)\psi_{n_y}(y)\right] \left[\psi^*_{n'_z}(z)\psi_{n_z}(z)\right] = \delta_{n'_x,n_x}\delta_{n'_y,n_y}\delta_{n'_z,n_z}$$

3. Unlike in 1D, there are energy degeneracies – solutions are no longer solely identified by their energies. For example the states labeled

$$(n_x, n_y, n_z) = \{(1,1,2),\ (1,2,1),\ (2,1,1)\}$$

   all have energy $E = \frac{3\hbar^2\pi^2}{ma^2}$. In 3D we generally will need to find additional quantum labels for our wave functions, as E does not suffice.

4. The solutions provide a complete basis for representing any wave packet satisfying the same boundary conditions. This property plus 1. and 2. allows us to implement the prime directive.

5. We made good use of parity in 1D and we have already exploited it here, solving the infinite cubic well. In 1D, the square well parity is $(-1)^{n+1}$.

$$\text{1D}: \quad \text{under } x \to -x,\ \psi_n(x) \to \psi_n(-x) = (-1)^{n+1}\psi_n(x)$$

   but in 3D, the cubic well parity is $(-1)^{n_x+n_y+n_z+1}$.

$$\begin{aligned}\text{3D}: \quad \text{under } \{x,y,z\} \to \{-x,-y,-z\},\ \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) &\to \psi_{n_x}(-x)\psi_{n_y}(-y)\psi_{n_z}(-z) \\ &= (-1)^{n_x+n_y+n_z+1}\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)\end{aligned}$$

These questions of normalization, orthonormality, completeness, and wave function labeling will come up in every 3D problem we tackle.

8.3 Quantum Mechanics with Spherical Symmetry

8.3.1 Symmetry and Spherical Coordinates

Many of the potentials we deal with in physics are spherically symmetric, requiring a different procedure for separating variables. In cases where the Schrödinger equation takes the form

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r}),$$

instead of using Cartesian coordinates (x, y, z), one uses coordinates better matched to the rotational symmetry of the problem – spherical coordinates (r, θ, ϕ), where

$$x = r\sin\theta\cos\phi \quad y = r\sin\theta\sin\phi \quad z = r\cos\theta \quad 0 \leq \theta \leq \pi \quad 0 \leq 0 \leq 2\pi$$

We separate the equation in spherical coordinates as follows

$$\left[\left(\left\{-\frac{\hbar^2}{2m}\nabla^2\right\}_r + V(r)\right) + \left\{-\frac{\hbar^2}{2m}\nabla^2\right\}_{\theta,\phi}\right]\psi(\vec{r}) = E\psi(\vec{r})$$

and look for a solution of the form

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

The angular solution $Y(\theta, \phi)$ will be a solution of Laplace's equation restricted to the 2D unit sphere – the second term in the Hamiltonian above – and will be valid for any problem where the potential is spherically symmetric, only depending on r. In contrast, the radial solution $R(r)$, corresponding to the first term in the Hamiltonian above, will depend on the potential. However, as an equation just in r, in general this solution is no more complex than those we encountered in 1D Quantum Mechanics. So although the separation takes a bit of algebra, the task we are about to undertake is conceptually simple.

The Laplacian in spherical coordinates is

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

from which obtain the explicit separation of the Hamiltonian,

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

We substitute $\psi(\vec{r}) = R(r)Y(\theta, \phi)$, after which we multiply on the left by $-mr^2/(\hbar^2 R(r)Y(\theta, \phi))$, similar to what we did with the infinite cubical box. This yields

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V(r)-E)\right\}+\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\psi^2}\right)\right\}=0$$

As the radial and angular terms are separate and can be varied independently, a solution requires both terms to be a constant. It proves convenient to use as that constant, $\ell(\ell+1)$. We then obtain

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V(r)-E)=\ell(\ell+1) \tag{8.1}$$

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right\}=-\ell(\ell+1) \tag{8.2}$$

8.3.2 The Spherical Harmonics

Before going into the details of finding the solutions $Y(\theta,\phi)$, I should stress that conceptually we are doing something simple – finding the solutions of Laplace's equation restricted to the surface of a sphere. Once we have those solutions, they will be common to all 3D QM problems in which the potential depends only on r.

We rewrite the angular equation as

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

then seek a separated solution

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

Plugging this in and dividing the left by $Y(\theta,\phi)$ yields

$$\frac{1}{\Theta(\theta)}\left\{\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\ell(\ell+1)\sin^2\theta\right\}\Theta(\theta)+\frac{1}{\Phi(\phi)}\left(\frac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)=0$$

Like we have seen before, each term can be varied independently, and so we must require that each is a constant, which we will call m^2. This yields

$$\frac{1}{\Phi(\phi)}\left(\frac{d^2}{d\phi^2}\right)\Phi(\phi)=-m^2 \qquad \frac{1}{\Theta(\theta)}\left\{\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)+\ell(\ell+1)\sin^2\theta\right\}\Theta(\theta)=m^2$$

The first equation requires

$$\frac{d^2\Phi(\phi)}{d\phi^2}=-m^2\Phi(\phi) \qquad \Rightarrow \qquad \Phi(\phi)=e^{im\phi}$$

There is also a boundary condition – our wave function must be continuous, so $\Phi(0) = \Phi(2\pi)$, so m must be an integer,

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

In the second equation, noting that

$$\sin\theta \frac{d}{d\theta} = \sin\theta \frac{d\cos\theta}{d\theta} \frac{d}{d\cos\theta} = -\sin^2\theta \frac{d}{d\cos\theta} = -(1-\cos^2\theta)\frac{d}{d\cos\theta}$$

we find

$$\left\{(1-\cos^2\theta)\frac{d}{d\cos\theta}\left((1-\cos^2\theta)\frac{d}{d\cos\theta}\right) + \ell(\ell+1)(1-\cos^2\theta)\right\}\Theta(\cos\theta) = m^2\Theta(\cos\theta) \Rightarrow$$

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

This is a famous equation whose solutions are single valued functions on the interval $-1 \leq \cos\theta \leq 1$. Provided ℓ is a non-negative integer, with $|m| \leq \ell$, it generates the associated Legendre functions

$$\Theta(\cos\theta) = A_{\ell m} P_\ell^m(\cos\theta)$$

These functions are defined in terms of the Legendre Polynomials $P_\ell(x)$,

$$P_\ell^m(x) \equiv (-1)^m(1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x) \qquad P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$$

Once can generate the Legendre Polynomials from the starting values and recursion relation

$$P_0(x) = 1 \quad P_1(x) = x \quad P_{n+1}(x) = \frac{1}{n+1}[(2n+1)xP_n(x) - nP_{n-1}(x)]$$

The overall solution up to normalization is thus

$$\Phi(\phi)\Theta(\theta) = A_{\ell m} e^{im\phi} P_\ell^m(\cos\theta)$$

The normalization is determined by the condition

$$\Psi(\vec{r}) \equiv R(r)\Phi(\phi)\Theta(\theta) \quad \Rightarrow \quad 1 = \int |\Psi(\vec{r})|^2\, d\vec{r} = \int_0^\infty r^2 |R(r)|^2\, dr \int |\Phi(\phi)\Theta(\theta)|^2\, d\Omega = 1$$

We impose the normalization constant on the radial and angular functions separately, so

$$\int_0^\infty r^2 |R(r)|^2 \, dr = 1 \qquad \int |\Phi(\phi)\Theta(\theta)|^2 \, d\Omega = \int \sin\theta |A_{\ell m} P_\ell^m(\cos\theta)|^2 \, d\theta d\phi = 1$$

The normalized solutions are called the *spherical harmonics*, $Y_{\ell m}(\theta, \phi)$.

Spherical Harmonics

$$Y_{\ell m} \equiv \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} e^{im\phi} P_\ell^m(\cos\theta) \qquad \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} |Y_{\ell m}(\theta,\phi)|^2 \, d\phi = 1$$

The $Y_{\ell m}$ are a complete orthonormal basis for the angular solutions of Schrödinger equation in any case where V is just a function of r. The orthonormality condition is

$$\int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} \, d\theta \int_0^{2\pi} Y_{\ell' m'}(\theta,\phi) Y_{\ell m} \, d\phi = \delta \ell' \ell \delta m' m \quad \ell = 0, 1, 2, \ldots \; m = -\ell, -\ell+1, \ldots, \ell-1, \ell$$

From the formulas we have given above, one can verify

$$Y^*_{\ell m}(\theta,\phi) = (-1)^m Y_{\ell -m}(\theta,\phi)$$

Note the subscript on the right side isn't literally $\ell - m$, but ℓ and $-m$ separately.
The first few spherical harmonics are

$$Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1m}(\theta,\phi) = \begin{cases} -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} & m = 1 \\ \sqrt{\frac{3}{4\pi}} \cos\theta & m = 0 \\ \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi} & m = -1 \end{cases}$$

$$Y_{2m}(\theta,\phi) = \begin{cases} \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\phi} & m = 2 \\ -\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{i\phi} & m = 1 \\ \sqrt{\frac{5}{16\pi}} (2\cos^2\theta - \sin^2\theta) & m = 0 \\ \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{-i\phi} & m = -1 \\ \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{-2i\phi} & m = -2 \end{cases}$$

But what are the spherical harmonics even about? Three important answers.

1. They are the complete orthonormal basis for the solution of Laplace's equation on the unit sphere and consequently provide the angular wave function one needs to create a complete basis of stationary states for any problem in which V solely depends on r.
2. They are the eigenstates of the total angular momentum operator $\vec{L}^2$ with eigenvalue $\hbar(\ell(\ell+1))$ and of the z-component of angular momentum L_z with eigenvalue $m\hbar$ – see below.
3. They provide additional quantum labels for our stationary states, augmenting the energy.

8.3.3 Angular Momentum

The angular momentum operator in position space is

$$\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times \frac{\hbar}{i}\nabla \quad L_i = \frac{\hbar}{i}\epsilon_{ijk} r_j \partial_k, \qquad \text{where } \{i,j,k\} \in \{x,y,z\}$$

which we stress is an operator orthogonal to the radius vector and thus associated with the tangential space of the sphere. We use the anti-symmetric epsilon tensor, defined by

$$\epsilon_{xyz} \equiv 1 \qquad \epsilon_{ijk} = -\epsilon jik$$

This leads to

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

And we can also define the total angular momentum operator

$$\vec{L}^2 \equiv \vec{L}_x^2 + \vec{L}_y^2 + \vec{L}_z^2$$

Using these expressions, one can calculate the commutation relations among these operators. One finds

$$[\vec{L}^2, L_x] = [\vec{L}^2, L_y], [\vec{L}^2, L_z] = 0 \qquad [L_x, L_y] = i\hbar L_z \quad [L_y, L_z] = i\hbar L_x \quad [L_z, L_x] = i\hbar L_y$$

Consequently one can select $\vec{L}^2$ and one of the others, by convention this is L_z – as commuting Hermitian operators. One can form bases of stationary states that are simultaneously eigenstates of both $\vec{L}^2$ and L_z.

In spherical coordinates,

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$L_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2 = \hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right)$$

With these spherical operator forms one can show

> The spherical harmonics are eigenstates of $\vec{L}^2$ with eigenvalues $\hbar^2\ell(\ell+1)$
>
> $$\vec{L}^2 Y_{\ell m}(\theta,\phi) = \hbar^2\ell(\ell+1) Y_{\ell m}(\theta,\phi)$$
>
> The spherical harmonics are eigenstates of L_z with eigenvalues $m\hbar$
>
> $$L_z Y_{\ell m}(\theta,\phi) = m\hbar Y_{\ell m}(\theta,\phi)$$

The expression of $\vec{L}^2$ should look very familiar. We now see

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\right] + V(r) + \frac{1}{2mr^2}\vec{L}^2$$

As $\vec{L}^2$ and L_z only act on angular variables, $[\hat{H}, \vec{L}^2] = [\hat{H}, L_z] = 0$ and $\vec{L}^2, L_z] = 0$. Thus $\hat{H}, \vec{L}^2$ and L_z are mutually commuting Hermitian operators.

When we solve the 1D radial equation, which depends on ℓ, we will typically get solutions indexed by some radial quantum numbers we will call n. Thus the energy eigenvalues can be labeled in general as $E_{n\ell}$. Note that $\hat{H}$ does not depend on L_z, yet L_z commutes with $\vec{L}^2$. So m is a wave function label, but as E does not depend on m, there is a $2\ell+1$ degeneracy of energy eigenvalues corresponding to the possible values of m. Thus we conclude that the stationary state solutions for any central potential will take the form

$$\psi = R_{n\ell}(r) Y_{\ell m}(\theta,\phi)$$

$$\hat{H}\psi_{n\ell m} = E_{n\ell}\psi_{n\ell m} \qquad \vec{L}^2\psi_{n\ell m}\psi_{n\ell m} = \hbar^2\ell(\ell+1)\psi_{n\ell m} \qquad \hat{L}_z\psi_{n\ell m}\psi_{n\ell m} = m\hbar\psi_{n\ell m}$$

8.4 3D Infinite Spherical Well

We consider the spherical analog of the 3D infinite square well we discussed previously. Namely,

$$V(r) = \begin{cases} 0 & \text{if } r < a \\ \infty & \text{otherwise} \end{cases}$$

The radial equation for $r < a$ becomes

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

8.4.1 *s-wave* case

We first consider the $\ell = 0$ case, which we call the *s-wave* case. (Hint: atomic s orbitals).

