University of California, Berkeley

Physics 137A-B

Quantum Mechanics

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April 25, 2024

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 $\hbar$.

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

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

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

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, treat-

ing 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.
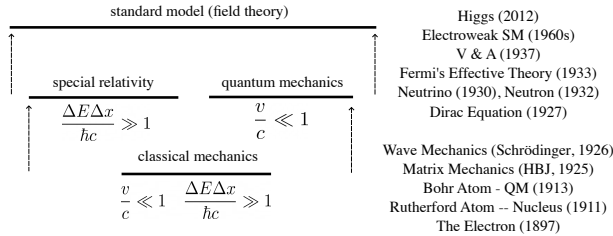

Figure 1.1: Summary of the developments leading up to and beyond wave mechanics and the Schroedinger equation

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 quasi-particles 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 acknowledge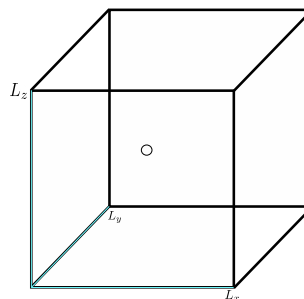d through a series of Nobel Prizes over the last thirty years recognizing the development of tools for *manipulating atoms* and other quantum matter, including the laser, the maser, quantum electronics, atom traps, optical tweezers, laser cooling, ultra-fast laser pulses, optical frequency combs, and 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.

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

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.

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/$m^2 K^4$. 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 princi-

ples, 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

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

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

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

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,

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

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:

$$\bar{E} = \frac{\sum_{n=0}^\infty nh\nu e^{-nh\nu/k_B T}}{\sum_{n=0}^\infty e^{-nh\nu/k_B T}}$$

$$= -\frac{1}{\sum_{n=0}^\infty e^{-nh\nu/k_B T}} \frac{d}{d\frac{1}{k_B T}} \sum_{n=0}^\infty e^{-nh\nu/k_B T}$$

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

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

and thus Planck obtained (in frequency form)

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

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

The Rayleigh-Jeans (classical) result is obtained for small frequencies, so we recognize $h \rightarrow 0$ 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.
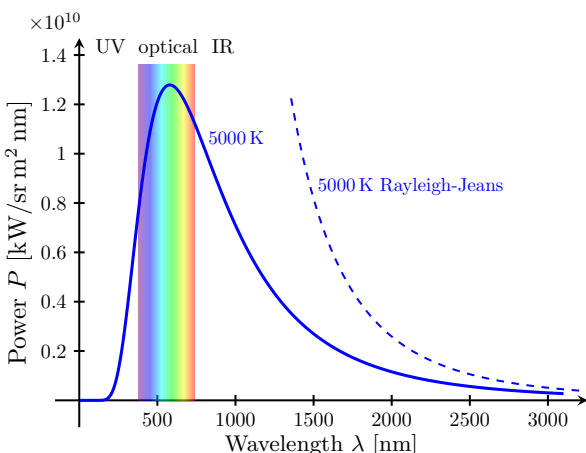
Rayleigh-Jeans' prediction diverges as the wavelength of light becomes small which goes against energy conservation. Planck's revision, however, viewing light as discrete packets of energy known as *quanta*, recovers the Stefan-Boltzmann law and is well-behaved.

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.
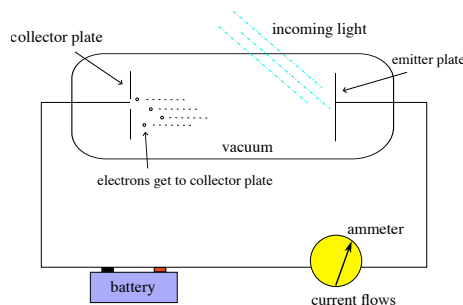

Figure 2.2: Basics of a photoelectric effect experimental setup

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

$$h\nu = KE_e + h\nu_0 \qquad (2.1)$$

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

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

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

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:

$$p_e = m_e v = \frac{h}{\lambda} \quad \Rightarrow \quad \lambda = \frac{h}{m_e v} \qquad (2.2)$$

