Quantum Physics 1

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1 The Wave Function

1.1 The Schrödinger Equation

The quantum description of a particle of mass m is given by the **wave function**, $\Psi(x, t)$.
It's dynamics, or time-evolution, are given by the **Schrödinger equation**:

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

Or:

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

The Schrödinger equation's complex conjugate is given by:

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

The wave function of a particle can be found by solving the Schrödinger equation.

Important to note here is the use of $\bar{h}$ which is Planck's constant divided by 2π:

$$\bar{h} = \frac{h}{2\pi} = 1.054572 \times 10^{-34}\,\text{J s}$$

1.2 The Statistical Interpretation

The probability of finding the particle between a and b, at time t is give by:

$$P = \int_a^b |\Psi(x, t)|^2 dx$$

Here we know that

$$|\Psi(x, t)|^2 = \Psi^* \Psi \qquad \text{or} \qquad |\Psi(x, t)|^2 = \Psi_{\text{Re}}^2 \cdot \Psi_{\text{Im}}^2$$

If $\Psi(x, t)$ isn't a complex number then $|\Psi(x, t)|^2 = \Psi \cdot \Psi$.

$|\Psi(x, t)|^2$ is also known as the **probability density**, $\rho(x)$. This statistical interpretation introduces a kind of **indeterminacy** into quantum mechanics.

There are three positions on where the particle was just before a measurement (where is was found at point C):

1. **Realist** (Einstein): the particle was at point C, but for this to be true quantum mechanics is an incomplete theory, there is some additional information (known as a **hidden variable**).

2. **Orthodox** (Bohr): the particle wasn't really anywhere, because of the measurement the particle was *forced* to be somewhere.

3. **Agnostic**: refuse to answer, simply because we can't know.

Experiments have confirmed the orthodox interpretation, when a measurement is done the wave function **collapses** to a spike at the point where the particle was measured to be.

1.3 Probability

1.3.1 Discrete Variables

The average value of some function of j is given by

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

The **variance** of a distribution is given by

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$$

Taking the square root of this gives the **standard deviation**

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

And since σ^2 is clearly non negative this implies that $\langle x^2 \rangle \geq \langle x \rangle^2$

1.3.2 Continuous Variables

The probability that x lies between a and b is given by the integral of the **probability density**

$$P_{a,b} = \int_a^b \rho(x) dx = \int_a^b |\Psi(x,t)|^2 dx$$

We also know that the probability that x lies between $-\infty$ and $+\infty$ is 1 (The particle has to be **somewhere**).

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

The weighted average also known as the **expectation value** or mean value.

$$\langle x \rangle = \int_{-\infty}^{+\infty} x \rho(x) dx$$

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 \rho(x) dx$$

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x) \rho(x) dx$$

1.4 Normalization

We now know that:

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

If you get a different finite result than 1, you can **normalize** Ψ, which is basically re-scaling Ψ, by adding an constant A, such that the equation above holds again. It has two constraints:

- Ψ needs to go to 0 at ∞

- Ψ must "fall" faster than $\frac{1}{\sqrt{x}}$

If $\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 dx$ gives ∞ or if Ψ has the trivial solution 0, the wave function is **non-normalizable**, because it represents nonphysical particles. Physically realizable states correspond to the **square-integrable** solutions to Schrödinger's equation.

Because the total probability is time-independent a wave function will stay normalized if it has been normalized once (*Proof in the book*).

1.5 Momentum

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

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

This expectation value is **not** the value that you are most likely to measure, nor will it be the average of subsequent measurements. Rather if you have an **ensemble** of particles, each in the same state Ψ, and measure the positions of all of them: $\langle x \rangle$ will be the average of these results.

By taking the *time derivative of the expectation value of the position* we find the **expectation value of the velocity**:

$$\langle v \rangle = \frac{\mathrm{d}}{\mathrm{d}t} \langle x \rangle$$
$$= \int x \frac{\partial}{\partial t} |\Psi|^2 dx$$
$$= \frac{-i\bar{h}}{m} \int \Psi^* \frac{\partial}{\partial x} \Psi dx$$

It is customary to work with **momentum**, which is given by:

$$\langle p \rangle = m \cdot \frac{\mathrm{d}}{\mathrm{d}t} \langle x \rangle = -i\bar{h} \int \left(\Psi^* \frac{\partial}{\partial x} \Psi \right) dx$$

Therefore, given a wave function, the expectation values for location and momentum are:

$$\langle x \rangle = \int \Psi^*(x)\Psi dx$$

$$\langle p \rangle = \int \Psi^* \left(\frac{\bar{h}}{i} \frac{\partial}{\partial x} \right) \Psi dx$$

Here the **operator** x "represents" position, and the operator $(h/i)(\partial/\partial x)$ "represents" momentum.

This can be generalized by remembering that any observable is a function of x and p. Therefore the expectation value of *any* such quantity, $Q = Q(x,p)$, can be calculated by

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

1.6 The Uncertainty Principle

A general property of waves is that they cannot have **both** a sharp position and wavelength.

The wavelength of Ψ is related to the momentum through the **de Broglie formula**:

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

Thus a spread in wavelength corresponds to a spread in momentum. From this follows Heisenberg's **uncertainty principle**:

$$\sigma_x \sigma_p \geq \frac{\bar{h}}{2}$$

2 Time-Independent Schrödinger Equation

2.1 Stationary States

Suppose that the potential specified in the Schrödinger equation is *independent of t*. In that case **separation of variables** can be used to solve the Schrödinger equation:

$$\Psi(x,t) = \psi(x)\varphi(t)$$

This gives the **time-independent Schrödinger equation**

$$-\frac{\bar{h}^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi$$

and the general solution of the temporal part:

$$\varphi(t) = e^{-itE/\bar{h}}$$

Now *what is so great about these separable solutions?* There are three properties that are really useful, which are

1. They are **stationary states**. The wave function itself of course depends on t, but the probability density doesn't.

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

   Following from this we get that *every expectation value is constant in time*. So nothing ever *happens* in a stationary state.

2. They are states of *definite total energy* ('energy eigenstates'). In classical mechanics the total energy is called the **Hamiltonian**, here the corresponding Hamiltonian *operator* is given by:

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

   This gives:

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

   And following from that we get

   $$\langle H \rangle = E \qquad\qquad \text{and} \qquad\qquad \langle H^2 \rangle = E^2$$

   So the variance of H is $\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = 0$, this gives the property that *every measurement of the total energy is certain to return the value E.*

3. The general solution is a **linear combination** of separable solutions. For every **allowed energy** there is a different wave function and combining these separable solutions can give us a more general solution.

   $$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-iE_n t/\bar{h}} = \sum_{n=1}^{\infty} c_n\Psi_n(x,t)$$

   In other words; the stationary states span a basis for all space.

Important to note is the fact that the separable solutions themselves are *stationary* states; all their probabilities and expectation values are independent of time, but this is not the case with the general solution.

The **boundary conditions** for $\psi(x)$ are that *both ψ and $d\psi/dx$ are continuous*. But where the potential goes to infinity only the first of these applies, which is important for some of the cases we will look at next.

2.2   The Infinite Square Well

Suppose we have the following potential

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

A particle in this potential is completely free, except at the two ends, where an infinite force prevents it from escaping.

Outside the well $\psi(x) = 0$, the probability of finding the particle there is zero. At the boundaries $x = 0$ and $x = a$ $\psi(x)$ is also zero, this is a physical requirement, ψ must be continuous.

Inside the well the time-independent Schrödinger equation will become a **simple harmonic oscillator**. The solutions for $\psi(x)$ inside the well are given by

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

And the possible values for the energy are given by

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

The wave function with the lowest energy, ψ_1 is called the **ground state**, the others are called **exited states**. As a collection the functions have some interesting properties:

1. They are alternately **even** and **odd**, with respect to the center of the well, starting with ψ_1, which is even.

2. Each successive state has one more **node** (zero-crossing), starting with ψ_1, which has none (the end points don't count).

3. They are **orthonormal** (both **orthogonal** and normalized), this is defined by the following statement:

$$\int_0^a \psi_m^*(x)\, \psi_n(x) dx = \delta_{mn}$$

   Here δ_{mn} of course is the **Kronecker delta**;

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

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

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

   If you've paid attention in you mathematics courses you'll recognize that this is just the **Fourier series** for $f(x)$.

