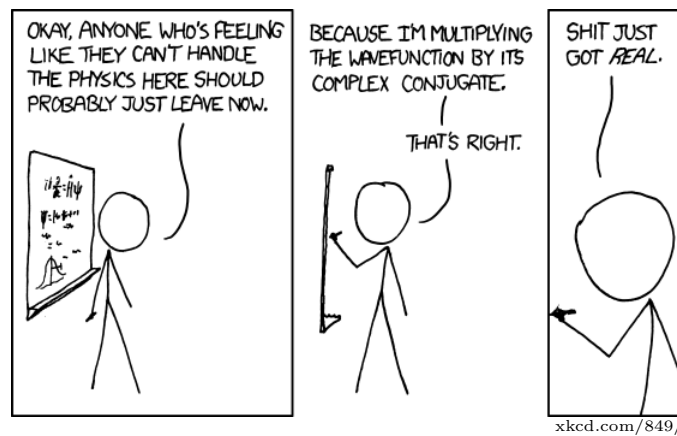# Physics GRE:

Quantum Mechanics

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xkcd.com/849/

Contents

1 Introduction

1.1 History Up through the early twentieth century there were several phenomena which could not be explained by classical mechanics: The photoelectric effect proved impossible for classical wave theory, descriptions of blackbodies were riddled with divergences, and orbiting electrons should spiral into the atomic nucleus.

There were several important milestones in the development of quantum mechanics:

~1805: Young's double-slit experiment. Showed wave nature of light.

1905: Photoelectric effect explained by Einstein, relying on quanta of light.

1911: Gold foil experiment by Rutherford, showing existence of nucleus.

1920: Stern-Gerlach experiment, showing quantization of spin.

In 1923 de Broglie introduced the idea of matter waves, proposing that not only photons but all types of matter have both a particle and a wave character. The wavelength and momentum of a particle are related by

$$p = \frac{h}{\lambda} \tag{1}$$

1.2 Photoelectric Effect The photoelectric effect posed a problem before the introduction of quantum mechanics. When light was shone on a metal it was observed that electrons were ejected only above a specific frequency of light, and that their maximum kinetic energy was independent of the intensity of the incident beam. In addition, there seemed no indication of a delay in ejection, as predicted by the well-accepted wave-model of light. The maximum kinetic energy of ejected electrons is given by

$$K_{\text{max}} = h\nu - W \tag{2}$$

where W is the work function, a property of the metal. One may observe this effect by shining light on one of two parallel plates and either measuring the current as electrons jump from on to the other, or increase the potential between the plates until no current flows. The point at which the current stops is known as the stopping potential, and is related to the maximum kinetic energy of the electrons by

$$K_{\text{max}} = eV_{\text{stop}} \tag{3}$$

1.3 Operators In a few words, operators are objects which act on functions and spit out functions. A common example is the derivative operator, D, defined by $D \cdot f(x) = f'(x)$. Another simple example is the identity operator, I, which acts as $I \cdot f(x) = f(x)$.

A Hilbert space H has an inner product, denoted $\langle \cdot, \cdot \rangle$. To each operator A we may associate another operator $A^\dagger$, known as its adjoint, defined to satisfy

$$\langle Au, v \rangle = \langle u, A^\dagger v \rangle \qquad \forall u, v \in H \tag{4}$$

An operator is called Hermitian if $A^\dagger = A$.

The commutator is defined as $[A, B] = AB - BA$. Some commutator identities are

$$[AB, C] = [A, C]B + A[B, C] \qquad [A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0 \tag{5}$$

Observable	Operator
x_i	x_i
p_i	$-i\hbar\frac{\partial}{\partial x^i}$
T	$\frac{p^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$
L_i	$(\boldsymbol{r} \times \boldsymbol{p})_i = \epsilon_{ijk}r^j p^k = \epsilon_{ijk}r^j\frac{\partial}{\partial x_k}$

Table 1: Common operators in the position basis.

The Heisenberg uncertainty principle is a general feature of wave-phenomena:

$$\Delta A \Delta B \geq \frac{1}{2}\left|\langle [A,B]\rangle\right| \tag{6}$$

The ability to measure two observables simultaneously is limited by the expectation value of their commutator! The commonly quoted version of this is

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \tag{7}$$

indicating that a state of both definite position and definite momentum is impossible.

For an operator Q we have that its expected value is

$$\langle Q\rangle = \langle\psi|Q|\psi\rangle = \int \psi^*(\boldsymbol{x})\hat{Q}\psi(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x} \tag{8}$$

This is different than the most probable, which would be the peak in the probability distribution for the values of measuring Q.

For example, if $|n\rangle$ are a set of orthonormal eigenfunctions of N with eigenvalues n, then the expectation value of N for the state $|\psi\rangle = \frac{1}{\sqrt{50}}\left(7\,|3\rangle - |4\rangle\right)$ is

$$\langle N\rangle = \langle\psi|N|\psi\rangle = \frac{1}{50}\left(7\,\langle 3| - \langle 4|\,\right)N\left(7\,|3\rangle - |4\rangle\right) \tag{9}$$

$$= \frac{1}{50}\left(49\,\langle 3|N|3\rangle - 7\,\langle 3|N|4\rangle - 7\,\langle 4|N|3\rangle + \langle 4|N|4\rangle\,\right) \tag{10}$$

$$= \frac{1}{50}\left(147\,\langle 3|3\rangle - 28\,\langle 3|4\rangle - 21\,\langle 4|3\rangle + 4\,\langle 4|4\rangle\,\right) \tag{11}$$

$$= \frac{1}{50}\left(147 + 4\right) \tag{12}$$

$$= 3.02 \tag{13}$$

Of course this is long-winded, and there is a short-cut when the basis is orthonormal: the square of a coefficient is the probability of measuring the corresponding eigenvalue. Here the probability of measuring 3 is $\frac{49}{50}$ and the probability of measuring 4 is $\frac{1}{50}$. Thus the expected value is

$$\langle N\rangle = 3 \cdot \frac{49}{50} + 4 \cdot \frac{1}{50} = \frac{151}{50} = 3.02 \tag{14}$$

Again, this trick only works when the basis set consists of orthonormal eigenvectors of the operator.

Recalling the classical mechanics result concerning time-evolution of functions:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \{f, H\} + \frac{\partial f}{\partial t} \tag{15}$$

The quantum mechanical analogue of this concerns the expected value of an operator:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = \frac{1}{i\hbar}\langle[A,H]\rangle + \left\langle\frac{\partial A}{\partial t}\right\rangle \tag{16}$$

This is the Ehrenfest theorem. A special case of this relates position and momentum in a familiar way for a particle moving in a time-independent potential V:

$$m\frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{x}\rangle = \langle\boldsymbol{p}\rangle \qquad \frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{p}\rangle = -\left\langle\frac{\partial V(\boldsymbol{x})}{\partial\boldsymbol{x}}\right\rangle \tag{17}$$

Namely, the expected values follow the classical equations of motion.

1.4   Postulates of Quantum Mechanics

- The state of a system is completely specified by a *wave/state-function*, $\Psi(\boldsymbol{r};t)$, that depends on the coordinates and on time. It is such that $\Psi^*\Psi\,\mathrm{d}\boldsymbol{r}$ represents the probability that the particles lies in the volume element $\mathrm{d}\boldsymbol{r}$ at the given time.

- Every observable quantity in classical mechanics corresponds to a linear, Hermitian operator in quantum mechanics (recall that Hermitian operators only have real-valued eigenvalues).

- A measurement of an observable with operator A will only ever result in one of its eigenvalues, a, satisfying $A\,|\Psi\rangle = a\,|\Psi\rangle$.

