PHYS401 Notes (Section 0101)

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1 Overview

Quantum mechanics is the theory that describes the microscopic world. It is governed by $\hbar$, Planck's constant. $\hbar = 1.05 \times 10^{-34}$ Joule seconds. This is a tiny number, it has units of action, or angular momentum.

When we solve in QM, the solutions are governed by Schrodinger's equation, with some operator acting on the wavefunction and the Hamiltonian acting on the wavefunction. A lot of 401 and 402 is just learning how to solve the equation and deriving intuition for how to go about solving the equation.

We will talk about how QM is a statistical theory, where we can only compute probabilities, it is not deterministic. It is at its base a theory about our knowledge of nature, not a theory about nature.

2 Pre-Quantum

2.1 Black Body Radiation

Physicists noticed that when objects were heated up, the color of the light emitted was independent of the material that was being heated.

Assume we have a box that is a perfect black body emitter, with light bouncing inside it, and some coming out. A perfect black body absorbs all the light entering and re-emits the light. It re-emits with only one parameter, the temperature of the box T. We want to compute the value of $\rho(\lambda, T)$, which is the power per unit area per wavelength for a certain temperature. IF we plot this function against wavelength, we obtain the blackbody curves that we are familiar with. As we get warmer and warmer, the peaks of the curves shift closer and closer to the visible spectrum (shorter wavelengths). Wien's displacement law states that $\lambda_{peak} T$ is a constant. If we integrate to get the total power emitted, we see that

$$\int_0^\infty \rho(\lambda, T)\, d\lambda = P(T) = A\sigma T^4$$

Where σ is the Stefan-Boltzmann constant, $\sigma = 5.67 \times 10^{-8}\, W/m^2/K^4$, and A is the area.

This still doesn't tell us what the shape of the spectrum is. Wien proposed a shape of the form

$$\rho(\lambda, T) = \frac{ae^{-b/\lambda T}}{\lambda^5}$$

This was just done via observation. If we try to check Wien's displacement law, via taking a derivative, we see that indeed the peak of this function is a constant. If we integrate the curve:

$$\int_0^\infty \rho(\lambda, T)\, d\lambda = \frac{6a}{b^9} T^4$$

This led to Rayleigh-Jeans, an attempt to figure out the spectrum without just fitting functions. Assume we have a box with EM waves in it. Inside we have different modes of the EM waves. We have the wave equation:

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2}$$

This has simple solutions, just sinusoids:

$$E = E_0 \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

If we plug this into the wave equation, we have that

$$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2}{\lambda^2}$$

In the end, the number of modes depends on the volume of the box and the wavelength:

$$N = \frac{8\pi L^3}{3\lambda^3}$$

If we take the number of modes per wavelength and distribute it across the volume, we get $\frac{8\pi}{\lambda^4}$. This leads to the energy density:

$$U = \frac{1}{L^3}\frac{dE}{d\Lambda} = k_B T \frac{1}{L^3}\frac{dN}{d\lambda} = \frac{8\pi k_b T}{\lambda^4}$$

This leads to Rayleigh-Jeans:

$$\rho = \frac{c}{4}U = \frac{2\pi c k_b T}{\lambda^4}$$

There are a couple problems with this, the first of which occurs when we take

$$\frac{d\rho}{d\lambda}_{\lambda \to 0} \to \infty$$

The issue is that if we take smaller wavelengths, the theory fails. This is known as the Ultraviolet Catastrophe. The second issue is that Rayleigh-Jeans does not match what Wien fit to the data.

In 1901, Max Planck finds the correct expression:

$$\rho(\lambda, T) = \frac{a}{\lambda^5} \frac{1}{e^{b/(\lambda T)} - 1}$$

He then tried to derive it from physical principles. He made an assumption that used quantized energies. Assume a collection of discrete oscillators. The energy of an oscillator was given by $\epsilon_n = nh\nu$. The change in energy is given by $\Delta\epsilon_n = h\nu$, where h is Planck's constant. To get around the UV Catastrophe, he assumed a Boltzmann distribution:

$$N(n) = N_0 e^{-\epsilon n/(kT)}$$

We can compute an average energy:

$$\bar{\epsilon} = \frac{\sum N(n)\epsilon_n}{\sum_{n=0}^{\infty} N(n)} = \frac{h\nu}{e^{h\nu/(kT)} - 1}$$

We then get that

$$\rho(\lambda, T) = n(\lambda)\bar{\epsilon}\frac{c}{4} = \frac{2\pi h c^2}{\lambda^5} \frac{1}{e^{hc/(\lambda k T)} - 1}$$

This solves the two issues that we had, but it assumes that the oscillators only exist at discrete energy levels, which went against everything that classical mechanics had assumed previously.

2.2 Photoelectric Effect

The photoelectric effect is the phenomenon in which light striking a piece of metal releases electrons. In 1905, Einstein wrote a paper which claimed that

$$\frac{1}{2}mv^2 = eV = h\nu - W$$

Where W is the work function, which is metal specific. Planck assumed that the oscillators were quantized, and now Einstein had assumed that light was quantized. This was even more crazy than what Planck did, as we already had EM, where waves were already well established.

The classical model was that the electron was essentially bound to the surface via a spring. They observed that there was some threshold frequency (metal dependent), below which the electrons would not be emitted. They also observed that the electrons were emitted instantly. They also noted that it was independent of the intensity of the light. This went against what the classical model would expect.

They also noted that the current increased with intensity, but is independent of frequency. The strangest was that the kinetic energy only depended on frequency.

In 1916, Millikan placed the nail in the coffin, fully backing up Einstein's findings. He was also very close to the modern day value of Planck's constant.

Compton scattering was the idea that solidified the idea of quantized light. The basis is that shining x-rays on a metal would scatter the light, and measuring the angle and the shifted wavelength of the reflected light. We begin with an x-ray with momentum $p = \frac{h}{\lambda_0}$, that strikes an electron, creating a photon moving at angle θ_p with some momentum and energy

$$p' = \frac{h}{\lambda'} \quad E' = h\nu'$$

And moving the electron at some angle θ_e with some kinetic energy, potential energy, and velocity. We can then do some momentum conservation:

$$p_0 = p' \cos\theta_p + p_e \cos\theta_e$$

$$0 = p' \sin\theta_p - p_e \sin\theta_e$$

Doing some algebra, we are left with

$$p_e^2 = p_0^2 - 2p_0 p' \cos\theta_p$$

We can then also write down energy conservation (note we are using the relativistic form for the electron energy, $E^2 = p_e^2c^2 + m^2c^4$):

$$p_0 p'(1 - \cos\theta_p) = mc(p_0 - p')$$

Then writing this in the traditional form (Compton was measuring the wavelength)

$$\lambda_0 - \lambda' = \frac{h}{mc}(1 - \cos\theta)$$

This is the Compton scattering relationship, and $\frac{h}{m_e c}$ is known as the Compton wavelength. This fit Einstein's theory very well, showing that light acts just like particles.

2.3 Atomic Spectra

Physicists had seen that heating up substances would generate distinct spectra, but had no idea why this was happening. In 1913, Bohr created his model of the atom.

We assume that the nucleus has a charge of $+Ze$, with mass M, and there is an electron moving around with charge e_- and mass m_e. This is a classical physics problem, and we can use Newton's second law:

$$\frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

We can also write down the kinetic energy of the electron, and equate it to the Coulomb energy:

$$\frac{1}{2}m_e v^2 = \frac{Ze^2}{8\pi\epsilon_0 r}$$

And the potential energy:

$$U = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

This gets the total energy to be

$$E = \frac{-Ze^2}{8\pi\epsilon_0 r}$$

Note that this is negative because the electron is bound, it requires energy to remove from the system.

We can then look at angular momentum:

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}\frac{(mvr)^2}{mr^2} = \frac{1}{2}\frac{L^2}{mr^2} = \frac{Ze^2}{8\pi\epsilon_0 r}$$

We can then solve for r:

$$r = \frac{4\pi\epsilon_0 L^2}{mZe^2}$$

We can plug this back into the total energy, and we get

$$E = \frac{-mZ^2e^4}{32\pi^2\epsilon_0^2 L^2}$$

Bohr then assumed that angular momentum is quantized, $L = \frac{nh}{2\pi} = n\hbar$. Plugging this in to the energy:

$$E_n = \frac{-mZ^2e^4}{32\pi^2\epsilon_0^2 n^2\hbar^2} = \frac{-Z^2}{2n^2}E_H$$

Where E_H is the Hartree energy:

$$E_H = m\left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2 = 27.2\,eV$$

This is the atomic unit of energy.

Now moving to spectra, we can define the Rydberg constant:

$$R = \frac{E_H}{4\pi\hbar c} = 10973731.56816\,m^{-1}$$

Which has units of m^{-1}. We can also define the Bohr radius a_0:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{mc^2} = 5.29 \times 10{-}11\,m$$

It can be shown that the radius of the orbit is given by

$$r_n = \frac{a_0 n^2}{Z}$$

We can also rewrite the energy in terms of the Bohr radius:

$$E_n = \frac{-1}{2}\frac{\hbar^2}{a_0 m}\frac{Z^2}{h^2}$$

Finally, we can define the fine structure constant α:

$$\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c} \approx \frac{1}{137} = 7.297352569 \times 10^{-3}$$

We can write the Hartree in terms of the fine structure constant:

$$E_H = mc^2\alpha^2$$

Bohr claimed that the spectral lines were created by the energy difference between two of the quantized states:

$$\Delta E_{nk} = E_n - E_k = -\frac{1}{2}E_H\left(\frac{1}{n^2} - \frac{1}{k^2}\right)$$

If we set $k = 1$, we obtain what is known as the Lyman series:

$$h\nu_n = -\frac{1}{2}E_H\left(\frac{1}{n^2} - 1\right)$$

If we go from $n = 2$ to $k = 1$, we get a wavelength of 121 nanometers, which is known as the Lyman α line for Hydrogen. If we use $k = 2$, we get what is known as the Balmer series. Bohr's model agreed almost perfectly with the observed series. The key to this was the assumption that the energy levels/angular momentum was quantized.

Bohr assumed several things, the first of which was that the Coulomb force provides the acceleration. He also assumed that the electron in an orbit does not radiate, which goes contrary to classical EM. He also assumed that $L = n\hbar$, and that emission/absorption occurs when electrons move between energy levels.

To do a quick summary of the lead up to QM, we had Planck who stated that radiators are quantized, to explain the black body problem. Einstein then said that light must be quantized, to explain the photoelectric effect. Compton then came along and experimentally showed that x-rays act like particles. Bohr then claimed that angular momentum was quantized, to explain the atomic spectra of atoms like Hydrogen.

In 1925, deBroglie in his PhD thesis assumed that electrons were waves, something that was pretty radical, we had already seen that they could be thought of as particles. If we then thought of an

electron moving around in its orbit, the wavelength had to be a certain set of values in order to create a stable orbit:

$$n\lambda_{dB} = 2\pi r$$

Taking what Bohr had ($mvr = n\hbar$), we have that

$$\lambda_{dB} = \frac{2\pi n\hbar}{nmv} = \frac{h}{mv} = \frac{h}{p}$$

Two years later, in 1927, Davisson and Germer scattered electrons off of crystals, and they observed Bragg diffraction/scattering, which is an interference phenomenon that occurs when x-rays scattering into a crystal lattice travels different lengths that can create constructive interference:

$$n\lambda = 2d\sin\theta$$

Davisson and Germer did this for electrons, and found a diffraction pattern, just like x-rays. This verified the deBroglie wave concept for electrons. This is now a standard surface science technique, LEED, Low Energy Electron Detection.

3 Quantum Mechanics

We need to define a wavefunction. We assume that the modulus squared is the probability of finding the particle at position x and time t. We can write a plane wave

$$\Psi(x,t) = \Psi_0 e^{i(kx-\omega t)} = \Psi_0 e^{i(xp-Et)/\hbar}$$

We can take the modulus:

$$|\Psi(x,t)|^2 = \Psi^*(x_1,t_1)\Psi(x_1,t_1)dx$$

The particle has to be somewhere, so the integral of this overall space must be 1. We define the probability density

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

And the integral of this must be 1

$$\int_{-\infty}^{\infty}\rho(x,t)\,dx = 1$$

We have normalized the wavefunction so that the probability is 1.

In general, we will work with wavefunctions that are normalized:

$$\int_{-\infty}^{\infty}|\Psi(x,t)|^2\,dx = 1$$

When light interferes, we have that the intensity is proportional to the sum of the energies squared, $I \propto |E_1 + E_2|^2$. The same is true of wavefunction interference:

$$\Psi(x,t) = \Psi_A(x,t) + \Psi_B(x,t)$$

$$\rho(x,t) = |\Psi_A|^2 + |\Psi_B|^2 + \Psi_A^*\Psi_B + \Psi_A\Psi_B^*$$

We can pick some values for Ψ_A and Ψ_B:

$$\Psi_a = \frac{1}{\sqrt{2}}\Psi_0 \quad \Psi_B = \frac{e^{i\theta}}{\sqrt{2}}\Psi_0$$

This gets us

$$\rho = \frac{1}{2} + \frac{1}{2} + \frac{1}{2}\Psi_0^* e^{i\theta}\Psi_0 + \frac{1}{2}e^{-i\theta}\Psi_0^*\Psi_0 = 1 + \cos\theta$$

This gets us the interference between wavefunctions.

3.1 Schrodinger Equation

We want a wave equation for our wavefunction to describe evolution in time and space. We want it to be linear, so if Ψ_1 and Ψ_2 are solutions then so is some linear combination of the two. We also want it to be a first order diffeq in time, because adding more orders adds more constants. We also need it to be consistent with the deBroglie relationship.

If we have a free particle, with no potentials of any kind, we have that $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$. We can write it as a plane wave:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}e^{-(kx-\omega t)}$$

Differentiating with respect to time:

$$\frac{\partial\Psi}{\partial t} = -i\omega\Psi = -\frac{i\hbar k^2}{2m}\Psi$$

Doing it once more:

$$\frac{\partial^2\Psi}{\partial x^2} = -k^2\Psi$$

Plugging this into the first derivative:

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

Which is conventionally written as

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

In 3 dimensions:

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

If we now include in a potential:

$$E = \frac{p^2}{2m} + V(x)$$

We add the potential in to obtain the full equation:

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

Where the right side can be compressed down using the Hamiltonian, $\hat{H}\Psi$.

3.2 Postulate Number 1

Postulate 1. *The state of a quantum system, including all the information you can know, is completely described by a wavefunction that is a vector in a complex Hilbert space.*

Suppose we have some Cartesian 2D vector space. A vector $\mathbf{v}$ can be written in terms of the basis vectors:

$$\mathbf{v} = a\hat{i} + b\hat{j}$$

The basis vectors should be, orthogonal, form a complete basis, and be unit vectors.

In QM, we use a Hilbert space, which is a linear vector space where the unit vectors are complete functions that are orthogonal and normalized.

We use Dirac notation, bras and kets. A ket:

$$|\Psi\rangle = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \\ a_n \end{bmatrix}$$

Which is the same as saying

$$|\Psi\rangle = a_1 |\varphi_1\rangle + a_2 |\varphi_2\rangle + \cdots + a_n |\varphi_n\rangle$$

Where φ_n are the basis functions of the Hilbert space.

3.3 Dirac Notation

The analogue for the dot product in a Hilbert space is the inner product:

$$\langle\alpha|\beta\rangle = \int_{-\infty}^{\infty} \alpha(x)^* \beta(x)\, dx$$

If $|\alpha\rangle = a_1 |\varphi_1\rangle + a_2 |\varphi_2\rangle + \dots$ and $|\beta\rangle = b_1 |\varphi_1\rangle + b_2 |\varphi\rangle + \dots$, we can write

$$\langle\alpha|\beta\rangle = a_1^* b_1 \langle\varphi_1|\varphi_1\rangle + a_2^* b_2 \langle\varphi_2|\varphi_2\rangle + \dots$$

We also have the relationship that the basis vectors are orthogonal:

$$\langle\varphi_m|\varphi_n\rangle = \delta_{mn}$$

Which turns the inner product into

$$\langle\alpha|\beta\rangle = a_1^* b_1 + a_2^* b_2 + \dots$$

We see that we have removed the need to do any integrals when computing an inner product.