Fourier's trick (named by our one and only Griffiths) is a method to evaluate the coefficients c_n for a given $f(x)$:

$$c_n = \int \psi_n(x)^* f(x)\, dx.$$

How should we interpret what c_n is? c_n basically tells you the "amount of ψ_n that is contained in Ψ". Following from this is that $|c_n|^2$ tells you the *probability that a measurement of the energy would yield the value E_n*. This of course gives that

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

Also the expectation value of the energy will be

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n$$

The fact that the probability of getting a particular energy is independent of time, is a manifestation of **conservation of energy** in quantum mechanics.

2.3   The Harmonic Oscillator

Next we want to look at the case where the potential is described by a harmonic oscillator. Clasically this motion is governed by **Hooke's law**, but the *quantum* problem is to solve the Schrödinger equation for the potential

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

This gives the following time-independent Schrödinger equation:

$$-\frac{\bar{h}^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi$$

There are two different approaches to solving this equation; a straightforward solution using the **power series method** and a diabolically clever algebraic technique, using so-called **ladder operators**. We'll follow the book of course and do the ladder operators first.

2.3.1   Algebraic Method

First we rewrite our Schrödinger equation to

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

In an ideal world we would be able to *factor* the Hamiltonian as follows:

$$H = \frac{1}{2m}\left[p^2 + (m\omega x)^2\right]$$
$$\neq \frac{1}{2m}\left(p + im\omega x\right)\left(p - im\omega x\right)$$

Sadly we don't live in an ideal world and this isn't possible because p and x are *operators* and not normal numbers. In general operators do not **commute** $(x \cdot p \neq p \cdot x)$. We can however still examine the quantities and define our **ladder operators** (more on the actual ladder part later):

$$a_\pm = \frac{1}{\sqrt{2m\bar{h}\omega}}(p \pm im\omega x)$$

Before we are going to continue we want to explore the wonderful world of **commutators**; commutators are a measure of how badly (some) operators *fail* to commute. In general the commutator of operators A and B is

$$[A, B] \equiv AB - BA.$$

So the commutator for x and p will be

$$[x, p] = x \cdot p - p \cdot x = i\bar{h},$$

this result is also known as the **canonical commutation relation**.

Now we can multiply a_+ and a_- with each other to find our Hamiltonian.

$$a_-a_+ = \frac{1}{2m\bar{h}\omega}(p + im\omega x)(p - im\omega x)$$
$$= \frac{1}{2m\bar{h}\omega}\left[p^2 + (m\omega x)^2\right] - \frac{i}{2\bar{h}}[x, p]$$
$$= \frac{1}{\bar{h}\omega}H + \frac{1}{2}$$

Note that the order of the ladder operators is important here, if you would reverse is this would give

$$a_+a_- = \frac{1}{\bar{h}\omega}H - \frac{1}{2}$$

So clearly

$$[a_+, a_-] = -1$$

In terms of $a_\pm$ we get a new form of the Schrödinger equation for the harmonic oscillator

$$\bar{h}\omega \left(a_\pm a_\mp \pm \frac{1}{2} \right) \psi = E\psi$$

Now we get to the ladder operator part! We call $a_\pm$ **ladder operators**, because they allow us to climb up and down in energy, that is *if ψ satisfies the Schrödinger equation with energy E, then $a_+\psi$ satisfies the Schrödinger equation with energy $(E + \bar{h}\omega)$.* In other words:

$$\text{if} \qquad H\psi = E\psi, \qquad \text{then} \qquad H(a_+\psi) = (E + \bar{h}\omega)(a_+\psi)$$

a_+ then is called the **raising operator**. The same goes for a_-, the **lowering operator**:

$$\text{if} \qquad H\psi = E\psi, \qquad \text{then} \qquad H(a_-\psi) = (E - \bar{h}\omega)(a_-\psi)$$

Important to note is the fact that a "lowest rung" (ψ_0) of our ladder exists, such that

$$a_-\psi_0 = 0$$

Using this we can find

$$\psi_0 = \left(\frac{m\omega}{\pi\bar{h}} \right)^{1/4} e^{-m\omega x^2/2\bar{h}} \qquad \text{and} \qquad E_0 = \frac{1}{2}\bar{h}\omega$$

And now that we know the equation of the "lowest rung", we can easily find all exited states

$$\psi_n(x) = A_n(a_+)^n\psi_0(x), \qquad \text{with } E_n = \left(n + \frac{1}{2} \right) \bar{h}\omega$$

Where A_n is the normalization constant. Some fancy algebraic footwork can also be used to find this normalization constant. The proof in the book first finds the following relations

$$a_+\psi_n = \sqrt{n+1}\psi_{n+1} \text{ and } a_-\psi_n = \sqrt{n}\psi_{n-1}.$$

From these relations follow that

$$\psi_n = \frac{1}{\sqrt{n!}}(a_+)^n\psi_0$$

As in the case of the infinite square well, the stationary states of the harmonic oscillator are orthonormal, so if we want we can Fourier's trick to evaluate the coefficients, when we expand $\Psi(x,0)$ as a linear combination of stationary states.

2.4   The Free Particle

Next we look at what you would think is the easiest case; the free particle. Here $V(x) = 0$ everywhere. This gives that the Schrödinger equation will reduce to the same form as inside the infinite square well. This time we will write our solutions in the exponential form:

$$\Psi_k(x,t) = Ae^{i(kx - \frac{\bar{h}k^2}{2m}t)}$$

with

$$k \equiv \pm\frac{\sqrt{2mE}}{\bar{h}}.$$

Now, *any* function of x and t that depends on these variables in the special combination, $x \pm vt$, represents a traveling wave of fixed profile (its shape **doesn't** change as it propagates), which travels in the $\mp x$ direction, at speed v. The direction in which the wave travels in our case is governed by k:

$$k > 0 \Rightarrow \text{ travelling to the right,}$$
$$k < 0 \Rightarrow \text{ travelling to the left.}$$

So clearly the "stationary states" of the free particle are propagating waves; their wavelength is $\lambda = 2\pi/|k|$, and they carry momentum

$$p = \bar{h}k.$$

Before we get to the velocities of these wave we'll look at another important thing. *This wavefunction is not normalizable.* So in the case of the free particle, the separable solutions do not represent physically realizable states. *There is no thing as a free particle with a definite energy.* But we can still use these separable solutions.

The general solution to the time-dependent Schrödinger equation is still a linear combination of separable solutions, only this time it's an integral over the *continuous* variable k:

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

Now this wave function can be normalized (for appropriate $\phi(k)$). But it necessarily carries a range of k's, and hence a range of energies and speeds. We call it a **wave packet**.

The question now is how to determine $\phi(k)$ so as to match the initial wave function

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

Well the answer to this is provided by **Plancherel's theorem**:

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

$F(k)$ is called the **Fourier transform** of $f(x)$; $f(x)$ is the **inverse Fourier transform** of $F(k)$ (the only difference is in the sign of the exponent). There is, of course, some restriction on the allowable functions: The integrals have to *exist*. This theorem gives

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

Now to the velocities. The speed of these waves is given by

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

But if we were to determiner the classical speed through $E = (1/2)mv^2$ we would get that

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

So apparently the quantum mechanical wave function travels at half the speed of the particle it is supposed to represent, how does this work? The essential idea is this: A wave packet is a superposition of sinusoidal functions whose amplitude is modulated by ϕ; it consists of "ripples" contained within an "envelope." What corresponds to the particle velocity is not the speed of the individual ripples (the **phase velocity**), but rather the speed of the envelope (the **group velocity**) which, can be greater than, less than, or equal to, the velocity of the ripples that go to make it up. So

$$v_{\text{classical}} = v_{group} = 2v_{phase} = 2v_{\text{quantum}}.$$

2.5   The Delta-Function Potential

2.5.1   Bound States and Scattering States

In classical mechanics a one-dimensional time-independent potential can give rise to two rather different kinds of motion. If $V(x)$ rises higher than the particle's total energy (E) on either side, then the particle is in a **bound state**. It is "stuck" in the potential well—it rocks back and forth between the **turning points**, but it cannot escape. If, on the other hand, E exceeds V (x) on one side (or both), then it is in a **scattering state**. The particle comes in from "infinity," slows down or speeds up under the influence of the potential, and returns to infinity.