- The expected value of the observable corresponding to $\hat{A}$ is given by

$$\langle A\rangle = \langle\Psi|\hat{A}|\Psi\rangle = \int\Psi^*\hat{A}\Psi\,\mathrm{d}\boldsymbol{r} \tag{18}$$

- The time evolution of the wavefunction is given by the time dependent Schrödinger equation.

1.5   Simultaneous Eigenstates
An important result is that if two operators commute, then there exists a so-called simultaneous eigenbasis consisting of eigenfunctions of both operators. Assume that A and B commute, and let $|a\rangle$ be an eigenstate of A with eigenvalue a. Then we have

$$A(B\,|a\rangle) = BA\,|a\rangle = Ba\,|a\rangle = a(B\,|a\rangle) \tag{19}$$

The state $B\,|a\rangle$ is an eigenstate of A with eigenvalue a: this means that it must be proportional to $|a\rangle$. We conclude that $B\,|a\rangle = b\,|a\rangle$ for some constant b. This is exactly what we wished to show, and now we write the state as $|a,b\rangle$ to label its two eigenvalues.

2   Schrödinger Equation

The Schrödinger equation is inspired by classical mechanics, in which the Hamiltonian of a system is related to the energy of the system. To transition to quantum mechanics we suppose that dynamical variables become operators. The most general form of the Schrödinger equation is

$$\hat{H}(t)\,|\psi\rangle = i\hbar\frac{\partial}{\partial t}\,|\psi\rangle \tag{20}$$

The solution is fairly easy to write down: it is

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar} \int_0^t \hat{H}(t')\,\mathrm{d}t'} |\psi(0)\rangle \tag{21}$$

However, often the integration and operator exponential are intractable and other methods are necessary. One common simplification is to consider systems consisting of non-relativistic particles, in which we classically have

$$H = \frac{p^2}{2m} + V(q) \tag{22}$$

for some pair of canonical coordinates q and p. For example, working in the position basis with cartesian coordinates x and momentum p means that H becomes the operator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(x) \tag{23}$$

For an angular variable, θ, the Hamiltonian would be

$$\hat{H} = -\frac{\hbar^2}{2ma^2}\frac{\partial^2}{\partial \theta^2} + \hat{V}(\theta) \tag{24}$$

for some fixed radius a. These generalize quite easily to multiple coordinates.

The time-dependent Schrödinger equation is:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x}) \right] \Psi(\boldsymbol{x}; t) = i\hbar \frac{\partial \Psi(\boldsymbol{x}; t)}{\partial t} \tag{25}$$

If we assume that Ψ is separable, namely that $\Psi(\boldsymbol{x}; t) = \psi(\boldsymbol{x})T(t)$, this reduces to the time-independent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x}) \right] \psi(\boldsymbol{x}) = E\psi(\boldsymbol{x}) \tag{26}$$

The time dependence of Ψ is $T(t) = e^{-iEt/\hbar}$. In order to be physical, we often require that both ψ and $\frac{\partial \psi}{\partial x_i}$ be continuous.

2.1 Probability Current Density From the Schrödinger equation we may form the conjugate equation, assuming that $V^*(x) = V(x)$:

$$-\frac{\hbar^2}{2m}\nabla^2 \Psi^*(\boldsymbol{x}) + V(x)\Psi^*(\boldsymbol{x}) = -i\hbar \frac{\partial}{\partial t}\Psi^*(\boldsymbol{x}) \tag{27}$$

Multiplying the Schrödinger equation by Ψ^* and the conjugate equation by Ψ gives

$$-\frac{\hbar^2}{2m}\Psi^*\left(\nabla^2\Psi\right) + V(x)\Psi^*\Psi = i\hbar\,\Psi^*\frac{\partial \Psi}{\partial t} \tag{28}$$

$$-\frac{\hbar^2}{2m}\left(\nabla^2\Psi^*\right)\Psi + V(x)\Psi^*\Psi = -i\hbar\frac{\partial \Psi^*}{\partial t}\Psi \tag{29}$$

Subtracting these two equations gives

$$i\hbar\left(\Psi^*\frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi\right) = -\frac{\hbar^2}{2m}\left(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*\right) \tag{30}$$

$$\frac{\partial(\Psi^*\Psi)}{\partial t} = -\frac{\hbar}{2mi}\boldsymbol{\nabla}\cdot(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*) \tag{31}$$

Rearranging results in

$$\frac{\partial(\Psi^*\Psi)}{\partial t} + \boldsymbol{\nabla}\cdot\left[\frac{\hbar}{2mi}(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*)\right] = 0 \tag{32}$$

Making the following associations,

$$\rho = \Psi^*\Psi \qquad \boldsymbol{j} = \frac{\hbar}{2mi}(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*) \tag{33}$$

we see that ρ and its associated current, $\boldsymbol{j}$, satisfy the continuity equation:

$$\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j} = 0 \tag{34}$$

The interpretation is that $\rho = \Psi^*\Psi$ is a probability density, meaning that $\boldsymbol{j}$ is the probability current density, showing how the probability density function is changing through time.

The probability current density is useful for calculating transmission and reflection coefficients. For a surface of interest, these are

$$T = \frac{\boldsymbol{j}_{\text{trans}}\cdot\hat{\boldsymbol{n}}}{\boldsymbol{j}_{\text{inc}}\cdot\hat{\boldsymbol{n}}} = \frac{|\boldsymbol{j}_{\text{trans}}|}{|\boldsymbol{j}_{\text{inc}}|} \qquad R = -\frac{\boldsymbol{j}_{\text{refl}}\cdot\hat{\boldsymbol{n}}}{\boldsymbol{j}_{\text{inc}}\cdot\hat{\boldsymbol{n}}} = \frac{|\boldsymbol{j}_{\text{refl}}|}{|\boldsymbol{j}_{\text{inc}}|} \tag{35}$$

2.2 One-Dimensional Potentials

There are several classic one-dimensional potentials which lend themselves to exact solutions.

2.2.1 Infinite Square Well

Here the form of the potential in Schrödinger's equation is

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases} \tag{36}$$

One may run into cases where the well is defined in the region $|x| \leq \frac{L}{2}$. This, of course, does not change the solutions but only their mathematical description.

We look for solutions to the time-independent Schrödinger equation. Outside of the box we must have $\psi = 0$. This means that we must solve the following constrained problem

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \qquad \psi(0) = \psi(L) = 0 \tag{37}$$

for x in the interval $[0, L]$. Notice that we cannot require the derivative of ψ to be continuous at the boundaries. This arises because we are considering an idealized, non-physical potential.

Keeping the constraint $\psi(0) = 0$ in mind, we have that the general solution at this point is

$$\psi(x) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}\,x\right). \tag{38}$$

Enforcing the second constraint, $\psi(L) = 0$, gives the condition

$$\sqrt{\frac{2mE}{\hbar^2}}\,L = n\pi \qquad n \in \{1, 2, 3, \ldots\}, \tag{39}$$
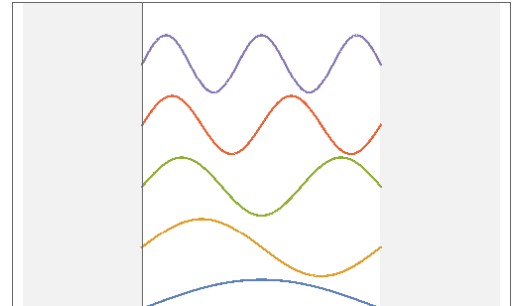

Figure 1: The first five eigenfunctions for the infinite square well.

from which we conclude that the energy is quantized as

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}. \tag{40}$$

Our solutions now stand as

$$\psi_n(x) = A_n \sin\left(\frac{n\pi x}{L}\right) \qquad n \in \{1, 2, 3, \ldots\}. \tag{41}$$