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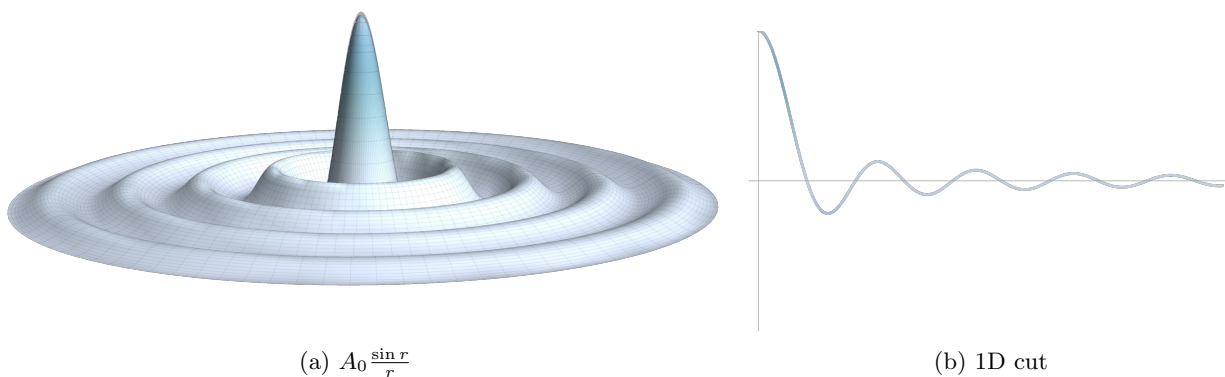
Figure 3.1: Example of a very intuitive wave phenomena, but mathematically a slightly complicated one. The one-dimensional cut of this wave shows the oscillation is damped.

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:
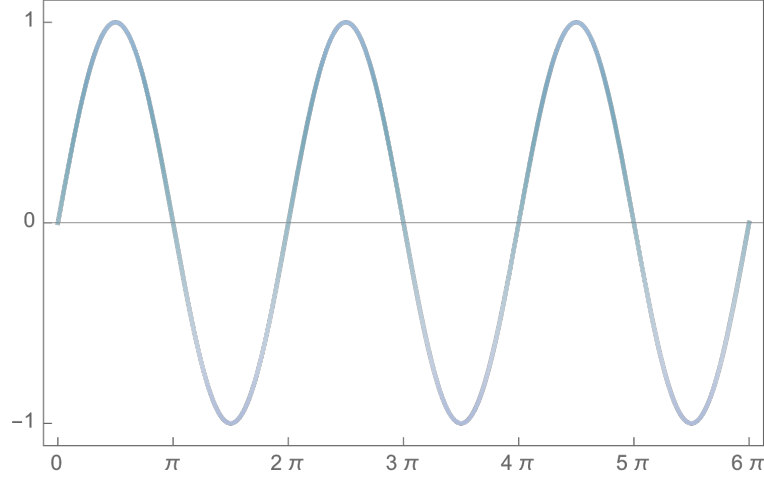
The wave function of the sinusoidal wave above is given by

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

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,

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

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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 *Rydberg atoms* . 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,

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

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

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,

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

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

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

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:

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

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,

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

23

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

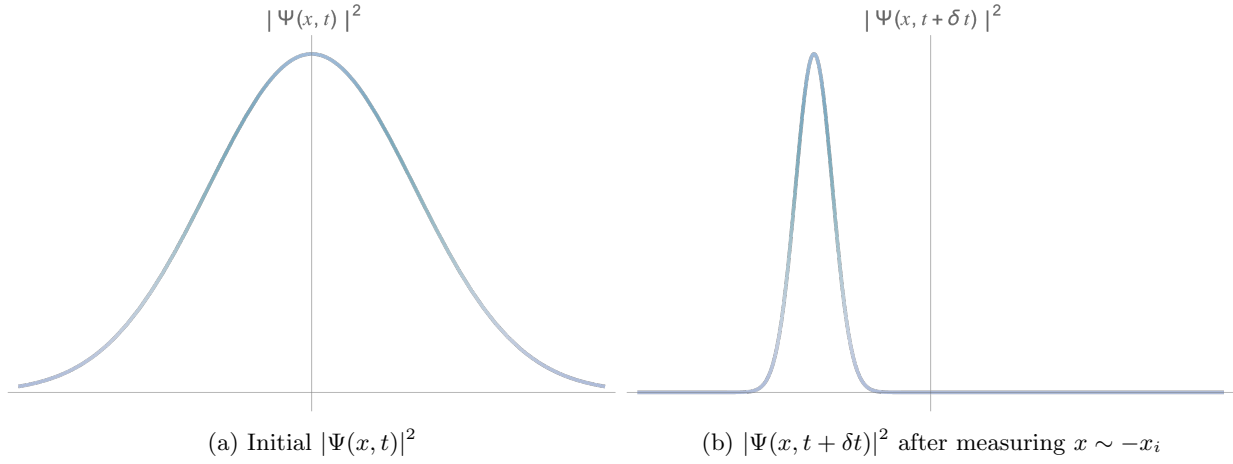(b) $|\Psi(x, t+\delta t)|^2$ after measuring $x \sim -x_i$