Substituting $u_\ell(r) = rR_\ell(r)$ in the above yields

$$\frac{d}{dr} r^2 \frac{d}{dr} \frac{u_\ell(r)}{r} = r \frac{d^2}{dr^2} u_\ell(r) \quad \Rightarrow \quad \frac{d^2}{dr^2} u_\ell(r) = -\frac{2mE}{\hbar^2} u_\ell(r) = -k^2 u_\ell(r) \quad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

The general solution is

$$u(r) = A \sin kr + B \cos kr \qquad \Rightarrow R(r) = A\frac{\sin kr}{r} + B\frac{\cos kr}{r}$$

We have boundary conditions at $r = 0$ and $r = a$. As the second term blows up at $r = 0$, we reject it as unphysical since $|R(r)|^2$ is infinite at the origin. The second constraint yields

$$\frac{\sin ka}{a} = 0 \quad \Rightarrow \quad ka = n\pi,\ n = 1, 2, 3, \ldots \quad \Rightarrow \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2},\ n = 1, 2, 3, \ldots$$

The normalization condition is

$$1 = \int_0^a r^2 |A|^2 \frac{\sin^2 kr}{r^2}\, dr = |A|^2 \left(\frac{a}{2} - \frac{\sin 2ak}{4k}\right) = |A|^2 \left(\frac{a}{2} - \frac{\sin 2n\pi}{4k}\right) = |A|^2 \frac{a}{2} \quad \Rightarrow A = \sqrt{\frac{2}{a}}$$

s-wave Spherical Well Solution

$$\ell = 0: \quad \psi_{n,\ell=0,m=0}(\vec{r}) = \sqrt{\frac{2}{a}} \frac{\sin\left(\frac{n\pi r}{a}\right)}{r} Y_{00}(\theta, \phi) = \frac{1}{\sqrt{2\pi a}} \frac{\sin\left(\frac{n\pi r}{a}\right)}{r} \qquad E_{n,\ell=0} = \frac{n^2\pi^2\pi^2}{2ma^2}$$

8.4.2 General Case

The full radial equation is

$$\left[\frac{d}{dr}\left(r^2 \frac{d}{dr}\right) + k^2 r^2\right] R_\ell(r) = \ell(\ell+1) R_\ell(r)$$

the general solution of which are the spherical Bessel and spherical Neumann functions

$$R_{n\ell}(r) = A j_\ell(kr) + B \eta_\ell(kr)$$

where j_ℓ is the solution regular at the origin

$$j_\ell(x) \to \frac{x^\ell}{(2\ell+1)!!} \qquad \eta_\ell(x) \to -\frac{(2\ell-1)!!}{x^{\ell+1}}$$

and thus is the solution we retain

$$j_0(x) = \frac{\sin x}{x} \quad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \qquad j_{\ell+1}(x) = \frac{2\ell+1}{x} j_\ell(x) - j_{\ell-1}(x)$$

Our boundary condition at $r = a$ requires $j_\ell(kr) = 0$. Denoting the ascending zeros, which one can find tabulated below, of the spherical Bessel function by

$$j_\ell(\beta_{n\ell}) \equiv 0, \ ; n = 1, 2, 3 \dots \quad \Rightarrow ka = \beta_{n\ell}$$

we then have the energy eigenvalues,

$$E_{n\ell} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \beta_{n\ell}^2}{2ma^2}, \quad n = 1, 2, 3, \dots \quad \ell = 0, 1, 2, \dots$$

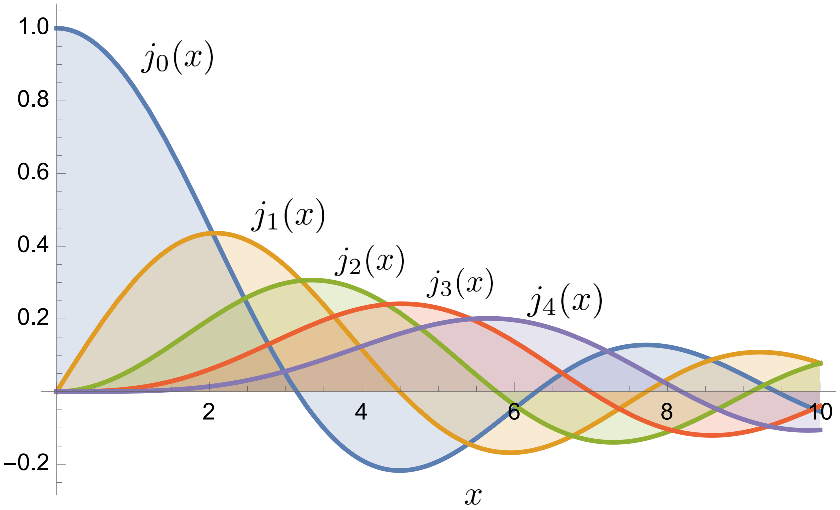


Figure 8.1: First few $j_\ell(x)$

The first few zeros $\beta_{n\ell}$

table of $\beta_{n\ell}$:

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$\ell = 0$	π	2π	3π	4π
$\ell = 1$	4.493	7.725	10.904	14.066
$\ell = 2$	5.763	9.095	12.323	15.515
$\ell = 3$	6.988	10.417	13.698	16.924
$\ell = 4$	8.183	11.705	15.050	18.301

As the spherical harmonics are properly normalized, the normalization condition is

$$|A_{n\ell}|^2 = \int_0^a r^2 \left[j_\ell(\beta_{n\ell}\frac{r}{a}\right]^2\, dr = |A_{n\ell}|^2 a^3 \int_0^1 y^2 [j_\ell(\beta_{n\ell} y)]^2\, dy = 1$$

where we substituted $r = ay$ above. Thus our full solution is

Full Spherical Well Solution

$$\psi_{n\ell m}(r,\theta,\phi) = A_{n\ell} j_\ell \left(\beta n\ell \frac{r}{a}\right) Y_{\ell m}(\theta,\phi) \qquad E_{n\ell} = \frac{\hbar^2 \beta_{n\ell}^2}{2ma^2}$$

These solutions form a complete orthonormal basis of stationary states for any wave packet satisfying the boundary condition that the wave function vanish at $r = a$. The orthonormality condition

$$1 = \int \psi^*_{n'\ell' m'}(r,\theta,\phi)\psi_{n\ell m}(r,\theta,\phi),\ d\vec{r} = A^*_{n'\ell'} A_{n\ell} \int_0^a r^2 j_{\ell'}\left(\beta_{n'\ell}\frac{r}{a}\right) j_\ell\left(\beta_{n\ell}\frac{r}{a}\right) dr \int Y_{\ell' m'}(\theta,\phi) Y_{\ell m}(\theta,\phi)\, d\Omega$$

$$= \delta_{\ell'\ell}\delta_{m'm} A^*_{n'\ell} A_{n\ell} \int_0^a r^2 j_\ell\left(\beta_{n'\ell'}\frac{r}{a}\right) j_\ell\left(\beta_{n\ell}\frac{r}{a}\right) dr$$

This then requires

$$A^*_{n'\ell} A_{n\ell} \int_0^a r^2 j_\ell\left(\beta_{n'\ell}\frac{r}{a}\right) j_\ell\left(\beta_{n\ell}\right) dr = A^*_{n'\ell} A_{n\ell} a^3 \int_0^1 y^2 j_\ell(\beta_{n'\ell} y) j_\ell(\beta_{n\ell} y)\, dy = \delta_{n'n} |A_{n\ell}|^2$$

which can be demonstrated by using recursion relations and partially integrating.

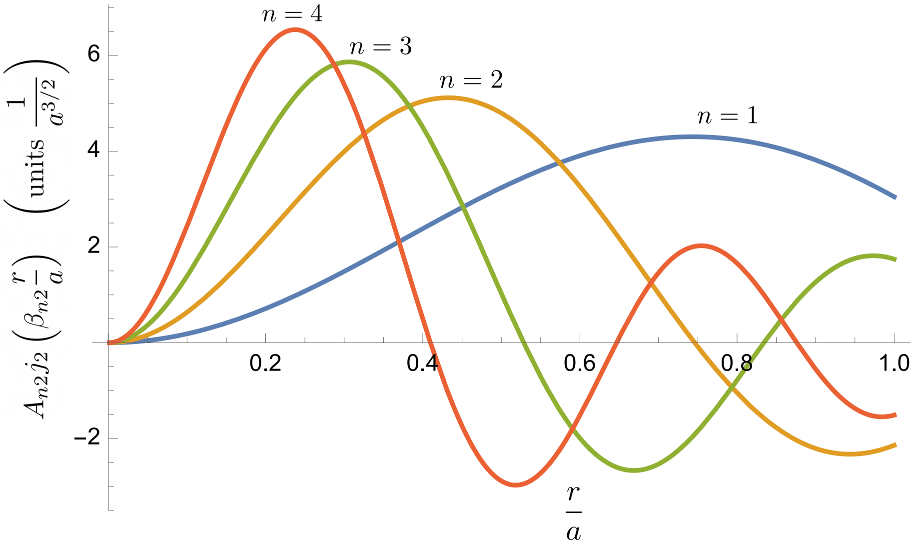


Figure 8.2: The normalized radial solutions for $\ell = 2$, $A_{n\ell} j_\ell \left(\beta_{n\ell}\frac{r}{a}\right)$

It is amusing to compare the two closely related 3D problems we have completed. In the case of the 3D Cartesian square well, there are three quantum numbers n_x, n_y, n_z associated with the three degrees of freedom, and $E = E(n_x, n_y, n_z)$. E was proportional to $n_x^2 + n_y^2 + n_z^2$ so there is an implicit energy degeneracy as several choices of these quantum numbers can give the same energy. This degeneracy includes all distinct permutations of $\{n_x, n_y, n_z\}$, but is not necessarily limited to such exchanges. These permutations correspond to various 90-degree rotations of the cube into itself, exchanging the axes.

In the spherical case, there are also three quantum numbers, n, ℓ, m, but $E = E_{n\ell}$. The degeneracy is explicit – the $2\ell + 1$ degeneracy is associated with m. This reflects rotational invariance – the physics of a rotationally invariant Hamiltonian cannot depend on the choice we make in locating the z-axis of our coordinate system.

8.5 The Hydrogen Atom

Now we tackle a problem that in some sense started quantum mechanics. A couple of preliminaries to simplify assumptions that Griffiths and/or we will make in treating the hydrogen atom.

1. To date we have discussed motions of particles in a fixed external field. However the hydrogen atom is more complex, consisting of an electron and a proton bound together, each orbiting the center of mass. However as $m_p \gg m_e$, the center of mass is *very* close to the proton, which allows Griffiths to treat the proton as an infinitely heavy static source of a Coulomb field. For consistency, we will do the same. However the true time-independent Schrödinger equation would be

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2_{\vec{r}_e} - \frac{\hbar^2}{2m_p}\nabla^2_{\vec{r}_p} + V(|\vec{r}_e - \vec{r}_p|)\right]\psi(\vec{r}_e, \vec{r}_p) = E\psi(\vec{r}_e, \vec{r}_p)$$

where here

$$\nabla^2_{\vec{r}_e} = \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}$$

and similarly with $\nabla^2_{\vec{r}_p}$. The equation requires six coordinate degrees of freedom. But because the potential involves only the relative coordinate, one can simplify things by transforming the relative $\vec{r}_e$ and center of mass $\vec{R}$ coordinates as follows:

$$\vec{r} \equiv \vec{r}_e - \vec{r}_p \quad M\vec{R} = m_e\vec{r}_e + m_p\vec{r}_p \quad M \equiv m_e + m_p$$

Using the chain rule one then finds

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{r}} - \frac{\hbar^2}{2M}\nabla^2_{\vec{R}} + V(r)\right]\psi(\vec{r}, \vec{R}) = E\psi(\vec{r}, \vec{R}) \quad \text{where } \mu \equiv \frac{m_e m_p}{m_e + m_p}$$

Then by writing $\psi(\vec{r}, \vec{R}) = \psi_{\text{rel}}(\vec{r})\psi_{CM}(\vec{R})$ one obtains

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2 + V(r)\right]\psi_{\rm rel}(\vec{r}) = E_{\rm rel}\psi_{\rm rel}(\vec{r}) \quad -\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\psi_{CM}(\vec{R}) = E_{CM}\psi_{CM}(\vec{R}) \quad E = E_{\rm rel} + E_{CM}$$

The second equation is easily solved. The center of mass of the atom travels as a plane and E_{CM} is the associated kinetic energy. But in general this is of no interest – we are instead concerned with the intrinsic excitations of the atom.

2. We will assume $V(r) \sim \frac{1}{r}$. The proton has a finite size, which modifies the $\frac{1}{r}$ behavior at very short distances of around 10^{-5} of the hydrogen atom's radius. Treating the Coulomb interaction as that from a point charge in the Schrödinger equation leads to solutions where the wave function remains finite at the origin – but this is not the case for its relativistic analog, the Dirac equation.

3. Griffiths uses SI units. We will write the attractive Coulomb potential in the form

$$V(r)_{\rm Griffiths} = -\left[\frac{e^2}{4\pi\varepsilon_0}\right]\frac{1}{r} = -\left[\frac{e^2}{4\pi\varepsilon_0\hbar c}\right]\frac{\hbar c}{r} = -\alpha\frac{\hbar c}{r} \equiv V(r)_{\rm us}$$

Here α is the dimensionless fine structure constant $\alpha \sim \frac{1}{137}$ which Holger Müller has measured to exquisite precision. For atom physics applications, we use $\hbar c = 1973$ eV Å, where an Åis $10^{-10} m$ as eV and Åare the natural energy and distance units in an atom.

If we plug in $R_\ell(r) = u_\ell(r)/r$ into our generic 3D radial equation

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \alpha\frac{\hbar c}{r} + \frac{\hbar^2}{2m}\frac{1}{r^2}\ell(\ell+1)\right]R_\ell = ER_\ell \quad \Rightarrow \tag{8.3}$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \alpha\frac{\hbar c}{r} + \frac{\hbar^2}{2m}\frac{1}{r^2}\ell(\ell+1)\right]u_\ell = Eu_\ell \tag{8.4}$$

The potential is shown below in Figure 8.3. It is much more extended than either the square well or the harmonic oscillator

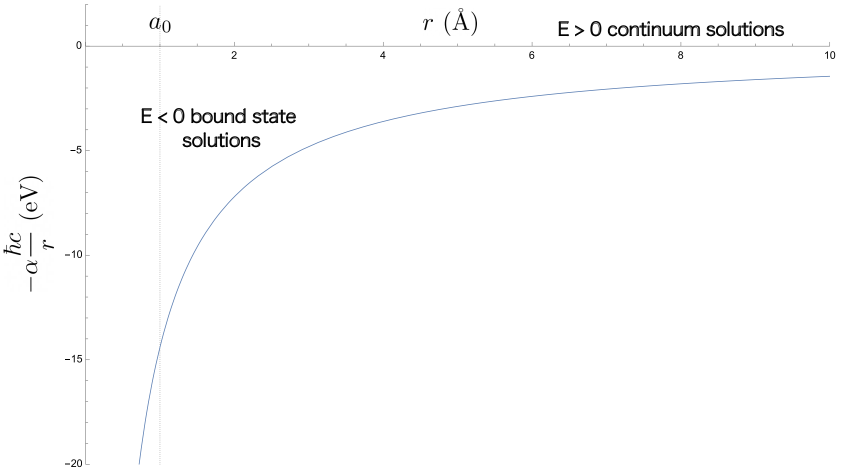


Figure 8.3: The Coulomb potential for the hydrogen atom, which generates an infinite number of bound and continuum states. The hydrogen Bohr radius a_0 is indicated. The $1s$ state binding energy is 13.6 eV.

cases we have discussed previously, where binding energies were proportional to n^2 and n respectively. We will find the Coulomb bound-state spectrum varies at $1/n^2$ leading to an infinite number of very weakly bound states.