Requiring that these states be normalized gives

$$1 = \int_0^L \psi^*(x)\psi(x)\,\mathrm{d}x = |A_n|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right)\,\mathrm{d}x = \frac{L}{2}|A_n|^2. \tag{42}$$

Choosing $A_n = \sqrt{\frac{2}{L}}$ yields the final result,

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \tag{43}$$

2.2.2 Finite Square Well
The potential here is given by

$$V(x) = \begin{cases} 0 & |x| < \frac{L}{2} \\ V_0 & |x| \geq \frac{L}{2} \end{cases} \tag{44}$$

where $V_0 > 0$. We are interested in looking for bound states, so consider a state with energy $E < V_0$. Write down the wavefunction in each of the regions as

$$\psi(x) = \begin{cases} A'e^{k_2 x} + B'e^{-k_2 x} & x < \frac{L}{2} \\ C'e^{ik_1 x} + D'e^{-ik_1 x} & |x| < \frac{L}{2} \\ F'e^{k_2 x} + G'e^{-k_2 x} & x > \frac{L}{2} \end{cases} \tag{45}$$

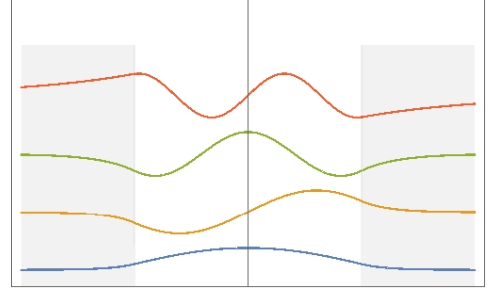$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \qquad k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \tag{46}$$

Figure 2: The *only* four bound states for a particular finite square well.

We must have $B' = F' = 0$ so that the wavefunction is bounded at $\pm\infty$, allowing it to be normalized. It is helpful to express the part of the wavefunction within the well in terms of sines and cosines instead. This gives

$$\psi(x) = \begin{cases} Ae^{k_2 x} & x < \frac{L}{2} \\ B \sin k_1 x + C \cos k_1 x & |x| < \frac{L}{2} \\ De^{-k_2 x} & x > \frac{L}{2} \end{cases} \tag{47}$$

In satisfying the boundary conditions at $x = \pm\frac{L}{2}$ we find two distinct sets of continuous solutions of definite parity:

$$\psi_S(x) = \begin{cases} Ae^{k_2 x} & x < -\frac{L}{2} \\ Ae^{-k_2 L/2} \frac{\cos k_1 x}{\cos\left(\frac{k_1 L}{2}\right)} & |x| < \frac{L}{2} \\ Ae^{-k_2 x} & x > \frac{L}{2} \end{cases} \qquad \psi_A(x) = \begin{cases} -Ae^{k_2 x} & x < -\frac{L}{2} \\ Ae^{-k_2 L/2} \frac{\sin k_1 x}{\sin\left(\frac{k_1 L}{2}\right)} & |x| < \frac{L}{2} \\ Ae^{-k_2 x} & x > \frac{L}{2} \end{cases} \tag{48}$$

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Enforcing continuity of $\frac{\partial \psi}{\partial x}$ gives the following conditions for the symmetric and antisymmetric solutions:

$$S: \quad k_2 = k_1 \tan\left(\frac{k_1 L}{2}\right) \qquad A: \quad k_2 = -k_1 \cot\left(\frac{k_1 L}{2}\right) \tag{49}$$

Recalling that both k_1 and k_2 are functions of E, we see that only discrete energies are possible: the solutions of these transcendental equations, which may be solved graphically. Doing so shows that there are only finitely many bound states, and that the number decreases to one as $V_0 \to 0$. There is *always* a symmetric bound state, no matter how small $V_0 > 0$ is. However, if V_0 is small enough there are no antisymmetric, bound states. Also, as $V_0 \to \infty$, we recover exactly the wavefunctions and energies of the infinite square well, as one might expect.

2.2.3 Step

Next we consider the following form for a one-dimensional potential:

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases} \tag{50}$$

We do not expect to find any bound states in this case, but given a particle initially with negative position moving to the right we may ask about the probability of finding it in the higher potential region continuing on its way to $+\infty$. We may write down the wavefunction:

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x} & x < 0 \\ Ce^{ik_2 x} & x \geq 0 \end{cases} \qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}} \qquad k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \tag{51}$$

There are two cases, corresponding to whether E or V_0 is larger:

- **Case I ($E > V_0$).** Here all wavenumbers are real, and all we must do is satisfy the boundary conditions at $x = 0$. Doing this gives

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + A\left(\frac{k_1 - k_2}{k_1 + k_2}\right)e^{-ik_1 x} & x < 0 \\ A\left(\frac{2k_1}{k_1 + k_2}\right)e^{ik_2 x} & x \geq 0 \end{cases} \tag{52}$$

  The reflection and transmission coefficients are

$$R = \frac{k_1}{k_1}\frac{|B|^2}{|A|^2} = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \qquad T = \frac{k_2}{k_1}\frac{|C|^2}{|A|^2} = \frac{4k_1 k_2}{(k_1 + k_2)^2} \tag{53}$$

  One may quickly check that $R + T = 1$, as expected.

- **Case II ($E < V_0$).** Here the wavenumber in the higher potential region is imaginary, and so we may write

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x} & x < 0 \\ Ce^{-k_2' x} & x \geq 0 \end{cases} \qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}} \qquad k_2' = \sqrt{\frac{2m|E - V_0|}{\hbar^2}} \tag{54}$$

  In the region $x > 0$ the wavefunction dies away quite quickly. Again the boundary conditions must be met. The result is

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + A\left(\frac{k_1 - ik_2'}{k_1 + ik_2'}\right)e^{-ik_1 x} & x < 0 \\ A\left(\frac{2k_1}{k_1 + ik_2'}\right)e^{-k_2' x} & x \geq 0 \end{cases} \tag{55}$$
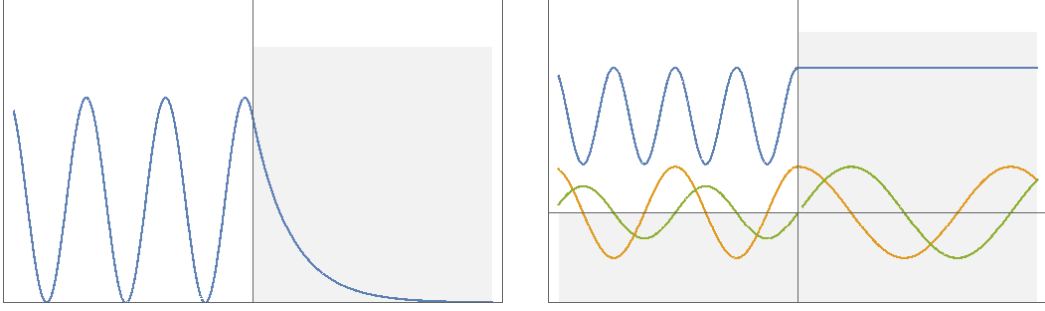
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Figure 3: Step potential probability densities for $E < V_0$ and $E > V_0$.

This gives for the reflection coefficients

$$R = \frac{k_1}{k_1} \frac{|B|^2}{|A|^2} = \left| \frac{k_1 - ik_2'}{k_1 + ik_2'} \right|^2 = 1, \tag{56}$$

from which we deduce the transmission coefficient is $T = 0$, matching our classical expectations.

2.2.4 Finite Barrier
Consider the finite barrier potential:

$$V(x) = \begin{cases} 0 & x < 0 \text{ or } x > L \\ V_0 & 0 \le x \le L \end{cases} \tag{57}$$

where $V_0 > 0$. We consider a particle initially with negative position moving to the right. As with the step potential above, there are two cases, depending on which of E and V_0 is larger.