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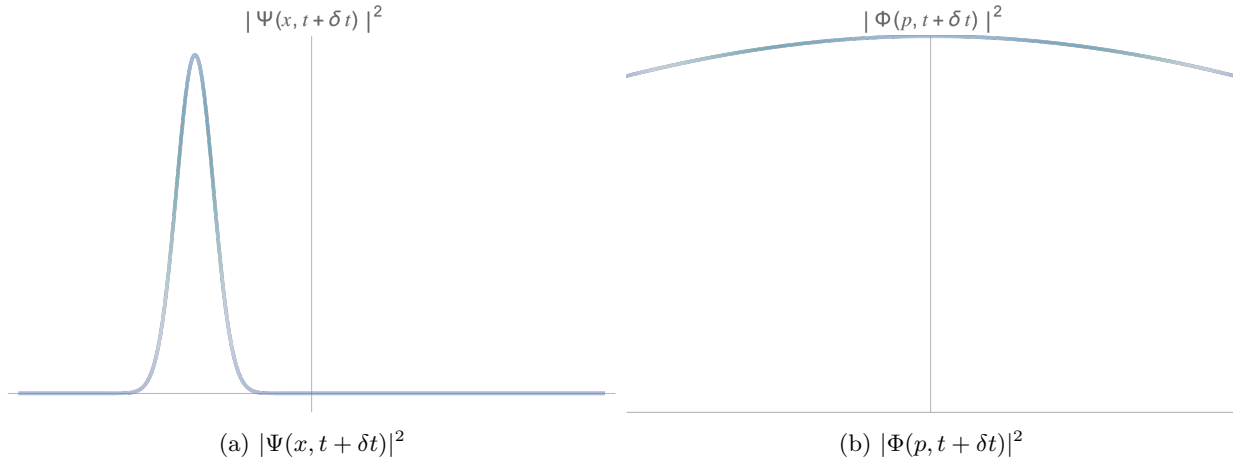
Figure 4.2: A narrow $|\Psi(x,t)|^2$ (a) implies a very spread $|\Phi(p,t)|^2$ (b). Since coordinate-space wave packets and momentum-space packets are inverse Fourier transforms of one another, $\Psi(x,t)$ and $\Phi(p,t)$ are inverse F.T's of one another. Note from this moment on Ψ refers to coordinate-space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

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

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

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

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

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

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

The LHS is seen to be

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

while the RHS can be manipulated into the form

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

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

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

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

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

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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 $e^{-iE_i t/\hbar}$ 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.

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

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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

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

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

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comes from time-varying interference.

Hence, according to our *prime directive*, to solve for the time dependent wave function of any particle orwave 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

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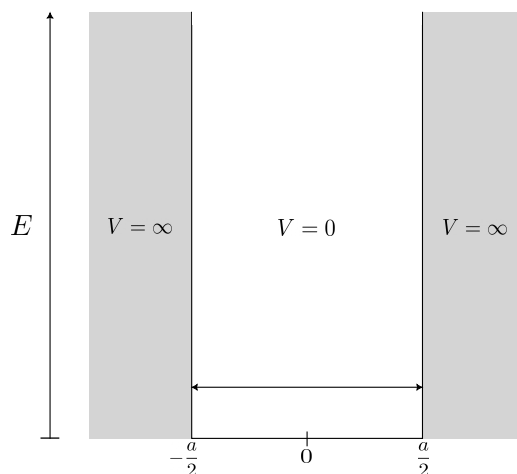