Since the basis functions form a complete basis, we can write any wavefunction as a linear combination of them:

$$|\psi\rangle = \sum_n a_n |\varphi_n\rangle$$

If we then take the inner product with a basis vector:

$$\langle \varphi_m | \psi \rangle = \sum_n a_n \langle \varphi_m | \varphi_n \rangle = a_m$$

We see that taking the inner product with a basis vector pulls out the coefficient for that basis vector.

Let's do a random but concrete example. Suppose we have a set of basis functions for $0 \leq x \leq 1$:

$$|\varphi_n\rangle = \sqrt{2}\sin(n\pi x)$$

We first can check it for normalization:

$$\langle \varphi_n | \varphi_n \rangle = \int_0^1 2\sin^2(n\pi x)\,dx = \int_0^1 1 - \cos(2n\pi x)\,dx$$

$$= \left[x - \frac{\sin(2n\pi x)}{2\pi n}\right]_0^1 = 1$$

Thus we see that the basis functions are indeed normalized. We can check orthogonality, by taking the inner product of two different basis states:

$$\langle \varphi_n | \varphi_m \rangle = 2\int_0^1 \sin(n\pi x)\sin(m\pi x)\,dx$$

If we do out this integral, we see that if $n = m$, we get 1, and if $n \neq m$, we get 0, showing that indeed

$$\langle \varphi_n | \varphi_m \rangle = \delta_{mn}$$

Thus we have shown that we have an orthonormal set of basis vectors.

Suppose we have a wavefunction

$$|\psi\rangle = \frac{1}{2}\sin(6\pi x) + \frac{e^{i\theta}}{2}\sin(17\pi x)$$

$$= \frac{1}{\sqrt{2}}|\varphi_6\rangle + \frac{e^{i\theta}}{\sqrt{2}}|\varphi_{17}\rangle$$

We can see that the wavefunction we have is normalized:

$$\langle \psi | \psi \rangle = \frac{1}{2}\langle \varphi_6 | \varphi_6 \rangle + \frac{e^{-i\theta}e^{i\theta}}{2}\langle \varphi_{17} | \varphi_{17} \rangle = 1$$

In general, for an orthonormal basis, we have that

$$\langle \psi | \psi \rangle = |a_1|^2 + |a_2|^2 + \dots$$

We have an inner product between a bra and a ket, $\langle \alpha | \beta \rangle = \int a^* b\,dx$. The ket $|\beta\rangle$ is a vector in the Hilbert space, and can be thought of as a column vector. $\langle \alpha |$ can be thought of as a row vector:

$$\langle \alpha | = \begin{pmatrix} a_1^* & a_2^* & \dots & a_n^* \end{pmatrix}$$

Mathematically, the space of bras is the dual space of the Hilbert space.

3.4 Operators

Suppose we have an operator $\hat{p} = |\alpha\rangle \langle\alpha|$. To understand what this does, we see how it acts on some wavefunction $|\beta\rangle$:

$$\hat{p} |\beta\rangle = |a\rangle \langle\alpha|\beta\rangle$$

We see that this is a matrix, which we call an operator in quantum mechanics. It takes a vector and transforms it into another vector. This is known as the projection operator, as it results in the piece of $|\beta\rangle$ in the "direction" of $|\alpha\rangle$.

We can do some math review on linear algebra. A matrix is defined as something that maps vectors to other vectors:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} a_{11}x + a_{12}y \\ a_{21}x + a_{22}y \end{pmatrix}$$

There are special vectors such that $M\alpha = \lambda\alpha$. We say that α is an eigenvector of M, and λ is the associated eigenvalue. We can compute the eigenvalues and eigenvectors:

$$M(\alpha) - \lambda I\alpha = 0$$

If $(M - \lambda I)^{-1}$ exists, then $\alpha = \mathbf{0}$. This is boring, so we want the inverse to not exist. This occurs when the determinant of this is 0:

$$det(M - \lambda I) = 0$$

We can solve this for the values of λ, and then we can substitute them back into the equation and solve the system the vectors that make the equation true for each λ.

We have an operator for measuring the spin along the y direction:

$$\hat{s}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

We could find the eigenvalues for this:

$$det \begin{pmatrix} -\lambda & -i\frac{\hbar}{2} \\ i\frac{\hbar}{2} & -\lambda \end{pmatrix} = \lambda^2 + i^2 \left(\frac{\hbar}{2}\right)^2 = 0 \rightarrow \lambda = \pm\frac{\hbar}{2}$$

Generally we write operators with hats on top of them, and can write them in terms of bras and kets:

$$|\beta\rangle = \hat{Q} |\alpha\rangle$$

3.5 Postulate Number 2

Postulate 2. *Observables are described by operators that are linear and Hermitian.*

In Dirac notation, operators always act from the left:

$$\hat{Q} |\psi\rangle = |\psi'\rangle$$

And can never act from the right, as this doesnt make sense (vector times matrix is not defined). Suppose we have a wavefunction $|\psi\rangle$:

$$|\psi\rangle = \sum_n \alpha_n |\varphi_n\rangle$$

We have that $|\psi'\rangle = \hat{Q}\,|\psi\rangle$:

$$|\psi'\rangle = \sum_n \beta_n\,|\varphi_n\rangle = \hat{Q}\sum_n \alpha_n\,|\varphi_n\rangle = \sum_n \alpha_n \hat{Q}\,|\varphi_n\rangle$$

Let us now take the inner product on both sides $|\varphi_n\rangle$:

$$\sum_n \beta_n\,\langle\varphi_m|\varphi_n\rangle = \sum_n \alpha_n\,\langle\varphi_m|\hat{Q}\varphi_n\rangle = \sum_n Q_{mn}\alpha_n$$

Thus we can relate β_n with α_n:

$$\beta_m = \sum_n Q_{mn}\alpha_n \qquad Q_{mn}\,\langle\varphi_m|\hat{Q}|\varphi_n\rangle$$

In other words, Q_{mn} is an element of the matrix representation of $\hat{Q}$ in the basis given by the functions $|\varphi_n\rangle$.

Operators are linear, which means that

$$\hat{Q}\,|A\psi_1 + B\psi_2\rangle = A\hat{Q}\,|\psi_1\rangle + B\hat{Q}\,|\psi_2\rangle$$

A Hermitian matrix is one such that $A^\dagger = A$, where $A^\dagger$ is the complex conjugate of the transpose of the matrix. Hermitian operators are nice because the eigenvalues of a Hermitian matrix are always real, which is something we want to be true of our observable values.

3.6 Postulate Number 3

Postulate 3. *The only possible outcome of a measurement of an observable corresponding to operator $\hat{A}$ is an eigenvalue a_n of operator $\hat{A}$.*

Suppose we have a classical probability distribution:

$$P(y) = e^{-(y-2)^2}$$

To find the mean of this, we would compute

$$\frac{\int_{-\infty}^{\infty} dy\, y e^{-(y-2)^2}}{\int_{-\infty}^{\infty} dy\, e^{-(y-2)^2}}$$

If we instead wanted the average of y^2, we'd do the same thing, just multiplying by y^2 instead of just y. This is essentially just a weighted average. In QM, we do the analogous method. The "expectation value" of a variable is defined as

$$\langle\hat{Q}\rangle = \langle\psi|\hat{Q}\psi\rangle = \int_{-\infty}^{\infty} \psi^*\hat{Q}\psi\,dx$$

Note that we have no normalization factor because the wavefunction is normalized. Since the operators are Hermitian, we must have that

$$\langle\hat{Q}\rangle = \langle\hat{Q}\rangle^*$$

If we want to take the complex conjugate of an inner product:

$$\langle m|n\rangle^* = \left(\int m^* n\, dx\right)^* = \int mn^*\, dx = \langle n|m\rangle$$

Using this, we see that taking the complex conjugate of an inner product allows us to just swap the order of the terms in the inner product.

$$\hat{Q} = \langle\psi|\hat{Q}|\psi\rangle = \langle\hat{Q}\psi|\psi\rangle$$

As $\hat{Q}$ is Hermitian.

Let us prove that eigenvalues of a Hermitian operator are real.

Proof. We have that $\hat{Q}\,|\psi_n\rangle = q_n\,|\psi_n\rangle$, and that $\hat{Q}^\dagger = \hat{Q}$. We can take the inner product with $\langle\psi_n|$ on both sides:

$$\langle\psi_n|\hat{Q}|\psi_n\rangle = \langle\psi_n|q_n\psi_n\rangle = q_n\,\langle\psi_n|\psi_n\rangle = q_n$$

If we instead start with the operator on the left side:

$$\langle\hat{Q}\psi_n|\psi_n\rangle = \langle q_n\psi_n|\psi_n\rangle = q_n^*\,\langle\psi_n|\psi_n\rangle = q_n^*$$

Thus we have that $q_n = q_n^*$, and thus $q_n \in \mathbb{R}$. □

Let us now prove that eigenvectors of a Hermitian operator are orthogonal if they correspond to distinct eigenvalues.

Proof. Assume we have that $\hat{Q}\,|\psi_i\rangle = q_i\,|\psi_i\rangle$ and $\hat{Q}\,|\psi_j\rangle = q_j\,|\psi_j\rangle$, where $q_i \neq q_j$. We also know that $\hat{Q}$ is Hermitian.

We can take the inner product with $|\psi_i\rangle$:

$$\langle\psi_i|\hat{Q}\psi_j\rangle = \langle\psi_i|q_j\psi_j\rangle = q_j\,\langle\psi_i|\psi_j\rangle$$

We also have

$$\langle\hat{Q}\psi_i|\psi_j\rangle = q_i\,\langle\psi_i|\psi_j\rangle$$

We then have

$$q_i\,\langle\psi_i|\psi_j\rangle = q_j\,\langle\psi_i|\psi_j\rangle$$

The only way for this to be true is if $\langle\psi_i|\psi_j\rangle = 0$, which implies orthogonality. □

We have defined the expectation value of an observable $\langle q\rangle = \langle\psi|\hat{Q}|\psi\rangle$, where q is the observable and $\hat{Q}$ is the operator associated with it.

The variance of an observable

$$\Delta q^2 = \langle\psi|\hat{Q}^2\psi\rangle - (\langle\psi|\hat{Q}|\psi\rangle)^2$$

Theorem 3.1. *$\Delta q^2 = 0$ iff $|\psi\rangle$ is an eigenstate of $\hat{Q}$.*

Proof. We have some operator $\hat{Q}$:

$$\hat{Q}\left|\psi\right\rangle = q_n\left|\psi\right\rangle$$

Computing the variance:

$$\hat{Q}^2\left|\psi\right\rangle = \hat{Q}\hat{Q}\left|\psi\right\rangle = \hat{Q}q_n\left|\psi\right\rangle = q_n^2\left|\psi\right\rangle$$

$$\langle q\rangle = \langle\psi|\hat{Q}\psi\rangle = \langle\psi|q_n\psi\rangle = q_n$$

And then

$$\langle q^2\rangle = \langle\psi|\hat{Q}^2\psi\rangle = q_n^2$$

Thus

$$\Delta q^2 = q_n^2 - q_n^2 = 0$$

□

We have some common operators:

$$\hat{x} = x \quad \hat{p} = -i\hbar\frac{\partial}{\partial x}$$

Remember that these operators are matrices, and they have elements

$$X_{ij} = \langle i|\hat{x}|j\rangle = \int dx\,\psi_i^* x\psi_j$$

and

$$P_{ij} = \langle i|\hat{p}|j\rangle = -i\hbar\int dx\,\psi_i^*\frac{\partial}{\partial x}\psi_j$$

Let's look at the position operator:

$$\langle\psi|\hat{x}|\psi\rangle = \int dx\,\psi^* x\psi = \int dx\,x\psi^*\psi = \int dx\,(x\psi^*)\psi = \langle\hat{z}\psi|\psi\rangle$$

Thus we have that

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

And thus we have that $x = x^*$, proving that $\hat{x}$ is Hermitian.

Lets look at the derivative operator, $\frac{\partial}{\partial x}$:

$$\langle\psi|\frac{\partial}{\partial x}|\psi\rangle = \int dx\,\psi^*\frac{\partial}{\partial x}\psi = [\psi^*\psi]_{-\infty}^{\infty} - \int\frac{\partial}{\partial x}\psi^*\psi\,dx$$

The left term must be 0, as the wavefunction must be normalized and must go to 0 at infinity and negative infinity. This means we are left with

$$= \int dx\,(\frac{\partial\psi}{\partial x})^*\psi = -\langle\frac{\partial}{\partial x}\psi|\psi\rangle$$

We see that this operator $\frac{\partial}{\partial x}$ is anti-Hermitian, and so we make it Hermitian by adding an i, to get $i\frac{\partial}{\partial x}$.

3.7 Postulate Number 4

Postulate 4. *The probability of finding the result a_n in a measurement is*

$$P_{a_n} = |\langle a_n|\psi\rangle|^2$$

where $\hat{A}|a_n\rangle = a_n|a_n\rangle$.

If we have a complete basis, we can always write out a wavefunction as a sum of basis vectors:

$$|\psi\rangle = \sum_n \alpha_n |a_n\rangle$$

If we operate from the left with $\langle a_m|$:

$$\langle a_m|\psi\rangle = \sum_n \alpha_n \langle a_m|a_n\rangle = \alpha_m$$

And $P_{a_m} = |\alpha_m|^2$.

If we have the wavefunction $|\psi\rangle = \frac{1}{\sqrt{2}}|a_1\rangle + \frac{1}{\sqrt{2}}|a_2\rangle$, with eigenvalues a_1 and a_2, we can get either eigenvalue as a result of a measurement, weighted equally because the basis vectors are equally weighted.

3.8 Postulate Number 5

Postulate 5. *Immediately after a measurement of observable A that yielded eigenvalue a_n, the wavefunction/system is now given by*

$$|\psi'\rangle = \frac{\hat{P}_n|a_n\rangle}{|\langle\psi|\hat{P}_n\psi\rangle|^{1/2}}$$

Where $\hat{P} = |a_n\rangle\langle a_n|$.

Suppose our system is

$$|\psi\rangle = \alpha|\varphi_1\rangle + \beta|\varphi_2\rangle + \gamma|\varphi_3\rangle$$

And we measure and obtain a_2, associated with $|\varphi_2\rangle$. This postulate tells us that our new state is

$$|\psi'\rangle = \frac{|\varphi_2\rangle\langle\varphi_2|\psi\rangle}{[\langle\varphi_2|\psi\rangle\langle\psi|\varphi_2\rangle]^{1/2}} = \frac{\beta|\varphi_2\rangle}{(\beta^2)^{1/2}} = |\varphi_2\rangle$$

The process of measurement has driven our system into an eigenstate of the operator, now any more measurements will return the same result. The act of measurement has now made it impossible to return to the state we were in before. This is known as collapsing the wavefunction.

3.9 Postulate Number 6

Postulate 6. *As long as there is no measurement, a wavefunction will evolve governed by Schrodinger's equation.*

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

Where $\hat{H}$ is the Hamiltonian.

3.10 Summary of the Postulates

1. Hilbert Space
2. Hermitian Operators
3. $\hat{A} \to a_n$
4. $P_{a_n} = |\langle a_n|\psi\rangle|^2$
5. $|\psi'\rangle = |a_n\rangle$, wavefunction collapse
6. Wavefunctions evolve according to the Schrodinger Equation

3.11 Stern-Gerlach Experiments

Atoms can have magnetic moments μ, and we can exert a force on something with a magnetic moment using a magnetic field. Recall that the energy is $-\mu \cdot \mathbf{B}$, meaning that we can have forces like

$$f_z = \frac{\partial}{\partial z}\mu \cdot \mathbf{B}$$

Stern and Gerlach had a pair of magnets, one of which was pointed (lets say the north magnet). If we draw out the field lines, the point concentrates the field, becoming stronger near the tip and falling off as we move further away, creating a field gradient $\frac{dB}{dz}$. Shooting a beam of atoms through the gap between them (generated by heating a lump of silver in an oven with a pinhole in it to generate a beam). The atoms would pass through the field and were deflected, based on the orientation of the magnetic moment. We can define a "spin" which relates to the magnetic moment:

$$\mu = g\frac{e}{2m_e}\mathbf{s}$$

where g is the gyromagnetic ratio, and is just a constant (around 2). Note that for silver atoms, $\mathbf{s} \in [-\frac{\hbar}{2}, \frac{\hbar}{2}]$.