The distinction is even cleaner in quantum, because the phenomenon of **tunneling** allows the particle

to "leak" through any finite potential barrier, so the only thing that matters is the potential at infinity. Since most potentials go to zero at infinity we get

$$
\begin{cases}
E < 0 \Rightarrow \ \text{bound state,} \\
E > 0 \Rightarrow \ \text{scattering state.}
\end{cases}
$$

Because the infinite square well and harmonic oscillator potentials go to infinity as x goes there too, they admit bound states only. Because the free particle potential is zero everywhere, it only allows scattering states.

2.5.2   The Delta-Function Well

We all already know the Dirac delta function, but let's give a quick overview anyway :)
The **Dirac delta function** is an infinitely high, infinitesimally narrow spike at the origin, whose area is 1

$$
\delta(x) \equiv
\begin{cases}
0, & \text{if } x \neq 0 \\
\infty, & \text{if } x = 0
\end{cases}, \quad \text{with } \int \delta(x)\,dx = 1.
$$

Remember that $\delta(x-a)$ would be a spike of area 1 at the point a. And that

$$
f(x)\delta(x-a) = f(a)\delta(x-a),
$$

in particular,

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

That's the most important property of the delta function: Under the integral sign it serves to "pick out" the value of $f(x)$ at the point a.

Let's consider a potential of the form
$$
V(x) = -\alpha\delta(x),
$$

where α is some positive constant. The Schrödinger equation for the delta-function well reads

$$
-\frac{\bar{h}^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \alpha\delta(x)\psi = E\psi,
$$

and it yields both bound and scattering states.

Bound States   We'll first look at the bound states, so $E < 0$. In the regions $x < 0$ and $x > 0$, $V(x) = 0$, so
$$
\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\bar{h}^2}\psi = \kappa^2\psi,
$$

where
$$
\kappa = \frac{\sqrt{-2mE}}{\bar{h}}.
$$

The solution for the bound states then becomes

$$
\psi(x) =
\begin{cases}
Be^{\kappa x}, & (x \leq 0), \\
Be^{-\kappa x}, & (x \geq 0).
\end{cases}
$$

The fact that both sides have the same constant follows from the boundary conditions for $\psi(x)$: *ψ is always continuous and $d\psi/dx$ is continuous except at points where the potential is infinite.*
These two parts of the wave function can in the end be expressed as one function. So the delta-function well has one bound state:
$$
\psi(x) = \frac{\sqrt{m\alpha}}{\bar{h}}e^{-m\alpha|x|/\bar{h}^2}; \ \text{with } E = -\frac{m\alpha^2}{2\bar{h}^2}.
$$

Scattering States   Now we will look at the scattering states, yay! Of course now $E > 0$. For $x < 0$ and $x > 0$, $V(x) = 0$, so

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\bar{h}^2}\psi = -k^2\psi,$$

where

$$k = \frac{\sqrt{2mE}}{\bar{h}}.$$

Then we get a solution of the form

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & (x < 0), \\ Fe^{ikx} + Ge^{-ikx}, & (x > 0). \end{cases}$$

Sadly no terms can be ruled out, since none blow up. Imposing boundary conditions gives us two equations:

$$F + G = A + B \qquad \text{and} \qquad F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \text{ with } \beta \equiv \frac{m\alpha}{\bar{h}^2 k}.$$

Now what do all these constants represent? Well A is the amplitude of a wave coming in from the left, B is the amplitude of a wave returning to the left, F is the amplitude of a wave traveling off to the right, and G is the amplitude of a wave coming in from the right. For a typical scattering experiments we know what 1 constant will be:

$$G = 0, \text{ (for scattering from the left).}$$

Then we know that A is the amplitude of the **incident wave**, B is the amplitude of the **reflected wave**, and F is the amplitude of the **transmitted wave**.

The relative probability that an incident particle will be reflected back is given by the **reflection constant**:

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2} = \frac{1}{1 + (2\bar{h}^2 E/m\alpha^2)}.$$

The probability of transmission is given by the **transmission coefficient**:

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2} = \frac{1}{1 + (m\alpha^2/2\bar{h}^2 E)}.$$

The higher the energy, the greater the probability of transmission.
Of course, the *sum* of these probabilities should be 1, and it *is*:

$$R + T = 1.$$

Important to notice is that these scattering wave functions are *not* normalizable, so they don't actually represent possible particle states. So we must form normalizable linear combinations of the stationary states, just as we did for the free particle, true physical particles are represented by the resulting wave packets.

Next we'll quickly look at the delta-function *barrier*, for this we only have to flip the sign of α. This kills the bound state, since $V_0 = 0$, but the scattering state remains unchanged. So the particle is just as likely to pass through the barrier as to cross over the well! The particle has some nonzero probability of passing through the potential even if $E < V_{\max}$. We call this phenomenon **tunneling**.

2.6   The Finite Square Well

The finite square well has a potential of the form

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

Bound States.   First we will look at the bound states; the **even** solutions for this case are given by

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & \text{for } x > a, \\ D\cos{(lx)}, & \text{for } 0 < x < a, \\ \psi(-x), & \text{for } x < 0. \end{cases}$$

Imposing the boundary conditions at $x = a$ gives us a transcendental equation for z as a function of z_0

$$\tan z = \sqrt{(z_0/z)^2 - 1} \text{ with } z = la, \text{ and } z_0 = \frac{a}{\bar{h}}$$

This can be solved numerically or by plotting both sides of the on the same grid and looking at the points of intersection.

the **odd** solutions for this case are given by

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & \text{for } x > a, \\ D\sin{(lx)}, & \text{for } 0 < x < a, \\ -\psi(-x), & \text{for } x < 0. \end{cases}$$

Here we also get a similar transcendental equation for (the same) z as a function of (the same) z_0

$$-\cot z = \sqrt{(z_0/z)^2 - 1},$$

which can be solved in the same way.

Two limiting cases are of special interest:

1. Wide, deep well.   If z_0 is very large, the intersections occur just slightly below $z_n = n\pi/2$, with n even or odd; it follows that

$$E_n + V_0 \cong \frac{n^2\pi^2\bar{h}^2}{em(2a)^2}.$$

2. Shallow, narrow well.   As z_0 decreases, there are fewer and fewer bound states, until finally (for $z_0 < \pi/2$, where the lowest odd state disappears) only one remains.

Scattering States.   For the scattering states $(E > 0)$ we will get a solution of the form

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & \text{for } x < -a, \\ C\sin{(lx)} + D\cos{(lx)}, & \text{for } -a < x < a, \\ Fe^{ikx}, & \text{for } x > a. \end{cases}$$

Like with the delta-function well we assume that there's no incoming wave from the right. Again A is the incident amplitude, B is the reflected amplitude, and F is the transmitted amplitude.
There are 4 boundary conditions which can be used to eliminate C and D, and solving them gives us two quite ugly equations:

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

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

The transmission coefficient $(T = |F|^2/|A|^2)$ is given by

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

Notice that $T = 1$ (the well becomes "transparent") whenever the sine is zero, which is to say, when

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

where n is any integer. The energies for perfect transmission, then, are given by

$$E_n + V_0 = \frac{n^2\pi^2\bar{h}^2}{2m(2a)^2},$$

which happen to be precisely the allowed energies for the *infinite* square well.

3 Formalism

Quantum theory is based on two constructs: *wave functions* and *operators*. The state of a system is represented by its wave function, observables are represented by operators. Mathematically, wave functions satisfy the defining conditions for abstract **vectors**, and operators act on them as **linear transformations**. So the natural language of quantum mechanics is **linear algebra**. So that's why we first have a recap on vector spaces and then continue on to some new concepts.

Recap on some Linear Algebra, which you should kind of know..

3.0.1 Vector Spaces

A **vector space** is a set of vectors $|\alpha\rangle, |\beta\rangle, ...$ and scalars $a, b, ...$ which is closed under some certain operations.