Figure 6.1: The Infinite Square Well

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
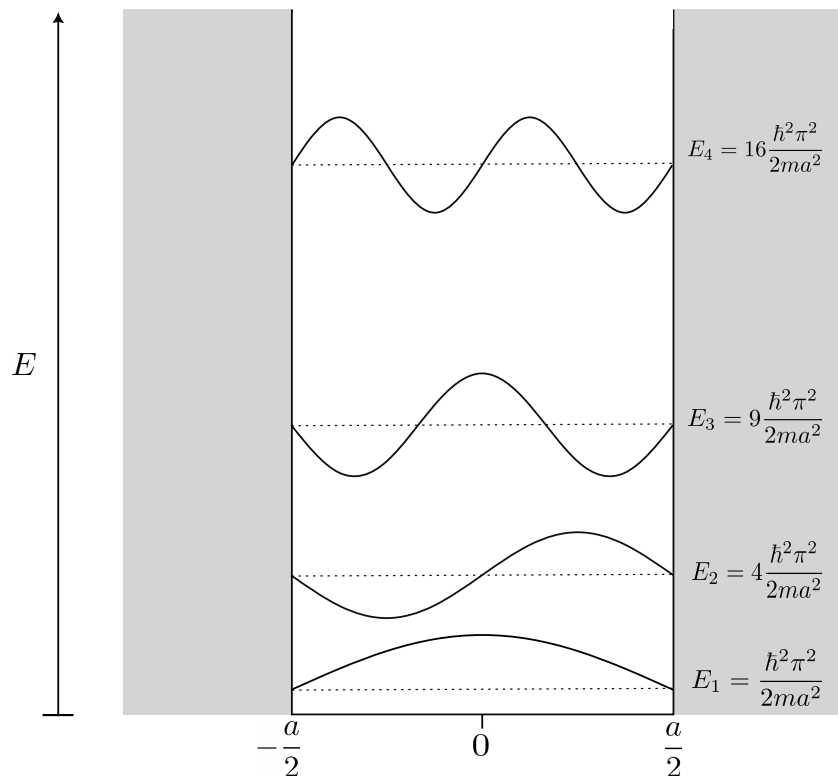
Figure 6.2: Infinite Square Well Stationary States

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

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

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.

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

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.

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

$$= |A|^2 \left(a^2 \frac{x^3}{3} - 2a \frac{x^4}{4} + \frac{x^5}{5} \right) \Big|_0^a = |A|^2 \left(\frac{a^5}{3} - \frac{2a^5}{4} + \frac{a^5}{5} \right) = |A|^2 \frac{a^5}{30} = 1 \tag{6.10}$$
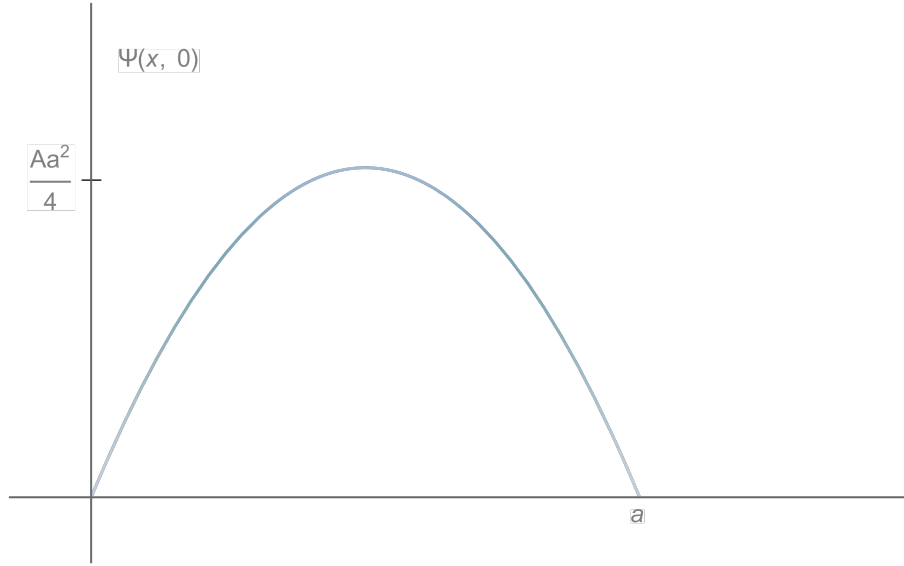
$$\Rightarrow |A| = \sqrt{\frac{30}{a^5}} \tag{6.11}$$

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

Now we can determine the coefficients c_n using Equation 5.12.