We look for bound-state solution. We introduce the dimensionless distance ρ and the dimensionless parameter ρ_0,

$$\rho \equiv \kappa r = \frac{\sqrt{-2m_e E}}{r} = \frac{\sqrt{2m|E|}}{r} \qquad \rho_0 \equiv \alpha \sqrt{\frac{2mc^2}{|E|}}$$

where $|E|$ is the binding energy, which leads to

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \alpha\frac{\hbar c}{r} + \frac{\hbar^2}{2m}\frac{1}{r^2}\ell(\ell+1)\right] u_\ell(\rho) = E u_\ell(\rho) \quad \Rightarrow$$

$$\left[-\frac{\hbar^2}{2m}\frac{2m|E|}{\hbar^2}\frac{d^2}{d\rho^2} - \alpha\frac{\sqrt{2m|E|}}{\hbar}\frac{\hbar c}{\rho} + \frac{\hbar^2}{2m}\frac{2m|E|}{\hbar^2}\frac{1}{\rho^2}\ell(\ell+1)\right] u_\ell(\rho) = -|E| u_\ell(\rho) \quad \Rightarrow$$

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

We can get insight into the solutions by examining limiting behavior. As $\rho \to \infty$,

$$\frac{d^2 u_\ell(\rho)}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u_\ell(\rho) \quad \Rightarrow \quad u_\ell(\rho) \sim A e^{-\rho} + B e^{\rho} \quad \rightarrow \quad u_\ell(\rho) \sim A e^{-\rho}$$

as we want the solution to be normalizable. But for $\rho \to 0$,

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

$$\Rightarrow \quad u_\ell(\rho) \sim C\rho^{\ell+1} + D\rho^{-\ell} \quad \Rightarrow \quad u_\ell(\rho) \sim C\rho^{\ell+1}$$

to avoid $R_\ell(r)$ blowing up as $r \to 0$.
The combination of these two limits prompts us to try a solution of the form

$$u_\ell(\rho) \sim \rho^{\ell+1}e^{-\rho}v_\ell(\rho) \quad \to$$

Plugging this in yields

$$\rho^\ell e^{-\ell}\left[\rho\frac{d^2}{d\rho^2} + 2(\ell+1-\rho)\frac{d}{d\rho} + \frac{\ell(\ell+1)}{\rho} - 2(\ell+1) + \rho\right]v_\ell(\rho) = \rho^\ell e^{-\rho}\left[\rho - \rho_0 + \frac{\ell(\ell+1)}{\rho}\right]v_\ell(\rho) \quad \Rightarrow$$

$$\left[\rho\frac{d^2}{d\rho^2} + 2(\ell+1-\rho)\frac{d}{d\rho} + \rho_0 - 2(\ell+1)\right]v_\ell(\rho) = 0$$

Just as we did in solving the harmonic oscillator in the "conventional way", we look for a power series solution

$$v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$$

$$\frac{dv(\rho)}{d\rho} = \sum_{j=0}^{\infty} c_j j\rho^{j-1} = \sum_{j=1}^{\infty} c_j j\rho^{j-1} = \sum_{j=0}^{\infty} c_{j+1}(j+1)\rho^j \quad \text{in the last step taking } j \to j+1$$

$$\frac{d^2v(\rho)}{d\rho^2} = \sum_{j=0} c_{j+1}j(j+1)\rho^{j-1}$$

Substituting this into our radial equation yields

$$\sum_{j=0}^{\infty}\left[c_{j+1}j(j+1)\rho^j + 2(\ell+1)c_{j+1}(j+1)\rho^j - 2c_j j\rho^j + (\rho_0 - 2(\ell+1))c_j p^j\right] = 0$$

where the color coding indicated which expressing for $\frac{dv(\rho)}{d\rho}$ has been used where. As all terms carry the same power in ρ^j, we conclude

$$c_{j+1}j(j+1) + 2(\ell+1)c_{j+1}(j+1) - 2c_j j + (\rho_0 - 2(\ell+1))c_j = 0 \quad \Rightarrow$$

$$c_{j+1}(j+1)(j+2\ell+2) - c_j(2j+2\ell+2-\rho_0) = 0 \quad \Rightarrow \quad c_{j+1} = \left[\frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}\right]c_j$$

For large j this relationship reduces to

$$c_{j+1} \sim \frac{2}{j+1} c_j \qquad \text{which we can iterate to get} \qquad c_{j+1} \sim \frac{2^{j+1}}{(j+1)!} c_0$$

Thus,

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \sim c_0 \sum_{j=0}^{\infty} \frac{(2\rho)^j}{j!} \sim c_0 e^{2\rho}$$

in which case

$$u_\ell(\rho) \sim \rho^{\ell+1} e^{-\rho} v_\ell(\rho) \sim \rho^{\ell+1} e^{-\rho} c_0 e^{2\rho} \sim c_0 \rho^{\ell+1} e^{\rho}$$

and our solution would not be normalizable. We conclude that $v(\rho)$ must truncate – it must be a polynomial. Thus our solutions must be

> Bound-state Coulomb solutions will be obtained for $c_j = 0, j = 1, 2, 3, \ldots$

Let's start finding out what these polynomials are.

8.5.1 Bound State Radial Wave Function

Let's quickly summarize what we just found. If we plug in $R_\ell(r) = u_\ell(r)/r$ in our generic 3D radial wave equation

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \alpha \frac{\hbar c}{r} + \frac{\hbar^2}{2m} \frac{1}{r^2} \ell(\ell+1) \right] R_\ell = E R_\ell \quad \Rightarrow$$

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \alpha \frac{\hbar c}{r} + \frac{\hbar^2}{2m} \frac{1}{r^2} \ell(\ell+1) \right] u_\ell = E u_\ell$$

We look for bound-state solutions. We introduce the dimensionless ρ and the dimensionless parameter ρ_0,

$$\rho \equiv \kappa r = \frac{\sqrt{-2m_e E}}{\hbar} r = \frac{\sqrt{2m|E|}}{\hbar} r \qquad \rho_0 \equiv \alpha \sqrt{\frac{2mc^2}{|E|}}$$

where $|E|$ is the binding energy, which leads to

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

We examined this equation for $\rho \to \infty$ and found that it must behave as

$$u_\ell(\rho) \sim Ae^{-\rho}$$

to be normalizable. We also examined the equation for $\rho \to 0$ and found that to remain infinite,

$$u_\ell(\rho) \sim C\rho^{\ell+1}$$

to avoid $R_\ell(r)$ blowing up as $r \to 0$.

We then decided to try a solution that builds in the proper large and small ρ behavior

$$u_\ell(\rho) \sim \rho^{\ell+1}e^{-\rho}v_\ell(\rho) \quad \Rightarrow$$

where $v_\ell(\rho)$ is yet to be determined. Plugging this in and doing a far amount of algebra led to the recursion relation

$$c_{j+1} = \left[\frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}\right]c_j$$

For large j this relationship reduces to

$$c_{j+1} \sim \frac{2}{j+1}c_j \quad \Rightarrow \quad c_{j+1} \sim \frac{2^{j+1}}{(j+1)!}c_0$$

Thus,

$$v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j \sim c_0\sum_{j=0}^{\infty}\frac{(2\rho)^j}{j!} \sim c_0e^{2\rho}$$

in which case

$$u_\ell(\rho) \sim \rho^{\ell+1}e^{-\rho}v_\ell(\rho) \sim \rho^{\ell+1}e^{-\rho}c_0e^{2\rho} \sim c_0\rho^{\ell+1}e^{\rho}$$

and our solution would not be normalizable. Therefore $v(\rho)$ must truncate as a polynomial.

If c_{jmax} is the last nonzero coefficient, then

$$2(j_{max}+\ell+1) = \rho_0, \quad j_{max} = 0, 1, 2, \ldots$$

This is an *eigenvalue equation*: ρ depends on the energy and must be an even positive integer (see below). Let's define $n \equiv j_{max} + \ell + 1$ – which we will call the principal quantum number. As j_{max} runs from 0 onward,

$$\ell = 0 \;\Rightarrow\; n = 1, 2, 3, \ldots \qquad \ell = 1 \;\Rightarrow\; n = 2, 3, 4, \ldots \qquad \text{in general } \;\ell\; n = \ell+1, \ell+2, \ldots$$

Then the condition is

$$2n = \rho_0 = \alpha\sqrt{\frac{2mc^2}{|E|}} \quad \Rightarrow \quad |E_n| = \frac{\alpha^2 mc^2}{2n^2} = -\frac{|E_1|}{n^2} \quad \text{depends on just} n$$

$$n = 1 \qquad |E_1| = \frac{\alpha^2 mc^2}{2} \qquad \ell = 0 \qquad 1s \tag{8.5}$$

$$n = 2 \qquad |E_2| = \frac{|E_1|}{4} \qquad \ell = 0, 1 \qquad 2s, 2p \tag{8.6}$$

$$n = 3 \qquad |E_3| = \frac{E_1|}{9} \qquad \ell = 0, 1, 2 \qquad 3s, 3p, 3d \tag{8.7}$$

As each ℓ has $2m + 1$ *magnetic* substrates – we'll get to the magnetic aspect later – we can calculate the total degeneracy of the level characterized by n,

$$\text{number of states with energy} E_n \ : \ \sum_{\ell=0}^{n-1}(2\ell + 1) = n^2$$

There is a natural distance scale for the hydrogen atom, based on the n = 1 s-wave orbit

$$1 = a_0\kappa_1 \equiv a_0\frac{\sqrt{2m|E_1|}}{\hbar} = a_0\frac{\alpha mc^2}{\hbar c} \qquad a_0 = \frac{\hbar c}{\alpha mc^2} \sim \frac{(137)(1973 \text{ eV Å})}{511000 \text{ eV}} \sim 0.529\text{Å}$$

This is called the *Bohr radius* for hydrogen. Similarly $|E_1| \sim 13.6$ eV.

Basic Scales in Hydrogen

1 s binding energy ~ 13.6 eV Bohr Radius ~ 0.529 Å 1 Å$= 10^{-10}$ m

Note then that

$$\rho = \kappa r = \frac{\sqrt{2m|E_n|}}{\hbar}r = \frac{\sqrt{2m|E_1|}}{n\hbar}r = \frac{1}{n}\frac{r}{a_0}$$

So the spectroscopy of the hydrogen atom – at the level where the interaction is just the Coulomb potential is shown below in Figure 8.4. Note that, apart from the ground state, there are multiple states of different *angular momenta* ℓ with the same energy. This degeneracy should surprise you, as the radial equation whose solutions determine the energy eigenvalues include an angular momentum barrier term $\ell(\ell + 1)/r^2$ that one might anticipate would distinguish eigenstates of different ℓ. Also note the pattern of bound states, the increasing density of states as one approaches $E \rightarrow 0$ from below.

Also remember there are continuum states of $E > 0$ that we have not discussed. These are scattering states of an interacting free electron with an interacting free proton. These states are not normalizable, but we could derive a basis, analogous to plane waves, that (together with the bound states) would be complete, allowing us to expand any wave packet describing a $E > 0$ state of an interacting electron and proton in terms of that basis. This basis would become our familiar plane wave basis – our momentum basis – were we to turn off the Coulomb interaction, by, for example, taking $\alpha \to 0$.

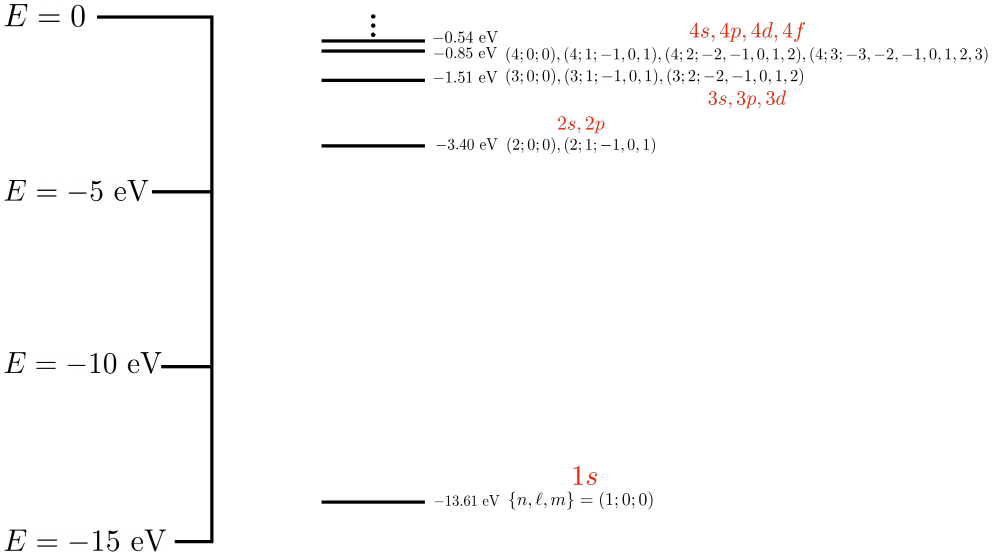


Figure 8.4: The spectroscopy of the hydrogen atom. Our treatment of the Hamiltonian includes just the Coulomb force between the proton and electron, treating the proton as a point particle. Corrections associated with the electron and nuclear spin – fine structure and hyperfine structure can be added to this simple picture.