Vector addition
$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle$$

Vector addition is *commutative*: $|\alpha\rangle + |\beta\rangle = |\beta\rangle + |\alpha\rangle$ and *associative*: $|\alpha\rangle + (|\beta\rangle + |\gamma\rangle)$. It works with the *null vector*: $|\alpha\rangle + |0\rangle = |\alpha\rangle$ and adding a vector to it's *inverse* gives the null vector: $|\alpha\rangle + |-\alpha\rangle = |0\rangle$.

Scalar Multiplication
$$a \cdot |\alpha\rangle$$

Scalar multiplication is *distributive*: $a \cdot (|\alpha\rangle + |\beta\rangle) = a \cdot |\alpha\rangle + a \cdot |\beta\rangle$, and also *associative* $a \cdot b \cdot |\alpha\rangle$. The *unit scalar* is given by $1 \cdot |\alpha\rangle = |\alpha\rangle$ and the *zero scalar* is given by $0 \cdot |\alpha\rangle = |0\rangle$.

A vector can be a **linear combination** of some vectors, if a vector isn't a linear combination it is called **linearly independent**. A collection of vectors **spans** the vector space if and only if every vector in the vector space is a linear combination of this collection of vectors:

$$|\alpha\rangle = \sum \alpha_i \cdot |e_i\rangle$$

Here the collection of vectors $|e_i\rangle$ is called a **basis** of the vector space and the number of vectors in this basis is the **dimension** of the vector space.
A vector space has an **orthonormal basis** when

$$\langle e_i | e_j \rangle = \delta_{ij}$$

3.0.2 Inner Product Spaces

Given two vectors, $|\alpha\rangle$ and $|\beta\rangle$, the **inner product**, $\langle \alpha | \beta \rangle$, will be the complex number

$$\langle \alpha | \beta \rangle = \sum_i \alpha_i^* \beta_i.$$

Two properties of the inner product are

$$\langle \alpha | \beta \rangle^* = \langle \beta | \alpha \rangle,$$

and

$$\langle \alpha | \alpha \rangle = \sum_i \alpha_i^* \alpha_i,$$

this second property is the same as the (square of the) norm of a vector, $||\alpha||^2$, and is real and non-negative.

Schwarz inequality says that
$$|\langle \alpha | \beta \rangle|^2 \leq \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle$$

Linear transformations, T, are represented by matrices, which act on vectors to produce new vectors.

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

3.1   Hilbert Space

Now we have looked at some linear algebra basics we can apply it to quantum mechanics. In quantum mechanics the "vectors" we encounter are *functions*, and they live in infinite-dimensional spaces. The collection of *all* functions of x constitutes a vector space, but for our purposes it is much too large. We will look at the set of all **square-integrable functions**, on a specified interval

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

which is called **Hilbert space**. So **wave functions live in Hilbert space.**

We define the **inner product of two functions**, $f(x)$ and $g(x)$, as follows:

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

The integral **Schwarz inequality** says

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

The inner product for integrals also has two notable properties which are very similar to their vector counterparts

$$\langle g|f \rangle = \langle f|g \rangle^* \qquad\qquad \text{and} \qquad\qquad \langle f|f \rangle = \int_a^b |f(x)|^2 dx$$

The inner product can also give you information about functions:

- a function is said to be **normalized** if $\langle f|f \rangle = 1$,
- two functions are **orthogonal** if $\langle f|g \rangle = 0$,
- a set of functions are **orthonormal** if $\langle f_m|f_n \rangle = \delta_{mn}$.

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

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

If the functions $f_n(x)$ are orthonormal, the coefficients are given by

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

3.2   Observables

3.2.1   Hermitian Operators

The expectation value of an observable $Q(x, p)$ can be expressed in inner-product notation:

$$\langle Q \rangle = \left\langle \Psi|\hat{Q}\Psi \right\rangle = \int \Psi^* \hat{Q}\Psi \, dx.$$

The expectation value has to be real, thus

$$\langle Q \rangle = \langle Q \rangle^*,$$

but the complex conjugate of an inner product reverses the order, so

$$\left\langle \Psi|\hat{Q}\Psi \right\rangle = \left\langle \hat{Q}\Psi|\Psi \right\rangle.$$

This must hold true for any wave function. **Observables are represented by hermitian operators**. An operator is **hermitian** if

$$\left\langle f|\hat{Q}g \right\rangle = \left\langle \hat{Q}f|g \right\rangle \qquad\qquad \text{for all } f(x) \text{ and all } g(x)$$

3.2.2   Determinate States

Determinate states for the observable Q are states where every measurement of Q is certain to return the same value q. We've seen an example of determinate states before with the stationary states, which are determinate states of the Hamiltonian.
Determinate states are eigenfunctions of $\hat{Q}$.

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

This is the **eigenvalue equation** for the operator $\hat{Q}$; Ψ is an **eigenfunction** of $\hat{Q}$, and q is the corresponding **eigenvalue** (a *number*). The collection of all the eigenvalues of an operator is called its **spectrum**. Sometimes two (or more) linearly independent eigenfunctions share the same eigenvalue; in that case the spectrum is said to be **degenerate**.

3.3   Eigenfunctions of a Hermitian Operator

Our attention is thus directed to the *eigenfunctions of hermitian operators*. These fall into two categories: If the spectrum is **discrete** (i.e., the eigenvalues are separated from one another) then the eigenfunctions lie in Hilbert space and they constitute physically realizable states. If the spectrum is **continuous** (i.e., the eigenvalues fill out an entire range) then the eigenfunctions are not normalizable, and they do not represent possible wave functions.

3.3.1   Discrete Spectra

Mathematically, the normalizable eigenfunctions of a hermitian operator have three important properties:

- **Realness**: Their eigenvalues are *real*.

- **Orthogonality**: Eigenfunctions belonging to distinct eigenvalues are *orthogonal*.

- **Completeness**: The eigenfunctions of an observable operator are *complete*: Any function (in Hilbert space, a *finite*-dimensional vector space) can be expressed as a linear combination of them.

Unfortunately this tells us nothing about degenerate states. But, if two (or more) eigenfunctions share the same eigenvalue, any linear combination of them is itself an eigenfunction, with the same eigenvalue, and we can use the **Gram-Schmidt orthogonalization procedure** to construct orthogonal eigenfunctions within each degenerate subspace. So *even in the presence of degeneracy* the eigenfunctions can be *chosen* to be orthogonal.

3.3.2   Continuous Spectra

If the spectrum of a hermitian operator is continuous (so the eigenvalues are labeled by a continuous variable, p or y, as in the examples in the book; or z, generically), the eigenfunctions are not normalizable, they are not in Hilbert space and they do not represent possible physical states; nevertheless, the eigenfunctions with *real* eigenvalues have **Dirac orthonormality**

$$\langle f'_z | f_z \rangle = \delta(z - z'),$$

which is strikingly reminiscent of true orthonormality, the indices are now continuous variables, and the Kronecker delta has become a Dirac delta. These eigenfunctions with *real* eigenvalues also are complete (with the sum now an integral).

3.4   Generalized Statistical Interpretation

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

$$|c_n|^2, \text{ where } c_n = \langle f_n | \Psi \rangle .$$

If the spectrum is continuous, with real eigenvalues $q(z)$ and associated Dirac orthonormalized eigenfunctions $f_z(x)$, the probability of getting a result in the range dz is

$$|c(z)|^2 dz, \text{ where } c(z) = \langle f_z | \Psi \rangle .$$

Upon measurement, the wave function "collapses" to the corresponding eigenstate, for continuous spectra the collapse is to a narrow range about the measured value.

The momentum space wave function, $\Phi(p,t)$, is given by

$$\Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} e^{-ipx/\hbar}\Psi(x,t)\,dx.$$

It is essentially the Fourier transform of the (position space) wave function $\Psi(x,t)$, which, by Plancherel's theorem, is its *inverse* Fourier transform:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} e^{ipx/\hbar}\Phi(p,t)\,dp.$$

According to the generalized statistical interpretation, the probability that a measurement of momentum would yield a result in the range dp is

$$|\Phi(p,t)|^2\,dp$$

3.5   The Uncertainty Principle

3.5.1   Proof of the Generalized Uncertainty Principle

The (generalized) **uncertainty principle** is given by

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

There is an "uncertainty principle" for *every pair of observables whose operators do not commute*, these observables are also known as **incompatible observables**. Incompatible observables do not have shared eigenfunctions, at least, they cannot have a complete set of common eigenfunctions. By contrast, *compatible* (commuting) observables *can* have complete sets of simultaneous eigenfunctions.
Note that the uncertainty principle is not an extra *assumption* in quantum theory, but rather a *consequence* of the statistical interpretation.