- **Case I ($E > V_0$).** Here all the wavenumbers are real, so we may immediately write down the wavefunction as

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x} & x < 0 \\ Ce^{ik_2 x} + De^{-ik_2 x} & 0 \le x \le L \\ Fe^{ik_1 x} & x > L \end{cases} \tag{58}$$

For $x > L$ there is only the right-moving piece since in this region there is nothing to have reversed the particle's direction. Satisfying the boundary conditions at $x = 0$ and $x = L$
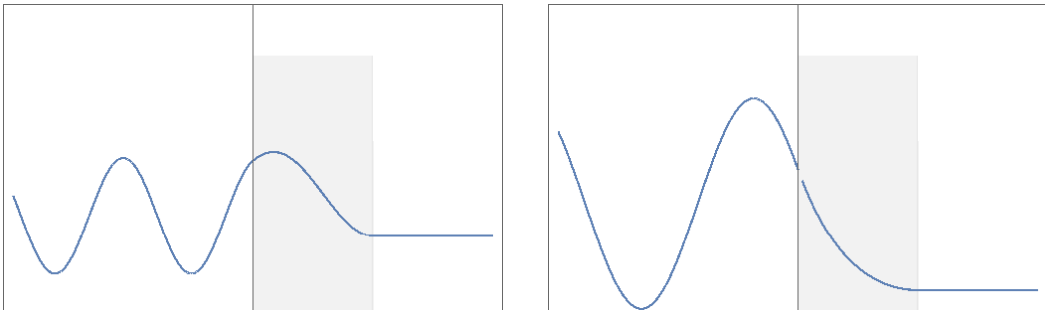

Figure 4: Finite barrier probability densities for $E > V_0$ and $E < V_0$.

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results in unenlightening expression for the coefficients. The takeaway is the transmission coefficient, i.e. the probability of passing the barrier:

$$T = \frac{1}{1 + \frac{V_0^2 \sin^2{(k_2 L)}}{4E(E - V_0)}} \tag{59}$$

Notice that when the system is "tuned" to have $\sin{(k_2 L)} = 0$, the transmission probability is exactly one.

- **Case II ($E < V_0$).** Here we get real exponentials within the barrier. In contrast with classical mechanics, there is a nonzero probability of passing through to $x > L$:

$$T = \frac{1}{1 + \frac{V_0^2 \sinh^2{(k_2 L)}}{4E(V_0 - E)}} \tag{60}$$

Note the similarity to the $E > V_0$ transmission coefficient. However, now there is no tuning that may be done to allow $T = 1$.

2.2.5 Dirac Delta

- **Repulsive.** We have a Dirac delta barrier given by

$$V(x) = \alpha \delta(x) \qquad \alpha > 0 \tag{61}$$

This may be thought of as a limiting case of the finite barrier with $L \to 0$ and $V_0 \to \infty$ but $L V_0 = \alpha$. Using the expression found above, we find the transmission and reflection coefficients to be

$$T = \frac{2E\hbar^2}{2E\hbar^2 + m\alpha^2} \qquad R = \frac{m\alpha^2}{2E\hbar^2 + m\alpha^2} \tag{62}$$

- **Attractive.** In the case where the potential forms a sharp "well", there is actually a bound state! If the potential is given by

$$V(x) = -\beta \delta(x) \qquad \beta > 0 \tag{63}$$

then the bound state is

$$\psi(x) = \sqrt{\Lambda} e^{-\Lambda |x|} \qquad \Lambda = \frac{m\beta}{\hbar^2} \tag{64}$$

2.3 Harmonic Oscillator The quantum harmonic oscillator lends itself to two methods of solving: one by sifting through tedious differential equations and the other through an elegant use of clever operators.

2.3.1 Differential Equation Method The time-independent Schrödinger equation for the one-dimensional harmonic oscillator is

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \right) \psi(x) = E\psi(x) \tag{65}$$

Writing $\xi = \sqrt{\frac{m\omega}{\hbar}} x$ cleans things up nicely:

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial \xi^2} + \frac{1}{2} \xi^2 \right) \psi(\xi) = \frac{E}{\hbar\omega} \psi(\xi) \tag{66}$$

For large ξ the function $e^{-\xi^2/2}$ is an approximate solution that is normalizable. To find exact solutions, write $\psi(\xi) = f(\xi)e^{-\xi^2/2}$, where f grows more slowly than $e^{\xi^2/2}$ for large ξ. Substituting this in gives the following differential equation for f:

$$f''(\xi) - 2\xi f'(\xi) + (2\mathcal{E} - 1) f(\xi) = 0 \qquad \mathcal{E} = \frac{E}{\hbar\omega} \tag{67}$$

Assuming a power-series solution of the form $f(\xi) = \sum_{n=0}^{\infty} a_n \xi^n$ leads to a recurrence relation for the coefficients:

$$a_{n+2} = \frac{2n - 2\mathcal{E} + 1}{(n+1)(n+2)} a_n \tag{68}$$

For large n, these grows as $a_{n+2} \sim \frac{2}{n} a_n$, leading to $f \sim e^{\xi^2}$. We disallowed this possibility when assuming f, so we conclude that the power series must terminate for some value of n. This forces either a_0 or a_1 to be zero, and requires the familiar condition: $\mathcal{E} = n + \frac{1}{2}$ for some $n \in \{0, 1, 2, \ldots\}$. The polynomials that result are the Hermite polynomials, $H_n(\xi)$. The full, normalized solutions are

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \sqrt[4]{\frac{m\omega}{\pi\hbar}} H_n(\xi)e^{-\xi^2/2} \qquad \xi = \sqrt{\frac{m\omega}{\hbar}} x \tag{69}$$

The first few eigenfunctions are

$$\psi_0(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}} e^{-\xi^2/2} \tag{70}$$

$$\psi_1(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}} \sqrt{2}\xi e^{-\xi^2/2} \tag{71}$$

$$\psi_2(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}} \frac{1}{\sqrt{2}} \left(2\xi^2 - 1\right) e^{-\xi^2/2} \tag{72}$$

$$\psi_3(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}} \frac{1}{\sqrt{3}} \left(2\xi^3 - 3\xi\right) e^{-\xi^2/2} \tag{73}$$

One may also see a potential that is for a harmonic oscillator in the region $x > 0$ but is infinite for $x < 0$. In this case everything above has been valid except for the new boundary condition at $x = 0$ and the normalization. Of the solutions we have found, only the odd solutions are now allowed, and so the new energy spectrum is

$$E_n' = \hbar\omega \left(n + \frac{1}{2}\right) \qquad n \in \{1, 3, 5, \ldots\} \tag{74}$$

2.3.2 Algebraic Method The harmonic oscillator Hamiltonian is

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2 \tag{75}$$

As a sum of squares this suggests a factorization of the form

$$H = (a\hat{x} - ib\hat{p})(a\hat{x} + ib\hat{p}) + c \qquad a, b, c \in \mathbb{R} \tag{76}$$

Some algebra gives

$$H = \frac{1}{2}m\omega^2 \left(\hat{x}^2 + i\frac{\hat{x}\hat{p} - \hat{p}\hat{x}}{m\omega} + \frac{\hat{p}^2}{m^2\omega^2}\right) - \frac{i\omega}{2}[\hat{x}, \hat{p}] \tag{77}$$

$$= \frac{1}{2}m\omega^2 \left(\hat{x} - \frac{i\hat{p}}{m\omega}\right)\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right) + \frac{\hbar\omega}{2} \tag{78}$$

Towards this goal, define the following dimensionless "ladder" operators:

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right) \qquad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right), \tag{79}$$

as well as the "number operator", $N = a^\dagger a$. We may now write the Hamiltonian in the compact form,

$$H = \hbar\omega\left(N + \frac{1}{2}\right) = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right). \tag{80}$$