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

$$c_n = \int \psi_n(x)\Psi(x,0)\,dx$$

$$= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}} x(a-x)\,dx$$

$$= \frac{2\sqrt{15}}{a^3} \left[a \int_0^a x \sin\left(\frac{n\pi}{a}x\right)\,dx - \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right)\,dx \right]$$

$$= \frac{2\sqrt{15}}{a^3} \left[a\left[\left(\frac{a}{n\pi}\right)^2 \sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi}\cos\left(\frac{n\pi}{a}x\right) \right]_0^a - \left[2\left(\frac{a}{n\pi}\right)^2 x \sin\left(\frac{n\pi}{a}x\right) - \frac{(n\pi xa)^2 - 2}{(n\pi a)^3}\cos\left(\frac{n\pi}{a}x\right) \right]_0^a \right]$$

$$= \frac{2\sqrt{15}}{a^3} \left[-\frac{a^3}{n\pi}\cos(n\pi) + a^3\frac{(n\pi)^2 - 2}{(n\pi)^3}\cos(n\pi) + a^3\frac{2}{(n\pi)^3}\cos(0) \right]$$

$$= \frac{4\sqrt{15}}{(n\pi)^3}[\cos(0) - \cos(n\pi)]$$

$$= \begin{cases} 0 & \text{if } n \text{ even} \\ \frac{8\sqrt{15}}{(n\pi)^3} & \text{if } n \text{ odd} \end{cases}$$

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

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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, "friggin' everything is a harmonic oscillator" – Reddit commenter. 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

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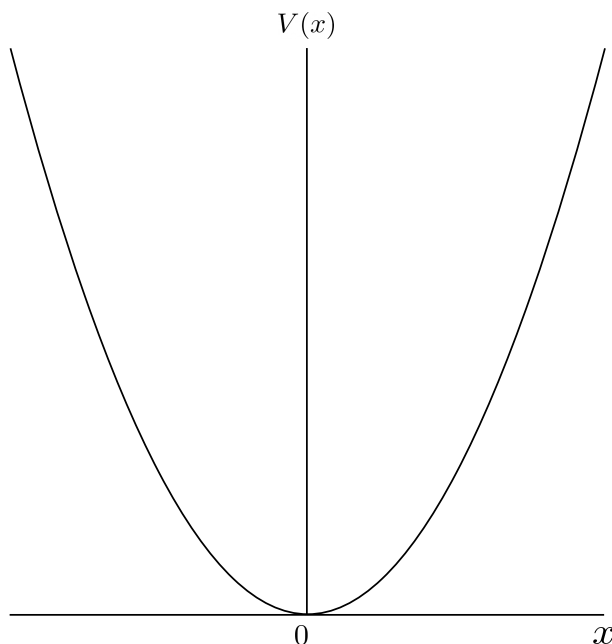

Figure 6.4: Quantum Harmonic Oscillator Potential

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 $\hat{a}_-\hat{a}_+$.

$$\hat{a}_-\hat{a}_+ = \frac{1}{2\hbar m\omega}(i\hat{p} + m\omega x)(-i\hat{p} + m\omega x) \tag{6.20}$$

$$= \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega x)^2 - im\omega(x\hat{p} - \hat{p}x)\right] \tag{6.21}$$

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

$$[x, \hat{p}]f(x) = \left[x(-i\hbar)\frac{d}{dx}f(x) - (-i\hbar)\frac{d}{dx}(xf)\right] \tag{6.24}$$

$$= -i\hbar\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right) \tag{6.25}$$

$$= i\hbar f(x) \tag{6.26}$$

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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.

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

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

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

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 $(E - \hbar\omega)$.

$$\hat{H}(\hat{a}_-\psi) = \hbar\omega\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\right)(\hat{a}_-\psi) = \hbar\omega\hat{a}_-\left(\hat{a}_+\hat{a}_- - \frac{1}{2}\right)\psi \tag{6.35}$$

$$= \hat{a}_-\left[\hbar\omega\left(\hat{a}_-\hat{a}_+ - 1 - \frac{1}{2}\right)\psi\right] = \hat{a}_-\left(\hat{H} - \hbar\omega\right)\psi = \hat{a}_-(E - \hbar\omega)\psi \tag{6.36}$$