3.5.2   The Minimum-Uncertainty Wave Packet

We have twice encountered wave functions that hit the position-momentum uncertainty limit: the ground state of the harmonic oscillator and the Gaussian wave packet for the free particle. This raises an interesting question: What is the most general minimum-uncertainty wave packet?

Tweaking the proof of the generalized uncertainty principle a little bit gives rise to the following condition for minimum uncertainty:

$$g(x) = iaf(x),\text{ where } a \text{ is real.}$$

(Also $f = (\hat{A} - \langle A\rangle)\Psi$ and $g = (\hat{B} - \langle B\rangle)\Psi$, this is shown in the proof of the generalized uncertainty principle in the book.)

For the position-momentum uncertainty principle this criterion becomes:

$$\left(\frac{\hbar}{i}\frac{d}{dx} - \langle p\rangle\right)\Psi = ia(x - \langle x\rangle)\Psi,$$

for which the general solution is

$$\Psi(x) = Ae^{-a(x-\langle x\rangle)^2/2\hbar}e^{i\langle p\rangle x/\hbar}.$$

Evidently the minimum-uncertainty wave packet is a *gaussian*—and the two examples we encountered earlier were *gaussians*.

3.5.3   The Energy-Time Uncertainty Principle

The position-momentum uncertainty principle is often paired with the **energy-time uncertainty principle**,

$$\Delta t\, \Delta E \geq \frac{\bar{h}}{2}.$$

In the context of special relativity the energy-time form might be thought of as a *consequence* of the position-momentum version, because x and t go together in the position-time four-vector, while p and E go together in the energy-momentum four-vector.

In the energy-time uncertainty principle Δt doesn't represent the standard deviation of a collection of time measurements, but it represents *the amount of time it takes the expectation value of Q to change by one standard deviation.* This is shown by the formula

$$\sigma_Q = \left| \frac{d\,\langle Q \rangle}{dt} \right| \Delta t.$$

And the time derivative of the expectation value of some operator, $Q(x, p, t)$, is given by

$$\frac{d}{dt}\langle Q \rangle = \frac{i}{\bar{h}} \left\langle [\hat{H}, \hat{Q}] \right\rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle.$$

3.6   Dirac Notation

The notation of the inner product, $\langle \alpha | \beta \rangle$, is called the **bra-ket**, or Dirac, notation and can be split into two pieces, **bra**, $\langle \alpha |$, and **ket**, $| \beta \rangle$. The ket is a "normal" column vector

$$|\alpha\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix},$$

and the corresponding bra is its **Hermitian conjugate** (†), which is the combination of the transpose ($^\top$) and the complex conjugate (*):

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

4   Quantum Mechanics in Three Dimensions

4.1   Schrödinger Equation in Spherical Coordinates

When generalizing to 3 dimensions, momentum becomes:

$$\mathbf{p} \to \frac{\bar{h}}{i} \nabla$$

Thus:

$$i\bar{h} \frac{\partial \Psi}{\partial t} = -\frac{\bar{h}^2}{2m} \nabla^2 \Psi + V \Psi.$$

Here

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

of course is the **Laplacian**. The potential energy and the wave function now are functions of $\mathbf{r} = (x, y, z)$ and t. The normalization condition now reads

$$\int |\Psi|^2 d^3\mathbf{r} =, 1$$

with the integral taken over all space and the infinitesimal volume $d^3\mathbf{r} = dx\,dy\,dz$. If the potential is independent of time we can still use the separation of variables and there will be a complete set of stationary states:

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})\, e^{-iE_n t/\hbar}.$$

And the the time-independent Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

4.1.1   Seperation of Variables

To make our lives easier in the long run we want to adopt **spherical coordinates**, (r, θ, ϕ),

$$x = r\sin\theta\cos\phi,$$
$$y = r\sin\theta\sin\phi,$$
$$z = r\cos\theta.$$

In spherical coordinates the Laplacian takes the form

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$

In spherical coordinates, then, the time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + V\psi = E\psi$$

We begin by looking for solutions that are separable into products:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Some derivation later gives us two equations, one that only depends on r and one that depends on θ and ϕ. Both must be a constant, we will write this "separation constant" in the form $l(l+1)$:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1);$$
$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -l(l+1).$$

4.1.2   The Angular Equation

First we will look at the angular equation, that depends on θ and ϕ. For this equation we can once again use separation of variables:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi).$$

This again gives us two equations, one that only depends on θ and one that only depends on ϕ. Again both must be a constant, this time we will call the separation constant m^2:

$$\frac{1}{\Theta}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta = m^2;$$
$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2.$$

The general solution of $\Phi(\phi)$ then is

$$\Phi(\phi) = e^{im\phi},$$

here m is an *integer* that can be positive and negative. Also it is natural to require that

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

The general solution of $\Theta(\theta)$ isn't that easy. The solution is

$$\Theta(\theta) = AP_l^m(\cos\theta),$$

here P_l^m is the associated **Legendre function**, defined by

$$P_l^m(x) \equiv (1 - x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x),$$

and $P_l(x)$ is the lth **Legendre polynomial**, defined by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l.$$

Important to note is that l must be a nonnegative *integer* and that the values of m range from $-l$ to l, with integer intervals, because of this for any given l there are $(2l + 1)$ possible values of m. Mathematically speaking there exist solutions for *any old* values of l and m, but physically speaking some solutions are unacceptable.

The normalized angular wave functions are called **spherical harmonics**:

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

here $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. These are automatically orthogonal, so

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \phi)]^* \left[Y_{l'}^{m'}(\theta, \phi) \right] \sin \theta \, d\theta \, d\phi = \delta_{ll'} \delta_{mm'}.$$

For historical reasons, l is called the **azimuthal quantum number**, and m the **magnetic quantum number**.

4.1.3   The Radial Equation

Notice that the *angular* part of the wave function, $Y(\theta, \phi)$, is the same for all spherically symmetric potentials; the actual shape of the potential, $V(r)$, affects only the *radial* part of the wave function, $R(r)$.
The **radial equation** is given by

$$-\frac{\bar{h}^2}{2m} \frac{d^2 u}{dx^2} + \left[V + \frac{\bar{h}^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu,$$

here the m's are masses and

$$u(r) \equiv rR(r).$$

As you can see the radial equation is *identical in form* to the one-dimensional Schrödinger equation, except that the effective potential contains an extra term called the **centrifugal term**. It tends to throw the particle outward (away from the origin).
For the radial equation the normalization condition becomes

$$\int_0^\infty |u|^2 \, dr = 1.$$

This is all we can do with the radial part of the wave function until a specific potential $V(r)$ is provided.

4.2   The Hydrogen Atom

The hydrogen atom consists of a heavy, essentially motionless proton, of charge e, together with a much lighter electron (charge $-e$) that orbits around it, bound by the mutual attraction of opposite charges. From Coulomb's law, the potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

4.2.1 The Radial Wave Function

The radial equation now is

$$-\frac{\bar{h}^2}{2m}\frac{\mathrm{d}^2 u}{\mathrm{d}x^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\bar{h}^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu,$$

and we will be looking at the discrete *bound* states, representing the hydrogen atom.

The allowed energies of this equation are given by the **Bohr formula**:

$$E_n = -\left[\frac{m}{2\bar{h}^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \text{ with } n = 1, 2, 3, ...$$

The energy of the **ground state** is given by:

$$E_1 = -\left[\frac{m}{2\bar{h}^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6 \text{ eV}$$

Evidently the **binding energy** of hydrogen (the amount of energy you would have to impart to the electron in the ground state in order to ionize the atom) is 13.6 eV.