These new operators satisfy the commutation relations

$$[a, a^\dagger] = 1 \qquad [N, a] = -a \qquad [N, a^\dagger] = a^\dagger. \tag{81}$$

a and $a^\dagger$ are not Hermitian operators ($a \neq a^\dagger$), and so are not observables. However, $N^\dagger = (a^\dagger a)^\dagger = a^\dagger a = N$, and so N is a Hermitian operator. Write the eigenstates of N as $|n\rangle$, so that $N|n\rangle = n|n\rangle$. Since $[H, N] = 0$, these satisfy also $H|n\rangle = \hbar\omega(n + \frac{1}{2})|n\rangle$. Using the commutation relations, we see

$$N(a|n\rangle) = (aN + [N, a])|n\rangle = aN|n\rangle - a|n\rangle = an|n\rangle - a|n\rangle = (n-1)(a|n\rangle) \tag{82}$$

$$N(a^\dagger|n\rangle) = (a^\dagger N + [N, a^\dagger])|n\rangle = a^\dagger N|n\rangle + a^\dagger|n\rangle = a^\dagger n|n\rangle + a^\dagger|n\rangle = (n+1)(a^\dagger|n\rangle) \tag{83}$$

The state $a|n\rangle$ has eigenvalue $n - 1$ and the state $a^\dagger|n\rangle$ has eigenvalue $n + 1$. We conclude that they must be proportional to the next-higher or next-lower eigenstate. The normalization may be found to be

$$a|n\rangle = \sqrt{n}\,|n-1\rangle \qquad a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle \tag{84}$$

The ladder operators "raise" and "lower" states from one into another, changing the energy by $\pm\hbar\omega$. However, since H is positive definite, we may not lower the energy indefinitely. There must exist some ground state, $|0\rangle$, such that $a|0\rangle = 0$. Any excited state is found by acting on the ground state with the raising operator.

$$a|0\rangle = 0 \qquad |n\rangle = \frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n|0\rangle \tag{85}$$

Notice that this gives a first-order ODE for the ground state, in contrast to the second-order equation of the previous section:

$$\left(x + \frac{\hbar}{m\omega}\frac{\partial}{\partial x}\right)|0\rangle = 0 \qquad \Longrightarrow \qquad \langle x|0\rangle = Ae^{-\frac{m\omega}{2\hbar}x^2} \tag{86}$$

3 Angular Momentum

3.1 Orbital Angular Momentum Classically, three-dimensional angular momentum is given by $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, so that $L_i = \epsilon_{ijk}r^j p^k$ (explicitly, $L_x = yp_z - zp_y$, $L_y = zp_x - xp_z$, $L_z = xp_y - yp_x$). We may use the commutation relations for $\boldsymbol{x}$ and $\boldsymbol{p}$ to find those for L_i when considering angular momentum quantum mechanically. For example,

$$[L_x, L_y] = [yp_z - zp_y, zp_x - xp_z] = y[p_z, z]p_x + x[z, p_z]p_y = i\hbar(xp_y - yp_x) = i\hbar L_z \tag{87}$$

In general, we have

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k \tag{88}$$

Total angular momentum, $L^2 = L_x^2 + L_y^2 + L_z^2$, commutes with each L_i. For example:

$$[L^2, L_x] = [L_x^2 + L_y^2 + L_z^2, L_x] = [L_y^2, L_x] + [L_z^2, L_x] \tag{89}$$

$$= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \tag{90}$$

$$= i\hbar\left(-L_yL_z - L_zL_y + L_zL_y + L_yL_z\right) = 0 \tag{91}$$

We see that L^2 and one of its components have a simultaneous eigenbasis. Conventionally we choose to single out L_z, and write

$$L^2\left|l, m\right\rangle = \hbar^2 l(l+1)\left|l, m\right\rangle \qquad L_z\left|l, m\right\rangle = \hbar m\left|l, m\right\rangle \tag{92}$$

The $\hbar$s are to carry the dimension, and the unusual '$l(l+1)$' is chosen to simplify later results. Now to find the allowed values of l and m.

Define the operators $L_\pm = L_x \pm iL_y$ with satisfy the following commutation relations:

$$[L_+, L_-] = 2\hbar L_z \qquad [J_z, J_\pm] = \pm\hbar L_\pm \qquad [L^2, L_\pm] = 0 \tag{93}$$

The use of these is shown in the following calculation:

$$L_z(L_\pm\left|l, m\right\rangle) = (L_\pm L_z + [L_z, L_\pm])\left|l, m\right\rangle \tag{94}$$

$$= (L_\pm L_z \pm \hbar L_\pm)\left|l, m\right\rangle \tag{95}$$

$$= \hbar(m \pm 1)(L_\pm\left|l, m\right\rangle) \tag{96}$$

We conclude that $L_\pm\left|l, m\right\rangle$ is an eigenstate of L_z with eigenvalue $m\pm1$. In addition, since $[L^2, L_\pm] = 0$, the state $L_\pm\left|l, m\right\rangle$ still has eigenvalue l, and so we conclude that it must be proportional to $\left|l, m \pm 1\right\rangle$. The normalization can be shown to be

$$L_\pm\left|l, m\right\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)}\left|l, m \pm 1\right\rangle \tag{97}$$

In addition, $L^2 - L_z^2 = L_x^2 + L_y^2$ is semi-positive definite (has non-negative real eigenvalues), and these ladder operators change the eigenvalue of L_z by one while keeping the eigenvalue of L^2 fixed. Thus it must be that at some point applying L_+ or L_- gives zero: no state at all! Indeed, $L_+\left|l, l\right\rangle = 0$ and $L_-\left|l, -l\right\rangle = 0$, which agrees with the normalization statement above.

3.2 Spin Angular Momentum Evidence for spin was displayed in the Stern-Gerlach experiment, in which silver atoms were passed through a non-uniform magnetic field and detected on a screen. The beam of atoms was split in two, showing that the atoms have an intrinsic magnetic momentum, related to what is now called spin angular momentum, or simply spin. Two distinct spots were observed on the screen, in contrast to a continuous smear predicted classically, suggesting that spin is quantized.

There is no evidence that particles have spin in the nonrelativistic theories, suggesting that this quantity is a purely relativistic effect. In the Schrödinger equation we make the association $H = \frac{p^2}{2m}$, but this is only valid for small p! To make a relativistic theory, time and space should be on equal footing. Using the relativistic equation $E^2 = (mc^2)^2 + (pc)^2$ and associating $E \leftrightarrow i\hbar\frac{\partial}{\partial t}$ and $\boldsymbol{p} \leftrightarrow -i\hbar\nabla$, we arrive at the Klein-Gordan equation:

$$\left[\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \left(\frac{mc}{\hbar}\right)^2\right]\psi = 0 \tag{98}$$

This, however, does not concern us here. One may also try using $E = \sqrt{(mc^2)^2 + (pc)^2}$, but square roots of operators are not so nice. With some fiddling one may write this, with the same associations, as

$$\left(\boldsymbol{\alpha} \cdot \boldsymbol{p}c + \beta mc^2\right)\psi = i\hbar\frac{\partial}{\partial t}\psi \qquad \{\alpha_i, \alpha_j\} = 2\delta_{ij} \qquad \{\beta, \alpha_i\} = 0 \qquad \beta^2 = 1 \tag{99}$$

where $\{A, B\} = AB + BA$ is the anticommutator. Clearly the constraints on $\boldsymbol{\alpha}$ and β cannot be met if they are complex numbers. However, matrices do the trick, implying that ψ is a matrix as well. Further analysis of this equation reveals that it describes particles with an intrinsic angular momentum of $\frac{1}{2}$: relativistic quantum mechanics predicts particle spin! Similarly, the Klein-Gordon equation has been found to describe spin-0 particles.