$$= (E - \hbar\omega)(\hat{a}_-\psi). \tag{6.37}$$

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,

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

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

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

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 $\frac{d^2h}{d\xi^2}$,

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

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

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

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

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

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

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.
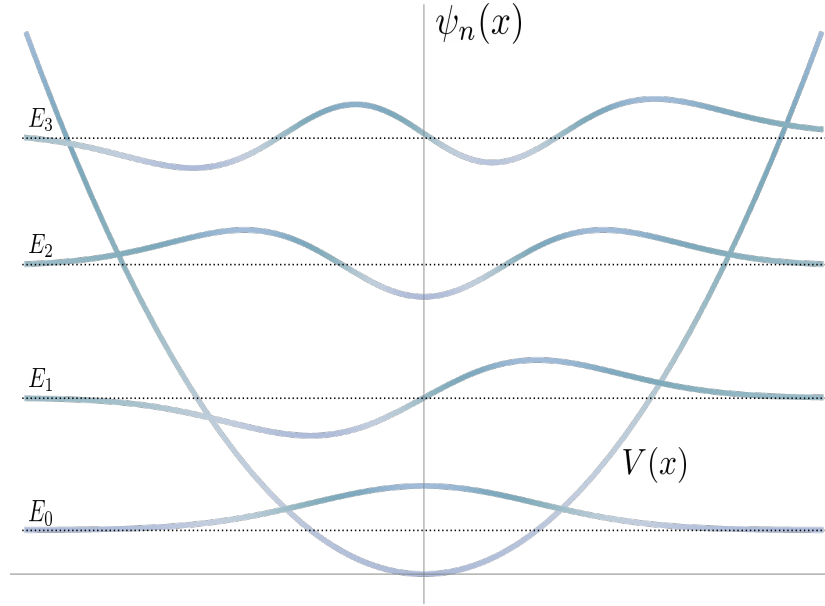

Figure 6.5: Stationary State Wave Functions for 1D Harmonic Oscillator

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.

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6.2.4   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

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

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).

$$k = +\frac{\sqrt{2mE}}{\hbar} > 0 \to \text{ traveling to the right } (+x)$$

$$k = -\frac{\sqrt{2mE}}{\hbar} < 0 \to \text{ traveling to the left } \quad (-x)$$

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*.

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

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

Worked Example

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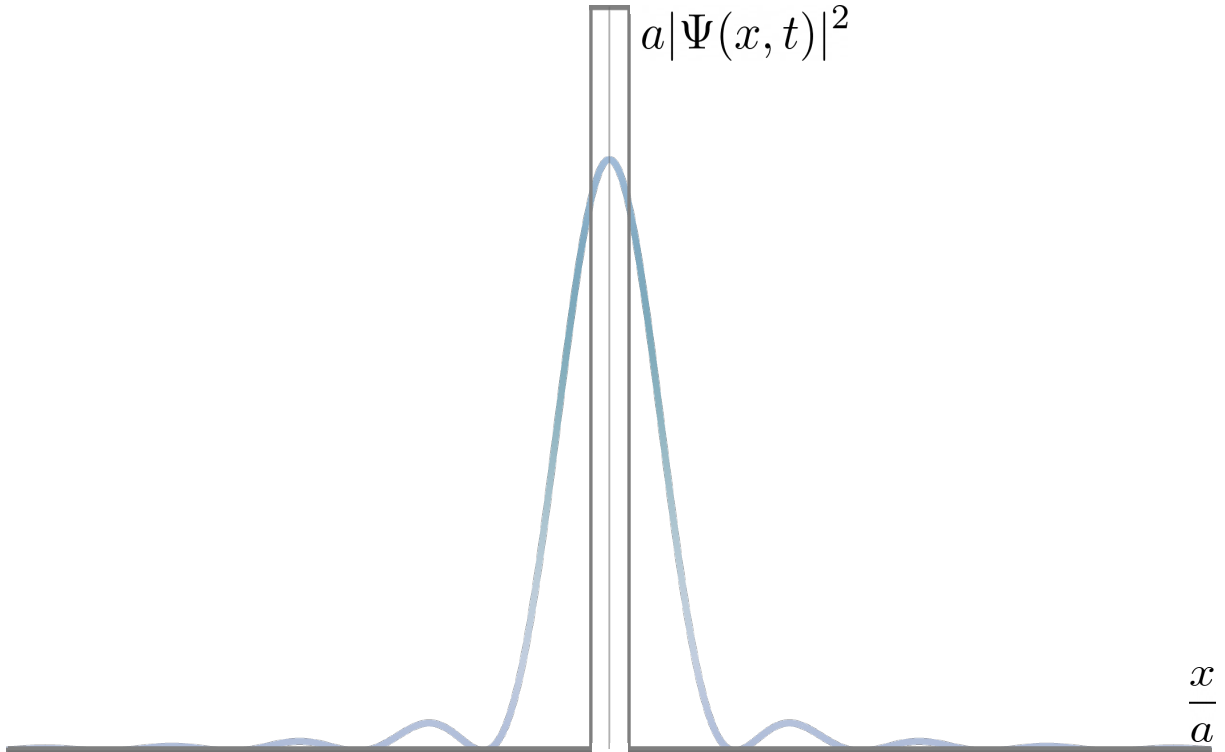
$$a|\Psi(x,t)|^2$$

$$\frac{x}{a}$$

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