The most probable distance between the nucleus and the electron in a hydrogen atom in its ground state is the so-called **Bohr radius** and is given by

$$a \equiv \frac{4\pi\epsilon_0\bar{h}^2}{me^2} = 0.529 \times 10^{-10} \text{ m}$$

The normalized hydrogen wave functions are

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$
$$= \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}e^{-r/na}\left(\frac{2r}{na}\right)^l\left[L_{n-l-1}^{2l+1}(2r/na)\right]Y_l^m(\theta,\phi).$$

Here

$$L_{q-p}^p(x) \equiv (-1)^p\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^p L_q(x)$$

is an **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^q (e^{-x}x^q)$$

is the qth **Laguerre polynomial**.

The ground state of hydrogen is given by

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

4.2.2 The Spectrum of Hydrogen

If you perturb an hydrogen atom (by collision with another atom, say, or by shining light on it), the electron may undergo a **transition** to some other stationary state—either by *absorbing* energy, and moving up to a higher-energy state, or by *giving off* energy (typically in the form of electromagnetic radiation), and moving down. In practice transitions are constantly occurring, the energy of the given off light (photons) corresponds to the difference in energy between the initial and final states:

$$E_\gamma = E_i - E_f = -13.6 \text{ eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right).$$

The Planck formula says that the energy of a photon is proportional to its frequency:

$$E_\gamma = h\nu.$$

And the **Rydberg formula** connects the wavelength to the principal quantum number

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),$$

where the **Rydberg constant** is given by:

$$R \equiv \frac{m}{4\pi c \bar{h}^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = 1.097 \times 10^7 \text{ m}^{-1}.$$

The different series of hydrogen transitions also have names:

- The **Lyman series** consists of transitions to the ground state ($n_f = 1$).
- The **Balmer series** consists of transitions to the first exited state ($n_f = 2$).
- The **Paschen series** consists of transitions to the second exited state ($n_f = 3$).

And the list goes on like that.

4.3   Angular Momentum

Classically, the angular momentum of a particle (with respect to the origin) is given by the formula

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}.$$

This gives us in quantum mechanics three angular momentum operators:

$$L_x = yp_z - zp_y, \qquad\qquad L_y = zp_x - xp_z, \qquad\qquad L_z = xp_y - yp_x,$$

with of course

$$p_x \to -i\bar{h}\,\partial/\partial x, \qquad\qquad p_y \to -i\bar{h}\,\partial/\partial y, \qquad\qquad p_z \to -i\bar{h}\,\partial/\partial z.$$

4.3.1   Eigenvalues

Our three angular momentum operators sadly do not commute:

$$[L_x, L_y] = i\bar{h}L_z, \qquad\qquad [L_y, L_z] = i\bar{h}L_x, \qquad\qquad [L_z, L_x] = i\bar{h}L_y.$$

This makes them *incompatible* observables. According to the generalized uncertainty principle,

$$\sigma_{L_x}\sigma_{L_x} \geq \frac{\bar{h}}{2}|\langle L_z \rangle|.$$

But introducing the square of the total angular momentum,

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2,$$

helps us immensely, since this *does* commute with all three angular momentum operators. With this we can find simultaneous eigenstates of L^2 and (let's say) L_z:

$$L^2 f = \lambda f \qquad\qquad \text{and} \qquad\qquad L_z f = \mu f.$$

We'll use a "ladder operator" technique like we've seen before

$$L_\pm \equiv L_x \pm iL_y.$$

This operator of is of course compatible with L^2 and its commutator with L_z is $[L_z, l_\pm] = \pm\bar{h}L_\pm$. If f is an eigenfunction of L^2 and L_z, so also is $L_\pm f$:

$$L^2(L_\pm f) = \lambda(L_\pm f), \qquad\qquad L_z(L_\pm f) = (\mu \pm \bar{h})(L_\pm f).$$

We call L_+ the "raising" operator, because it *increases* the eigenvalue of L_z by $\bar{h}$, and L_- the "lowering" operator, because it *lowers* the eigenvalue by $\bar{h}$. In contrary to the harmonic oscillator ladder this ladder has both a top and a bottom rung, such that

$$L_+ f_{\text{top}} = 0 \hspace{4cm} L_- f_{\text{bottom}} = 0$$

The eigenvalues of L^2 and L_z are given by

$$L^2 f_l^m = \bar{h}^2 l(l+1) f_l^m \hspace{2cm} \text{and} \hspace{2cm} L_z f_l^m = \bar{h} m f_l^m,$$

where

$$l = 0, 1/2, 1, 3/2, ...; \hspace{3cm} m = -l, -l+1, ..., l-1, l,$$

and the eigenfunctions are characterized by the numbers l and m. For a given value of l, there are $2l+1$ different values of m (i.e., $2l+1$ "rungs" on the "ladder").

4.3.2 Eigenfunctions

The operator L_z is given by

$$L_z = \frac{\bar{h}}{i} \frac{\partial}{\partial \phi}$$

and the operator L^2 is given by

$$L^2 = -\bar{h}^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right].$$

But we've solved this before! The result (appropriately normalized) is the spherical harmonic, $Y_l^m(\theta, \phi)$. Conclusion: Spherical harmonics are eigenfunctions of L^2 and L_z. There is a curious final twist to this story, for the *algebraic* theory of angular momentum permits l (and hence also m) to take on *half*-integer values, whereas separation of variables yielded eigenfunctions only for *integer* values.

4.4 Spin

In classical mechanics, a rigid object admits two kinds of angular momentum: **orbital** ($\mathbf{L} = \mathbf{r} \times \mathbf{p}$), associated with the motion *of* the center of mass, and **spin** ($\mathbf{S} = I\omega$), associated with motion *about* the center of mass. Elementary particles carry **intrinsic** angular momentum ($\mathbf{S}$) in addition to their "extrinsic" angular momentum ($\mathbf{L}$). The *algebraic* theory of spin is a carbon copy of the theory of orbital angular momentum, beginning with the fundamental commutation relations:

$$[S_x, S_y] = i\bar{h}S_z, \hspace{2cm} [S_y, S_z] = i\bar{h}S_x, \hspace{2cm} [S_z, S_x] = i\bar{h}S_y.$$

It follows (as before) that the eigenvectors of S^2 and S_z satisfy

$$S^2 \left| s\, m \right\rangle = \bar{h}^2 s(s+1) \left| s\, m \right\rangle; \hspace{2cm} S_z \left| s\, m \right\rangle = \bar{h} m \left| s\, m \right\rangle;$$

and

$$S_\pm \left| s\, m \right\rangle = \bar{h}\sqrt{s(s+1) - m(m \pm 1)} \left| s\, (m \pm 1) \right\rangle,$$

with $S_\pm \equiv S_x \pm iS_y$ and

$$s = 0, 1/2, 1, 3/2, ...; \hspace{3cm} m = -s, -s+1, ..., s-1, s.$$

It so happens that every elementary particle has a *specific and immutable* value of s, which we call the **spin** of that particular species, some particles include:

- spin 0: pi mesons,

- spin 1/2: proton, neutron, electron, neutrino, and quarks,

- spin 1: photon, Z and W bosons, gluons,

- spin 3/2: deltas,

- spin 2: gravitons.

4.4.1   Spin 1/2

When you have a particle with spin 1/2 then there are just two eigenstates:

$$\textbf{Spin up} \ : \ \left|\frac{1}{2}\frac{1}{2}\right\rangle \text{ and}$$

$$\textbf{Spin down} \ : \ \left|\frac{1}{2}\left(-\frac{1}{2}\right)\right\rangle.$$

Using these as basis vectors, the general state of a spin-1/2 particle can be expressed as a two-element column matrix (or **spinor**):

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-,$$

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ representing spin up, and}$$

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ representing spin down.}$$

Then using the eigenvalues of the operators S^2, $S_\pm$ and S_z we can find the matrix representation for the spin operators. For this we get:

$$\mathbf{S}^2 = \frac{3}{4}\bar{h}^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad\qquad \mathbf{S}_+ = \bar{h} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad\qquad \mathbf{S}_- = \bar{h} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

For $\mathbf{S}_x$, $\mathbf{S}_y$ and $\mathbf{S}_z$ it is neater to write $\mathbf{S} = \left(\frac{\bar{h}}{2}\right)\sigma$, with

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad\qquad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad\qquad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These last three matrices are the **Pauli spin matrices**.
Note that $\mathbf{S}_x$, $\mathbf{S}_y$, $\mathbf{S}_z$ and S^2 are *hermitian*, since they represent observables and $S_\pm$ *aren't* hermitian, thus not observable.