Classically the force is

$$F_z = \mu \cdot \frac{\partial \mathbf{B}}{\partial z}$$

If we placed a screen behind the experiment, we would expect some continuous distribution of particles striking, based on the spin of the outgoing atom. Instead, they obtained two peaks at $\pm\frac{\hbar}{2}$, instead of the distribution they expected. This makes sense when we look at it from a quantum measurement perspective, where there are only two potential outputs, $\pm\frac{\hbar}{2}$, where the experiment measures each particle. We haven't really defined a wavefunction for the particles, but it turns out that we have something of the form

$$|\psi\rangle = \alpha\,|+\rangle_z + \beta\,|-\rangle_z$$

If we then send one of the split peaks into its own S-G experiment, say the $|+\rangle$ peak, then all of the particles will return the $|+\rangle$ again, and none will return the $|-\rangle$ state.

If we instead rotated the second S-G experiment to the x basis, then what happens when the $|+\rangle_z$ particles pass through the x S-G experiment? We have collapsed the spin to an eigenvalue in the z basis, but in the x basis, the wavefunction is still split evenly. Thus when measuring through the x S-G experiment, we still get a 50/50 split, so 25% and 25%:

$$|+\rangle_z = \alpha\,|+\rangle_x + \beta\,|-\rangle_x$$

where $|\alpha|^2 = |\beta|^2 = \frac{1}{2}$.

We also have what's known as a "quantum eraser", which essentially recombines the outputs of a S-G machine. We see that this does not collapse the wavefunction.

3.12 Commutativity of Operators

We want to look at non-commuting observables, i.e. whether the order you measure two observables matters. The Cauchy-Schwarz inequality is useful:

$$|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle$$

We can prove it:

Proof. Suppose we have the state

$$|\gamma\rangle = |\beta\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}|\alpha\rangle$$

Computing $\langle\gamma|\gamma\rangle$:

$$\langle\gamma|\gamma\rangle = \langle\beta|\beta\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}\langle\beta|\alpha\rangle - \frac{\langle\beta|\alpha\rangle}{\langle\alpha|\alpha\rangle}\langle\alpha|\beta\rangle + \frac{\langle\beta|\alpha\rangle\langle\alpha|\beta\rangle\langle\alpha|\alpha\rangle}{\langle\alpha|\alpha\rangle^2} = \langle\beta|\beta\rangle - \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle}$$

Since we know that $\langle\gamma|\gamma\rangle \geq 0$ because it is a magnitude, then we know that

$$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$$

□

Recall that the variance of an observable A is

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

For some other observable B, we can also define the variance $\sigma_B^2 = \langle g|g\rangle$, with $g = (\hat{B} - \langle\hat{B}\rangle)|\psi\rangle$. We can then compute

$$\langle f|g\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\psi|\hat{B}\psi\rangle - \langle\hat{B}\rangle\langle\hat{A}\psi|\psi\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle\langle\psi|\psi\rangle$$

We know that $\langle\psi|\hat{B}\psi\rangle = \langle\hat{B}\rangle$, and since $\hat{A}$ is Hermitian, we know that $\langle\hat{A}\psi|\psi\rangle = \langle\psi|\hat{A}\psi\rangle = \langle\hat{A}\rangle$:

$$\langle f|g\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle$$

If we then compute $\langle g|f\rangle$, we see that we obtain:

$$\langle g|f\rangle = \langle\hat{B}\hat{A}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle$$

If we then compute $\langle f|g\rangle - \langle g|f\rangle$, we see that we have

$$\langle f|g\rangle - \langle g|f\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{B}\hat{A}\rangle$$

This is known as the commutator:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Now using the Cauchy-Schwarz inequality:

$$\sigma_A^2\sigma_B^2 = \langle f|f\rangle \langle g|g\rangle \geq |\langle f|g\rangle|^2$$

Now using the fact that $|z|^2 = Re(z)^2 + Im(z)^2 = \left(\frac{1}{2i}(z-z^*)\right)^2$ for any $z \in \mathbb{C}$:

$$\sigma_A^2\sigma_B^2 \geq \frac{1}{2i}\left(\langle f|g\rangle - \langle g|f\rangle\right)^2 \rightarrow \sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\right)^2 \langle[\hat{A},\hat{B}]\rangle^2$$

In other words:

$$\boxed{\sigma_A\sigma_B \geq \frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle}$$

We see that we have derived the Heisenberg Uncertainty Principle.

To point out that this isn't that weird, consider two arbitrary matrices M and N. We know that $MN \neq NM$ in general. You can also think of operators as functions, such as $\hat{x} = x$ and $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, Suppose $|\psi\rangle = f(x)$. If we look at $\langle\hat{x}\hat{p}\rangle$ versus $\langle\hat{p}\hat{x}\rangle$:

$$\int f(x)x\frac{df}{dx}\,dx \neq \int f(x)\frac{d}{dx}xf(x)\,dx$$

And thus we have the fact that $\hat{x}$ and $\hat{p}$ do not commute. This relationship holds for any two observables, not just position and momentum. This stems from the fact that quantum mechanics uses matrices to describe operators, and matrices don't commute.

3.13 Unitary Operators

Unitary operators transform one basis to another.

$$|\psi_i'\rangle = \sum_j U_{ij}^*|\psi_j\rangle$$

If we look at the inner product of the old basis and the new basis:

$$\langle\psi_i'|\psi_j'\rangle = \delta_{ij}$$

$$\langle\sum_k U_{ik}|\psi_k|\sum_l U_{il}^*\psi_l\rangle = \delta_{ij}$$

$$\sum_{k,l} U_{ik}U_{il}^*\langle\psi_k|\psi_l\rangle$$

Due to orthogonality:

$$= \sum U_{ik}U_{jk}^* = \sum U_{ik}U_{kj}^* = \delta_{ij}$$

This tells us that $UU^\dagger = \mathbb{1}$, and is the definition of a unitary matrix.

Looking at how unitary operators act on basis vectors:

$$|\psi_i'\rangle = \hat{U}|\psi_i\rangle$$

$$|\psi_i\rangle = \hat{U}^\dagger|\psi_i'\rangle$$

And transforming operators:

$$\hat{Q}' = \hat{U}\hat{Q}\hat{U}^{-1}$$

And the other way around:

$$\hat{Q} = \hat{U}^{-1}\hat{Q}\hat{U}$$

Thinking about a Cartesian rotation matrix, we want to map $a\hat{i} + b\hat{j}$ to the same vector in another basis, $a'\hat{i}' + b'\hat{j}'$. We can do this with a rotation matrix:

$$R = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

Note that this is not Hermitian, in general, unitary matrices don't have to be Hermitian, and will oftentimes not be Hermitian. We can check that it is unitary:

$$R^\dagger R = \mathbb{1}$$

We have said that inner products are independent of basis, that is

$$\langle \alpha' | \beta' \rangle = \langle \alpha | \beta \rangle$$

And likewise the eigenvalues or outcomes of measurements are independent of the basis we are working in.

We can define a unitary time evolution operator $\hat{U}(t, t_0)$

$$|\psi(t)\rangle = \hat{U}(t, t_0)\,|\psi(t_0)\rangle$$

We can look at the inner product of $|\psi(t)\rangle$ with itself, and this must be equal to the inner product of $|\psi(t_0)\rangle$ with itself:

$$\begin{aligned} \langle \psi(t)|\psi(t)\rangle &= \langle \psi(t_0)|\psi(t_0)\rangle \\ &= \langle \hat{U}(t,t_0)\psi(t_0)|\hat{U}(t,t_0)\psi(t_0)\rangle \\ &= \langle \psi(t_0)|\hat{U}^\dagger\hat{U}|\,|\psi(t_0)\rangle\rangle = \hat{U}^\dagger\hat{U} = \mathbb{1} \end{aligned}$$

We expect that $\hat{U}(t_0, t_0) = 1$. If we plug this into the Schrodinger equation:

$$i\hbar\frac{\partial}{\partial t}U(t, t_0)\,|\psi(t_0)\rangle = \hat{H}\hat{U}(t, t_0)\,|\psi(t_0)\rangle$$

$$\frac{\partial}{\partial t}\hat{U}(t, t_0) = -\frac{i}{\hbar}\hat{H}\hat{U}(t, t_0)$$

Assuming that $\hat{H}$ is time-independent, we then get

$$\boxed{U(t, t_0) = e^{-i(t-t_0)\hat{H}/\hbar}}$$

3.14 Review of Dirac Notation

Let us assume we are in a 2D Hilbert space. Kets are column vectors in the Hilbert space, and bras are row vectors in the Hilbert space. To convert between a ket and bra, we take the Hermitian conjugate, bringing along a complex conjugate. To take the inner product of two kets, turn the first one into a bra and then FOIL out all the terms, removing certain terms due to orthonormality of the basis vectors. Also remember that pulling scalars out of a bra requires a complex conjugate and does not require one when pulling it out of the ket.

If $\hat{Q}$ is an operator, its matrix elements are given by $Q_{ij} = \langle i|\hat{Q}|j\rangle$. The expectation value $\langle\hat{Q}\rangle = \langle\psi|\hat{Q}|\psi\rangle$. The commutator of two operators $\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$. The anti-commutator is $\{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$.

If $|\phi_i\rangle$ are basis vectors and eigenfunctions of $\hat{Q}$:

$$\hat{Q} = q_1 |\phi_1\rangle \langle\phi_1| + q_2 |\phi_2\rangle \langle\phi_2|$$

Note that the matrix representation of an operator will be diagonal if the basis vectors are eigenfunctions of the operator.

3.15 Quantum 2-Level Systems

An example of a 2-level system would be spin, which was first described in 1925, when Uhlenbeck and Goudsmit proposed the idea. Spin is essentially the intrinsic angular momentum of a particle. In particular, they were describing the electron, which is a spin-$\frac{1}{2}$ particle.

We can also think of polarized photons as a 2-level system, being either horizontally or vertically polarized. Another case is anytime we have a quantum system that can be isolated down to just two levels, we can treat it as if it is a spin system. For example, if we have a Sodium atom, with many different energy levels, if we isolate just the ground state and the first excited state, we have a 2-level system. These are pseudo-spin systems, as we can think of them as if they were spin systems, but they aren't actually spin systems.

We have two states, $|+\rangle = \begin{bmatrix}1\\0\end{bmatrix}$ and $|-\rangle = \begin{bmatrix}0\\1\end{bmatrix}$.

If we have some general matrix M:

$$M = \begin{bmatrix}a+d & b-ic\\ b+ic & a-d\end{bmatrix}$$

We can decompose this using the set of matrices known as the Pauli matrices:

$$M = a\mathbb{1} + b\sigma_1 + c\sigma_2 + d\sigma_3$$

Where $\sigma_1 = \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$, $\sigma_2 = \begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}$, and $\sigma_3 = \begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$. With these (and the identity), we can decompose any 2-level matrix.

We can define the spin operators:

$$\hat{S}_x = \frac{\hbar}{2}\sigma_1 \quad \hat{S}_y = \frac{\hbar}{2}\sigma_2 \quad \hat{S}_z = \frac{\hbar}{2}\sigma_3$$

We can see how $\hat{S}_z$ operates on the basis states:

$$\hat{S}_z \left|\pm\right\rangle = \pm\frac{\hbar}{2}$$

It can be shown that

$$\left|+\right\rangle_x = \frac{1}{\sqrt{2}}(\left|+\right\rangle_z + \left|-\right\rangle_z) \qquad \left|-\right\rangle_x = \frac{1}{\sqrt{2}}(\left|+\right\rangle_z - \left|-\right\rangle_z)$$

And

$$\left|\pm\right\rangle_y = \frac{1}{\sqrt{2}}(\left|+\right\rangle_z \pm i\left|-\right\rangle_z)$$

We can write some commutation relations as well:

$$[\hat{S}_x, \hat{S}_y] = \frac{\hbar^2}{4}(\sigma_1\sigma_2 - \sigma_2\sigma_1) = \frac{i\hbar^2}{4}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} = \frac{\hbar^2}{2}i\sigma_3 = i\hbar\hat{S}_z$$

It can also be shown that

$$[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x \quad [\hat{S}_x, \hat{S}_z] = i\hbar\hat{S}_y$$

Relating this back to the uncertainty principle:

$$\Delta\hat{S}_x^2\Delta\hat{S}_y^2 \geq \left(\frac{\hbar}{2}\hat{S}_z\right)^2$$

The total spin is given as

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

We can compare the commutator of the total spin with the individual spins:

$$[\hat{S}^2, \hat{S}_x] = 0$$

And in fact this holds for $\hat{S}_y$ and $\hat{S}_z$ as well.

Let us now look at the matrix for the total spin:

$$\hat{S}^2 = \frac{3\hbar^2}{4}\mathbb{1}$$

Where we have leveraged the fact that $\sigma^2 = \mathbb{1}$ for all 3 Pauli matrices. Note that the eigenvalue for $\hat{S}^2$ is $\lambda = 3\frac{\hbar^2}{4}$. Computing the magnitude of the total spin vector, we have $|S| = \frac{\sqrt{3}}{2}\hbar$. We also know that $|S_z| = \frac{\hbar}{2}$. This is kind of odd, and this implies that spins cannot be perfectly aligned with an axis. Also note that the spin operators are Hermitian, as is $\hat{S}^2$. They also commute with each other.

What about measuring spin along an arbitrary direction?

$$\mathbf{b} = b_x\sin\theta + b_z\cos\theta$$

Then

$$\hat{S}_\theta = \hat{S}_x\sin\theta + \hat{S}_z\cos\theta = \frac{\hbar}{2}\begin{pmatrix}\cos\theta & \sin\theta\\ \sin\theta & -\cos\theta\end{pmatrix}$$

If we find the eigenvalues of this operator, we find what we expect, $\lambda = \pm\frac{\hbar}{2}$. If we solve for the eigenvectors, we have

$$\begin{pmatrix} \sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix}$$

We can then write down the basis states:

$$|+\rangle_\theta = \cos\frac{\theta}{2}|+\rangle_z + \sin\frac{\theta}{2}|-\rangle_z$$

And

$$|-\rangle_\theta = \sin\frac{\theta}{2}|+\rangle_z - \cos\frac{\theta}{2}|-\rangle_z$$

We have the idea of completeness,

$$\sum_i |\psi_i\rangle\langle\psi_i| = \mathbb{1}$$

Working in the z basis, if we do the matrix math out:

$$|+\rangle_z\langle+|_z + |-\rangle_z\langle-|_z = \mathbb{1}$$

If we looked at the eigenvectors for the $\hat{S}_x$ operator, we'd get

$$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

Some more useful things are that

$$[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\epsilon_{ijk}\sigma_k$$

The anti-commutator is

$$\{\hat{\sigma}_i, \hat{\sigma}_j\} = 2\delta_{ij}\mathbb{1}$$

And the trace of the Pauli matrices is 0:

$$\mathrm{Tr}(\hat{\sigma}_i) = 0$$

And finally

$$\hat{\sigma}_i^2 = \mathbb{1}$$

3.16 Multiple Degrees of Freedom

So far we have only dealt with 1 variable, such as the spin of a particle, or the position, but what if we have 2 variables, like the spin and position of an atom, or the frequency and polarization of a photon. What do we do if we have 2 or more particles?

The Hilbert space is a tensor product space. This means that a wavefunction for 2 particles with positions x_1 and x_2 is

$$\psi(x_1, x_2) = \sum_{m,n} c_{mn}\varphi_m(x_1)\otimes\varphi_n(x_2)$$

This gives us 4 possible basis states:

$$|+\rangle_1\otimes|+\rangle_2 \quad |+\rangle_1\otimes|-\rangle_2 \quad |-\rangle_1\otimes|+\rangle_2 \quad |-\rangle_1\otimes|-\rangle_2$$

A wavefunction in this space will be a column vector of size 4.