8.5.2 *s-wave* Solutions

We can generate a few examples of s-wave radial states

$$s\text{–wave:} \quad c_{j+1} = \left[\frac{2(j+1) - 2n}{(j+1)(j+2)} \right] c_j$$

and calling the j_{max} as the last nonzero term $c_{j_{max}}$,

$$j_{max} = 0 \qquad n = 1 \qquad v(\rho) = c_0$$

$$j_{max} = 1 \qquad n = 2 \qquad v(\rho) = c_0(1 - \rho) = c_0 \left(1 - \frac{1}{2} \frac{r}{a_0} \right)$$

$$j_{max} = 2 \qquad n = 3 \qquad v(\rho) = c_0\left(1 - 2\rho + \frac{2}{3}\rho^2\right) = c_0\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)$$

and so on. Now as

$$R_\ell(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v_\ell(\rho) \qquad \Rightarrow \qquad R_0(r) = \frac{1}{r}\rho e^{-\rho}v_0(\rho)$$

So

$$R_{n=1\ell=0} \sim c_0 e^{-r/a_0} \quad R_{n=2\ell=0} \sim c_0 e^{-r/2a_0}\left(1 - \frac{1}{2}\frac{r}{a_0}\right) \qquad R_{n=3\ell=0} \sim c_0 e^{-r/3a_0}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)$$

Finally we determine c_0 via normalization in each case above

$$\int_0^\infty r^2|R_{n\ell=0}(r)|^2\,dr = 1$$

which yields

$$R_{n=1\ell=0} = \frac{2}{\sqrt{a_0^3}}e^{-r/a_0} \qquad R_{n=2\ell=0} = \frac{2}{\sqrt{(2a_0)^3}}e^{-r/2a_0}\left(1 - \frac{1}{2}\frac{r}{a_0}\right)$$

$$R_{n=3\ell=0} = \frac{2}{\sqrt{(3a_0)^3}}e^{-r/3a_0}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)$$

and of course the full 3D normalized stationary bound states are

$$R_{n=1\ell=0} = \frac{2}{\sqrt{a_0^3}}e^{-r/a_0}Y_{00}(\theta,\phi) \qquad R_{n=2\ell=0} = \frac{2}{\sqrt{(2a_0)^3}}e^{-r/2a_0}\left(1 - \frac{1}{2}\frac{r}{a_0}\right)Y_{00}(\theta,\phi)$$

$$R_{n=3\ell=0} = \frac{2}{\sqrt{(3a_0)^3}}e^{-r/3a_0}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)Y_{00}(\theta,\phi)$$

8.5.3 General Solution

The recursion for the polynomial $v(\rho)$ can be evaluated for any ℓ and n. The results are the associated Laguerre polynomials

$$v(\rho) = L^{2\ell+1}_{n-\ell-1}(2\rho) \quad \text{where} \quad L^p_q(x) \equiv (-1)^p\left(\frac{d}{dx}\right)^p L_{p+q}(x)$$

Here $L_{p+q}(x)$ is the Laguerre polynomial,

$$L_q(x) = \frac{e^x}{q!}\left(\frac{d}{dx}\right)^q (e^{-x}x^q) \qquad L_0(x) = 1 \quad L_1(x) = 1 - x \quad L_2(x) = 1 - 2x + \frac{1}{2}x^2 + \cdots$$

Combining these and bringing derivatives across the first exponential yields simpler expressions

$$L_q^p(x) = \frac{x^{-p}e^x}{q!}\left(\frac{d}{dx}\right)^q e^x x^{p+q}$$

$$v(\rho) = \frac{1}{(n-\ell-1)!}\rho^{-2\ell-1}e^{2\rho}\left(\frac{d}{d\rho}\right)^{n-\ell-1} e^{-2\rho}\rho^{n+\ell}$$

The normalization can be done, and the full 3D stationary states are formed. The result is

Hydrogen Bound-State Wave Functions

$$\psi_{n\ell m} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-r/na_0}\left(\frac{2r}{na_0}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}(2r/na_0)\right] Y_{\ell m}(\theta,\phi)$$

$$\int r^2 \psi_{n\ell m}^*(\vec{r})\psi_{n\ell m}(\vec{r})\, dr d\Omega = \delta_{n'n}\delta_{\ell'\ell}\delta m'm$$

A lot remains to be discussed. Our goal is now to understand the electron's quantum mechanical *spin*.

Chapter 9

Angular Momentum and Spin

9.1 Angular Momentum

9.1.1 Addition of Angular Momentum

Much of the interesting physics of the hydrogen atom and other atomic systems derives from interactions that involve both orbital motion and the electron spin (as well as the nuclear total angular momentum). This problem leads us to describe systems with more than one angular momentum operator. We describe here the coupling of two commuting angular momentum operators $\hat{J}_1$ and $\hat{J}_2$. An understanding of this two-angular-momenta system will allow us to proceed to other problems of much greater complexity – by successively coupling angular momenta in pairs.

The orthonormal eigenstates of $\hat{J}_1^{\,2}$ and J_{1z} we will denote by $|j_1 m_1\rangle$: $\hat{J}_2$ will have no effect on these states. Similarly $\hat{J}_2$ and J_{2z} will have the eigenstates $|j_2 m_2\rangle$ and $\hat{J}_1$ will have no effect on them. That is, these operators act in a direct product space

$$\Sigma = \Sigma_{j_1} \otimes \Sigma_{j_2}$$

corresponding to the state vectors

$$|j_1 m_1; j_2 m_2\rangle \equiv |j_1 m_1\rangle |j_2 m_2\rangle$$

The wave function labels come from the full set of four commuting operators $\hat{J}_1^{\,2}, J_{1z}, \hat{J}_2^{\,2}$, and J_{2z}. The Hilbert space of a physical problem may involve other degrees of freedom. For example, if one is describing a particle according to its location in 3D space and its spin, then its wave function could be represented as

$$|\vec{r_1} s_1 = \frac{1}{2} m_{s_1}\rangle \to |n_1 \ell 1 m_1 s_1 = \frac{1}{2} m_{s_1}\rangle$$

Or one could have two electrons, with a possible set of labels for the full Hilbert space being

$$|\vec{r_1} s_1 = \frac{1}{2} m_{s_1}\rangle |\vec{r_2} s_2 = \frac{1}{2} m_{s_2} \equiv \begin{cases} |\vec{r_1} s_1 m_{s_1}; \vec{r_2} s_2 m_{s_2} \\ |\vec{r_1}\rangle |s_1 m_{s_1}\rangle |\vec{r_2}\rangle |s_2 m_{s_2}\rangle \end{cases}$$

That is, we can think of this as a single Hilbert space for the problem, or alternatively as a direct product space involving the kets for particle 1 and particle 2, or alternatively, the ket for each particle can be viewed as a *product* of kets describing the particle's spatial and spin degrees of freedom.

Another example would be the case where $\hat{J}_1$ and $\hat{J}_2$ might represent the orbital and spin angular momentum carried by a single particle. This would correspond to one of the electrons described above, but where the nature of the problem (e.g., motion in a central field) allows us to further decompose the state vector $|\vec{r_1}\rangle$. In this case the full set of labels for our Hilbert space could be taken to be

$$|\vec{r_1} s_1 m_{s_1}\rangle \to |n_1 \ell_1 m_{\ell_1} s_1 m_1\rangle$$

Both of the examples described above involve Hilbert spaces that are infinite, if all degrees of freedom are considered. In many cases we may want to focus only on the angular momentum quantum numbers – and often only the magnetic quantum numbers, as we may be working in subspaces with fixed j_1 and j_2. In that case we may put aside the other quantum numbers that may be carried along (implicitly) and focus on just the angular momentum degrees of freedom. In the following we thus will suppress the accompanying quantum numbers.

If we have commuting angular momenta $\hat{J}_1$ and $\hat{J}_2$, then when we form $\hat{J} = \hat{J}_1 + \hat{J}_2$,

$$[J_{1i}, J_{1j}] = i\epsilon_{ijk} J_{1k} \quad [J_{2i}, J_{2j}] = i\epsilon_{ijk} J_{2k} \quad \Rightarrow \quad [J_i, J_j] = [J_{1i}, J_{1j}] + [J_{2i}, J_{2j}] = i\epsilon_{ijk}(J_{1k} + J_{2k}) = \epsilon_{ijk} J_k$$

we have another angular momentum. The "coupled representation" corresponds to a direct sum of subspaces having definite j

$$|(j_1 j_2) jm\rangle \quad \Leftrightarrow \quad \Sigma = \Sigma_{|j_1 - j_2|} \oplus \cdots \oplus \Sigma_{j_1 + j_2} \qquad |j_1 - j_2| \leq j \leq j_1 + j_2$$

The wave function has been labeled by the eigenvalues of another set of four commuting operators $\hat{J}_1^{\,2}, \hat{J}_2^{\,2}, \hat{J}^2$, and J_z. Thus the eigenvalues j_1 and j_2 are held in common in the coupled and uncoupled representations. Previously we counted the number of distinct magnetic substates in the uncoupled representation –

$$(2j_1 + 1)(2j_2 + 1)$$

and of course we have the same number of states in the coupled representation,

$$\sum_{j=|j_1 - j_2|}^{j_1 + j_2} (2j + 1) = (j_1 + 1)(j_2 + 1)$$

Which basis should we use? It depends on one's problem. For the simple Coulomb hydrogen atom problem, the interaction had no dependence on spin, so we worked in the uncoupled representation – and could forget entirely about the spin degree of freedom. If we include spin, all we have to remember is that each state is actually two, one with spin up, and one with spin down. But they have the same energy.

However, had we considered corrections to the hydrogen atom Hamiltonian associated with the electron's velocity, we would have encountered new contributions to the Hamiltonian, such as an interaction proportional to $\vec{\ell} \cdot \vec{s}$ that couples the electron's angular momentum to its spin. The eigenstates can no longer be written as single uncoupled states, but instead take on the coupled form,

$$|(\ell s) j m_j\rangle$$

where j is the total angular momentum we get by coupling ℓ to $s = \frac{1}{2}$, so $j = \ell \pm \frac{1}{2}$. Thus the six uncoupled $2p$ states in hydrogen:

$$2p: \quad |n=2, \ell=1, m\rangle |s = \frac{1}{2} m_s\rangle \rightarrow \begin{cases} |n \left(\ell \frac{1}{2}\right) j = \frac{3}{2} m\rangle \\ |n \left(\ell \frac{1}{2}\right) j = \frac{1}{2} m\rangle \end{cases}$$

are reshuffled to produce two subsets of states that transform as $j = \frac{1}{2}$ and $\frac{3}{2}$ amplitudes. These states – not the uncoupled ones – are the stationary state basis Nature chooses and thus we must also. The problem is rotationally invariant, and Nature knows that. In this sense, our ability to solve the hydrogen atom in the uncoupled basis was the result of an "accidental" degeneracy. "Accident" is in quotes because the accident was on we created – by ignoring the fine-structure interactions that break the degeneracy of these states.

9.1.2 Transformations Between Coupled and Uncoupled Bases

Because the coupled and uncoupled bases of states span equivalent spaces, we can expand any state in one basis relative to the other.

Clebsch-Gordan Coefficients

Unitary transformations from the uncoupled to the coupled representations are accomplished with Clebsch-Gordan coefficients

$$|(\ell_1 \ell_2) j m_j\rangle = \sum_{m_1=-\ell_1}^{\ell_1} \sum_{m_2=-\ell_2}^{\ell_2} |\ell_1 m_1 \ell_2 m_2\rangle \langle \ell_1 m_1 \ell_2 m_2 | (\ell_1 \ell_2) j m_j\rangle$$

The transformation coefficients in red – numbers that conventionally are real, as we will see – are the Clebsch-Gordan coefficients. They are nonzero only if $m_j = m_1 + m_2$. We stress that the result in the box above is simply a unitary transformation that does not alter the portion of the Hilbert space being spanned. But the coupled representation breaks the Hilbert space into a block-diagonal form, with each block labeled by one of the allowed values of $j, |\ell_1 - \ell_2| \leq \ell_1 + \ell_2$.

The inverse transformation is

$$|\ell_1 m_1 \ell_2 m_2\rangle = \sum_{j=|\ell_1-\ell_2|}^{\ell_1+\ell_2} \sum_{m_j=-j}^{j} |(\ell_1\ell_2)jm_j\rangle\langle(\ell_1\ell_2)jm_j|\ell_1 m_1 \ell_2 m_2\rangle$$

The statements of unitary follow from the orthogonality of the states in either basis, namely

$$\delta_{m_1' m_1}\delta_{m_2' m_2} = \langle \ell_1 m_1' \ell_2 m_2' | \ell_1 m_1 \ell_2 m_2\rangle = \sum_{j=|\ell_1-\ell_2}^{\ell_1+\ell_2} \sum_{m_j=-j}^{j} \langle \ell_1 m_1' \ell_2 m_2' |(\ell_1\ell_2)jm_j\rangle\langle(\ell_1\ell_2)jm_j|\ell_1 m_1 \ell_2 m_2\rangle$$

$$\delta_{jj'}\delta_{m_j' m_j} = \langle(\ell_1\ell_2)j'm_j'|(\ell_1\ell_2)jm_j\rangle = \sum_{m_1=-\ell_1}^{\ell_1} \sum_{m_2=-\ell_2}^{\ell_2} \langle(\ell_1\ell_2)j'm_j'|\ell_1 m_1 \ell_2 m_2\rangle\langle \ell_1 m_1 \ell_2 m_2|(\ell_1\ell_2)jm_j\rangle$$

It is understood in the last relation that j satisfies the triangle condition, $|\ell_1 - \ell_2| \leq j \leq \ell_1 + \ell_2$.

9.1.3 Angular Momentum & Rotations of States

Let's now try to make the connections to rotations more explicit.

We used rotational symmetry to simplify our treatment of the general central force problem, but in a hidden way, a consequence of our separation of variable in spherical coordinates. We found that all 3D central-force problems can be reduced to 1D radial equations, with the angular behavior encoded in wave functions $|\ell m\rangle$ whose position representations are the $Y_{\ell m}$s.

$$\langle\theta,\phi|\ell m\rangle = Y_{\ell m}(\theta,\phi)$$

1. The angular solutions are universal, valid for any central-force problems we decide to do.
2. Infinite-dimensional physics is factored into finite-dimensional subspaces, blocks labeled by ℓ containing $2\ell+1$ magnetic substates labeled by m. This revealed an energy degeneracy associated with m.
3. ℓ and m are quantum labels of our orthonormal stationary states.

The $Y_{\ell m}$s are angular momentum eigenstates for our coordinate system – the magnetic number m is defined with respect to the z axis we picked.

Because these eigenfunctions are associated with a particular z-axis – yet clearly the physics can not depend on the choice of coordinate system – it is natural to ask what happens were we to rotate to a different coordinate system. Under an arbitrary rotation $\hat{U}$, the state $|\ell m\rangle$ will *remain in the subspace* defined by $\{|\ell m\rangle, m = -\ell, \cdots, \ell\}$. That is,

$$\hat{U}(\hat{n},\phi)|\ell m\rangle = \sum_{m'=-\ell}^{\ell} |\ell m'\rangle\langle\ell m'|\hat{U}|\ell m\rangle \equiv \sum_{m'=-\ell}^{\ell} |\ell m'\rangle D^{\ell}_{m'm}(\hat{n},\phi)$$

The rotation operator here has been defined by an axis $\hat{n}$ about which we rotate and an angle ϕ specifying the number of radians in the rotation (with the direction of rotation conventionally defined by right hand rule). The unitary operator that accomplishes this is

$$\hat{U}(\hat{n},\phi) = \exp\left[-\frac{i}{\hbar}\phi\hat{n}\cdot\hat{L}\right] \rightarrow \exp\left[-\frac{i}{\hbar}\phi\hat{n}\cdot\hat{J}\right]$$

where here we replaced $\hat{L}$ with $\hat{J}$ because we intend the discussion to apply to *any* angular momentum operator. What is important about this? The numerical coefficients describing the rotation, the $D^j_{m'm}(\hat{n},\phi)$ depend on the rotation and on j, but not on details of the state being rotated. It could be a Coulomb state, a 3D harmonic oscillator state, etc.