The so-called Pauli matrices are handy for continuing a discussion of the Dirac equation, and come in handy when considering spin-$\frac{1}{2}$ particles:

$$\sigma_1 = \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma_2 = \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma_3 = \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{100}$$

These are a set of three Hermitian, 2×2 matrices which satisfy the required properties above:

$$\det \sigma_i = -1 \qquad \operatorname{tr} \sigma_i = 0 \qquad \{\sigma_i, \sigma_j\} = 2\delta_{ij}\mathbb{I}_2 \qquad [\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma^k \tag{101}$$

where $\mathbb{I}_2$ is the identity matrix and $\{A, B\} = AB + BA$ is the anticommutator. Each has a set of orthonormal eigenvectors:

$$\psi_{x+} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix} \qquad\qquad \psi_{y+} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix} \qquad\qquad \psi_{z+} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{102}$$

$$\psi_{x-} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix} \qquad\qquad \psi_{y-} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \end{bmatrix} \qquad\qquad \psi_{z-} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{103}$$

Define the spin operator $\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$. Using the properties of the Pauli matrices we see that the components of $\boldsymbol{S}$ satisfy the commutation relations of an angular momentum: $[S_i, S_j] = i\hbar\epsilon_{ijk}S^k$. This explains the terminology "orbital angular momentum" and "spin angular momentum" to distinguish $\boldsymbol{L}$ and $\boldsymbol{S}$. Their sum is also an angular momentum and is denoted $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$.

So-called spinors form a basis for S^2 and S_z:

$$|\uparrow\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad\qquad |\downarrow\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{104}$$

These obviously satisfy the following:

$$S^2 |\uparrow\rangle = \frac{3\hbar^2}{4}|\uparrow\rangle \qquad\qquad S^2 |\downarrow\rangle = \frac{3\hbar^2}{4}|\downarrow\rangle \tag{105}$$

$$S_z |\uparrow\rangle = \frac{\hbar}{2}|\uparrow\rangle \qquad\qquad S_z |\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle \tag{106}$$

These are eigenstates of the z-component of spin. What are the possible values of the x-component of spin for $|\uparrow\rangle$?

$$|\uparrow\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1 \\ 1 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 1 \\ -1 \end{bmatrix} = \frac{1}{\sqrt{2}}\left(\psi_{x+} + \psi_{x-}\right) \tag{107}$$

We see that it is equally likely to measure the x-component of the spin to be $+\frac{\hbar}{2}$ as $-\frac{\hbar}{2}$.

13

Suppose we have a two particle system with Hamiltonian

$$H = -a\boldsymbol{S}_1 \cdot \boldsymbol{S}_2, \tag{108}$$

describing a spin interaction. A good method of attack is to rewrite the dot product in a convenient way. Introduce $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$, so that

$$S^2 = S_1^2 + S_2^2 + 2\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 \tag{109}$$

This allows us to write the Hamiltonian as

$$H = -\frac{a}{2}\left(S^2 - S_1^2 - S_2^2\right) \tag{110}$$

The values of S_i^2 are fixed because these are simply inherent properties of the particles. Writing $S^2 |s\rangle = s(s+1) |s\rangle$, the possible values for s are $\{|s_1 - s_2|, \ldots, s_1 + s_2\}$. The ground state will the the value for s which minimizes the energy:

$$E_{gs} = -\frac{a}{2}\Big[(s_1 + s_2)(s_1 + s_2 + 1) - s_1(s_1 + 1) - s_2(s_2 + 1)\Big] \tag{111}$$

Such addition of angular momenta tricks work because $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$ still satisfies the algebra that defines an angular momentum.

4 Wavefunction Symmetries

Consider a two-particle state whose constituents are indistinguishable: interchanging the particles should have no effect on any observables. Define the "swapping" operator, Σ, by

$$\Sigma\Psi(\alpha, \beta) = \Psi(\beta, \alpha) \tag{112}$$

where α and β characterize the quantum states of the two identical particles. Clearly, we have

$$\Sigma\Sigma\Psi(\alpha, \beta) = \Psi(\alpha, \beta) \qquad \Longrightarrow \qquad \Sigma^2 = \mathbb{I} \tag{113}$$

From these properties we see that Σ has eigenvalues 1 and -1. A general eigenstate is of the form

$$\Psi_S(\alpha, \beta) = \frac{1}{\sqrt{2}}\Big[\psi_1(\alpha)\psi_2(\beta) + \psi_1(\beta)\psi_2(\alpha)\Big] \tag{114}$$

$$\Psi_A(\alpha, \beta) = \frac{1}{\sqrt{2}}\Big[\psi_1(\alpha)\psi_2(\beta) - \psi_1(\beta)\psi_2(\alpha)\Big] \tag{115}$$

where S and A label the wavefunctions as symmetric or antisymmetric. These satisfy

$$\Sigma\Psi_S(\alpha, \beta) = \Psi_S(\alpha, \beta) \qquad \Sigma\Psi_A(\alpha, \beta) = -\Psi_A(\alpha, \beta) \tag{116}$$

Note, however, that the squares of ψ_S and ψ_A, or probability densities, do not change upon particle exchange: the particles are indistinguishable. One consequence of the antisymmetric wavefunction is that if $x_1 = x_2$ the probability density vanishes, seemingly describing particles which cannot be in the same place: this is a manifestation of the Pauli exclusion principle. Bosons, described by a symmetric wavefunction, have integral spin and do not follow the Pauli exclusion principle. Fermions, described by an antisymmetric wavefunction, have half-integral spin and follow the Pauli exclusion principle.

5 Time-Independent Non-Degenerate Perturbation Theory

If we have a Hamiltonian which is very close to one that we are able to solve exactly, we expect the solutions to not differ from these by much. We would like to solve

$$H \ket{n} = E_n \ket{n} \qquad H = H_0 + \lambda H' \tag{117}$$

The constant λ is a placeholder that eventually will be set to one. It serves to keep track of the order of each term. We assume that we have a basis $\ket{n^{(0)}}$ satisfying

$$H_0 \ket{n^{(0)}} = E_n^{(0)} \ket{n^{(0)}}, \tag{118}$$

and write both $\ket{n}$ and E_n as series expansions:

$$\ket{n} = \ket{n^{(0)}} + \lambda \ket{n^{(1)}} + \lambda^2 \ket{n^{(2)}} + \cdots \tag{119}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{120}$$

The task then is to find expressions for $\ket{n^{(k)}}$ and $E_n^{(k)}$. Substitute these two expressions into the original eigenvalue problem:

$$(H_0 + \lambda H') \left(\ket{n^{(0)}} + \lambda \ket{n^{(1)}} + \lambda^2 \ket{n^{(2)}} + \cdots \right) \tag{121}$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \right) \left(\ket{n^{(0)}} + \lambda \ket{n^{(1)}} + \lambda^2 \ket{n^{(2)}} + \cdots \right) \tag{122}$$

Collecting powers of λ,

$$H_0 \ket{n^{(0)}} + \lambda \left(H_0 \ket{n^{(1)}} + H' \ket{n^{(0)}} \right) + \cdots \tag{123}$$

$$= E_n^{(0)} \ket{n^{(0)}} + \lambda \left(E_n^{(0)} \ket{n^{(1)}} + E_n^{(1)} \ket{n^{(0)}} \right) + \cdots \tag{124}$$