If you measure S_z on a particle in the general state χ, you could get $+\bar{h}/2$, with probability $|a|^2$, or $-\bar{h}/2$, with probability $|b|^2$. Since these are the only possibilities we get,

$$|a|^2 + |b|^2 = 1$$

4.4.2   Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole moment**, μ, is proportional to its spin angular momentum, $\mathbf{S}$:

$$\mu = \gamma\mathbf{S},$$

here γ is called the **gyromagnetic ratio**.
When a magnetic dipole is placed in a magnetic field $\mathbf{B}$, it experiences a torque, $\mu \times \mathbf{B}$, which tends to line it up parallel to the field (just like a compass needle). The energy associated with this torque is

$$H = -\mathbf{mu} \cdot \mathbf{B},$$

so the Hamiltonian of a spinning charged particle, at rest in a magnetic field $\mathbf{B}$, is

$$H = -\gamma\mathbf{B} \cdot \mathbf{S}.$$

4.4.3 Addition of Angular Momenta

Suppose now that we have two spin-1/2 particles—for example, the electron and the proton in the ground state of hydrogen. Each can have spin up or spin down, so there are four possibilities in all:

$$\uparrow\uparrow,\ \uparrow\downarrow,\ \downarrow\uparrow,\ \downarrow\downarrow,$$

where the first arrow refers to the electron and the second to the proton. This combination of two spin-1/2 particles can carry a total spin of 1 or 0. The three states with $s = 1$ are

$$\left.\begin{cases} |1\,1\rangle & =\uparrow\uparrow \\ |1\,0\rangle & =\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\,-1\rangle & =\downarrow\downarrow \end{cases}\right\}\ s = 1\ (\text{the } \textbf{triplet}\ \text{combination}).$$

The orthogonal state with $m = 0$ carries $s = 0$:

$$\left\{|0\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)\right\}\ s = 0\ (\text{the } \textbf{singlet}).$$

So in a more general form: If you combine spin s_1 with spin s_2, the total spins you can get are

$$s = (s_1 + s_2),\ (s_1 + s_2 - 1),\ (s_1 + s_2 - 2),\ldots,\ |s_1 - s_2|$$

(Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another, and the lowest occurs when they are antiparallel.)

5 Identical Particles

5.1 Two-Particle Systems

The state of a two-particle system is a function of the coordinates of particle one ($\mathbf{r}_1$), the coordinates of particle two ($\mathbf{r}_2$), and the time:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t).$$

Its time evolution is determined (as always) by the Schrödinger equation:

$$i\bar{h}\frac{\partial \Psi}{\partial t} = H\Psi$$

where H is the Hamiltonian for the whole system:

$$H = -\frac{\bar{h}^2}{2m_1}\nabla_1^2 - \frac{\bar{h}^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$$

The statistical interpretation carries over in the obvious way:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

is the probability of finding particle 1 in the volume $d^3\mathbf{r}_1$ and particle 2 in the volume $d^3\mathbf{r}_2$; evidently Ψ must be normalized in such a way that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 1$$

5.1.1 Bosons and Fermions

In quantum mechanics particles are *indistinguishable in principle*. Because of this the wave function of particle 1 that is in the (one-particle) state $\psi_a(\mathbf{r})$, and particle 2 that is in the state $\psi_b(\mathbf{r})$ isn't simply a *product*:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) \neq \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\ (\text{if particles are indistinguishable}).$$

Because we can't do this we need to construct a wave function that is *noncommittal* as to which particle is in which state. There are actually *two* ways to do it:

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]$$

Thus the theory admits two kinds of identical particles: **bosons**, for which we use the plus sign, and **fermions**, for which we use the minus sign. It so happens that

$$\begin{cases} \text{all particles with } integer \text{ spin are bosons, and} \\ \text{all particles with } half\ integer \text{ spin are fermions.} \end{cases}$$

This connection between **spin and statistics** can be *proved* in *relativistic* quantum mechanics; in the nonrelativistic theory it is taken as an axiom.

The famous **Pauli exclusion principle** states that *two or more identical fermions cannot occupy the same state*;

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_a(\mathbf{r}_1)] = 0.$$

This doesn't go for bosons, because there we add the products of the states together.

There is a more general (and more sophisticated) way to formulate this problem. Let us define the **exchange operator**, P, which interchanges the two particles:

$$Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1)$$

Clearly, $P^2 = 1$, and it follows that the eigenvalues of P are ± 1. Now, if the two particles are identical, the Hamiltonian must treat them the same: $m_1 = m_2$ and $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$. It follows that P and H are compatible observables and hence we can find a complete set of functions that are simultaneous eigenstates of both. That is to say, we can find solutions to the Schrödinger equation that are either symmetric (eigenvalue +1) or antisymmetric (eigenvalue -1) under exchange:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi(\mathbf{r}_2, \mathbf{r}_1).$$

For identical particles the wave function is required to satisfy this **symmetrization requirement**. Bosons will get the plus sign and fermions the minus sign.

5.1.2   Exchange Forces

Next we're gonna look at a simple one-dimensional example, to get some sense of what the symmetrization requirement actually *does*.
Suppose one particle is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalized. If the two particles are distinguishable, then the combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2),$$

for identical bosons we get

$$\psi_+(x_1, x_2) = A[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_2)\psi_a(x_1)],$$

and for identical fermions we get

$$\psi_-(x_1, x_2) = A[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_2)\psi_a(x_1)].$$

Now let's calculate the expectation value of the square of the separation distance between the two particles,

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$$

Case 1: Distinguishable particles.   For distinguishable particles the expectation value of the square of the separation distance between the two particles becomes

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b.$$

Case 2: Identical particles.   For identical particles the expectation value of the square of the separation distance between the two particles becomes

$$\langle (x_1 - x_2)^2 \rangle_\pm = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2.$$

It is clear that the only difference resides in the final term:

$$\left\langle (x_1 - x_2)^2 \right\rangle_{\pm} = \left\langle (x_1 - x_2)^2 \right\rangle_d \mp 2|\langle x \rangle_{ab}|^2.$$

Identical bosons (the upper signs) tend to be somewhat closer together, and identical fermions (the lower signs) somewhat farther apart, than distinguishable particles in the same two states. Notice that this only makes a difference when the two wave functions actually *overlap*, if the wavefunctions *don't* overlap $\langle x \rangle_{ab}$ *vanishes*. As a practical matter, therefore, it's okay to pretend that electrons with nonoverlapping wave functions are distinguishable.

The interesting case is when there is some overlap of the wave functions. The system behaves as though there were a "force of attraction" between identical bosons, pulling them closer together, and a "force of repulsion" between identical fermions, pushing them apart. We call it an **exchange force**.

So far we've been ignoring spin. The complete state of the electron includes not only its position wave function, but also a spinor, describing the orientation of its spin:

$$\psi(\mathbf{r})\chi(\mathbf{s}).$$

When we put together the two-electron state, it is the whole works, not just the spatial part, that has to be antisymmetric with respect to exchange. Now, a glance at the composite spin states reveals that the singlet combination is *antisymmetric* (and hence would have to be joined with a *symmetric* spatial function), whereas the three triplet states are all *symmetric* (and would require an *antisymmetric* spatial function).

5.2 Atoms

A neutral atom, of atomic number Z, consists of a heavy nucleus, with electric charge Ze, surrounded by Z electrons (mass m and charge $-e$). The Hamiltonian for this system is

$$H = \sum_{j=1}^{Z} \left\{ -\frac{\bar{h}^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right)\sum_{j \neq k}^{Z}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}.$$

The term in curly brackets represents the kinetic plus potential energy of the jth electron, in the electric field of the nucleus; the second sum (which runs over all values of j and k except $j = k$) is the potential energy associated with the mutual repulsion of the electrons (the factor of $1/2$ in front corrects for the fact that the summation counts each pair twice). The problem is to solve Schrödinger's equation for the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)$. Because electrons are identical fermions, however, not all solutions are acceptable: only those for which the complete state (position and spin),

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_Z),$$

is antisymmetric with respect to interchange of any two electrons. In particular, no two electrons can occupy the same state.