Given a Hilbert space and an operator acting in that Hilbert space, if there exists a subset of the Hilbert space in which the operator, acting on that subspace, generates states that are also in that Hilbert subspace, we say that this subspace is invariant under that operator. Thus under rotations, the states of definite $\ell, m = -\ell, \cdots, \ell$ are invariant subspaces.

We can do a very simple example of a rotation. Suppose we have picked a set of axes and made measurements, but someone else has chosen different x, y axes, but hasn't changed the z axis. What would our states look like in the other person's coordinate system? The solution in our coordinate system can be transformed to the other coordinate system by a rotation by some angle ϕ around our mutual z axis, to align the x, y axes. As an exponentiated operator is defined by the corresponding power series, for this case

$$\hat{U}(\hat{n},\phi) = \exp\left[-\frac{i}{\hbar}\phi\hat{n}\cdot\hat{J}\right] = \exp\left[-\frac{i}{\hbar}\phi\hat{J}_z\right]$$

But if we apply $(\hat{J}_z)^n$ on $|jm\rangle$ it returns m^n. So on re-exponentiating,

$$D^j_{m'm}(\hat{n},\phi) = \langle jm'|\hat{U}|jm\rangle = \langle jm'|\mathrm{exp}[-i\phi m]|jm\rangle = \delta_{m'm}\mathrm{exp}[-im\phi]$$

Because the two experimentalists agree on a common z axis, they also have a common set of quantum numbers. The transformed solution differs from the original only by a phase. This expression is easily computed as a function of ϕ.

How difficult is it to generalize this?

1. What must we do to describe a rotation from one coordinate system to another that share the same origin but otherwise can differ in arbitrary ways?
2. Once we figure out how to characterize the rotation, can we evaluate the expressions for $D^j_{m'm}(\hat{n},\phi)$, as we did with our simple rotation above?

Without derivation, the answers are:

1. Using techniques you may have seen in classical mechanics, one coordinate system (x, y, z) can be put into alignment with a second coordinate system (x', y', z') via a series of three sequential rotations about the axes of the original system – these are the Euler angle rotations. The rotations are
    - A rotation of γ about the z axis

- A rotation of β around the y axis
- A rotation of α around the z axis

This means that the general $\hat{U}$ takes the form

$$\hat{U}(\alpha,\beta,\gamma) = \exp\left[-\frac{i}{\hbar}\alpha\hat{J}_z\right]\exp\left[-\frac{i}{\hbar}\beta\hat{J}_y\right]\exp\left[-\frac{i}{\hbar}\gamma\hat{J}_z\right], \quad 0 \le \alpha,\gamma \le 2\pi, 0 \le \beta \le \pi$$

and consequently

$$D^j_{m'm}(\alpha,\beta,\gamma) = \langle jm'|\hat{U}(\alpha,\beta,\gamma)|jm\rangle = \exp[-i\alpha m]d^j_{m'm}(\beta)\exp[-i\gamma m]$$

where

$$d^j_{m'm}(\beta) = \langle jm'|\exp\left[-\frac{i}{\hbar}\beta\hat{J}_y\right]|jm\rangle$$

2. an we evaluate expressions like that directly above? As we will discuss soon, $\hat{J}_y$ can be expressed in terms of raising and lowering operators that have a simple matrix element in our angular momentum subspaces, which when we expand our exponentiated operator in a power series, allows the power series to be evaluated term by term and summed. All this has been done and tabulated for our use. So the answer is yes. For $j = \frac{1}{2}$, for example, one can show

$$d^{\frac{1}{2}}_{m'm}(\beta) = \begin{pmatrix} \cos\beta/2 & -\sin\beta/2 \\ \sin\beta/2 & \cos\beta/2 \end{pmatrix}$$

9.1.4 Review So Far

We described how the states of a system with two angular momenta be represented either in the coupled or uncoupled representations within the same subspace of the Hilbert space, but with the former more useful in systems where the total angular momenta is conserved.

Clebsch-Gordan Coefficients

Unitary transformations from the uncoupled to the coupled representations are accomplished with Clebsch-Gordan coefficients

$$|(\ell_1\ell_2)jm_j\rangle = \sum_{m_1=-\ell_1}^{\ell_1}\sum_{m_2=-\ell_2}^{\ell_2}|\ell_1m_1\ell_2m_2\rangle\langle\ell_1m_1\ell_2m_2|(\ell_1\ell_2)jm_j\rangle$$

We also described how the rotational symmetry of the eigenstates we derived in the central force problem, the position-space states $Y_{\ell m}$, remain in the subspace $\{|\ell m\rangle, m = -\ell, \cdots, \ell\}$ under rotations. This is what it means to be an angular momentum eigenstate. So

$$\hat{U}(\hat{n},\phi)|\ell m\rangle = \sum_{m'=-\ell}^{\ell} |\ell m'\rangle\langle \ell m'|\hat{U}|\ell m\rangle \equiv \sum_{m'=-\ell}^{\ell} |\ell m'\rangle D^{\ell}_{m'm}(\hat{n},\phi)$$

$$\hat{U}(\hat{n},\phi) = \exp\left[-\frac{i}{\hbar}\phi\hat{n}\cdot\hat{L}\right]$$

We also noted that the most general rotation of axes can be described by three Euler angles defining sequential rotations about the $\hat{z}, \hat{y}$ and $\hat{z}$ axes of the initial axes,

$$\hat{U}(\alpha,\beta,\gamma) = \exp\left[-\frac{i}{\hbar}\alpha\hat{J}_z\right]\exp\left[-\frac{i}{\hbar}\beta\hat{J}_y\right]\exp\left[-\frac{i}{\hbar}\gamma\hat{J}_z\right], \quad 0 \le \alpha,\gamma \le 2\pi, 0 \le \beta \le \pi$$

$$D^{j}_{m'm}(\alpha,\beta,\gamma) = \langle jm'|\hat{U}(\alpha,\beta,\gamma)|jm\rangle = \exp[-i\alpha m]d^{j}_{m'm}(\beta)\exp[-i\gamma m]$$

$$d^{j}_{m'm}(\beta) = \langle jm'|\exp\left[-\frac{i}{\hbar}\beta\hat{J}_y\right]|jm\rangle$$

9.1.5 Constructing Spherical Tensor Operators

The discussion so far shows that states of good angular momentum not only factorize the Hilbert space into subspaces, but that this factorization is preserved under rotations – the subspaces are invariant. If we can take one more step – figure out how to form operators that behave in the same way – we will be able to greatly simplify our calculations of observables (matrix elements).

Why have we not previously talked about the angular momentum operator? – how to formulate such operators so they transform simply under rotations? The simple reason is that our 3D work thus far has been on Hamiltonian, which are scalars and thus do not change under rotations. For our central force problem

$$\langle \ell' m|\hat{H}|\ell m\rangle \to \langle \ell m|\hat{H}|\ell m\rangle \to \langle \ell|\hat{H}|\ell\rangle$$

There is no dependence on m and thus no dependence on the choice of coordinate system. But we have need in Quantum Mechanics for many types of operators, and most do carry nonzero angular momentum. It is clear we need to understand how both state vectors *and* operators transform under rotations, if we are to treat matrix elements involving both states and operators – and observables correspond to matrix elements. This is clear because

$$\langle j'm|\hat{T}|jm\rangle = \langle j'm'|\hat{U}^{-1}\hat{U}\hat{T}\hat{U}^{-1}\hat{U}|jm\rangle$$

$$\text{transformed operator: } \hat{T}' = \hat{U}\hat{T}\hat{U}^{-1}$$

What requirement should we place on this transformation? It is the following:

Spherical Tensor Operators

An irreducible spherical tensor operator of rank k, denoted $\hat{T}^k_q$, is a set of $2k+1$ operators, $q = -k, -k+1, \cdots, k-1, k$ that transforms according to

$$\hat{U}(\alpha,\beta,\gamma)\hat{T}^k_q\hat{U}^{-1}(\alpha,\beta,\gamma) = \sum_{q'} T^k_{q'} D^k_{q'q}(\alpha,\beta,\gamma) \tag{9.1}$$

That is, components of spherical tensor operators transform under rotations of the coordinate frame just like the components of the states $|jm_j\rangle$ we previously discussed.

As in the case of choosing the representation $|(\ell_1\ell_2)jm\rangle$ not $|\ell_1 m_1 \ell_2 m_2\rangle$, this is largely a matter of properly grouping the components of our operators. For example, we can rearrange the components of the rank-one operator $\hat{r}$ – so the Cartesian components (x, y, z) transform into the components of a spherical tensor:

$$\begin{pmatrix} r_1 \\ r_0 \\ r_{-1} \end{pmatrix} = \begin{pmatrix} -\frac{1}{\sqrt{2}}(x+iy) \\ z \\ \frac{1}{\sqrt{2}}(x-iy) \end{pmatrix} = r\sqrt{\frac{4\pi}{3}} \begin{pmatrix} Y_{11}(\theta,\phi) \\ Y_{10}(\theta,\phi) \\ Y_{1-1}(\theta,\phi) \end{pmatrix}$$

But what about more complicated operators – quantum systems may have dipoles, quadropoles, octupoles, etc. diagonal moments, and more important, these operators govern the *transitions* between quantum states. Is there some general procedure for grouping components to create spherical tensors that transform simply and link only invariant subspaces?

Before answering this question, let's look at a few examples to get a better idea of what we want to do. Suppose, for example, we had two factors of $\vec{r}$, two rank-one operators we want to combine. From the Cartesian components we can construct six independent bilinears,

$$(x^2, xy, xz, y^2, yz, z^2)$$

And the spherical regrouping? It is

$$(x^2, xy, xz, y^2, yz, z^2) \quad \leftrightarrow \quad \begin{cases} (r^2 Y_{00}) & J = 0 \\ (r^2Y_{22}, r^2Y_{21}, r^2Y_{20}, r^2Y_{2-1}, r^2Y_{2-2}) & J = 2 \end{cases}$$

There are six independent Cartesian bilinears on the left, and two spherical operators on the right, one with a single component ($J = 0$), and one with five ($J = 2$). Note that when we couple $\hat{r}$ to itself, only even-parity spherical tensors are generated – and only six Cartesian bilinears arise. If we had coupled $\hat{r}$ to the Pauli matrices $\hat{\sigma}$ (we'll get to Pauli later), nine Cartesian bilinears would result, and a $J = 1$ spherical tensor operator would also be generated.

Let's try three. The Cartesian trilinears we can now form are these 10,

$$(x^3, x^2y, x^2z, xy^2, xz^2, y^3, y^2z, yz^2, z^3) \quad \leftrightarrow \quad \begin{cases} r^3 Y_{1m} & J=1, m=-1,0,1 \\ r^2 Y_{3m} & J=3, m=3,2,1,0,-1,-2,-3 \end{cases}$$

Again, the two representations agree on the number of trilinear operators. In this case, the use of three powers of the same vector leads to only odd spherical harmonics.

These examples reflect a general procedure that can be used to generate more complicated spherical tensor operators from elementary ones like $\hat{r}, \hat{p}$, and $\hat{\sigma}$. One can show

> If $\hat{A}_{\ell_1 m_1}$ and $\hat{B}_{\ell_2 m_2}$ are spherical tensor operators, so too is
>
> $$\hat{C}_{\ell m} = \sum_{m_1 m_2} \hat{A}_{\ell_1 m_1} \hat{B}_{\ell_2 m_2} \langle \ell_1 m_1 \ell_2 m_2 | (\ell_1 \ell_2) \ell m \rangle$$

Our friend the Clebsch-Gordan coefficients show up again.

9.2 The Wigner-Eckart Theorem

Finally, we come to the real payoff of using states and operators that transform under rotations like our friends, the $Y_{\ell m}$s. The evaluation of matrix elements via Wigner-Eckart describes a powerful factorization of matrix elements into a piece that is operator dependent but frame independent, and a piece that is specific to the quantization axis the experimentalist has chosen, but independent of the operator apart from its angular momentum rank. This second term, again given in terms of Clebsch-Gordan coefficients, encodes all of the geometry of rotation. Two forms are given,

> **Wigner-Eckart Theorem**
>
> $$\begin{aligned} \langle n'j'm'|\hat{T}_{kq}|njm\rangle &= \frac{(-1)^{j-m}}{\sqrt{2k+1}} \langle j'm'j-m|(j'j)kq\rangle \langle nj'||\hat{T}_k||nj\rangle \\ &= \frac{(-1)^{k-j+j'}}{\sqrt{2j'+1}} \langle kqjm|(kj)j'm'\rangle \langle nj'||\hat{T}_k||nj\rangle \end{aligned}$$

Although we will not derive this here, the results should look reasonable to you, at least from a coupling perspective. Consider the second form: it states that if one operators on a state of angular momenta j, m with a spherical operator carrying angular momenta k, q, the only way this is going to connect to a final state characterized by $j'm'$ is if j, m and k, q are coupled to $j'm'$.

Why is this a powerful result? There are a total of $(2j'+1)(2j+1)(2k+1)$ matrix elements above. (The ones where $q+m-m' \neq 0$ are zero though). To determine these, only one measurement or one calculation is needed. One measurement for a specific m', m and q determines the "reduced matrix element" $\langle nj'||\hat{T}_k||nj\rangle$, a quantity independent of magnetic quantum numbers. And once that quantity is known, all other matrix elements are then determined. This makes sense. Suppose, for example, you make a measurement with one coordinate system, and want to know what the answer is in another. As bra, ket, and operators all transform under the rules of rotation, you can envision rotating your axes to the new axes to determine the answer. That is just geometry, not a function of operator physics. The Wigner-Eckart theorem just tells one the geometry is really as simple as a Clebsch-Gordan coefficient.

9.3 Orbital Angular Momenta & Ladder Operators

We previously discussed the commutation relations among the orbital angular momentum operators

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k \quad \text{and} \quad [\hat{L}^2, \hat{L}_i] = 0$$

and then the convention choice to take $\hat{L}^2$ and L_z as the maximal set of commuting operators. We are then able to adopt a basis labeled by these quantum numbers – our stationary states are eigenfunctions of both operators.

From the unused operators $\hat{L}_z, \hat{L}_y$ we form the linear combinations

$$\hat{L}_\pm \equiv \hat{L}_x \pm iL_y$$

and then we study their properties.