Common tensor product notation is

$$|u\rangle_1 \otimes |v\rangle_2 = |u\rangle_1 |v\rangle_2 = |u_1, v_2\rangle = |u_1 v_2\rangle$$

If we have two wavefunctions:

$$|\psi\rangle = |u\rangle |v\rangle \qquad |\psi'\rangle = |u'\rangle |v'\rangle$$

and we take the inner product:

$$\langle\psi|\psi'\rangle = \langle u'|u\rangle \langle v'|v\rangle$$

We also have the tensor product of an operator:

$$\hat{C} = \hat{A}_1 \otimes \hat{B}_2$$

$$\hat{C} |uv\rangle = \hat{A}_1 |u\rangle \otimes \hat{B}_2 |v\rangle$$

We see that adding more particles drastically increases the dimension of the Hilbert space, 2^N for N particles. For 300 spin-1/2 particles, we have a 2^{300} dimensional Hilbert space.

Consider two spin-1/2 particles. The wavefunction for this system is a 4d column vector:

$$|\psi\rangle = \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = a |{+}{+}\rangle + b |{+}{-}\rangle + c |{-}{+}\rangle + d |{-}{-}\rangle$$

Suppose we have that

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}(|+\rangle_1 + |-\rangle_1)$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}(|+\rangle_2 + |-\rangle_2)$$

We can compute the tensor product of the two:

$$|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle = \frac{1}{2}(|{+}{+}\rangle + |{+}{-}\rangle + |{-}{+}\rangle + |{-}{-}\rangle)$$

This is a separable state, because we can write it as a tensor product of the wavefunctions of two particles.

If we have the state

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|{+}{+}\rangle + |{-}{-}\rangle)$$

we cannot write this as the tensor product of the wavefunctions of the two particles. This is known as an entangled state.

3.17 Bell's Inequality

Consider the state

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle)$$

If we measure the first particle, and find that it is in state $|0\rangle$, then we immediately know that B is in state $|1\rangle$, because of the entangled state.

If we measure the spin along some arbitrary direction with an operator $\mathbf{n}\hat{\sigma}$:

$$n_x\hat{\sigma}_x + n_y\hat{\sigma}_y + n_z\hat{\sigma}_z$$

We can then write the old basis vectors in terms of the new basis vectors:

$$|0\rangle = \alpha\,|a\rangle + \beta\,|b\rangle \qquad |1\rangle = \gamma\,|a\rangle + \delta\,|b\rangle$$

Let us now rewrite the wavefunction in terms of the new basis:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left[(\alpha\,|a\rangle + \beta\,|b\rangle)(\gamma\,|a\rangle + \delta b) - (\gamma\,|a\rangle + \delta\,|b\rangle)(\alpha\,|a\rangle + \beta\,|b\rangle)\right]$$

If we expand all of this out and then simplify, all the cross-terms cancel:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(\alpha\delta - \beta\gamma\right)\left(|ab\rangle - |ba\rangle\right)$$

If we look at this term at the front, it is the determinant of a matrix:

$$\begin{pmatrix}\alpha & \beta\\ \gamma & \delta\end{pmatrix}$$

Since the transformation matrix between two bases must be unitary, this matrix must be unitary, and unitary matrices have determinants of magnitude 1, so we have that

$$\alpha\delta - \beta\gamma = e^{i\theta}$$

Essentially, the determinant adds in a phase factor:

$$|\psi\rangle = \frac{e^{i\theta}}{\sqrt{2}}(|ab\rangle - |ba\rangle)$$

We see that the anti-correlation in the new basis is the same as it was in the original basis. In 1935, Einstein, Podolsky, and Rosen (Often abbreviated as EPR) wrote a paper in which they were very bothered by this result. This originated the phrase "spooky action at a distance". Einstein was never comfortable with quantum mechanics, and one conclusion of this paper was that "the wavefunction does not provide a complete description of reality". Einstein was wrong.

In 1964, John Bell came up with Bell's Inequality, which is effectively an implicit proof that Einstein's claim of a hidden variable could not be true.

Bell had to assume locality or causality (no time travel), and Einstein's objective reality, and he found that QM will not work unless he removed one of those assumptions.

We start with an experiment, where Alice and Bob each get a single photon from a pair of entangled photons. They both make measurements in two bases, and they both can make either one of two measurements for each basis.

Alice will choose one of two possible measurements, which have physical properties P_A and P_B, and Bob does the same thing, for P_C and P_D, and he does it at a causally disconnected time.

We can form a quantity E:

$$E = AC + BC + BD - AD = (A + B)C + (B - A)D$$

Since by definition, the measurements are all ± 1, the only outcomes allowed for E are ± 2.

We can now define the probability $P(a, b, c, d)$ that before the measurement, $A = a$, $B = b$, $C = C$, and $D = d$.

We can compute the average value of E classically:

$$\langle E \rangle = \sum_{a,b,c,d} P(a, b, c, d)(ac + bc + bd - ad) = \sum P(a, b, c, d)(\pm 2) \leq 2$$

This gets us

$$\boxed{\langle E \rangle_{clas} = \langle AC \rangle + \langle BC \rangle + \langle BD \rangle - \langle AD \rangle \leq 2}$$

Let us now go through the same thing but use a QM approach, using entanglement:

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle)$$

For A, let's say we use σ_z, and for B we use σ_x. On Bob's side, we do measurements that are superpositions of σ_z and σ_x:

$$C = -\frac{1}{\sqrt{2}}(\sigma_z + \sigma_x) \quad D = \frac{1}{\sqrt{2}}(\sigma_z - \sigma_x)$$

We can compute the 4 correlators:

$$\langle AC \rangle = -\frac{1}{\sqrt{2}}(\langle \psi | \sigma_{zA}\sigma_{zB} + \sigma_{zA}\sigma_{xB} | \psi \rangle)$$

If we now plug in $|\psi\rangle$, and then apply the Pauli matrices to the vectors, using the fact that σ_{zA} commutes with σ_{xB} and σ_{zB}, we are eventually left with

$$\langle AC \rangle = \frac{1}{\sqrt{2}}$$

We can do this grind of algebra for each commutator, and we find that

$$\langle E \rangle_{qm} = 2\sqrt{2}$$

Thus we have shown that quantum mechanics violates Bell's Inequality.

When Bell made the inequality, he had 2 assumptions, locality, and objective reality. QM has said that we can violate the inequality, so they cannot both be true.

In 1982, Alain Aspect and his colleagues placed a calcium atom (3 states) to naturally generate entangled pairs of photons. Using polarizers and detectors, they were able to do what we described in the Bell thought experiment. Doing this over and over again yielded $\langle E \rangle = 2.7 \pm 0.015$, verifying that QM violates Bell's Inequality.

3.18 Quantum Cryptography

We begin with the no-cloning theorem, first devised in 1982 by Wooters and Zurek. We begin with defining a copier operator $\hat{C}$:

$$\hat{C}\left|b\right\rangle\left|\psi_1\right\rangle = \left|\psi_1\right\rangle\left|\psi_1\right\rangle$$

Where $|b\rangle$ is a blank state, it can be anything. Essentially, the operator copies the state of the second ket onto the first ket. Lets act this on a superposition state:

$$\left|\psi_3\right\rangle = a\left|\psi_1\right\rangle + b\left|\psi_2\right\rangle$$

$$\hat{C}\left|b\right\rangle\left|\psi_3\right\rangle = \left|\psi_3\right\rangle\left|\psi_3\right\rangle = a^2\left|\psi_1\right\rangle\left|\psi_1\right\rangle + ab\left|\psi_1\right\rangle\left|\psi_2\right\rangle + ba\left|\psi_2\right\rangle\left|\psi_1\right\rangle + b^2\left|\psi_2\right\rangle\left|\psi_2\right\rangle$$

We can also use linearity, and just distribute the operator:

$$\hat{C}\left|b\right\rangle\left|\psi_3\right\rangle = a\left|\psi_1\right\rangle\left|\psi_1\right\rangle + b\left|\psi_2\right\rangle\left|\psi_2\right\rangle$$

Thus we see that these two are different, and thus we have proved that such an operator cannot exist, and thus you cannot perfectly copy an unknown quantum state. This has implications for quantum communication, as now long distance quantum communication is hard, as we cannot copy states to amplify them. However, it also benefits us because we can do quantum cryptography.

In 1984, Bennett and Brassard came up with an algorithm for Quantum Key Distribution (QKD), which is known as BB84. We encode the information in two non-orthogonal bases.

Alice wants to send a message to Bob. She generates a random bitstring to choose which of the two bases to encode her message in (A or B) for each photon. She then uses the bitstring to encode the message, and sends it to Bob. Bob measures using a random choice of basis for each photon. Alice then publicly announces her choices for the bases. Bob then also publicly discloses the bases that he used to measure the photons. They then choose to only keep the cases where the bases are the same. Alice then randomly announces her bits publicly. They then check, and if the error is below a threshold, they use the rest of the bits for the key.

If Eve tries to intercept, and measures a photon, she will collapse the wavefunction, and 50% of the time, she will introduce an error. This makes QKD provably secure, as it can check whether or not an eavesdropper was intercepting messages.

There is also the Ekert Protocol, where Alice generates N entangled states, and she sends the second particle to Bob, who then conducts EPR-type measurements on half the pairs, and if Bell's inequality is violated, then we know we have a quantum connection, rather than a classical one.

3.19 Quantum Information

A classical computer uses bits that are valued at either 0 or 1. If we think quantum mechanically, and take a spin-$\frac{1}{2}$ system, we have two basis states, but we also have states that are a superposition of these basis states. If we look at the logic behind classical computation, we have logic gates, such as the NOT gate and the AND gate. It can be shown that the NAND gate (NOT AND) is universal, which means that any other boolean logic gate can be built from NAND gates. For quantum computation, the universal set is arbitrary qubit-rotations and the CNOT gate.

We can see that the $\hat{\sigma}_x$ acts like a classical NOT gate, it maps $|0\rangle$ to $|1\rangle$, and $|1\rangle$ to $|0\rangle$.

Let's talk a bit about the physical realization of a qubit. The PSC has ion trapped qubits, with pulses of laser light tuned on the resonance of the gap from $|0\rangle$ and $|1\rangle$, such that when the $|0\rangle$ state

absorbs the laser photon, it has a 100% probability to reach the excited state $|1\rangle$, and vice versa. The action of applying this laser pulse is a NOT gate.

The Y gate is $\hat{\sigma}_y$, and $Z = \hat{\sigma}_z$. There are also some useful gates like

$$\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix} = \frac{1}{\sqrt{2}}(X+Z)$$

and the phase gate S:

$$S = \begin{pmatrix}1 & 0\\ 0 & i\end{pmatrix}$$

Which is also known as the square root of Z gate ($S^2 = Z$). The T gate is the $\frac{\pi}{8}$ gate:

$$T = \begin{pmatrix}1 & 0\\ 0 & e^{i\pi/4}\end{pmatrix}$$

We can think of the state of a qubit as a point on a sphere, which is known as a Bloch sphere. The position on a sphere corresponds to the state of the qubit:

$$|\psi\rangle = \alpha\,|0\rangle + e^{i\phi}\beta\,|1\rangle$$

Oftentimes we place $|0\rangle$ as the south pole and $|1\rangle$ as the north pole, making the equator the set of all equal superpositions of the two states.

It can be shown that we can write arbitrary rotations as

$$R_n(\alpha) = \cos\frac{\alpha}{2}\mathbb{1} - i\sin\frac{\alpha}{2}\mathbf{n}\cdot\hat{\sigma}$$

This rotates by angle α around a normal vector $\mathbf{n}$.

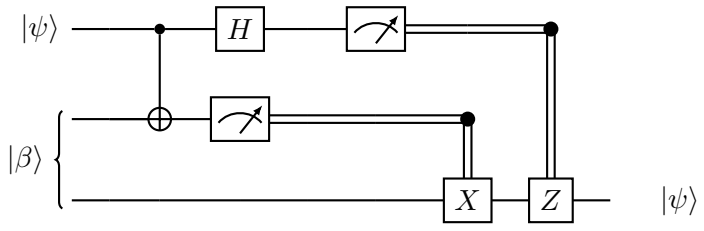
For 2-qubit gates, we have the controlled-NOT gate, or the CNOT gate. We have two qubits, the control and the target qubit. If the control is $|1\rangle$, we return the result of a NOT gate on the target, and if the control is $|0\rangle$ we do nothing and return the target's current value.

It can be shown that the CNOT can generate entanglement. Suppose we act on a superposition state and the $|0\rangle$ state:

$$CNOT((|0\rangle + |1\rangle)\otimes|0\rangle) = |00\rangle + |11\rangle$$

We can then think of our operations as a circuit, with lines being qubits, and we place boxes with letters in them on the lines to represent gates. We do multi qubit gates by using vertical lines to connect two qubits together. Measurement is represented by a box with a meter in it, and the output of measurement is given as a double line classical bit.

"Teleportation" is sending an arbitrary state $|\psi\rangle$ from Alice to Bob. They first share an entangled state (Bell state), with Alice getting one particle and Bob getting the other.



In 1994, Peter Shor proved that using the rules of quantum mechanics, we can factor large numbers exponentially faster than classically. Algorithms fit into different complexity classes, based on how difficult they are, which is measured by how they scale when we make the problem larger. Problems in the P class scale polynomially, and NP problems can be verified in polynomial time, but they scale exponentially. Factoring a large number is an NP problem, as it is hard to factor a large number, but it is easy to verify whether a solution is correct. Shor showed that a quantum computer could solve this polynomially, rather than the exponential complexity that classical computers could do.

A challenge to a physical construction of these quantum computers is noise, such as noise introduced by accident or external interactions. To fix these issues, we apply classical error correction and apply it to a quantum system. In 1948, Claude Shannon created the field of Information Theory, which allowed for the creation of optimal methods for protecting against noise being introduced into the system. A basic solution is to encode the same information using multiple qubits, and then using the majority value of the qubits. There also exist Hamming Codes, such as a $(7, 4)$ code, which uses 7 bits to encode the information stored in 4 bits. This is more efficient in terms of bits, and can detect and correct for flips.

If you want to build a physical quantum computer, you must satisfy the Divencenzo criteria:

1. Scalable physical system of qubits
2. Ability to initialize a state
3. Decoherence time that is much longer than the gate time
4. A universal set of gates
5. Have to be able to measure your qubits

This third one is one of the most challenging, because decoherence generally occurs from interactions from the outside, and yet we still want to be able to control the system. With all of these satisfied, you can build a quantum computer.

3.20 Fourier Transforms

We begin with some periodic function $f(x)$, with period $2L$. f must also be continuous and differentiable. We can write this function in terms of a Fourier series:

$$f(x) = \sum_{-\infty}^{\infty} c_n e^{in\pi x/L}$$

We can write this out

$$f(x) = \frac{a_0}{2} + \sum a_b \cos\frac{n\pi x}{L} + b_n \sin\frac{n\pi x}{L}$$

Where $a_n = c_n + c_{-n}$ and $b_n = i(c_n - c_{-n})$.

We know that the basis functions are orthonormal:

$$\frac{1}{2L}\int_{-L}^{L} e^{in\pi x/L} e^{-im\pi x/L}\, dx = \delta_{mn}$$

We can find the coefficients:

$$c_n = \frac{1}{2L}\int f(x) e^{-in\pi x/L}\, dx$$

We can then expand this to infinite bounds, and we want to be able to handle non-periodic functions. Note that our function must be square integrable over the reals. This gets us that

$$f(x) = \frac{1}{2\pi} \sum_{-\infty}^{\infty} \Delta k \int_{-L}^{L} dx' f(x') e^{in\pi(x-x')/L}$$

Where $\Delta k = \frac{\pi}{L}$. Letting the integral now go to infinity:

$$f(x) = \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx' f(x') e^{ik(x-x')}$$

We can write this in a symmetric form:

$$f(x) = \frac{1}{\sqrt{2\pi}} \int dk\, g(k) e^{ikx}$$

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

These are Fourier transform pairs. This allows us to essentially find how much in a different basis that we need to build a function, such as finding what frequency components we need to build a time-dependent signal.

Some pairs that are useful to have in mind are

$$e^{i\omega_0 t} \to 2\pi\delta(\omega - \omega_0)$$

$$\cos\theta \to \pi(\delta(\omega - \omega_0) + \delta(\omega + \omega_0))$$

$$e^{-\gamma t} \to \frac{2\gamma}{\gamma^2 + \omega^2}$$

$$e^{-t^2/2\sigma^2} \to \sqrt{2\pi}\sigma e^{-\sigma^2\omega^2/2}$$

A square pulse of length T maps to $T \operatorname{sinc} \frac{\omega T}{2\pi}$.