5.2.1 Helium

After hydrogen, the simplest atom is helium ($Z = 2$). The Hamiltonian,

$$H = \left\{ -\frac{\bar{h}^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\bar{h}^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

consists of two hydrogenic Hamiltonians (with nuclear charge $2e$), one for electron 1 and one for electron 2, together with a final term describing the repulsion of the two electrons. If we ignore this last term we can separate the Schrödinger equation, and the solutions can be written as products of hydrogen wave functions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{lnm}(\mathbf{r}_1)\psi_{l'n'm'}(\mathbf{r}_2).$$

This will have only half the Bohr radius, and four times the Bohr energies. The total energy would be

$$E = 4(E_n E_{n'}), \text{ with } E_n = \frac{-13.6}{n^2} \text{ eV}.$$

In particular, the ground state would be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a}, \text{ with } E_0 = -109 \text{ eV.}$$

ψ_0 is a symmetric function, so the spin state has to be *antisymmetric*, so it should be a *singlet* configuration. The *actual* ground state of helium is indeed a singlet, but the experimentally determined energy is -78.975 eV, so ignoring the repulsion of the two electrons didn't give a good value in that regard.
The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited state:

$$\psi_{nlm}\psi_{100}$$

We can construct both symmetric and antisymmetric combinations, in the usual way; the former go with the *antisymmetric* spin configuration (the singlet), and they are called **parahelium**, while the latter require a *symmetric* spin configuration (the triplet), and they are known as **orthohelium**. The ground state is necessarily parahelium; the excited states come in both forms.

5.2.2 The Periodic Table

To first approximation (ignoring their mutual repulsion altogether), individual electrons occupy one-particle hydrogenic states (n, l, m), called **orbitals**. Only two electrons can occupy any given orbital (one with spin up, and one with spin down—or). There are n^2 hydrogenic wave functions (all with the same energy E_n) for a given value of n, so the $n = 1$ shell holds 2 electrons, the $n = 2$ shell holds 8, $n = 3$ takes 18, and in general the nth shell can accommodate $2n^2$ electrons. Qualitatively, the horizontal rows on the **Periodic Table** correspond to filling out each shell, but the electron-electron repulsion throws this counting off.

The state of a particular electron is represented by the pair nl, with n (the number) giving the shell, and l (the letter) specifying the orbital angular momentum; the magnetic quantum number m is not listed, but an exponent is used to indicate the number of electrons that occupy the state in question. This is shown in the following table.

n \ l	s	p	d	f	g
1	2				
2	2	6			
3	2	6	10		
4	2	6	10	14	-

The numbers in the table indicate the total number of atoms that each shell can hold and the arrows indicate the order in which the shells get filled, so the $1s$ shell gets filled first, then $2s$, $2p$, $3s$ and so on.

Another way to express the state of an atom is using the following notation:

$$^{2S+1}L_J,$$

with S as the total spin, L as the total orbital angular momentum and J as the grand total (orbital plus spin).

12 Afterword

In this section we look at some paradoxes that will conclude whether the **realist** viewpoint (did the physical system "actually have" the attribute in question *prior* to the measurement) or the **orthodox** position (did the act of measurement itself "create" the property, limited only by the statistical constraint imposed by the wave function) is the right one.

12.1   EPR paradox

The **EPR paradox** (or the Einstein-Podolsky-Rosen Paradox) is a thought experiment intended to demonstrate an inherent paradox in the early formulations of quantum theory. It is among the best-known examples of quantum entanglement.
Consider the decay of a neutral pi meson into an electron and a positron:

$$\pi^0 \rightarrow e^- + e^+.$$

Both sides will have spin 0, so the electron and positron are in the singlet configuration:

$$\frac{1}{\sqrt{2}}(\uparrow_-\downarrow_+ - \downarrow_-\uparrow_+)$$

The two particles are entangled. If the electron is found to have spin up, the positron must have spin down and vice versa, no matter the distance if you measure spin up for the electron, you will immediately know that the positron will have spin down. For the realists this is logical, the particles will have had their spins from the moment they were created, quantum mechanics just didn't know it. But for the "orthodox" view this is a problem; your measurement of the electron collapsed the wave function, and *instantaneously* "produced" the spin of the positron 20 meters (or 20 light years) away. The fundamental assumption on which the EPR argument rests is that no influence can propagate faster than the speed of light. We call this the principle of **locality**, but the collapse of the wave function-whatever its ontological status-is instantaneous.

12.2   Bell's theorem

Bell suggested a generalization of the EPR/Bohm experiment: Instead of orienting the electron and positron detectors along the same direction, he allowed them to be rotated independently. The first measures the component of the electron spin in the direction of a unit vector $\mathbf{a}$, and the second measures the spin of the positron along the direction $\mathbf{b}$. Bell proposed to calculate the average value of the product of the spins, for a given set of detector orientations. Call this average $P(\mathbf{a}, \mathbf{b})$. For arbitrary orientations, quantum mechanics predicts

$$P(\mathbf{a}, \mathbf{b}) = -\mathbf{a} \cdot \mathbf{b}$$

What Bell discovered is that this result is incompatible with *any local hidden variable theory*.
The famous **Bell inequality** is given by

$$|P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c})| \leq 1 + P(\mathbf{b}, \mathbf{c}).$$

This holds for any local hidden variable theory, but it is easy to show that the quantum mechanical prediction is incompatible with Bell's inequality.

With Bell's modification, then, the EPR paradox proves something far more radical than its authors imagined: If they are right, then not only is quantum mechanics *incomplete*, it is downright *wrong*. On the other hand, if quantum mechanics is right, then no hidden variable theory is going to rescue us from the nonlocality. The results of the experiment were in excellent agreement with the predictions of quantum mechanics, and clearly incompatible with Bell's inequality. So *nature itself is fundamentally nonlocal*. Causality is of course still a thing, causal influences cannot propagate faster than light, but "ethereal" influences (like the entanglement) seemingly can.

12.3   No-clone theorem

You don't need to know this section for the exam

Quantum measurements are typically **destructive**, in the sense that they alter the state of the system measured. This is how the uncertainty principle is enforced in the laboratory. You might wonder why we don't just make a bunch of identical copies (**clones**) of the original state, and measure them, leaving the system itself unscathed. It can't be done. Indeed, if you could build a cloning device, quantum mechanics would be out the window. For example you would be able to send messages using the EPRB experiment and we just figured out that is a no-no. You can make a machine to clone spin-up electrons and spin-down electrons, but it's going to fail for any nontrivial linear combinations.

12.4   Schrodinger's cat

You don't need to know this section for the exam

A cat is penned up in a steel chamber, along with the following device (which must be secured against direct interference by the cat): in a Geiger counter, there is a tiny bit of radioactive substance, so small, that perhaps in the course of the hour one of the atoms decays, but also, with equal probability, perhaps none; if it happens, the counter tube discharges and through a relay releases a hammer that shatters a small flask of hydrocyanic acid. If one has left this entire system to itself for an hour, one would say that the cat still lives if meanwhile no atom has decayed. The first atomic decay would have poisoned it. The psi-function of the entire system would express this by having in it the living and dead cat mixed or smeared out in equal parts.

$$\psi = \frac{1}{\sqrt{2}}(\psi_{\text{alive}} + \psi_{\text{dead}})$$

12.5   Quantum Zeno paradox

You don't need to know this section for the exam

In 1977 Misra and Sudarshan proposed what they called the **quantum Zeno effect** as a dramatic experimental demonstration of the collapse of the wave function. Their idea was to take an unstable system (an atom in an excited state, say), and subject it to repeated measurements. Each observation collapses the wave function, resetting the clock, and it is possible by this means to delay indefinitely the expected transition to the lower state. Proof shows that a continuously observed unstable system never decays at all, but for this to work the measurements must be made extremely rapidly.

As it turns out, the experiment is impractical for spontaneous transitions, but it can be done using induced transitions, and the results are in excellent agreement with the theoretical predictions. Unfortunately, this experiment is not as compelling a confirmation of the collapse of the wave function as its designers hoped; the observed effect can be accounted for in other ways.