1. $L_\pm$ *is an eigenstate* of $\hat{L}^2$ – As $[\hat{L}^2, L_i] = 0$, clearly $[\hat{L}^2, L_\pm] = 0$. Further we find

   $$[\hat{L}_z, \hat{L}_\pm] = [\hat{L}_z, \hat{L}_x] \pm i[\hat{L}_z, \hat{L}_y] = i\hbar\hat{L}_y \pm \hbar\hat{L}_x = \pm\hbar(\hat{L}_x \pm i\hat{L}_y = \pm\hbar\hat{L}_\pm$$

   So suppose we act on on an eigenstate of $\hat{L}^2$ and $\hat{L}_z$, $|n\ell m\rangle$, by $\hat{L}_\pm$:

   $$\hat{L}^2\hat{L}_\pm|n\ell m\rangle = \hat{L}_\pm\hat{L}^2|n\ell m\rangle = \hat{L}_\pm\hbar^2\ell(\ell+1)|n\ell m\rangle = \hbar^2\ell(\ell+1)\hat{L}_\pm|n\ell m\rangle$$

   which states that $\hat{L}_\pm|n\ell m\rangle$ is an *eigenstate* of $\hat{L}^2$. So $\hat{L}_\pm$ produces a state within the selected invariant subspace.

2. $\hat{L}_\pm$ *raises/lowers* m by one unit;

   $$\langle n\ell m'|\hat{L}_z\hat{L}_\pm - \hat{L}_\pm\hat{L}_z|n\ell m\rangle = \pm\hbar\langle n\ell m'|\hat{L}_\pm|n\ell m\rangle$$

   $$\Rightarrow \hbar(m'-m)\langle n\ell m'|\hat{L}_z|n\ell m\rangle = \pm\hbar\langle n\ell m|\hat{L}_\pm|n\ell m\rangle \quad \Rightarrow \quad m'-m = \pm 1$$

   So $\hat{L}_+$ raises m by one unit while $\hat{L}_-$ lowers m by one unit.

3. The raising/lowering amplitudes *are related.*

   $$\hat{L}_+|n\ell m\rangle = x_m|n\ell m+1\rangle \quad \hat{L}_-|n\ell m\rangle = x'_m|n\ell m-1\rangle$$

Therefore, x'_m

$$x'_m = \langle n\ell m-1|\hat{L}_-|n\ell m\rangle = \langle n\ell m-1|\hat{L}_x - i\hat{L}_y|n\ell m\rangle$$
$$= \langle(\hat{L}_x + i\hat{L}_y)n\ell m-1|n\ell m\rangle = \langle\hat{L}_+ n\ell m-1|n\ell m\rangle = x^*_{m-1}$$

Consequently,

$$x^{'}_{m+1} = x^*_m \quad \Rightarrow \quad \hat{L}_+|n\ell m\rangle = x_m|n\ell m+1\rangle \quad \hat{L}_-|n\ell m\rangle = x^*_{m-1}|n\ell m-1\rangle$$

Note again that the statevector is defined by quantum numbers n, ℓ and $m \pm 1$; it is not literally $n\ell m - 1$ as an algebraic expression.

4. From the commutation relations one can show $\hat{L}_+\hat{L}_- - \hat{L}_-\hat{L}_+ = 2\hbar L_z$. And

$$\langle n\ell m|\hat{L}_+\hat{L}_- - \hat{L}_-\hat{L}_+|n\ell m\rangle = x^*_{m-1}\langle n\ell m|\hat{L}_+|n\ell m-1\rangle - x_m\langle n\ell m|\hat{L}_-|n\ell m+1\rangle = |x_{m-1}|^2 - |x_m|^2$$

And

$$\langle n\ell m|2\hbar L_z|n\ell m\rangle = 2\hbar^2 m$$

Therefore

$$|x_m|^2 - |x_{m-1}|^2 = -2\hbar^2 m \quad \Rightarrow \quad |x_m|^2 = (C - m(m+1))\hbar^2$$

One can show $C = \ell(\ell+1)$ based on the fact that $\hat{L}_+$ annihilates $|n\ell\ell\rangle$. Consequently,

Unfixed Angular Momentum Ladder Operators

$$\hat{L}_+|n\ell m\rangle = e^{i\beta_m}\hbar\sqrt{\ell(\ell+1) - m(m+1)}|n\ell m+1\rangle \tag{9.2}$$
$$\hat{L}_-|n\ell m\rangle = e^{-i\beta_{m-1}}\hbar\sqrt{\ell(\ell+1) - m(m-1)}|n\ell m-1\rangle \tag{9.3}$$

5. *Phase choices of Condon and Shortley*: We adopt a phase convention for fixing the relative phases $e^{i\beta_m}$ and $e^{-i\beta_{m-1}}$. The relations above involve 2ℓ phases $\{\beta_{\ell-1}, \cdots \beta_{-\ell}$ and we have 2ℓ relative phases at our disposal. We can get rid of all the phases recursively, starting with $m = \ell$ and $m = \ell - 1$, where we have

$$\hat{L}_-|n\ell\ell\rangle = e^{-i\beta_{\ell-1}}\hbar\sqrt{\ell(\ell+1)-\ell(\ell-1)}|n\ell\ell-1\rangle \tag{9.4}$$

$$\hat{L}_+|n\ell\ell-1\rangle = e^{i\beta_{\ell-1}}\hbar\sqrt{\ell(\ell-1)-\ell(\ell-1)}|n\ell\ell\rangle \tag{9.5}$$

the relations involving these states would read

$$\hat{L}_-|n\ell\ell\rangle = \hbar\sqrt{\ell(\ell+1)-\ell(\ell-1)}|n\ell\ell-1\rangle' \quad \hat{L}_+|n\ell\ell-1\rangle' = \hbar\sqrt{\ell(\ell+1)-\ell(\ell-1)}|n\ell\ell\rangle$$

as desired. The relation between states with $m = \ell - 1$ and $m = \ell - 2$ would then read

$$\hat{L}_-|n\ell\ell-1\rangle' = e^{-\beta(\beta_{\ell-2}+\beta_{\ell-1})}\hbar\sqrt{\ell(\ell+1)-(\ell-1)(\ell-2)}|n\ell\ell-2\rangle \tag{9.6}$$

$$\hat{L}_+|n\ell\ell-2\rangle = e^{i(\beta_{\ell-2}+\beta_{\ell-1})}\hbar\sqrt{\ell(\ell+1)-(\ell-1)(\ell-2)}|n\ell\ell-1\rangle' \tag{9.7}$$

and we could absorb this shifted phase into $|n\ell\ell-2\rangle$ without affecting what we did above,

$$|n\ell\ell-2\rangle' = e^{-i(\beta_{\ell-2}+\beta_{\ell-1})}|n\ell\ell-2\rangle$$

and so on. We adopt such a phase convention for fixing relative phases, leaving one overall phase still arbitrary, yielding the conventional fixed angular momentum operators

Angular Momentum Operators

$$\hat{L}_+|n\ell m\rangle = \hbar\sqrt{\ell(\ell+1)-m(m+1)}|n\ell m+1\rangle \tag{9.8}$$

$$\hat{L}_-|n\ell m\rangle = \hbar\sqrt{\ell(\ell+1)-m(m-1)}|n\ell m-1\rangle \tag{9.9}$$

This choice is incorporated in definitions of the $Y_{\ell m}$s for example. Now with these definitions we see

$$\hat{L}_+|n\ell\ell\rangle = 0 \qquad \hat{L}_-|n\ell-\ell\rangle = 0$$

like I mentioned above.

6. *Matrix Elements of $\hat{L}_x$ and $\hat{L}_y$.* As

$$\hat{L}_x = \frac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right) \quad \text{and} \quad \hat{L}_y = \frac{1}{2i}\left(\hat{L}_+ - \hat{L}_-\right)$$

one finds

$$\hat{L}_x|\ell m\rangle = \frac{\hbar}{2}\sqrt{\ell(\ell+1)-m(m+1)}|\ell m+1\rangle + \frac{\hbar}{2}\sqrt{\ell(\ell+1)-m(m-1)}|\ell m-1\rangle \tag{9.10}$$

$$\hat{L}_y|\ell m\rangle = \frac{\hbar}{2i}\sqrt{\ell(\ell+1)-m(m+1)}|\ell m+1\rangle - \frac{\hbar}{2i}\sqrt{\ell(\ell+1)-m(m-1)}|\ell m-1\rangle \tag{9.11}$$

So these are tri-diagonal Hermitian matrices but with zeros down the diagonal. For example, we have the following analogs of the $\ell = \frac{1}{2}$ Pauli matrices,

$$L_x = \frac{\hbar}{2}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix} \qquad L_x = \begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix}$$

As the orbital angular momentum comes from $\hat{r} \times \hat{p}$, we can transform into spherical coordinates and derive the position-space representations of the various components

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \qquad \hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right) \qquad \hat{L}_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_\pm + \pm\hbar e^{\pm i\phi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi}\right)$$

These acting on the $Y_{\ell m}$s for $\ell = 1$ will generate the same matrices deduced above.

9.4 Generating the Clebsch-Gordan Coefficients

While I won't go through the derivation of Clebsch-Gordan coefficients in detail, I do want to stress that the raising/lowering operator properties derived above, including the Condon and Shortley phase convention, is all one needs to derive numerical values for the Clebsch-Gordan coefficients while showing that they are real. The procedure is basically an algorithm that can be executed using the lowering operator. (For practical purposes just use Wolfram Mathematica to calculate them for you).

I will sketch the algorithm for the coupling of two angular momenta $\ell_1 = 1$ and $\ell_2 = 1$. One begin with the state of maximum total $L_z = 2$ which demands that ℓ_{12} also be maximum.

$$|(\ell = 1\ell_2 = 1)\ell_{12} = 2m_{12} = 2\rangle \quad = \quad |\ell_1 = 1m_1 = 1\ell_2 m_2 = 1\rangle \tag{9.12}$$

These two states are identified with each other and in each representation they are the unique states with the L_z eigenvalue of $2\hbar$. Consequently, (with the sign in this part of the CS phase convention),

$$\langle(\ell_1 = 1\ell_2 = 1)\ell_{12} = 2m_{12} = 2|\ell_1 = 1m_1 = 1\ell_2 = 1m_2 = 1\rangle = 1$$

Now we lower both sides of Equation 9.12. $L_{12-} = L_{1-} + L_{2-}$, and we use the left form on the left and right form on the right. This yields

$$2\hbar|(\ell_1 = 1\ell_2 = 1)\ell_{12} = 2m_{12} = 1\rangle = \sqrt{2}\hbar(|\ell_1 = 1m_1 = 0el_2 = 1m_2 = 1\rangle + |\ell_1 m_1 = 1\ell_2 = 1m_2 = 0\rangle) \tag{9.13}$$

If we contract both sides of Equation 9.13 with $\langle\ell_1 = 1m_1 = \hat{0}\ell_2 = 1m_2 = 1|$ we obtain

$$\langle\ell_1 = 1m_1 = 0\ell_2 = 1m_2 = 1|(\ell_1 = 1\ell_2 = 1)\ell_{12} = 2m_{12} = 1\rangle = \frac{1}{\sqrt{2}}$$

and if we contract both sides of Equation 9.13 with $\langle\ell_1 = 1m_1 = 1\ell_2 = 1m_2 = 0|$ we obtain

$$\langle\ell_1 m_1 = 1\ell_2 = 1m_2 = 0|(\ell_1 = 1\ell_2 = 1)\ell_{12} = 2m_{12} = 1\rangle = \frac{1}{\sqrt{2}}$$

But examining Equation 9.13 we see that there are two other normalized states of $L_z = 1$ that do not appear, that are orthogonal to the states in 9.13, and thus these must be uniquely identified with each other. That is, we find

$$|(\ell = 1\ell_2 = 1)\ell_{12} = 1m_{12} = 1\rangle = \frac{1}{\sqrt{2}}(-|\ell_1 = 1m_1 = 0\ell_2 = 1m_2 = 1\rangle + |\ell_1 = 1m_1 = 1\ell_2 = 1m_2 = 0\rangle) \tag{9.14}$$

from which we deduce

$$\langle\ell_1 = 1m_1 = 0\ell_2 = 1m_2 = 1|(\ell_1 = 1\ell_2 = 1)\ell_{12} = 1m_{12} = 1\rangle = -\frac{1}{\sqrt{2}} \tag{9.15}$$

$$\langle\ell_1 = 1m_1 = 1\ell_2 = 1m_2 = 0|(\ell_1 = 1\ell_2 = 1)\ell_{12} = 1m_{12} = 1\rangle = \frac{1}{\sqrt{2}} \tag{9.16}$$

Notice that, even with the assumption that the Clebsch-Gordan coefficients are real, the sign chosen on the RHS of Equation 9.14 appears arbitrary. This is again part of the CS phase convention: the component with the maximum m on the RHS was taken to have the positive sign.

The point here is not to have you calculate all of the CG coefficients – that is what Mathematica is for – but instead for you to understand that they can be derived using properties of the lowering operator combined with a convention for fixing various signs/phases.

9.5 Spin

9.5.1 Some History

In the early 1920s experimentalists studied the splitting of the lines of hydrogen and other atoms when the atoms were placed in a magnetic field. The external field defines a direction, and thees breaks rotational symmetry, and as a consequence, previously degenerate states split into their magnetic sub components, $-\ell \leq m \leq \ell$. The number of distinct lines produced exceeded the number that would be expected based on the description of the hydrogen atom we have developed so far.

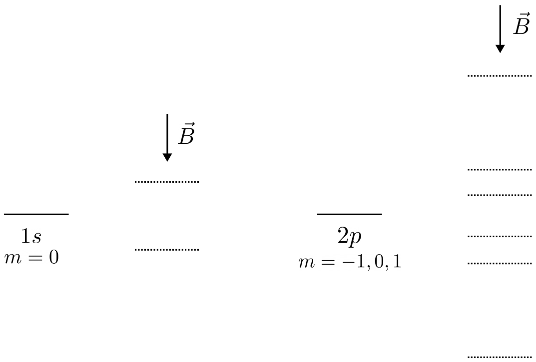


Figure 9.1: Zeeman Splittings in Hydrogen

Alfred Lande, an experimentalist based at Tübingen University, had developed an empirical model describing the Zeeman splittings, not based in theory. Pauli had concluded the necessary theory was one that introduced an additional electron quantum number that could take on only two values. A 20-year-old student Kronig, visiting Lande at the time Pauli also came for discussions, interpreted Pauli's idea as an electron having a "spin" $s = \frac{1}{2}$. Kronig shared his ideas with Pauli, whose objections included

1. the discrepant values needed for g_s.
2. the physical requirements for generating the needed magnetic moment were unrealistic – Pauli argued that the only radius one could construct for the electron, $r \sim \frac{e^2}{mc^2} \sim \alpha\frac{\hbar c}{mc^2}$ was so small that the electron's surface would need to rotate at 100s of c to generate the magnetic moment.