3.21 Free Particle

We can write down the Schrodinger equation for a free particle:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$

Which we know has the solution

$$|\psi\rangle = e^{ikx - \omega t}$$

Where $\omega = \frac{\hbar k^2}{2m}$ and $k = \frac{p}{\hbar}$. However, we have issues with normalization. We can instead create a wave packet, a superposition of plane waves such that the frequencies die down as we get further away from the center:

$$|\psi(x,t)\rangle = \int_{\mathbb{R}} dp\ |\varphi(p,t)\rangle\, e^{ipx/\hbar}$$

This looks familiar, because this is just the Fourier transform of the position wavefunction. If we take $|\,|\varphi(p,t)\rangle\,|^2$, this gives us the probability of momentum p at time t.

The momentum operator $\hat{p}$ can be given by $\frac{d\langle\hat{x}\rangle}{dt}$, which we can compute:

$$\frac{d\langle\hat{x}\rangle}{dt} = \frac{d}{dt}\int \psi^* x\psi\, dx = \int x\left(\psi^*\frac{\partial\psi}{\partial t} + \frac{\partial\psi^*}{\partial t}\psi\right) dx$$

Taking the Schrodinger equation with $V = 0$ and plugging in the relationship that gives us, and then integrating by parts:

$$-\frac{i\hbar}{2m}\int \psi^*\frac{\partial\psi}{\partial x} = \langle\hat{p}\rangle$$

This tells us that

$$\hat{p} = -\frac{i\hbar}{2m}\frac{\partial}{\partial x}$$

We can then write down Fourier transform pairs for our wavefunction;

$$\varphi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int dx\,\psi(x,t)e^{-ipx/\hbar}$$

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int dp\,\varphi(p)e^{ipx/\hbar}$$

We can take a Gaussian wavefunction:

$$|\psi\rangle = \frac{1}{(2\pi s)^{1/4}}e^{-x^2/4s^2}$$

We can compute $\sigma_x^2 = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2$, where the second term is 0. We then get that

$$\sigma_x^2 = \int_{\mathbb{R}} \frac{1}{(2\pi s)^{1/2}}x^2e^{-x^2/2s^2} = s^2$$

We can compute the variance in p:

$$\sigma_p^2 = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2 = -\hbar^2\int dx\,\psi\frac{\partial^2}{\partial x^2}\psi = \frac{\hbar^2}{4s^2}$$

We see that $\sigma_p\sigma_x = \frac{\hbar}{2}$, thus telling us that we are in a minimum uncertainty state (according the the uncertainty principle, this is the least uncertainty we can get in a state).

3.22 Time Dependence

If we add in time dependence:

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

where our Hamiltonian is given by

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

The Hamiltonian is the total energy operator, and is an observable, and thus must be Hermitian. The eigenstates of the Hamiltonian gives us the energies:

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$$

And thus we can write our wavefunction in terms of time independent terms:

$$|\psi(x,t)\rangle = \sum_n c_n(t)\,|\varphi_n(x)\rangle$$

If we then plug this into the Schrodinger equation:

$$i\hbar\frac{\partial}{\partial t}\sum_n c_n(t)\,|\varphi_n\rangle = \sum_n c_n(t)\,|\varphi_n\rangle\,E_n$$

Multiplying by $\langle\psi_n|$ and doing some math, we are left with

$$i\hbar\frac{\partial c_k(t)}{\partial t} = c_k(t)E_k$$

We can then compute this partial derivative:

$$\frac{\partial c_k}{\partial t} = -i\frac{E_k}{\hbar}c_k$$

And then this gives us that

$$c_k(t) = c_0 e^{-iE_k t/\hbar}$$

This means that we can write out the time dependent wavefunction:

$$|\Psi(x,t)\rangle = |\psi_n(x)\rangle\,e^{-iE_n t/\hbar}$$

This is stationary, as we can see that $\langle\Psi|\Psi\rangle = 1$.

Suppose we have the system

$$|\Psi(0)\rangle = c_1\,|\psi_1\rangle + c_2\,|\psi_2\rangle$$

We can write out the time dependent wavefunction as

$$|\Psi(t)\rangle = c_1 e^{-iE_1 t/\hbar}\,|\psi_1\rangle + c_2 e^{-iE_2 t/\hbar}\,|\psi_2\rangle$$

If we measure at some time t_1, and we find E_1, we know that the probability of this is still

$$P = |c_1|^2$$

We see that measuring the energy is not time dependent, the phase factors just cancel out when taking the inner product.

Thus we have that we can write a time dependent wavefunction as a time independent wavefunction times the time evolution:

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

Let us consider the following. Suppose we have an operator $\hat{A}$ such that

$$\hat{A}\,|\varphi_m\rangle = a_m\,|\varphi_m\rangle$$

Where $|\varphi_m\rangle = \alpha_1\,|\phi_1\rangle + \alpha_2\,|\psi_2\rangle$. We can see that $\hat{A}$ will not commute with the Hamiltonian, since the basis vectors are each not eigenstates of the energy operator (they're a superposition of two

energy eigenstates, rather than being just 1 eigenstate). The probability of measuring a_1 for some $|\Psi(x,t)\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle$:

$$P_{a1} = |\langle\varphi_1|\Psi(x,t)\rangle|^2 = \left|\alpha_1^* c_1 e^{-iE_1 t/\hbar} + \alpha_2^* c_2 e^{-iE_2 t/\hbar}\right|^2$$

$$= |\alpha_1|^2|c_1|^2 + |\alpha_2|^2|c_2|^2 + 2\mathrm{Re}\left[\alpha_1 c_1^* \alpha_2 c_2 e^{-i\Delta E t/\hbar}\right]$$

We see that we have an oscillating time dependent term. So we have that the probabilities are not always time independent.

Going back to a spin-$\frac{1}{2}$ particle, we have the Hamiltonian:

$$\hat{H} = -\mu \cdot \mathbf{B} = \omega_0 \hat{S}_z$$

For an electron, we have that $\omega_0 = \frac{eB}{m_e}$. We know the eigenvalues and eigenkets:

$$\hat{H} |\pm\rangle_Z = \pm\frac{\hbar\omega_0}{2} |\pm\rangle_Z$$

If we prepare a state in $|+\rangle_Z$ at $t = 0$, we have the wavefunction

$$|\Psi(x,t)\rangle = e^{-i\omega_0 t/\hbar} |+\rangle_Z$$

We can see by inspection that we will have a 100% chance of measuring the $|+\rangle_Z$ state.

If we instead start with the system in state

$$|\Psi(0)\rangle = \cos\theta |+\rangle_z + \sin\theta |-\rangle_z$$

If we now measure in the z basis again:

$$|\langle +_z|\Psi(t)\rangle|^2 = \cos^2\theta$$

And we still have no time dependence. This is because we measured in the z basis, and the Hamiltonian is in the z basis. The energy eigenstates are the basis vectors of the system. Had we instead measured along the x basis:

$$\langle +\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle_z + |-\rangle_z)$$

Thus taking the measurement gets us

$$\langle +_x|\Psi\rangle = \frac{1}{\sqrt{2}}(\langle +|_z + \langle -|_z)(\cos\theta |+\rangle_z e^{-i\omega_0 t/\hbar} + \sin\theta |-\rangle_z e^{i\omega_0 t/\hbar})$$

$$= \frac{1}{2}\left|\cos\theta + e^{i\omega_0 t}\sin\theta\right|^2 = \frac{1}{2}(1 + 2\cos\theta\sin\theta\cos\omega_0 t)$$

And we see that the measurement gives us a time dependence in the probabilities.

Going back to the free particle, we have that Schrodinger's equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}|\psi\rangle = E|\psi\rangle$$

Using the deBroglie relationship, we have that $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $E = \frac{\hbar^2 k^2}{2m}$. This makes the equation

$$-\frac{\partial^2}{\partial x^2}|\psi\rangle = -k^2|\psi\rangle$$

This has general solution

$$|\psi\rangle = Ae^{ikx} + Be^{-ikx}$$

Where each of these is a valid solution, and thus the linear combination is also a valid solution. We then make it time dependent:

$$|\Psi(x,t)\rangle = Ae^{ikx-iEt/\hbar} + Be^{-ikx}e^{-iEt/\hbar} = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)}$$

If we think of these as waves, we have that the wave speed is $\frac{\hbar k}{2m}$ for each wave, with one traveling left and the other traveling to the right.

We have to normalize this state, and we begin to run into trouble:

$$|\Psi(x,t)|^2 = \int_{\mathbb{R}} \Psi^*\Psi\, dx = \int_{\mathbb{R}} dx = \infty$$

This state is not normalizable. This is the first problem with this state. The second problem is that the speed of the wave is $v_q = \frac{\hbar k}{2m} = \sqrt{\frac{E}{2m}}$. However, classically, $\frac{1}{2}mv_c^2 = E$, which says that $v_C = \sqrt{\frac{2E}{m}}$. It seems as though our quantum velocity is half of the classical velocity.

3.23 Wave Packets

We begin our construction of a simple wave packet with 3 terms:

$$|\Psi(x,0)\rangle = \frac{1}{\sqrt{2\pi}}\left[\frac{1}{2}e^{i(k_0-\delta k)x} + e^{ik_0x} + \frac{1}{2}e^{i(k_0+\delta k)x}\right]$$

We have made a wave packet out of 3 slightly different frequency waves, at differing amplitudes. We can write this down with the phase factors:

$$|\Psi(x,t)\rangle = \frac{1}{\sqrt{2\pi}}\left[\frac{1}{2}e^{i(k_0-\delta k)x-\frac{i\hbar}{2m}(k_0-\delta k)^2t} + e^{ik_0x-\frac{i\hbar k_0^2}{2m}t} + \frac{1}{2}e^{i(k_0+\delta k)x-\frac{i\hbar(k_0+\delta k)^2}{2m}t}\right]$$

We now assume that $\delta k \ll k_0$, letting us ignore $(\delta k)^2$. We can then factor and we are left with

$$\approx \frac{1}{\sqrt{2\pi}}e^{ik_0(x-\frac{\hbar k_0}{2m})t}\left[1 + \cos\delta k\left(x - \frac{\hbar k_0}{m}t\right)\right]$$

We see that we have two velocities, the phase velocity and the group velocity, with the phase velocity being the one in the phase, and the other velocity being the group velocity, which if we plotted the wave packet, is the velocity of the envelope function. This doesn't look like a particle, because we only used 3 terms, and if we imagine the Fourier limit we have something that looks like the movement of a particle, moving at a velocity that agrees with the classical velocity of the wave.

A useful integral relation to know is that

$$\int e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}}e^{b^2/4a^2}$$

3.24 Infinite Square Well

Suppose we have a potential function that is ∞ everywhere except the bounds of the well

$$V = \begin{cases} 0, & -\frac{a}{2} < x < \frac{a}{2} \\ \infty, & \text{else} \end{cases}$$

We can write down the TISE:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}|\psi\rangle = E|\psi\rangle = \frac{\hbar^2 k^2}{2m}|\psi\rangle$$

We can rewrite this as

$$\frac{\partial^2}{\partial x^2}|\psi\rangle = -k^2|\psi\rangle$$

And we have a set of boundary conditions now. The solutions to this are combinations of moving plane waves:

$$|\psi\rangle = Ae^{ikx} + Be^{-ikx}$$

We know that $|\psi(x = \pm\frac{a}{2})\rangle = 0$:

$$\psi\left(\frac{a}{2}\right) = 0 \to Ae^{-ika/2} + Be^{ika/2} = 0$$

$$\psi\left(-\frac{a}{2}\right) = 0 \to Ae^{ika/2} + Be^{-ika/2} = 0$$

If we then add these two equations, we have that

$$0 = A\left(e^{-ika/2} + e^{ika/2}\right) + B\left(e^{ika/2} + e^{-ika/2}\right)$$

Which tells us that $A = -B$. this then tells us that

$$|\psi(x)\rangle = 2iA\sin(kx)$$

Setting this equal to 0 at the boundary, we know that $\psi\left(\frac{a}{2}\right) = 0$, which means that $\frac{ka}{2} = \frac{n\pi}{2}$ for even n. Thus we have that

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \quad (n\,\text{even})$$

For the odd solutions, we just subtract the equations, we find that $A = B$, and we then get a cosine instead of a sine:

$$\psi(x) = \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi x}{a}\right) \quad (n\,\text{odd})$$

Note that because of the conditions on n, we have discretized k, meaning that we have discrete energies:

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

Also note that the lowest energy state in the system is not 0:

$$E_1 = \frac{\hbar^2\pi^2}{2ma}$$

This is also known as the ground state, or the zero-point energy, and is sometimes written as E_0.

3.25 Harmonic Oscillator

The square well is one of the most important quantum systems, along with a spin-1/2 system. Another very important system is the quantum harmonic oscillator, which has 2 reasons for its importance. The potential for the harmonic oscillator has potential $V = \frac{1}{2}m\omega^2x^2$, and it turns out we can approximate almost potential with a minimum using a harmonic oscillator. The second reason is more subtle, and is that if we increase the energy, we pick up an $\hbar\omega$. This means that we can model other systems that add discrete amounts of energy, like photons and phonons.

We begin with the Schrodinger equation:

$$H\left|\psi\right\rangle = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left|\psi\right\rangle + \frac{1}{2}m\omega^2x^2\left|\psi\right\rangle$$

Dividing both ides by $\frac{\hbar\omega}{2}$:

$$\varepsilon\left|\psi\right\rangle = -\frac{\hbar}{m\omega}\frac{d^2}{dx^2} + \frac{m\omega}{\hbar}x^2\left|\psi\right\rangle$$

Where $\varepsilon = \frac{2E}{\hbar\omega}$. We can define $\alpha = \frac{m\omega}{\hbar}$:

$$\varepsilon\left|\psi\right\rangle = -\frac{1}{\alpha}\left|\psi\right\rangle + \alpha x^2\left|\psi\right\rangle$$

We now switch to dimensionless units, by using the fact that α has units of one over meters squared, so we define $q = \sqrt{\alpha}x$, which gets us that $x^2 = \frac{q^2}{\alpha}$. Taking the second derivative of this, and inserting it into the equation, we have that

$$\frac{d^2}{dq^2}\left|\psi\right\rangle = (q^2 - \varepsilon)\left|\psi\right\rangle$$

If we look at the asymptotic limit with $q \to \infty$, we have that $\frac{d^2}{dq^2} \approx q^2\left|\psi\right\rangle$, which gets us that $|\psi\rangle \approx Ae^{-q^2/2} + Be^{q^2/2}$, where we must set $B = 0$ because that explodes to infinity.

However, we can do it using the operator method, which gets us raising and lowering operators which are quite useful. We can think of q as an operator:

$$\hat{q} = \sqrt{\alpha}\hat{x}$$

and $\rho = \frac{1}{\hbar\sqrt{\alpha}}\hat{p} = -i\frac{d}{dq}$. This leaves the equation as

$$\left(-\frac{d^2}{dq^2} + q^2\right)\left|\psi\right\rangle = (\hat{\rho}^2 + \hat{q}^2)\left|\psi\right\rangle$$

One can find that the operators do not commute, with $[\hat{\rho}, \hat{q}] = -i$. This means that we cannot factor the sum of the squares like so:

$$\hat{\rho}^2 + \hat{q}^2 \neq (\hat{q} + i\hat{\rho})(\hat{q} - i\hat{\rho})$$

We can define two new operators:

$$\hat{a} = \frac{1}{\sqrt{2}}(\hat{q} + i\hat{\rho}) \quad \hat{a}^\dagger = \frac{1}{\sqrt{2}}(\hat{q} - i\hat{\rho})$$

And now we have that

$$\hat{\rho}^2 + \hat{q}^2 = \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}$$

Note that $[\hat{a}, \hat{a}^\dagger] = 1$. We can then rewrite the Schrodinger equation

$$(\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a})\,|\psi\rangle = \varepsilon\,|\psi\rangle$$

And can be rewritten in two more ways, using the commutator of the two operators:

$$\hat{a}\hat{a}^\dagger\,|\psi\rangle = \left(\frac{\varepsilon}{2} + \frac{1}{2}\right)|\psi\rangle$$

$$\hat{a}^\dagger\hat{a}\,|\psi\rangle = \left(\frac{\varepsilon}{2} - \frac{1}{2}\right)|\psi\rangle$$

If we then take the first of these, and then apply $\hat{a}^\dagger$ on both sides from the left, we can use the commutator:

$$\hat{a}^\dagger\hat{a}\hat{a}^\dagger\,|\psi\rangle = \left(\frac{\varepsilon}{2} + \frac{1}{2}\right)\hat{a}^\dagger\,|\psi\rangle$$

$$\hat{a}\hat{a}^\dagger(\hat{a}^\dagger\,|\psi\rangle) = \left(\frac{\varepsilon}{2} + \frac{3}{2}\right)(\hat{a}^\dagger\,|\psi\rangle)$$

We see that we increased the eigenvalue. This is why $\hat{a}^\dagger$ is known as the raising operator. $\hat{a}$ is known as the lowering operator, since it takes us down a single state.