The zeroth-order term reproduces what we already know:

$$H_0 \ket{n^{(0)}} = E_n^{(0)} \ket{n^{(0)}} \tag{125}$$

To gain information from the first-order, multiply on the left by $\bra{n^{(0)}}$. This gives:

$$\bra{n^{(0)}}H_0\ket{n^{(1)}} + \bra{n^{(0)}}H'\ket{n^{(0)}} = \bra{n^{(0)}}E_n^{(0)}\ket{n^{(1)}} + \bra{n^{(0)}}E_n^{(1)}\ket{n^{(0)}} \tag{126}$$

$$E_n^{(0)} \braket{n^{(0)}|n^{(1)}} + \bra{n^{(0)}}H'\ket{n^{(0)}} = E_n^{(0)} \braket{n^{(0)}|n^{(1)}} + E_n^{(1)} \braket{n^{(0)}|n^{(0)}} \tag{127}$$

$$\bra{n^{(0)}}H'\ket{n^{(0)}} = E_n^{(1)} \tag{128}$$

This expresses the first-order correction to the energy in terms of only the perturbing Hamiltonian and the unperturbed states! Now multiply on the left by $\bra{m^{(0)}}$ instead, with $m \neq n$:

$$\bra{m^{(0)}}H_0\ket{n^{(1)}} + \bra{m^{(0)}}H'\ket{n^{(0)}} = \bra{m^{(0)}}E_n^{(0)}\ket{n^{(1)}} + \bra{m^{(0)}}E_n^{(1)}\ket{n^{(0)}} \tag{129}$$

$$E_m^{(0)} \braket{m^{(0)}|n^{(1)}} + \bra{m^{(0)}}H'\ket{n^{(0)}} = E_n^{(0)} \braket{m^{(0)}|n^{(1)}} + E_n^{(1)} \braket{m^{(0)}|n^{(0)}} \tag{130}$$

$$\braket{m^{(0)}|n^{(1)}} = \frac{\bra{m^{(0)}}H'\ket{n^{(0)}}}{E_n^{(0)} - E_m^{(0)}} \tag{131}$$

Since $|m^{(0)}\rangle$ form a complete set, this gives

$$|n^{(1)}\rangle = \sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)}|n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle m^{(0)}|H'|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle \tag{132}$$

Notice that due to the denominator above, we run into trouble if we have degenerate energy states in the unperturbed system. A similar analysis shows that the second-order correction to the energy is

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle m^{(0)}|H'|n^{(0)}\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} \tag{133}$$

If both the unperturbed and perturbing Hamiltonians have the same parity, then the parity of the eigenstates will be unchanged when applying this procedure.

As an example, consider a harmonic oscillator with perturbing Hamiltonian

$$H' = V_0 \left(\tfrac{2m\omega}{\hbar} \right)^2 \hat{x}^4 \tag{134}$$

As in most cases for the harmonic oscillator, it is much cleaner to work with the ladder operators. Rewrite the perturbation as

$$H' = V_0 \left(a + a^\dagger \right)^4 \tag{135}$$

Following the prescription above, the first-order correction to the energy is

$$E_n^{(1)} = V_0 \langle n| \left(a + a^\dagger \right)^4 |n\rangle \tag{136}$$

Since only terms with an equal number of raising and lowering operators will be nonzero, we have

$$E_n^{(1)} = V_0 \langle n| a^2 a^{\dagger 2} + a a^\dagger a a^\dagger + a a^{\dagger 2} a + a^\dagger a^2 a^\dagger + a^\dagger a a^\dagger a + a^{\dagger 2} a^2 |n\rangle \tag{137}$$

$$= V_0 \left[(n+1)(n+2) + (n+1)^2 + n(n+1) + n(n+1) + n^2 + n(n-1) \right] \langle n|n\rangle \tag{138}$$

$$= 3V_0 \left(2n^2 + 2n + 1 \right) \tag{139}$$

6 Hydrogen

6.1 Non-Relativistic Solution Consider a central potential for a two-particle system, which gives the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + U(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \right] \psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = E\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{140}$$

Making a change of variables to R, the center of mass, and r the vector between the two particles, this becomes

$$\left[-\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + U(r) \right] \psi(\boldsymbol{R}, \boldsymbol{r}) = E\psi(\boldsymbol{R}, \boldsymbol{r}) \tag{141}$$

where $M = m_1 + m_2$ is the total mass and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass. Separation of variables gives

$$-\frac{\hbar^2}{2M} \nabla^2 \phi(\boldsymbol{R}) = E_R \phi(\boldsymbol{R}) \qquad \left[-\frac{\hbar^2}{2\mu} \nabla^2 + U(r) \right] \psi(\boldsymbol{r}) = E_r \psi(\boldsymbol{r}) \tag{142}$$

These describe the freely-moving center of mass and a single particle moving in a static potential, respectively. By going into a frame in which the center of mass is stationary, we may assume that

a two-particle system may be described completely by an effective one-particle system with mass μ. In the case of the Coulomb potential, $U(r) = \frac{Ze^2}{r}$, separation of variables leads to the solutions

$$\psi_{nlm}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \, \rho^l e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho) Y_l^m(\theta,\phi) \tag{143}$$

$$\rho = \frac{2r}{na_0} \qquad E_n = -\frac{\mu e^4}{2\hbar^2} \frac{1}{n^2} \approx -\frac{13.6\,\text{eV}}{n^2} \tag{144}$$

where $a_0 = \frac{\hbar^2}{m_e e^2}$ is the Bohr radius, L_k^α are generalized Laguerre polynomials and Y_l^m are spherical harmonics. The three quantum numbers may be:

$$n \in \{1, 2, 3, \ldots\} \qquad l \in \{0, 1, \ldots, n-1\} \qquad m \in \{-l, \ldots, l\} \tag{145}$$

This would imply that the degeneracy of the nth level is $\sum_{l=0}^{n-1}(2l+1) = n^2$; the inclusion of spin bumps this up to a degeneracy of $2n^2$.

Often one will only need the radial portion of a solution, which is

$$R_{nl}(r) \propto \rho^l e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho) \tag{146}$$

and goes as $R_{nl} \sim \rho^l$ near the origin. Often the ground state, $(n, l, m) = (1, 0, 0)$, suffices and this is given by

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \tag{147}$$

Considering Hydrogen-like atoms (one electron, Z protons) changes the energy levels to

$$E_n(Z) = -\frac{\mu Z^2 e^4}{2\hbar^2} \frac{1}{2} = -13.6\,\text{eV}\,\frac{Z^2}{n^2} = Z^2 E_n(1) \tag{148}$$

The important proportionalities are summarized by

$$E_n(Z) \propto \frac{\mu Z^2}{n^2} \tag{149}$$

Another expression for the energy levels of Hydrogen is

$$E_n = -\frac{1}{2} mc^2 \alpha^2 \frac{1}{n^2} \qquad \alpha = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} \approx \frac{1}{137} \tag{150}$$

where α is known as the fine structure constant. Relativistic corrections give terms proportional to α^4, plus higher-order terms.

A common question involves positronium, the bound state of and electron and positron pair. Everything above holds except for the energy levels, stemming from the change to the reduced mass. Since the mass of a positron is the same as that of an electron, we have

$$\mu = \frac{m_e m_e}{m_e + m_e} = \frac{m_e}{2} \tag{151}$$

This means that energy levels are shifted by a factor of two. In particular, the ground state energy is $-6.8\,\text{eV}$ instead of $-13.6\,\text{eV}$ for Hydrogen.

6.2 Fine Structure The fine structure in the Hydrogen energy spectrum arises through considering relativistic corrections and interactions between the spin angular momentum and the orbital angular momentum, aka spin-orbit coupling. This may be treated using perturbation theory, and gives a correction to the energy of

$$\Delta E_{nj} = -\frac{1}{2}mc^2\alpha^4\frac{1}{n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) = -\frac{2E_n^2}{mc^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) \qquad j = \left|l \pm \tfrac{1}{2}\right| \tag{152}$$

Notice that this always lowers the energy.