Kronig's idea was also met with skepticism from Niels Bohr, and was never published.

Nine month's later the same idea was generated by two young theorists in Holland, graduate students Uhlenbeck and Goudsmit, who described the notion of spin to Ehrenfest. He told the two that the idea was "either nonsense, or something important" and urged them to write a paper. Uhlenbeck and Goudsmit consulted Lorentz, the leading Dutch theorist of the time, who raised objections similar to those of Pauli. They returned to Ehrenfest, asking him to return their paper, but he had already submitted it, and advised his students not to worry as they were young enough to be forgiven for stupidity.

In 1926, Thomas identified a relativistic correction, a spin-orbit contribution to the Hydrogen atom Hamiltonian that removed the need for a state-dependent magnetic moment – they key objection both Pauli and Lorentz raised. That plus the acceptance that the electron spin was not some analog of classical spin, but a uniquely quantum phenomena of the electron, resolved earlier objections.

9.5.2 Quantum Mechanical Spin

Spin in Quantum Mechanics is defined by an algebra borrowed from orbital angular momentum:

$$[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}S_k \quad \Rightarrow \quad [\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z \quad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x \quad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$$

which leads to the familiar relations we have derived

$$\hat{S}^2|sm_s\rangle = \hbar^2 s(s+1)|sm_s\rangle \quad \hat{S}_z|sm_s\rangle = \hbar m_s|sm_s\rangle \quad \hat{S}_\pm|sm_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}|sm_s \pm 1\rangle$$

Elementary particles in the standard model come with an intrinsic spin. All particles that make up physical matter have spin $s = \frac{1}{2}$ and are called *fermions.* They include charged *leptons* (which only have electromagnetic weak interactions)

$$e^- \quad e^+ \quad \mu^- \quad \mu^+ \quad \tau^- \quad \tau^+$$

and their neutral partners, the *neutrinos*

$$\nu_e \quad \bar{\nu}_e \quad \nu_\mu \quad \bar{\nu}_\mu \quad \nu_\tau \quad \bar{\nu}_\tau$$

and the *quarks*, which have strong interactions and their antiparticles

$$u \quad d \quad s \quad c \quad t \quad b \qquad\qquad \bar{u} \quad \bar{d} \quad \bar{s} \quad \bar{c} \quad \bar{t} \quad \bar{b}$$

We also have the particles that mediate the forces, which carry spin $s = 1$,

weak interactions: $W^\pm$, Z electromagnetic interactions: γ strong interactions: g

and finally we have the *Higgs boson* which generates the masses of the charged fermions, which is the standard model's only spinless $s = 0$ particle.

The nucleon is a “composite fermion” – like an elementary fermion, only one composite fermion at a time can occupy a given quantum state. Its spin is made up of the spin of its elementary quark components, the angular momentum of the quarks, and the “glue” (gluons) that hold the nucleon together.

9.5.3 Spin $\frac{1}{2}$

The $s = \frac{1}{2}$ case is the most interesting for us as this is the intrinsic spin of the electron and all other elementary fermions, and because of its simplicity. First envision an arbitrary spin state, which we might denote $|\vec{s}\rangle$. Now we select a basis by first introducing a coordinate system, and choosing $\hat{s}$ and s_z as our eigenstate labels. Then, with the basis, our state (assumed normalized) can be represented

$$|\vec{s}\rangle = \sum_{m_s} |\frac{1}{2} m_s\rangle\langle\frac{1}{2} m_s|\vec{s}\rangle$$

There are two $\hat{s}_z$ basis states can be expressed in terms of what are called Pauli spinors:

$$|\frac{1}{2} m_s = \frac{1}{2}\rangle \leftrightarrow \begin{pmatrix}1\\0\end{pmatrix} \equiv \chi_+ \qquad |\frac{1}{2} m_s = -\frac{1}{2}\rangle \leftrightarrow \begin{pmatrix}0\\1\end{pmatrix} \equiv \chi_-$$

Here χ_+ and χ_- are the two special states where the spin points up or down, respectively with respect to the chosen z axis. The general normalized spin-1/2 state can be written

$$\chi_{\alpha,\beta} = \begin{pmatrix}\alpha\\\beta\end{pmatrix} = \alpha\chi_+ + \beta\chi_- \quad \text{with } |\alpha|^2 + |\beta|^2 = 1$$

That is, in the first equation above, the expansion coefficients in this basis are

$$\langle\frac{1}{2} m_s = \frac{1}{2}\rangle\vec{s}\rangle = \alpha \qquad \langle\frac{1}{2} m_s = -\frac{1}{2}|\vec{s}\rangle = \beta$$

From the general expression of spin, one has for the case of $s = \frac{1}{2}$,

$$\hat{S}^2|sm_s\rangle = \hbar^2 s(s+1)|sm_s\rangle \quad \Rightarrow \quad \hat{S}^2\chi_+ = \frac{3\hbar^2}{4}\chi_+ \quad \hat{S}^2\chi_- = \frac{3\hbar^2}{4}\chi_- \tag{9.17}$$

$$\hat{S}_z|sm_s\rangle = \hbar m_s|sm_s\rangle \quad \Rightarrow \quad \hat{S}_z\chi_+ = \frac{\hbar}{2}\chi_+ \quad \hat{S}_z\chi_- = -\frac{\hbar}{2}\chi_- \tag{9.18}$$

so in the spin-1/2 representations, $\hat{S}^2$ and $\hat{S}_z$ correspond to the matrices

$$\hat{S}^2 = \frac{3\hbar^2}{4}\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} \qquad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$

Similarly,

$$\hat{S}_+|sm_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s+1)}|sm_s+1\rangle \quad \Rightarrow \quad \hat{S}_+\chi_+ = 0 \quad \hat{S}_+\chi_- = \hbar\chi_+ \tag{9.19}$$

$$\hat{S}_-|sm_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s-1)}|sm_s+1\rangle \quad \Rightarrow \quad \hat{S}_-\chi_+ = \hbar\chi_- \quad \hat{S}_-\chi_- = 0 \tag{9.20}$$

Therefore,

$$\hat{S}_+ = \hbar\begin{pmatrix}0 & 1 & 0 & 0\end{pmatrix} \qquad \hat{S}_- = \hbar\begin{pmatrix}0 & 0 & 1 & 0\end{pmatrix}$$

And as $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$, then $\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-)$ and $\hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-)$, or

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \end{pmatrix} \qquad \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i & i & 0 \end{pmatrix}$$

Conventionally, $\hat{S}_x, \hat{S}_y$, and $\hat{S}_z$ are expressed in terms of the Pauli matrices $\vec{\sigma}$ as

Pauli Spin Matrices

$$\hat{S} = \frac{\hbar}{2}\vec{\sigma} \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These are Hermitian operators, as are the matrices representing observables $\hat{S}^2$ and $\hat{S}_z$.

9.5.4 Spin Measurements

We noted above that the most general normalized statevector can be expressed as

$$\chi_{\alpha,\beta} \equiv \alpha\chi_+ + \beta\chi_- = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \qquad |\alpha|^2 + |\beta|^2 = 1$$

We will be interested in measuring spin relative to some direction, e.g., the x, y or z axis. And when we do any such measurement, the answer is binary – either $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$, with respective probabilities that will depend on the state we are in. The z axis is particularly simple because its the axis of our angular momentum quantization. If we calculate the expectation value of $\hat{S}_z$ in the general state described above,

$$\langle \hat{S}_z \rangle \equiv \chi^\dagger_{\alpha,\beta}\hat{S}_z\chi_{\alpha,\beta} = (\alpha^* \;\; \beta^*)\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\hbar}{2}(|\alpha|^2 - |\beta|^2)$$

From this result, we can see choices corresponding to states of definite spin along z – the case where every measurement will give the same result, either always $\hbar/2$ or always $-\hbar/2$ – are

$$\alpha = 1,\ \beta = 0 \quad \text{corresponds to spin aligned with } z\text{:} \quad \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\alpha = 0,\ \beta = 1 \quad \text{corresponds to spin anti-aligned with } z\text{:} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

(up to an overall phase). Of course, this was obvious from the start.

But now we can do the same thing with x to find the states aligned with or against x. Taking the expectation value of $\hat{S}_x$,

$$\langle \hat{S}_x \rangle \equiv \chi^\dagger_{\alpha,\beta}\hat{S}_x\chi_{\alpha,\beta} = (\alpha^* \;\; \beta^*)\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\hbar}{2}(\alpha^*\beta + \alpha\beta^*) = \hbar\mathrm{Re}[\alpha\beta^*]$$

So the state with $\alpha = \beta = \frac{1}{\sqrt{2}}$ has $\langle \hat{S}_x \rangle = \frac{\hbar}{2}$ and the state with $\alpha = -\beta = \frac{1}{\sqrt{2}}$ has $\langle \hat{S}_x \rangle = -\frac{\hbar}{2}$. Thus

$$\chi^x_+ = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \quad \chi^x_- = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \quad \Rightarrow \quad \chi_+ = \frac{1}{\sqrt{2}}(\chi^x_+ + \chi^x_-) \quad \chi_- = \frac{1}{\sqrt{2}}(\chi^x_+ - \chi^x_-)$$

For a system quantizing along z, χ^x_+ and χ^x_- are states pointing up and down along x. And we can do the exercise a third time, taking the expectation value of $\hat{S}_y$ in the general state:

$$\langle \hat{S}_y \rangle \equiv \chi^\dagger_{\alpha,\beta} \hat{S}_y \chi_{\alpha,\beta} = (\alpha^* \quad \beta^*) \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\hbar}{2}(-i\alpha^*\beta + i\alpha\beta^*) = \hbar \text{Re}[i\alpha\beta^*]$$

So the state with $\alpha = \frac{1}{\sqrt{2}}, \beta = \frac{i}{\sqrt{2}}$ has $\langle \hat{S}_y \rangle = \frac{\hbar}{2}$ and the state with $\alpha = \frac{1}{\sqrt{2}}, \beta = -\frac{i}{\sqrt{2}}$ has $\langle \hat{S}_y \rangle = -\frac{\hbar}{2}$. Therefore

$$\chi^y_+ = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{pmatrix} \quad \chi^y_- = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \end{pmatrix} \quad \Rightarrow \quad \chi_+ = \frac{1}{\sqrt{2}}(\chi^y_+ + \chi^y_-) \quad \chi_- = \frac{i}{\sqrt{2}}(\chi^y_- - \chi^y_+)$$

So our general state can be expressed in several equivalent ways

General Quantum Statevector

$$\chi_{\alpha,\beta} \equiv \alpha\chi_+ + \beta\chi_- = \left(\frac{\alpha+\beta}{\sqrt{2}}\right)\chi^x_+ + \left(\frac{\alpha-\beta}{\sqrt{2}}\right)\chi^x_- = \left(\frac{\alpha-i\beta}{\sqrt{2}}\right)\chi^y_+ + \left(\frac{\alpha+i\beta}{\sqrt{2}}\right)\chi^y_-$$

9.5.5 Example – Wave Packet Collapse

These results allow one to quickly compute various examples, including the collapse of a wave packet.

1. Suppose the initial state is pointed along the positive z axis – that is, the initial state is $|\chi_+\rangle$. Then a measurement of $\hat{S}_x$ yields $+\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$ with probabilities

$$|\langle \chi^x_+ | \chi_+ \rangle|^2 = |\frac{1}{\sqrt{2}}(\chi_+ + \chi_-)|\chi_+\rangle|^2 = \frac{1}{2} \quad \text{and} \quad |\langle \chi^x_- | \chi_+ \rangle|^2 = |\langle\frac{1}{\sqrt{2}}(\chi_+ - \chi_-)|\chi_+\rangle|^2 = \frac{1}{2}$$

2. If the initial state is χ_+, then a measurement of $\hat{S}_y$ yields $+\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$ with probabilities

$$|\langle \chi^y_+ | \chi_+ \rangle|^2 = |\langle\frac{1}{\sqrt{2}}(\chi_+ + i\chi_-)|\chi_+\rangle|^2 = \frac{1}{2} \quad \text{and} \quad |\langle \chi^y_- | \chi_+ \rangle|^2 = |\langle\frac{1}{\sqrt{2}}(\chi_+ - i\chi_-)|\chi_+\rangle|^2 = \frac{1}{2}$$

3. And collapse: the state is initially $|\chi_+\rangle$, but a measurement of $\hat{S}_x$ is done yielding the answer $|\chi^x_+\rangle$. If another measurement is done to see if the spin is aligned along z, the answer will be

$$|\langle \chi_+ | \chi^x_+ \rangle|^2 = |\langle\frac{1}{\sqrt{2}}(\chi^x_+ + \chi^x_-)|\chi^x_+\rangle|^2 = \frac{1}{2}$$

So half the time the electron will be anti-aligned with z, even though it started out aligned.

9.6 Larmor Precession & Prime Directive

A charged particle with spin generates a magnetic dipole moment μ proportional to its spin

$$\mu = \gamma \vec{S}$$

where γ is the geomagnetic ratio (nearly exactly e/m for the electron). This magnetic momentum responds to an applied magnetic field $\vec{B}$, yielding

$$\hat{H} = -\mu \cdot \vec{B} = -\gamma \vec{B} \cdot \hat{\vec{S}}$$

If we define our z-axis along $\vec{B} = B\hat{z}$, this becomes

$$\hat{H} = -\gamma B \hat{S}_z = -\frac{\gamma \hbar B}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

yielding the stationary states and eigenvalues

$$\chi_+, \quad E_+ = -\frac{\gamma B \hbar}{2} \qquad \chi_-, E_- = \frac{\gamma B \hbar}{2}$$

so χ_+, with its spin pointing along the z-axis, in the direction of $\vec{B}$, has the lower energy. At time $t = 0$, if we are given an arbitrary wave packet

$$\chi(0) = \alpha\chi_+ + \beta\chi_- \equiv \cos\left(\frac{\theta}{2}\right)\chi_+ + \sin\left(\frac{\theta}{2}\right)\chi_-$$

where we have used the constraint $|\alpha|^2 + |\beta|^2 = 1$ and the ability to absorb phases into the basis states to write this in terms of a "mixing angle". This angle is the one between $\vec{B}$ and the spin. The prime directive then gives us the general solution for how this wave packet evolves in time in the presence of $\vec{B}$, with the z-axis pointing along $\vec{B}$:

$$\chi(t) = \alpha\chi_+ + \beta\chi_- \equiv \cos\left(\frac{\theta}{2}\right) e^{i\gamma Bt/2} + \sin\left(\frac{\theta}{2}\right)\chi_- e^{-i\gamma Bt/2} = \begin{pmatrix} \cos\left(\frac{\theta}{2}\right) e^{i\gamma Bt/2} \\ \sin\left(\frac{\theta}{2}\right) e^{-i\gamma Bt/2} \end{pmatrix}$$

Just as we did previously, we can calculate the expectation value of $\hat{S}_x$

$$\langle \hat{S}_x(t) \rangle = \chi(t)^\dagger \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \chi(t) = \frac{\hbar}{2} \sin\theta \cos\gamma Bt$$

and also $\hat{S}_y$,

$$\langle \hat{S}_y(t) \rangle = \chi(t)^\dagger \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \chi(t) = -\frac{\hbar}{2} \sin\theta \sin\gamma B t$$

and also $\hat{S}_z$,

$$\langle \hat{S}_z(t) \rangle = \chi(t)^\dagger \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \chi(t) = \frac{\hbar}{2} \cos\theta$$

These are the formulae for a classical precessing gyroscope. The angle θ and thus the projection on the z-axis remains constant while the projection onto the $x - y$ plane precesses with an angular frequency γB, the Larmor frequency.