If we apply the raising operator n times, we have the eigenvalue $\frac{\varepsilon}{2} + \frac{2n+1}{2}$ (for $\hat{a}\hat{a}^\dagger$), and eigenvalue $\frac{\varepsilon}{2} - \frac{2n-1}{2}$ (for $\hat{a}^\dagger\hat{a}$), and the eigenvalues for the Hamiltonian becomes $\varepsilon + 2n$. What is the ground state for the harmonic oscillator? We have that $\hat{a}\,|\psi_0\rangle = 0$:

$$\hat{a}^\dagger\hat{a}\,|\psi\rangle = 0 = \left(\frac{\varepsilon_0}{2} - \frac{1}{2}\right)|\psi\rangle$$

Which gets us that $\varepsilon_0 = 1 = \frac{2E_0}{\hbar\omega}$, which gets us that $E_0 = \frac{\hbar\omega}{2}$. We have the energy of the ground state, but what is the wavefunction for the ground state? We have that $\hat{a} = \frac{1}{\sqrt{2}}\left(q + \frac{d}{dq}\right)$, so we have that

$$\frac{d}{dq}\,|\psi_0\rangle + q\,|\psi_0\rangle = 0 \to \frac{d\psi_0}{dq} = -q$$

Integrating this gets us that $\ln|\psi_0\rangle = -\frac{q^2}{2}$, telling us that

$$\psi_0 = \frac{1}{\pi^{1/4}}e^{-q^2/2}$$

From this ground state, we can apply the raising operator and get all successive states and their wavefunctions and energies:

$$|\psi_n\rangle = \frac{c_n}{c_0}(\hat{a}^\dagger)^n\,|\psi_0\rangle = c_n(\hat{a}^\dagger)^n e^{-q^2/2} = \frac{c_n}{\sqrt{2^n}}\left(q - \frac{d}{dq}\right)^n e^{-q^2/2}$$

This is a Hermite polynomial generating function:

$$H_n(q) = e^{q^2/2}\left(q - \frac{d}{dq}\right)^n e^{-q^2/2}$$

After computing the normalization via $\langle\psi_n|\psi_n\rangle$, we have that the wavefunction is

$$\boxed{|\psi_n\rangle = \left(\frac{1}{2^n n!\sqrt{\pi}}\right)^{1/2} H_n(q)e^{-q^2/2}}$$

We can then get the energy of the nth state:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

And the raising and lowering operators work as follows:

$$\boxed{\hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle \qquad \hat{a}^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle}$$

What is the expectation value of x?

$$\langle\hat{x}\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\langle\psi_n|\hat{a}\psi_n\rangle + \langle\psi_n|\hat{a}^\dagger\psi_n\rangle\right) = \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n}\,\langle\psi_n|\psi_{n-1}\rangle + \sqrt{n+1}\,\langle\psi_n|\psi_{n+1}\rangle)$$

These are both 0, and thus $\langle\hat{x}\rangle = 0$. Note that we have used the fact that $\hat{x} \propto \hat{a} + \hat{a}^\dagger$. If we do the same thing for $\hat{p}$, we can use the fact that $\langle\hat{p}\rangle \propto \langle\hat{a} - \hat{a}^\dagger\rangle = 0$. What about the expectation value of $\hat{x}^2$ for the ground state ($|0\rangle$):

$$\langle 0|\hat{x}^2 0\rangle = \frac{\hbar}{2m\omega}(\hat{a} + \hat{a}^\dagger)^2$$

This is

$$= \frac{\hbar}{2m\omega}\,\langle 0|\hat{a}\hat{a} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}^\dagger|0\rangle = \frac{\hbar}{2m\omega}\,\langle 0|\hat{a}\hat{a}^\dagger|0\rangle = 1$$

Using the same logic, we can compute $\langle p^2\rangle$, and we will see that we get -1. If we then multiply the two expectation values, we see that we get $\frac{\hbar^2}{4}$, which is the state of minimum uncertainty.

Doing this for the excited states, we see that we get an extra term, because the lowering operator now drops us from $|n\rangle$ to $|n-1\rangle$ instead of doing nothing. We will see that $\langle x^2\rangle = 2n + 1$. When we compute the uncertainty product, we see that we get $\frac{\hbar}{2}(2n+1)$, indicating that we are no longer in a minimum uncertainty state.

3.26 Coherent States

We can see that the ground state is an eigenstate of the lowering operator:

$$\hat{a}\,|0\rangle = 0\,|0\rangle$$

Can we find another eigenstate?

$$\hat{a}\,|\alpha\rangle = \alpha\,|\alpha\rangle$$
$$\langle\alpha|\hat{a}^\dagger\hat{a}|\alpha\rangle = \alpha\,\langle\alpha|\hat{a}^\dagger\alpha\rangle$$
$$= \alpha\,\langle\hat{a}\alpha|\alpha\rangle$$
$$= \alpha\alpha^*\,\langle\alpha|\alpha\rangle = |\alpha|^2$$

Where we have assumed α is normalized. We can compute $\hat{x}$:

$$\hat{x} \to \langle\alpha|\hat{a} + \hat{a}^\dagger|\alpha\rangle = \alpha + \alpha^*$$

And we can also find that $\hat{p} = \alpha - \alpha^*$. If we want to compute the uncertainties, we want to compute $\langle \hat{x}^2 \rangle$ and $\langle \hat{p}^2 \rangle$:

$$\sigma_x^2 = \langle \hat{x}^2 \rangle + \langle \hat{x} \rangle^2 = \frac{\hbar}{2m\omega}$$

And we find that $\sigma_p^2 = \frac{\hbar m \omega}{2}$, and thus we have that

$$\sigma_x \sigma_p = \frac{\hbar}{2}$$

telling us that this state is a minimum uncertainty state. This is known as a coherent state. Let us now find this state:

$$|\alpha\rangle = \sum_n c_n |n\rangle$$

$$\hat{a} |\alpha\rangle = \alpha \sum_n c_n |n\rangle$$

$$\hat{a} \sum_n c_n |n\rangle = \alpha \sum_n c_n |n\rangle$$

$$\sum_n c_n \sqrt{n} |n-1\rangle = \alpha \sum_n c_n |n\rangle$$

Operating on both sides with $\langle m|$:

$$\sum_n c_n \sqrt{n} \langle m|n-1\rangle = \alpha \sum_n c_n \langle m|n\rangle$$

$$c_{m+1}\sqrt{m+1} = \alpha c_m$$

$$c_m = \frac{\alpha}{\sqrt{m}} c_{m-1}$$

This tells us a recurrence relation, which we can tie to the ground state:

$$c_n = \frac{\alpha^n}{\sqrt{n!}} c_0$$

And we can solve for the ground state coefficient:

$$\langle \alpha|\alpha\rangle = 1 = |c_0|^2 \sum_{m,n} \frac{\alpha^{m*}\alpha^n}{\sqrt{m!n!}} \langle m|n\rangle$$

$$= |c_0|^2 \sum \frac{\alpha^{2n}}{\sqrt{n!}} = |c_0| e^{|\alpha|^2}$$

Telling us that

$$c_0 = e^{-\frac{|\alpha|^2}{2}}$$

Putting this all together, we have that

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$

This is a coherent state.

Coherent states are interesting because they are not orthogonal. If we have two coherent states α_a and α_b:

$$\langle \alpha_a | \alpha_b \rangle = e^{-\frac{|\alpha_a|^2+|\alpha_b|^2}{2}} \sum_{n,m} \frac{\alpha_a^{*n}\alpha_b^n}{\sqrt{m!n!}} \langle m|n\rangle = e^{-|\alpha_a-\alpha_b|^2} \neq 0$$

If we look at the time dependence for a coherent state:

$$|\psi(x,0)\rangle = |\alpha_0\rangle$$

$$|\psi(x,t)\rangle = e^{-|\alpha|^2/2} \sum \frac{\alpha_0^n}{\sqrt{n!}} e^{-i\omega(n+1/2)t} |n\rangle = |\alpha_0 e^{-i\omega t}\rangle$$

Now that we have our raising and lowering operators, anytime we have a Hamiltonian of the form (provided that $\hat{P}$ and $\hat{Q}$ commute in the correct way)

$$\hat{H} = \hat{P}^2 + \hat{Q}^2$$

We can solve this using the harmonic oscillator solution. This works for photons, phonons, magnetic spin waves, etc.

3.27 Delta Function

Imagine we had a potential well that is not infinitely tall, rather it is only some V_0 deep. This system has bound states as well as free states, the states with energy inside the potential are bound, while states above the well are free.

Also note that if we placed a classical particle in a harmonic oscillator potential, there will be some turning point past which the particle will never go. However, if we look at the quantum result, the wavefunction has tails that go past the classical turning point now that the well is not infinite anymore.

Suppose we take this finite square well, and we make it deeper and shrink it such that the area covered by the well remains constant. Our potential becomes

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

We can solve this for the bound states, which will have energy below 0:

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

For $x < 0$, we essentially have the free particle:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}|\psi\rangle = \kappa^2|\psi\rangle$$

where $\kappa = \sqrt{\frac{-2mE}{\hbar^2}}$. This diffeq has the solution:

$$|\psi\rangle = Ae^{-\kappa x} + Be^{\kappa x}$$

For the $x < 0$ case, we have that $A = 0$:

$$|\psi(x<0)\rangle = Be^{\kappa x}$$

And if we do something for the positive x case:

$$|\psi(x>0)\rangle = Ce^{-\kappa x}$$

And by the total symmetry of this system, we must have that $B = C$. We can normalize this:

$$\langle\psi|\psi\rangle = 2B^2\int_0^\infty e^{-2\kappa x} \to B^2 = \kappa$$

This gets us that $|\psi(x)\rangle = \sqrt{\kappa}e^{-\kappa|x|}$.

We now need to find the energy. We integrate Schrodinger's equation along some small region around 0:

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

And then take the limit as the region goes to 0. We see via inspection that the first integral on the right will be 0, because ψ is continuous, and we can evaluate the rest of the integrals:

$$\left[\frac{d\psi}{dx}\right]_{-\epsilon}^{\epsilon} = \frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon}V(x)\psi(x)\,dx \to \left[\frac{d\psi_+}{dx} - \frac{d\psi_-}{dx}\right]_0 = -\frac{2m\alpha}{\hbar^2}\psi(0)$$

We can just plug in our wavefunction now:

$$\left[-\sqrt{\kappa}\kappa e^{-\kappa x} - \sqrt{\kappa}\kappa e^{\kappa x}\right]_0 = -\frac{2m\alpha}{\hbar^2}\sqrt{\kappa}$$

This gets us that

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

We see that there is no reliance on n, meaning that the delta function potential has only a single bound state, and we see that α is a "strength" of sorts for the delta function.

3.28 Finite Square Well

Suppose we have some finite potential well centered at $x = 0$, from $-\frac{a}{2}$ to $\frac{a}{2}$, and with some depth $-V_0$. We expect that for deep wells, we will see the same solution as the infinite square well. We have 3 regions, to the left of the well, the well, and the right of the well. We first define $L = \sqrt{-\frac{2mE}{\hbar^2}}$ (which is just from the free particle relation that $E = \frac{\hbar^2L^2}{2m}$).

In region 1, we expect the wave function to just be exponentials

$$|\psi(x<-\frac{a}{2})\rangle = Ae^{Lx} + Be^{-Lx}$$

We need the term that blows up to be 0, so $B = 0$, and we are left with

$$|\psi(x<-\frac{a}{2})\rangle = Ae^{Lx}$$

And for region 3, we have

$$|\psi(x>\frac{a}{2})\rangle = Fe^{-Lx}$$

For the middle region,

$$|\psi(-\frac{a}{2}<x<\frac{a}{2})\rangle = e^{ikx} + De^{-ikx}$$

Where $k = \sqrt{\frac{2m(V_0+E)}{\hbar^2}}$. We now need to find the constants to connect them together to get a single wavefunction. We can use symmetries, as we see that the solutions must have good parity, since we have a symmetric potential. From parity alone, we can say that $A = \pm F$, since the two sides be either the same or flipped. Similarly, in the middle we need $C = \pm D$, to either get a sine or a cosine.

We now look at the boundary continuity requirements for the wavefunction. Looking at the right edge of the well we need the two wavefunctions to be equal, and we also need their derivatives to be equal.

For even solutions, the well solution uses a $+$, giving a cosine:

$$2C\cos\left(\frac{ka}{2}\right) = Ae^{-L\frac{a}{2}}$$

And the derivatives

$$-2Ck\sin(\frac{ka}{2}) = -LAe^{-\frac{La}{2}}$$

And for the odd solutions we have that

$$2iC\sin\left(\frac{ka}{2}\right) = Ae^{-\frac{La}{2}}$$

$$2ikC\cos\left(\frac{ka}{2}\right) = -LAE^{-L\frac{a}{2}}$$

Now in both cases dividing one equation by the other, for the evens we have that

$$-k\tan\left(\frac{ka}{2}\right) = -L$$

and for the odds we have that

$$k\cot\frac{ka}{2} = -L$$

We know that

$$L^2 = -\frac{2mE}{\hbar^2}$$

and

$$k^2 = \frac{2mV_0}{\hbar^2} + \frac{2mE}{\hbar^2}$$

We can call the first term here k_0^2, and we have that

$$k_0^2 = k^2 + L^2$$

If we then rewrite this a bit to make a circle equation in k, L space:

$$\left(\frac{k_0a}{2}\right)^2 = \left(\frac{ka}{2}\right)^2 + \left(\frac{La}{2}\right)^2$$

If we then plot the equations for the even and odd relationships for k and L, and then add the equation of the circle in the space (with radius $\frac{k_0a}{2}$) we will see that we have 3 solutions, as we have 3 intersections with our even and odd functions. This determines the bound states, and we see that for this finite square well potential, the number of bound states depends on the radius, which is related to V_0.

If we take $V_0 \to \infty$, then $\frac{ka}{2} \to \frac{n\pi}{2}$. We then have that $k^2 = \frac{n^2\pi^2}{a^2}$, and we see that we have

$$V_0 + E = \frac{\hbar^2\pi^2}{2ma^2}n^2$$

Which is the infinite square well relationship. We see that as we take the limit, the tails of the well wavefunction disappear.

How can we count the number of bound states? As we increase the value of V_0, we have more and more bound states, and we want to maximize k, which is $k_{max} = \frac{k_0}{2}$, when the circle hits the x-axis. We can then count up the number of points we crossed a period of a tan or cotan, $n\pi$, which tells us that the number of bound states is

$$\frac{k_0}{a} = n_{max}\pi = \sqrt{\frac{2mV_0}{\hbar^2}}a$$

and we see that $n_{max}^2 = \frac{V_0}{E_0}$. For the infinite square well, we had that $E_n = n^2E_0$. And this approximates the number of bound states that we have.

3.29 Double Well

Suppose we have the molecule NH_3. This is an Ammonia molecule. We can imagine a potential landscape, which is a function of the position of the N atom. This is a double well potential, say with wells at $x = -b$ and $x = b$. For Ammonia, $b = 0.4$ Å, and the peak in between the two wells is .25 eV. We can approximate this as an infinite square well with a wall of height V_0 in the middle, of size $\Delta = 2b - a$, where b is the location of the center of the wells and a is the width of the sub-wells. We have 3 regions. In the right well, we have just the free particle

$$|\psi\rangle_{\text{right}} = A\sin(k(b + \frac{a}{2} - x))$$

Where $k = \sqrt{\frac{2mE}{\hbar^2}}$, and we have chosen the sine term so that the wavefunction goes to 0 when moving into the infinite potential. The wavefunction for the left well is similar:

$$|\psi\rangle_{\text{left}} = B\sin(k(b + \frac{a}{2} + x))$$

For the middle, we have

$$|\psi\rangle_{\text{middle}} = Ce^{Lx} + De^{-Lx}$$

Where $L = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$. Note that we have assumed that the energy is less than the wall potential, $E < V_0$.