7 Special Functions

7.1 Hermite Polynomials The Hermite polynomials arise when solving the Schrödinger equation for a one-dimensional harmonic oscillator. The are the solutions to the following differential equation:

$$f''(x) - 2xf'(x) + 2nf(x) = 0 \tag{153}$$

The solutions, H_n, are orthogonal with respect to the weight function e^{-x^2}:

$$\int_{-\infty}^{\infty} e^{-x^2} H_n(x)H_m(x)\,\mathrm{d}x = \sqrt{\pi}\,2^n n!\delta_{nm} \tag{154}$$

The first few are:

$$H_0(x) = 1 \qquad H_1(x) = 2x \qquad H_2(x) = 4x^2 - 2 \qquad H_3(x) = 8x^3 - 12x \tag{155}$$

Notice that they have definite parity.

7.2 Spherical Harmonics Spherical harmonics arise when solving the Schrödinger equation in spherical coordinates with a spherically symmetric potential, $V(r)$. Separation of variables gives the differential equations

$$m^2 = -\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + l(l+1)\sin^2\theta, \tag{156}$$

of which $Y_l^m(\theta,\phi) = \Theta_l^m(\theta)\Phi_m(\phi)$ are solutions. They take the form

$$Y_l^m(\theta,\phi) = (-1)^m\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}\,P_l^m(\cos\theta)e^{im\phi}, \tag{157}$$

where P_l^m are the associated Legendre polynomials. Notice that the only ϕ dependence is $e^{im\phi}$. The normalization is such that they are orthonormal over the sphere:

$$\int_{4\pi} Y_l^{m*}Y_{l'}^{m'}\,\mathrm{d}\Omega = \delta_{ll'}\delta_{mm'} \tag{158}$$

The first few (good to know up to normalization) are:

$$Y_0^0(\theta,\phi) = \sqrt{\frac{1}{4\pi}} \qquad\qquad\qquad Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{159}$$

$$Y_1^{-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi} \qquad\qquad Y_1^1(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} \qquad (160)$$

These functions are eigenfunctions of both L^2 and L_z:

$$L^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi) \qquad L_z Y_l^m(\theta, \phi) = \hbar m Y_l^m(\theta, \phi) \qquad (161)$$

Notice that if a wavefunction is proportional to $\sin\theta \sin\phi$ or $\sin\theta \cos\phi$, then it is a linear combinations of $l = 1$ spherical harmonics:

$$\sin\theta \sin\phi = i\sqrt{\frac{2\pi}{3}}\left(Y_1^1 + Y_1^{-1}\right) \qquad \sin\theta \cos\phi = \sqrt{\frac{2\pi}{3}}\left(Y_1^1 - Y_1^{-1}\right) \qquad (162)$$

A Summary

$$p = \frac{h}{\lambda} \qquad \text{(de Broglie Wavelength)}$$

$$K_{\max} = h\nu - W = eV_{\text{stop}} \qquad \text{(Photoelectric Effect)}$$

Operators

$$\langle A \rangle = \langle A | \Psi \rangle = \int \Psi^* A \psi \, \mathrm{d}\boldsymbol{r} \qquad \text{(Expected Value)}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle A \rangle = \frac{1}{i\hbar} \langle [A, H] \rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle \qquad \text{(Ehrenfest Theorem)}$$

$$p_i = -i\hbar \frac{\partial}{\partial x^i} \qquad \text{(Momemtum Operator)}$$

$$T = \frac{\boldsymbol{p} \cdot \boldsymbol{p}}{2m} = -\frac{\hbar^2}{2m} \nabla^2 \qquad \text{(Kinetic Energy)}$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi} \qquad \text{(Angular Momentum)}$$

$$H = T + V(x) = -\frac{\hbar^2}{2m} \nabla^2 + V(x) \qquad \text{(Nonrelativistic Hamiltonian)}$$

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{ip}{m\omega} \right) = \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{\hbar}{m\omega} \frac{\partial}{\partial x} \right) \qquad \text{(Harmonic Oscillator)}$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(x - \frac{ip}{m\omega} \right) = \sqrt{\frac{m\omega}{2\hbar}} \left(x - \frac{\hbar}{m\omega} \frac{\partial}{\partial x} \right)$$

$$H = \hbar\omega \left(N + \frac{1}{2} \right) = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right)$$

$$[x_i, p_j] = i\hbar \delta_{ij} \qquad \text{(Cannonical coordinates)}$$

$$[f(x), p_x] = i\hbar f'(x) \qquad \text{(Function of position)}$$

$$[x, g(p_x)] = i\hbar g'(p_x) \qquad \text{(Function of momentum)}$$

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L^k \qquad \text{(Angular momentum)}$$

$$[L^2, L_i] = 0$$

$$[a, a^\dagger] = 1 \qquad \text{(Ladder Operators)}$$

$$[N, a] = -a$$

$$[N, a^\dagger] = a^\dagger$$

One-Dimensional Potentials

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \qquad n \in \{1, 2, 3, \ldots\} \qquad \text{(Infinite square well)}$$

$$R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \qquad T = \frac{4k_1 k_2}{(k_1 + k_2)^2} \qquad \text{(Step: } E > V_0\text{)}$$

$$T = \left[1 + \frac{V_0^2 \sin^2(k_2 L)}{4E(E - V_0)}\right]^{-1} \qquad \text{(Finite Barrier: } E > V_0\text{)}$$

$$T = \left[1 + \frac{V_0^2 \sinh^2(k_2 L)}{4E(V_0 - E)}\right]^{-1} \qquad \text{(Finite Barrier: } E < V_0\text{)}$$

$$\psi(x) = \sqrt{\Lambda}\, e^{-\Lambda|x|} \qquad \Lambda = \frac{m\beta}{\hbar^2} \qquad V(x) = -\beta\delta(x) \qquad \text{(Delta Well Bound State)}$$

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \sqrt[4]{\frac{m\omega}{\pi\hbar}}\, H_n(\xi) e^{-\xi^2/2} \qquad \xi = \sqrt{\frac{m\omega}{\hbar}}\, x \qquad \text{(Harmonic Oscillator)}$$

$$E_n = \hbar\omega\left(n + \tfrac{1}{2}\right) \qquad n \in \{0, 1, 2, \ldots\}$$

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}} |0\rangle \qquad a|0\rangle = 0$$

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right) \qquad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right)$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(a^\dagger + a\right) \qquad p = i\sqrt{\frac{\hbar m\omega}{2}}\left(a^\dagger - a\right)$$

Angular Momentum & Spin

$$L^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle \qquad \text{(Eigenvalue Expressions)}$$

$$L_z |l, m\rangle = \hbar m |l, m\rangle$$

$$L_\pm |l, m\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)}\, |l, m \pm 1\rangle \qquad \text{(Ladder Operators)}$$

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \text{(Pauli Matrices)}$$

$$\sigma_i^2 = \mathbb{I}_2 \qquad \det \sigma_i = -1 \qquad \operatorname{tr} \sigma_i = 0$$

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}\mathbb{I}_2 \qquad [\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma^k$$

$$\boldsymbol{A} \cdot \boldsymbol{B} = \frac{1}{2}\left(C^2 - A^2 - B^2\right) \qquad \boldsymbol{C} \equiv \boldsymbol{A} + \boldsymbol{B} \qquad \text{(The ``Trick'')}$$

Time-Independent Non-Degenerate Perturbation Theory

$$E_n^{(1)} = \langle n^{(0)} | H' | n^{(0)} \rangle \qquad \text{(1st-order energy correction)}$$

$$|n^{(1)}\rangle = \sum_{k \neq n} \frac{\langle k^{(0)} | H' | n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle \qquad \text{(1st-order eigenstate correction)}$$

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle k^{(0)} | H' | n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \qquad \text{(2^{d}-order energy correction)}$$