9.7 Applications of the Addition of Angular Momenta

An interesting example of what we discussed previously about the addition of angular momenta is having two particles each with a spin-1/2. In general (not only spin-1/2), states in the uncoupled representation are eigenstates of four operators:

$$\begin{aligned}
(\hat{S}^{(1)})^2 \, |s_1 m_1 s_2 m_2\rangle &= s_1(s_1+1)\hbar^2 \, |s_1 m_1; s_2 m_2\rangle \\
(\hat{S}^{(2)})^2 \, |s_1 m_1 s_2 m_2\rangle &= s_2(s_2+1)\hbar^2 \, |s_1 m_1; s_2 m_2\rangle \\
\hat{S}_z^{(1)} \, |s_1 m_1 s_2 m_2\rangle &= m_1 \hbar \, |s_1 m_1; s_2 m_2\rangle \\
\hat{S}_z^{(2)} \, |s_1 m_1 s_2 m_2\rangle &= m_2 \hbar \, |s_1 m_1; s_2 m_2\rangle
\end{aligned}$$

while in the coupled representation,

$$\begin{aligned}
(\hat{S}^{(1)})^2 |(s_1 s_2) s m_s\rangle &= s_1(s_1+1)\hbar^2 |(s_1 s_2) s m_s\rangle \\
(\hat{S}^{(2)})^2 |(s_1 s_2) s m_s\rangle &= s_2(s_2+1)\hbar^2 |(s_1 s_2) s m_2 s\rangle \\
\hat{S}^2 \, |(s_1 s_2) s m_s\rangle &= s(s+1)\hbar^2 \, |(s_1 s_2) s m_s\rangle \\
\hat{S}_z \, |(s_1 s_2) s m_s\rangle &= m_s \hbar \, |(s_1 s_2) s m_s\rangle
\end{aligned}$$

where $\hat{S} = \hat{S}^{(1)} + \hat{S}^{(2)}$.

Specializing to spin-1/2, a case that will be useful when we discuss the Helium atom later, we can form either $s = 1$ (spin symmetric) triplet states of an $s = 0$ (spin antisymmetric) singlet state. Using our Clebsch-Gordan tech, we write these states in terms of their uncoupled equivalents. For the triplet case,

$$| \left(\frac{1}{2}\frac{1}{2}\right) s = 1 m_s\rangle = \sum_{m_1 m_2} \langle \frac{1}{2} m_1 \frac{1}{2} m_2 | \left(\frac{1}{2}\frac{1}{2}\right) s m_s \rangle | \frac{1}{2} m_1 \frac{1}{2} m_2 \rangle = \begin{cases} |\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle m_s & = 1 \\ \tfrac{1}{\sqrt{2}}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2} - \tfrac{1}{2}\rangle + \tfrac{1}{\sqrt{2}}|\tfrac{1}{2} - \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle m_s & = 0 \\ |\tfrac{1}{2} - \tfrac{1}{2}\tfrac{1}{2} - \tfrac{1}{2}\rangle m_s & = -1 \end{cases}$$

While for the singlet case,

$$|\left(\frac{1}{2}\frac{1}{2}\right)s=0m_s=0\rangle = \sum_{m_1m_2}\langle\frac{1}{2}m_1\frac{1}{2}m_2|\left(\frac{1}{2}\frac{1}{2}\right)00\rangle|\frac{1}{2}m_1\frac{1}{2}m_2\rangle = \frac{1}{\sqrt{2}}|\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}\rangle - \frac{1}{\sqrt{2}}|\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}\rangle$$

In summary

Symmetric Spin Triplet $(s=1)$ States

$$|\uparrow;\uparrow\rangle = \left|\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{1}{2}\right\rangle = \left|\left(\frac{1}{2}\frac{1}{2}\right)s=1\,m_s=1\right\rangle \qquad m_s=1$$

$$\frac{1}{\sqrt{2}}\left(|\uparrow;\downarrow\rangle+|\downarrow;\uparrow\rangle\right) = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\frac{1}{2};\frac{1}{2}-\frac{1}{2}\right\rangle + \left|\frac{1}{2}-\frac{1}{2};\frac{1}{2}\frac{1}{2}\right\rangle\right) \equiv \left|\left(\frac{1}{2}\frac{1}{2}\right)s=1\,m_s=0\right\rangle \qquad m_s=0$$

$$|\downarrow;\downarrow\rangle = \left|\frac{1}{2}-\frac{1}{2};\frac{1}{2}-\frac{1}{2}\right\rangle = \left|\left(\frac{1}{2}\frac{1}{2}\right)s=1\,m_s=-1\right\rangle \qquad m_s=-1$$

Antisymmetric Spin Singlet $(s=0)$ State

$$\frac{1}{\sqrt{2}}\left(|\uparrow;\downarrow\rangle-|\downarrow;\uparrow\rangle\right) = \left(\left|\frac{1}{2}\frac{1}{2};\frac{1}{2}-\frac{1}{2}\right\rangle - \left|\frac{1}{2}-\frac{1}{2};\frac{1}{2}\frac{1}{2}\right\rangle\right) \equiv \left|\left(\frac{1}{2}\frac{1}{2}\right)s=0\,m=0\right\rangle \qquad m_s=0$$

9.8 Review

9.8.1 Clebsch-Gordan Coefficients

Now that we have introduced quantum mechanical spin, we can "close the loop" on our previous discussion of Clebsch-Gordan coefficients, using spin-$\frac{1}{2}$ as an example. The two cases we will address are the coupling of two spins (very relevant to our future discussion of the ground state of Helium with its two electrons) and the coupling of orbital angular and spin momentum for a single electron (important for our subsequent treatment of spin-orbit interactions in Helium). We will also summarize here the key relationships you might need when utilizing Clebsch-Gordan coefficients. This summary might be particularly helpful for those of you following the discussion in Griffiths. Griffiths has a rather intimidating table of Clebsch-Gordan coefficients – that is, intimidating if your eyes are keen enough to read print that small. Griffiths also uses a notation that doesn't help with transparency. He writes

$$|sm\rangle = \sum_{m_1+m_2=m} C^{(s_1s_2)s}_{m_1m_2m}|s_1s_2m_1m_2\rangle$$

A more common notation that I feel better captures the meaning of the coefficients are the expansion coefficients of the states of the orthonormal coupled basis in terms of the states of the orthonormal uncoupled basis -

$$|(s_1 s_2)sm\rangle = \sum_{m_1, m_2, m_1+m_2=m} |s_1 m_1 s_2 m_2\rangle\langle s_1 m_1 s_2 m_2|(s_1 s_2)sm\rangle$$

Here $\vec{S} = \vec{S}^{(1)} + \hat{S}^{(2)}$, the basis states are eigenstates of

$$\begin{gathered} \text{coupled} - \text{basis: } \hat{S}^{(1)}, \hat{S}^{(2)}, \hat{S}, \hat{S}_z \\ \text{uncoupled basis: } \hat{S}^{(1)}, \hat{S}_z^{(1)}, \hat{S}^{(2)}, \hat{S}_z^{(2)} \end{gathered}$$

As $\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}$, we have the restriction in the sum that $m = m_1 + m_2$. And the expansion coefficients – analogous to the c_is when we expanded a wave packet in terms of a complete set of stationary states – are the Clebsch-Gordan coefficients.

$$\langle s_1 m_1 s_2 m_2|(s_1 s_2)sm\rangle$$

We have previously described some of the properties of Clebsch-Gordan coefficients. As

$$\langle (s_1 s_2)s'm'|(s_1 s_2)sm\rangle = \delta_{s's}\delta_{m'm} \quad \Rightarrow \quad \delta_{s's}\delta_{m'm} \tag{9.21}$$

$$\Rightarrow \sum_{m_1, m_2,\ m_1+m_2=m} |\langle s_1 m_1 s_2 m_2|(s_1 s_2)sm\rangle|^2 = 1 \tag{9.22}$$

But in fact the coefficients are defined as real, which is possible because phases can be absorbed into the states. So

$$\langle s_1 m_1 s_2 m_2|(s_1 s_2)sm\rangle^* = \langle s_1 m_1 s_2 m_2|(s_1 s_2)sm\rangle$$

Also, we can expand the uncoupled states in terms of the coupled states, the reverse of what we did above.

$$|s_1 m_1 s_2 m_2\rangle = \sum_{s,m,\ m=m_1+m_2} |(s_1 s_2)sm\rangle\langle (s_1 s_2)sm|s_1 m_1 s_2 m_2\rangle$$

Some further properties of Clebsch-Gordan coefficients that we have not explicitly derived, but follow from the same discussion include

$$\begin{gathered} \langle j_1 m_1 j_2 m_2|(j_1 j_2)jm\rangle = (-1)^{j_1+j_2-j}\langle j_2 m_2 j_1 m_1|(j_2 j_1)jm\rangle \\ \langle j_1 m_1 j_2 m_2|(j_1 j_2)jm\rangle = (-1)^{j_1+j_2-j}\langle j_1 - m_1 j_2 - m_2|(j_1 j_2)j - m\rangle \end{gathered}$$

9.9 Addition of Momenta

9.9.1 Addition of Two Spins with Spin $\frac{1}{2}$

We have stressed that the Clebsch-Gordan coefficients describe the orthogonal transformation between the uncoupled and coupled bases. We can write this out explicitly f or the case of two spin-1/2 particles.

i

$$\begin{pmatrix} \left|\left(\frac{1}{2}\frac{1}{2}\right)1\,1\right\rangle \\ \left|\left(\frac{1}{2}\frac{1}{2}\right)1\,0\right\rangle \\ \left|\left(\frac{1}{2}\frac{1}{2}\right)0\,0\right\rangle \\ \left|\left(\frac{1}{2}\frac{1}{2}\right)1\,-1\right\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} & 0 \\ 0 & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \left|\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\rangle \\ \left|\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}\right\rangle \\ \left|\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\rangle \\ \left|\frac{1}{2}-\frac{1}{2}\frac{1}{2}-\frac{1}{2}\right\rangle \end{pmatrix}$$

This matrix is the matrix of corresponding Clebsch-Gordan coefficients

$$\begin{pmatrix} \left\langle\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\right|\left(\frac{1}{2}\frac{1}{2}\right)11\rangle & 0 & 0 & 0 \\ 0 & \left\langle\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}\right|\left(\frac{1}{2}\frac{1}{2}\right)10\rangle & \left\langle\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}\right|\left(\frac{1}{2}\frac{1}{2}\right)10\rangle & 0 \\ 0 & \left\langle\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}\right|\left(\frac{1}{2}\frac{1}{2}\right)00\rangle & \left\langle\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}\right|\left(\frac{1}{2}\frac{1}{2}\right)00\rangle & 0 \\ 0 & 0 & 0 & \left\langle\frac{1}{2}-\frac{1}{2}\frac{1}{2}-\frac{1}{2}\right|\left(\frac{1}{2}\frac{1}{2}\right)1-1\rangle \end{pmatrix}$$

9.9.2 Addition of Orbital Angular Momentum and Spin

Here we consider the application to a single particle that has both spin and angular momentum. We can add these to form a total angular momentum

$$\hat{j} = \hat{\ell} + \hat{s}$$

For the spin-$\frac{1}{2}$ electron with definite ℓ there would be $(2\ell+1)(2)$ possibilities for j. If $\ell = 0$ there is a single possibility:

$$|(\ell = 0s)j = \frac{1}{2}m_j = \pm\frac{1}{2}\rangle$$

But for $\ell > 0$, two multiplets are formed – spin aligned and spin antialigned. From the $2(2\ell+1)$ states,

$$(\ell s)j = \ell + \frac{1}{2}m_j\rangle \quad 2\ell + 2 \text{ states}$$

$$|(\ell s)j = \ell - \frac{1}{2}m_j\rangle \quad 2\ell \text{ states}$$

Thus in a hydrogen atom, once spin is considered, the states of good angular momenta are

$$1s_{\frac{1}{2}} : |n = 1(\ell = 0 s = \frac{1}{2})j = \frac{1}{2} m_j\rangle$$

$$2s_{\frac{1}{2}} : |n = 2(\ell = 0 s = \frac{1}{2})j = \frac{1}{2} m_j\rangle \quad 2p_{\frac{1}{2}} : |n = 2(\ell = 1 s = \frac{1}{2})j = \frac{1}{2} m_j\rangle \quad 2p_{\frac{3}{2}} : |n = 2(\ell = 1 s = \frac{1}{2})j = \frac{3}{2} m_j\rangle$$

$$3s_{\frac{1}{2}} : |n = 2(\ell = 0 s = \frac{1}{2})j = \frac{1}{2} m_j\rangle \quad 3p_{\frac{1}{2}} : |n = 2(\ell = 1 s = \frac{1}{2})j = \frac{1}{2} m_j\rangle \quad 3p_{\frac{3}{2}} : |n = 2(\ell = 1 s = \frac{1}{2})j = \frac{3}{2} m_j\rangle$$

$$3d_{\frac{3}{2}} : |n = 2(\ell = 2 s = \frac{1}{2})j = \frac{3}{2} m_j\rangle \quad 3d_{\frac{5}{2}} : |n = 2(\ell = 2 s = \frac{1}{2})j = \frac{5}{2} m_j\rangle$$

This concludes the first half of UC Berkeley's Physics 137 Quantum Mechanics course sequence – 137A. Usually part A ends with a discussion of the Helium Atom and Identical Particles, along with an introduction to perturbation theory. However these topics will be covered in more detail in 137B. So I will leave it for the next book.

Quantum Mechanics I

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