By parity, we can write that $A = \pm B$, and $C = \pm D$. Also note that the lowest energy state will always be an even parity state.

Doing the even solution, at $x = b - \frac{a}{2} = \frac{\Delta}{2}$, by wavefunction continuity we have that

$$A\sin(ka) = C\left(e^{L\frac{\Delta}{2}} + e^{-L\frac{\Delta}{2}}\right) = 2C\cosh(k\Delta/2)$$

Doing the same for the derivative:

$$-kA\cos(ka) = -\frac{2k}{L}\sinh(L\Delta/2)$$

Dividing these two equations:

$$\tan(ka) = -\frac{k}{L}\coth\left(\frac{L\Delta}{2}\right)$$

We can make some approximations to gain some more insight. If we assume that $E \ll V_0$, and we assume that the barrier is wide, $L\Delta \gg 1$. Writing out the hyperbolic cotangent, and plugging in the approximations, we have that the relationship becomes:

$$\tan(ka) = -\frac{k}{L}(1 \pm 2e^{-L\Delta})$$

Where the $-$ comes from the odd solution (we do the same process and make the same approximations). If we then plot these and see where they intersect, we see that we get pairs of solutions, even and odd. We find that for the lowest energy state, the solutions are very close to $ka = \pi$. If we then use the fact that $La \gg ka$, we see that the slopes of the lines are very close to horizontal.

Looking back at our definitions, and recalling that $L \gg k$ because $L = \left[\frac{2mV_0}{\hbar^2}\right]^{1/2}$ and $k = \left[\frac{2mE}{\hbar^2}\right]^{1/2}$, and $E \ll V_0$. We can write down the even energies:

$$E_{\text{even}} = \frac{\hbar^2\pi^2}{2a^2m}\left(\frac{1}{1+\varepsilon_e}\right)^2$$

And for the odds:

$$E_{\text{odd}} = \frac{\hbar^2\pi^2}{2a^2m}\left(\frac{1}{1+\varepsilon_o}\right)^2$$

Where $\varepsilon_{\text{e,o}} = \frac{1}{ka}(1 \pm 2e^{-L\Delta})$.

If we add up the energies:

$$E_0' = \frac{1}{2}(E_{\text{e}} + E_{\text{o}}) = \frac{\hbar^2\pi^2}{2ma^2}\left(1 - \frac{2}{La}\right)$$

And if we take the differences:

$$\Delta E = \frac{\hbar^2\pi^2}{2ma^2}\frac{4}{La}e^{-L\Delta}$$

We see that in both terms we have the energy of the infinite square well.

We see that the ground state is in both wells at the same time, while the odd solutions are in just 1 of the wells. Also note that we have quantum tunneling, where the wavefunction is not 0 in the classically forbidden region, the wall between the two wells.

Suppose we are given some state

$$|\psi_L\rangle = \frac{1}{\sqrt{2}}(|\psi_e\rangle - |\psi_o\rangle)$$

And another state

$$|\psi_R\rangle = \frac{1}{\sqrt{2}}(|\psi_e\rangle + |\psi_0\rangle)$$

The first wavefunction should be mostly in the left well, and the second wavefunction should be mostly in the right well.

Let us now go to our time dependent solution. If we begin in $|\psi_R\rangle$:

$$|\psi(x,0)\rangle = |\psi_R(x)\rangle$$

We can add time dependence by adding in our phase factors:

$$|\psi(x,t)\rangle = \frac{1}{\sqrt{2}}\left(|\psi_e\rangle\, e^{-iE_e t/\hbar} + |\psi_o\rangle\, e^{-iE_o t/\hbar}\right)$$

If we use the fact that the two phase factors are off by just some phase:

$$= \frac{e^{-iE_e t/\hbar}}{\sqrt{2}}(|\psi_e\rangle + e^{-i\omega t}\,|\psi_o\rangle)$$

If we set $t = \frac{\pi}{\omega}$, we see that we are left with

$$|\psi(x, \frac{\pi}{\omega})\rangle = e^{i\phi}\,|\psi_L\rangle$$

Where ϕ is some phase we don't really care about. We see that after a certain amount of time has passed, we went from mostly in the right well to mostly in the left well. The wavefunction "tunnelled" through the wall and is now in the other well. For the Ammonia molecule, if we plug in the numers, we find that $\frac{\omega}{2\pi} = \nu = 24$ GHz. This means that the wavefunction oscillates at 24 GHz. This is the Ammonia maser frequency standard, and is how the first atomic clocks were made.

For a 3-well system, we would expect triplets of states, and for a 4-well system, we expect groups of 4 states. If we take the limit with a periodic potential, this models a solid state crystal, giving a continuum of states with gaps, which is known as band structure. This underlies all of the electronic properties of materials that we use.

3.30 Bound States

Suppose we have a double delta function potential well:

$$V = -\delta(x-a) - \delta(x+a)$$

We have two wells centered around 0, located at $x = -a$ and $x = a$. We can make our regions, and then use wavefunction continuity and derivative continuity:

$$\psi_{\text{left}} = Ae^{\kappa x}$$

$$\psi_{\text{right}} = De^{-\kappa x}$$

$$\psi_{\text{middle}} = Be^{\kappa x} + Ce^{-\kappa x}$$

Now using parity we know that $A = \pm D$ and $B = \pm C$. Using continuity and derivative continuity, we are left with

$$\frac{\hbar^2\kappa}{m\alpha} = 1 + e^{-2\kappa a}$$

for the even parity states. If we let $z = 2\kappa a$, and we plot the function that we have ($e^{-z} = cz - 1$) where we have collapsed constants into c, we see that we are guaranteed a collision between our functions, guaranteeing an even parity bound state. If we plot this in limiting behavior, we see that when the two wells are far apart, we just have two delta function solutions, and as they get closer, they merge with each other.

3.31 Scattering

Suppose we have our delta function potential $V = -\alpha\delta(x)$. What if instead of having $E < 0$, we have $E > 0$? We no longer have a bound state solution. We have a plane wave solution:

$$\psi(x < 0) = Ae^{ikx} + Be^{-ikx}$$

$$\psi(x > 0) = Fe^{ikx} + Ge^{-ikx}$$

From wavefunction continuity, we have that

$$A + B = F + G$$

For the derivatives, we have to be careful of the discontinuity, so we look at the derivatives approaching from both sides:

$$\frac{\partial\psi_-}{\partial x} = ik(A - B)$$

$$\frac{\partial\psi_+}{\partial x} = ik(F - G)$$

We then have that the difference between the two derivatives is equal to the delta function applied to ψ:

$$\frac{\partial\psi_-}{\partial x} - \frac{\partial\psi_+}{\partial x} = ik(F - G) - ik(A - B) = \delta(x)\psi(x) = \frac{2m\alpha}{\hbar}$$

We can define the transmission, which is $T = \frac{|F|^2}{|A|^2}$ (amount that moves past the barrier over the amount that came in) and the reflection $R = \frac{|B|^2}{|A|^2}$ (amount that bounces back over the amount that came in). We also know that $G = 0$, because we can't have anything bouncing back from behind the barrier, that just doesn't make sense. After solving, we find that $T = 1 - R = \frac{1}{\beta^2}$ where $\beta = \frac{m\alpha}{\hbar^2 k}$:

$$T = \frac{1}{1 + \frac{m\alpha^2}{2\hbar^2 E}} \qquad R = \frac{1}{1 + \frac{2\hbar^2 E}{m\alpha^2}}$$

Let's look at another potential. Suppose we have a step potential, which is V_0 for all x before $x = 0$, and is 0 afterwards.

In the left region, we have

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad k = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

And in the right region we have

$$\psi = Fe^{ik'x} \qquad k' = \sqrt{\frac{2mE}{\hbar^2}}$$

By wavefunction continuity we have that

$$A + B = F$$

And by the derivative continuity we have

$$ik(A - B) = ik'F$$

Adding these two equations gets us that

$$2A = F(1 + \frac{k'}{k})$$

and subtracting gets us that

$$2B = (1 - \frac{k'}{k})F$$

Now taking the ratio between the coefficients:

$$R = \frac{|B|^2}{|A|^2} = \frac{\left(1 - \frac{k'}{k}\right)^2}{\left(1 + \frac{k'}{k}\right)^2} = \left(\frac{\sqrt{E - V_0} - \sqrt{E}}{\sqrt{E - V_0} + \sqrt{E}}\right)^2$$

Classically we would expect the particle to just continue off the edge of the potential, but in the quantum case we see that we have a reflection. Also note that we can completely reflect if we have E closer and closer to V_0.

Let's do a barrier potential. We have a barrier of height V_0, and a particle coming in with energy $E < V_0$. We have the barrier centered at 0, going from $-a$ to a.

We have 3 regions, and on the left we have plane waves:

$$\psi_{\text{left}} = Ae^{ikx} + Be^{-ikx}$$

For the barrier:

$$\psi_{\text{barrier}} = Ce^{\kappa x} + De^{-\kappa x}$$

And for region past the barrier:

$$\psi_{\text{right}} = Fe^{ikx}$$

By wavefunction continuity and derivative continuity, we generate 4 equations:

$$Ae^{-ika} + Be^{ika} = Ce^{-\kappa a} + De^{\kappa a}$$
$$ik(Ae^{-ika} - Be^{ika}) = \kappa(Ce^{-\kappa a} - De^{\kappa a})$$
$$Ce^{\kappa a} + De^{-\kappa a} = Fe^{ika}$$
$$\kappa(Ce^{\kappa a} - De^{-\kappa a}) = ikFe^{ika}$$

Doing a bunch of algebra, dividing the equations with each other, and also assuming that $A = 1$ (since we only care about ratios), we find that

$$T = \frac{2k\kappa}{(k^2 + \kappa^2)\sinh^2(2\kappa a) + (2k\kappa)^2} = \frac{4\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)}{\sinh^2(2\kappa a) + \frac{4E}{V_0}\left(1 - \frac{E}{V_0}\right)}$$

If we now assume that $\kappa a \gg 1$ (which means we have either a tall or wide barrier), we see that the transmission is given by

$$T \approx 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)e^{-4\kappa a}$$

Let's take the other case, where $E > V_0$. We get similar expressions, but the sinh functions turn into sin functions, and we find that

$$T = \frac{\frac{4E}{V_0}\left(1 - \frac{V_0}{E}\right)}{\sin^2(2k'a) + \frac{4E}{V_0}\left(1 - \frac{V_0}{E}\right)}$$

If we plot this, we see that we have interference effects, with some points where we have perfect transmission, $T = 1$. This is known as the Ramsauer-Townsend Effect.

3.32 3D Free Particle

We now move away from 1 dimensional problems, and towards higher dimensions. For a free particle in 3D, we can write down Schrodinger's equation:

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

We can write a solution for this, its just a 3D plane wave:

$$\Psi(x,y,z)=Ne^{i\mathbf{k}\cdot\mathbf{r}}=Ne^{ik_xx}e^{ik_yy}e^{ik_zz}=\varphi_x(x)\varphi_y(y)\varphi_z(z)$$

Where $\mathbf{k}=(k_x,k_y,k_z)$. Also note that $E=E_x+E_y+E_z$.

If we add some potential $V(x,y,z)$, and assume that $V(x,y,z)=V_1(x)+V_2(y)+V_3(z)$ (i.e. the potential function is separable), we can write out Schrodinger's equation:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+V_1(x)\right)-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial y^2}+V_2(y)\right)-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial z^2}+V_3(z)\right)\right]\psi=E\psi$$

If we look at this, we see that this separates into 3 different equations, one for equation direction.

3.33 3D Harmonic Oscillator

We have a potential given by

$$V=\frac{1}{2}m\omega_x^2x^2+\frac{1}{2}m\omega_y^2y^2+\frac{1}{2}m\omega_zz^2$$

We will have that

$$\psi=\phi_{n_x}(x)\phi_{n_y}(y)\phi_{n_z}(z)$$

where ϕ is a 1D harmonic oscillator solution. If we now stipulate that the system is isotropic, $\omega_x=\omega_y=\omega_z$, we find that

$$E=E_x+E_y+E_z=(n_x+n_y+n_z)\hbar\omega+\frac{3}{2}\hbar\omega$$

We can see that the ground state has energy $\frac{3}{2}\hbar\omega$, 3 times what the 1D ground state is. We see that states can be specified by the 3 quantum numbers, and we have degenerate states, states with the same overall quantum number:

$$E_{100}=E_{010}=E_{001}$$

3.34 Particle in a Box (3D Infinite square well)

The 3D version of the infinite square well is given by a potential that is 0 inside a cube of space, and infinity elsewhere:

$$V=\begin{cases}0 & 0<x<L\,0<y<L\,0<z<L\\ \infty\end{cases}$$

The solutions to this have energies that are given by

$$E_{n_x,n_y,n_z}=\frac{\pi^2\hbar^2}{2mL^2}(n_x^2+n_y^2+n_z^2)$$

3.35 Finite Square Well

For the 2D finite square well, we need the potential to be some $-V_0$ inside, and 0 outside. We can attempt to construct this with

$$\begin{cases} V_x(x) = -\frac{V_0}{2} & 0 < x < L \\ V_y(y) = -\frac{V_0}{2} & 0 < y < L \end{cases}$$

However we see that when we sum these, we have regions outside the well in which we have nonzero potentials. It turns out that there is no way to write a potential such that $V = V_x + V_y$ for a 2D finite square well. This means that the only way to solve this would be to use a nonseparable potential and do it all in one go. This is not doable analytically.

3.36 Relative Motion

Before we get to the Hydrogen atom, we have to talk about relative motion. For a two body system in 3D, we have

$$\left[-\left(\frac{\hbar^2}{2m_1}\nabla_1^2 + \frac{\hbar^2}{2m_2}\nabla_2^2\right) + V(\mathbf{r})\right]\psi = E\psi$$

where $\mathbf{r}$ is a relative coordinate, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$.

We can write down the total kinetic energy:

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = KE$$

We can write down center of mass coordinates:

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$$

$$P = p_1 + p_2$$

and relative coordinates:

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

$$\mathbf{p} = \frac{m_1\mathbf{p_1} - m_2\mathbf{p}_2}{m_1 + m_2}$$

Now rewriting the kinetic energy, using the reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$:

$$KE = \frac{P^2}{2(m_1 + m_2)} + \frac{p^2}{2\mu}$$

We can now look at the commutation relationships between these operators:

$$[\hat{X}_i, \hat{P}_j] = i\hbar\delta_{ij} \qquad [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{i,j}$$

And we see that

$$[\hat{X}_i, \hat{p}_j] = 0 \qquad [\hat{x}_1, \hat{P}_j] = 0$$

where the relative and center of mass operators commute, we can separate out the motion of the center of mass from relative motion.

The Hamiltonian for the center of mass motion is just

$$\hat{H} = \frac{\hat{P}^2}{2(m_1 + m_2)}$$

which has solution

$$\Psi(\mathbf{R},\mathbf{r}) = e^{i\mathbf{K}\cdot\mathbf{R}}\psi(\mathbf{r})$$

We see that the center of mass motion just tacks on an exponential to the relative solution, so from now on we will just work in the relative coordinates.

$$E = \frac{\hbar^2 K^2}{2(m_1+m_2)} + E_{rel}$$

Now looking at the potential, in classical mechanics we have that

$$\mathbf{F} = -\nabla V = \frac{\partial V}{\partial r}\mathbf{e}_r$$

where $\mathbf{e}_r$ is the radial unit vector. We also have the angular momentum:

$$\mathbf{L} = \mathbf{r}\times\mathbf{p} \to \frac{d\mathbf{L}}{dt} = \mathbf{r}\times\frac{d\mathbf{p}}{dt} = \mathbf{r}\times\mathbf{F} = 0$$

We can split the momentum into two directions, the transverse and the radial:

$$\mathbf{p}_r = \mathbf{e}_r\mathbf{p}\mathbf{e}_r \quad \mathbf{p}_\perp = \mathbf{p} - \mathbf{p}_r$$

We have that

$$|\mathbf{L}| = r\mathbf{p}_\perp \to \mathbf{p}_\perp = \frac{\mathbf{L}}{\mathbf{r}}$$

We then have

$$\frac{|\mathbf{p}|^2}{2\mu} = \frac{p_r^2}{2\mu} + \frac{p_\perp^2}{2\mu} = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r^2}$$

Now swapping to spherical, we have that

$$x = r\sin\theta\cos\varphi$$

$$y = r\sin\theta\sin\varphi$$

$$z = r\cos\theta$$

We can write out our radial unit vector:

$$\mathbf{e}_r = \frac{\mathbf{r}}{|\mathbf{r}|} = \sin\theta\cos\varphi\mathbf{e}_x + \sin\theta\sin\varphi\mathbf{e}_y + \cos\theta\mathbf{e}_z$$

We can then write out the Laplacian in spherical coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial}{\partial\varphi}\right]$$

We can rewrite this as

$$\nabla^2 = \mathscr{R} + \frac{\mathscr{L}^2}{r^2}$$

where

$$\mathscr{R} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$$

and

$$\mathscr{L} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial}{\partial\varphi}$$

Let us assume that the total wavefunction will be written with a radial component and an angular piece:

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$$

Plugging this back into the Hamiltonian, we are left with

$$\left[-\frac{\hbar^2}{2\mu}\mathscr{R}R(r)\right]Y(\theta,\varphi) - \frac{\hbar^2}{2\mu}\left[\mathscr{L}^2Y(\theta,\varphi)\right]R(r) + V(r)R(r)Y(\theta,\varphi) = ER(r)Y(\theta,\varphi)$$

We then multiply both sides by $\frac{2\mu r^2}{\hbar^2}\frac{1}{R(r)Y(\theta,\varphi)}$:

$$\frac{r^2\mathscr{R}R(r)}{R(r)} + \frac{2\mu r^2}{\hbar^2}(E - V(r)) = -\frac{\mathscr{L}^2Y(\theta,\varphi)}{Y(\theta,\varphi)}$$

This left side depends only on r, and the right side only depends on θ and φ. The only way for this to be true is if they are both equal to a constant, Λ, known as the separation constant. This gives us two equations, a radial diffeq and an angular diffeq.

Note that we don't have to worry about the factor of r^2 under the $\mathscr{L}^2$, because $[\hat{p}^2, \hat{L}] = 0$, thus $[\hat{H}, \hat{L}^2] = 0$.

Also note that the angular portion will be the same for any spherically symmetric potential, since we have no dependence on V.

We begin by solving the angular equation. We start by multiplying by $\sin^2$:

$$\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}Y(\theta,\varphi) + \frac{\partial^2}{\partial\varphi^2}Y(\theta,\varphi) = -\Lambda\sin^2\theta Y(\theta,\varphi)$$

Now once again using separation of variables and assuming that $Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$:

$$\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta(\theta) + \Lambda\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2}$$

We say that each of these is equal to a new separation constant m^2:

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = m^2$$

$$\Phi = e^{im\varphi}$$

Note that this is why we chose m^2 and not m, we would have had a $\sqrt{m}$ in the exponential. We know that the angles are periodic variables, so

$$\Phi(\varphi + 2\pi) = \Psi(\varphi) \to e^{im(\varphi+2\pi)} = e^{im\varphi} \to e^{2i\pi m} = 1 \to m \in \mathbb{Z}$$

Thus we have a quantum number m.

From the cross product definition of the angular momentum and the momentum:

$$\hat{L} = \mathbf{r}\times\mathbf{p} \qquad \hat{p}_j = -i\hbar\frac{\partial}{\partial j}$$

We will find that the commutators of the angular momenta in every direction can be given by

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_z$$

and similarly for $\hat{L}_z$ and $\hat{L}_x$.

We know that $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$, and we can use the fact that

$$\hat{L} = -i\hbar(\mathbf{r} \times \nabla)$$

and now using the definition of ∇ in spherical, we find that

$$\hat{L} = \frac{\hbar}{i}\left(\hat{\varphi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

where $\hat{\theta} = \cos\theta\cos\varphi\hat{x} + \cos\theta\sin\varphi\hat{y} - \sin\theta\hat{z}$, and $\varphi = -\sin\varphi\hat{x} + \cos\varphi\hat{y}$. We will find that if we define the operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \qquad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

and we write use what we have just found to write out $\hat{L}_x$ and $\hat{L}_y$:

$$\hat{L}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_y = -i\hbar\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

Now writing out our newly defined operators:

$$\hat{L}_+\hat{L}_- = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right)$$

From this, we find that L^2 is actually just the angular equation times a constant:

$$\hat{L}^2 = -\hbar^2\mathscr{L}^2$$

And from this we find that

$$\hat{L}^2Y(\theta,\varphi) = \Lambda\hbar Y(\theta,\varphi)$$

And now moving back to the raising and lowering operators:

$$\hat{L}_z(\hat{L}_+Y^{(m)}) = (m+1)\hbar(\hat{L}_+Y^{(m)})$$

$$\hat{L}_z(\hat{L}_-Y^{(m)}) = (m-1)\hbar(\hat{L}_-Y^{(m)})$$

We can also find the value for Λ, using the fact that $\hat{L}_x^2$ and $\hat{L}_y^2$ must have positive eigenvalues:

$$(\hat{L}_x^2 + \hat{L}_y^2)Y^{(m)} = (\Lambda - m^2)\hbar^2Y^{(m)}$$

We see that $\Lambda \geq m^2$.

We have some maximum angular momentum and some minimum, l_{max} and l_{min}, which we can find by using the raising and lowering operators until we cannot anymore:

$$\hat{L}_+Y^{(l_{max})} = 0 \qquad \hat{L}_-Y^{(l_{min})} = 0$$

Now using the definitions we've found before:

$$\hat{L}^2 = \hat{L}_-\hat{L}_+ + \hbar\hat{L}_z + \hat{L}_z^2 \to \hat{L}^2 Y^{(l_{max})} = \Lambda\hbar^2 Y^{(l_{max})}$$

and similarly for l_{min}, and we find that $\Lambda = l(l+1)$.

We see that angular momentum is quantized, with a value of l, and the projection of angular momentum is also quantized, with a value of m, which can range over all integers between $-l$ and l. We now have a value for Λ, and so we can solve the angular equation for $\Theta(\theta)$, and we find that solution is

$$\Theta(\theta) = AP_l^m(\cos\theta)$$

where P_l^m are the associated Legendre polynomials:

$$P_l^m(x) = (1-x^2)^{|m|/2}\frac{d|m|}{dx}P_l(x)$$

where $P_l(x)$ are the Legendre polynomials.

Now putting together all of the angular solution:

$$\boxed{Y_l^m(\theta,\varphi) = \varepsilon\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2} e^{im\varphi}P_l^m(\cos\theta)}$$

where $\varepsilon = (-1)^m$ for $m \geq 0$, and 1 for $m \leq 0$. This is what is known as spherical harmonics, which can be thought of as the 3-D version of Fourier series.

Now we have to solve the radial equation. We can do this by inserting $u_l = rR_l(r)$, and inserting this into the radial equation:

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right]u_l = Eu_l$$

We can see we have a effective potential, which has this added term which is known as the centrifugal barrier. This prevents the particle from reaching $r = 0$, because the higher the angular momentum the higher the barrier. If we set the radial potential to 0, $V(r) = 0$, we have that

$$\frac{d^2u}{dr^2} = \left(\frac{l(l+1)}{r^2} - k^2\right)u$$

where $k^2 = \frac{2\mu E}{\hbar^2}$. For the $l = 0$ case, we have the solution $u = A\sin kr + B\cos kr$. Remembering that $R = \frac{u}{r}$, and we don't want the solution to diverge at $r = 0$, we must have that $B = 0$. Thus we have that

$$R = \frac{A\sin kr}{r} = 2iA\left(\frac{e^{ikr}}{r} - \frac{e^{-ikr}}{r}\right)$$

We see that we have two spherical waves, one going out and one going in, respectively.

For $l > 0$, we have special functions, j_l, which are the spherical Bessel functions and n_l, which are the spherical Neumann functions:

$$u = A_l j_l(kr) + B_l n_l(kr)$$

where

$$n_l = -(-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos x}{x}$$

$$j_l = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x}$$

Note that $n_l(x)$ diverges as $x \to 0$, so we have that $B_l = 0$ for the free particle.

In the end, for the free particle case:

$$\Psi_{klm} = |klm\rangle = A_l j_l(kr) Y_l^m(\theta, \varphi)$$

$$\hat{H}\,|klm\rangle = \frac{\hbar^2 k^2}{2\mu}\,|klm\rangle$$

$$\hat{L}^2\,|klm\rangle = \hbar^2 l(l+1)\,|klm\rangle$$

$$\hat{L}_z\,|klm\rangle = \hbar m\,|klm\rangle$$

Note that we have 3 quantum numbers, and k is continuous while l and m are discretized.

3.37 Infinite Spherical Well

We can think of trapping a particle in a sphere:

$$\begin{cases} V(r) = 0 & r < a \\ V(r) = \infty & r > a \end{cases}$$

Thus we need the radial component to be 0:

$$R_l(a) = 0 \to j_l(ka) = 0$$

This tells us that k is quantized:

$$k_{nl} = \frac{1}{a}\beta_{nl}$$

where β gives the zeros of j_l. From this we have that

$$|nlm\rangle = A_{nl} j_{nl}\left(\frac{\beta_{nl} r}{a}\right) Y_l^m$$

with energies

$$E = \frac{\hbar \beta_{nl}^2}{2\mu a^2}$$

3.38 Finite Spherical Well

We need a decaying solution outside the sphere, so we have that $B = iA$. This adds a new special function to our solution:

$$h_l^{(1)} = j_l + i n_l$$

Which is known as the spherical Hankel function of the first kind. We can write out our solution:

$$R_l = A h_l^{(1)}(\kappa r) \qquad \kappa = \frac{-2\mu E}{\hbar^2}$$

We can set conditions on k and κ by matching the inner solutions to the outer solutions.

3.39 Deuteron

We can crudely model the deuteron using the finite spherical potential well. The deuteron is a bound proton and neutron, with binding energy $E_{\text{bind}} = -2.26$ MeV. We assume that it is a $l = 0$ case. We will then find that

$$u = A \sin kr \quad (r < a) \qquad = Be^{-\kappa r} \quad (r > A)$$

Which leads to the relationship

$$k \cot ka = -\kappa a$$

If we plug in the numbers, we find that $a \approx 10^{-15}m$, and $V_0 \approx -100MeV$.

3.40 The Hydrogen Atom

We have that

$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

And looking at the mass:

$$\mu = \frac{m_p m_e}{m_p + m_e} \approx m_e$$

We define $\kappa = \frac{-2\mu E}{\hbar^2}$, and then removing constants by making a variable:

$$\rho = \kappa r \quad \rho_0 = \frac{\mu e^2}{2\pi\varepsilon_0 \hbar^2 \kappa}$$

This gets the equation

$$\frac{d^2u}{d\rho^2} - \left[\frac{l(l+1)}{\rho^2} - \frac{\rho_0}{\rho} + 1\right] u = 0$$

For large ρ, we have that $u \approx e^{-\rho}$. For small ρ, we have that $u \approx \rho^{l+1}$.

We assume that $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$, where we expand this term $v(\rho)$ as $\sum_j c_j \rho^j$. We can get a recursive relation for the coefficients of the expansion:

$$\frac{c_{j+1}}{c_j} = \frac{2(j + l + 1) - \rho_0}{(j+1)(j+2l+2)}$$

We need this expansion to stop at some point, which gives us

$$2(j_{max} + l + 1) = \rho_0 = 2n$$

Where we have let $j_{max} + l + 1 = n$.

We can compute the energies:

$$E = -\frac{\hbar^2\kappa^2}{2\mu} = -\left(\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\right)\frac{1}{n^2}$$

This tells us that $E_1 = 13.6$ eV. This is a pretty accurate approximation, and the reason it is off is because we neglected relativity.

From the relation from the coefficients of the expansion, we also have that $l \leq n - 1$. This tells us that for the hydrogen atom, we have some maximum angular momentum.

What were the polynomials in the expansion? They were the associated Laguerre polynomials

$$L_n^{2l+1} = \left(\frac{d}{dx}\right)^{2l+1} \left[e^x \left(\frac{d}{dx}\right)^{n+l} \left(x^{n+l} e^{-x}\right)\right]$$

Putting it all together, we have that a solution to the hydrogen atom system takes the form

$$|nlm\rangle = \left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta,\varphi)\right]$$

Where a_0 is the Bohr radius.

If we compute the probability with respect to the radius, we have that

$$P(r) = r^2 \left|R_{nl}\right|^2$$

Where R_{nl} is the radial wavefunction. This is because the integral of the spherical harmonics portion is 1 since they are normalized.

We also find that

$$\langle r\rangle = \frac{a_0}{2}\left[3n^2 - l(l+1)\right]$$

$$\langle r^2\rangle = \frac{a_0^2 n^2}{2}[5n^2 + 1 - 3l(l+1)]$$

3.41 Band Structure

Suppose we have some periodic potential given by a series of positive ions aligned in a series. This is essentially the Ammonia molecule with more than 2 wells. For 4 wells we have a ground state of 4 wavefunctions, one in each well. The first excited state will be odd, and we see that we can have 4 states. If we plot the energy levels, we have 4 closely spaced energy levels with a gap given by the individual well energy, and then another 4 energy levels. This is known as a band. This also generalizes to more wells.

We can look at the Schrodinger equation for this situation:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x)$$

By periodicity of the potential, we have that $V(x+a) = V(a)$, where a is the lattice spacing. We then define a translation operator:

$$\hat{T}_a\left|\psi\right\rangle = \left|\psi(x+a)\right\rangle$$

By the periodicity, we have that $[\hat{H}, \hat{T}_a] = 0$. Thus the translation operator should have an eigenstate:

$$\hat{T}_a\psi(x) = \lambda\psi(x)$$

From this, if we apply the operator n times:

$$\psi(x+na) = \lambda^n\psi(x)$$

This tells us that $|\lambda| = 1$, and $\lambda = e^{iqa}$. We see that since the translation operator is not Hermitian, the eigenvalue can be complex, and we see that the translation just picks up an overall phase term.

From this we have that

$$\psi(x) = e^{iqx}U(x)$$

where $U(x+a) = U(x)$. This is known as Bloch's theorem.

If we take Bloch's theorem and insert it into Schrodinger's equation, we have a diffeq in terms of $U(x)$, with a new term that seems to take the place of momentum, known as the crystal momentum or quasi-momentum. When doing this out, we are left with a set of coupled linear equations. This eventually gets a solution with energies in terms of the quasi-momentum governed by a discrete band index.

3.42 Schrodinger's Cat

We have a cat in a sealed steel box. There is a mechanism to observe an isotope that is decaying, and if it has decayed, the mechanism swings a hammer and breaks a glass of hydrogen cyanide, killing the cat. Our wavefunction is given as

$$|\psi\rangle = |1\rangle\,|\text{alive}\rangle + |0\rangle\,|\text{dead}\rangle$$

We have an entangling of a nuclear isotope and the cat (where $|0\rangle$ means that the isotope has decayed and $|1\rangle$ means that it is still there).

We have something known as the density matrix or density operator, which is defined as

$$\hat{\rho} = \sum_i P_i\,|\psi_i\rangle\,\langle\psi_i|$$

Where P_i is the probability of being in state i. From this we can write out the expectation value of an operator:

$$\langle\hat{A}\rangle = \text{Tr}(\hat{A}\hat{\rho})$$

and we can write out Schrodinger's equation

$$i\hbar\frac{\partial}{\partial t} = [\hat{H}, \hat{\rho}]$$

Density matrices are useful when talking about subsystems, where we can define a reduced density matrix. Suppose we have two systems, A and B. We have that

$$\hat{\rho}_A = \text{Tr}_B(\hat{\rho}) \quad \hat{\rho}_B = \text{Tr}_A(\hat{\rho})$$