Exploring Quantum Physics

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Chapter 1

Wavefunctions and Schrödinger Equations

1.1 Pioneering Experiments

There are many experiments today that exhibit quantum effects. But hundreds of years ago, manifestations of quantum physics were very subtle, due to the lack of precision in experiments and apparatus. In fact, the pre-20th century outlook was that a classical "theory of everything" had already been discovered. However, there were a few theories that exhibited anomalous behavior:

- Black-body radiation
- Quantization of atomic spectra
- Photoelectric effect
- Accident at Bell Labs showed electrons behave like waves (electron diffraction)

Photoelectric Effect Two separated metal plates connected to a voltage source, with UV light illuminating the plates. According to the classical theory of light, increasing the intensity of the light should lead to more energetic photoelectrons emitted from one plate to another. Furthermore, intense light of any frequency should allow some electrons to bridge the gap. However,

- Energy of electrons did not depend on the intensity of the light
- No photoelectrons produced if frequency was smaller than a certain critical value

Einstein's explanation: **photons**. Einstein introduced the idea of energy **quanta**, i.e. energy comes in "packets". This implied a formula of the sort $E = hc/\lambda$, where $h = 2\pi\hbar = 6.626 \times 10^{-34} J \cdot s$.

Davidson and Germer's Experiment Bombarding a nickel target with an electron beam produced diffraction patterns which changed upon annealing the target. The resulting diffraction pattern had peaks in specific angles: this phenomenon is something only waves can exhibit. So they concluded that their electron beam was behaving as if it were a wave. **de Broglie** predicted this earlier by $\lambda = h/mv$.

Summary We have seen there is clear experimental evidence that light sometimes behaves as a beam of particles carrying energy quanta, with $E = hc/\lambda = \hbar\omega$. On the other hand, there is also evidence that electrons sometimes behave as waves, with $\lambda = h/mv$. What is going on?

1.2 "Deriving" the Schrödinger Equation

Before we begin, consider the question: "what is more fundamental, particles or waves?" A **particle** has a well-defined velocity and position at any given time. In contrast, a **wave** is characterized by

$$u(x,t) = A_0 \sin(kx - \omega t + \phi_0) = A_0 \mathrm{Im}\{e^{i(kx-\omega t+\phi_0)}\}$$

And therefore it does not really make sense to ask where the wave is located, though we can identify the wave velocity and the wave vector. Recall that $\lambda = 2\pi/k$, and $\omega = ck$, where c is the wave speed.

Representation It is difficult to represent a wave as particles, but we can decompose a localized particle into waves using a **Fourier transform**:

$$f(x) = \int dk\, A_k e^{ikx}$$

Deriving wave equation from its solution Based on this, it seems reasonable to try to describe our quantum mechanical objects as waves. Consider Davidson and Germer's experiment. We postulate that for an electron, its **wave function** is

$$\Psi(x,t) = Ce^{i(kx-\omega t)}$$

To relate this to some quantities, recall that $p = \hbar k$, and $E = \hbar\omega$. Then Ψ becomes

$$\Psi(x,t) = Ce^{\frac{i}{\hbar}(px-Et)}$$

But what equation does Ψ satisfy? Well, we have the kinetic energy of a free particle $K = mv^2/2 = p^2/2m$ (since $p = mv$). We demand that whatever equation we get must give Ψ as a solution, but furthermore, we enforce that whatever E comes out, it must satisfy $p^2/2m$. A reasonable, naive guess is to assume that the electron wave-function satisfies the usual wave equation:

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\Psi = 0$$

But plugging Ψ in, we find that $\omega = ck$, and $E = cp$, which works for electromagnetic waves, but is not what we want for E. It turns out that the simplest such equation satisfying the desired properties can be constructed by noting that

$$\frac{\partial}{\partial t}\Psi = -\frac{i}{\hbar}E\Psi$$
$$\frac{\partial}{\partial x}\Psi = \frac{i}{\hbar}p\Psi$$

Hence we have $E = i\hbar\partial/\partial t$, and $\hat{p} = -i\hbar\partial/\partial x$, or, in multiple dimensions, $\hat{\vec{p}} = -i\hbar\nabla$. If we want to enforce that $E = p^2/2m$, we get

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

Rearranging, we get

$$\left(i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2\nabla^2}{2m}\right)\Psi = 0$$

This is the **free Schrödinger equation**. We are going to identify the right hand side with the **Hamiltonian** $\hat{H}$, which for an interacting particle is $\hat{H} = \hat{\vec{p}}^2/2m + V(\vec{r})$, and so the equation is better written as

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

Note that we can't actually derive a fundamental law of physics like this. But this is a good guess.

1.3 Spreading of quantum wave packets

Let's use the Schrödinger equation (abbreviated S.Eq. from now on) we just derived to do something useful. Assume we have a Gaussian wave-packet at $t = 0$, described by

$$\Psi(x, 0) = A \exp\left(-\frac{x^2}{2d^2}\right)$$

It turns out that solving the S.Eq. with this initial condition, we get the unstable solution

$$|\Psi(x, t)|^2 \propto \exp\left(-\frac{x^2}{d^2(1 + t^2/\tau^2)}\right) \qquad \tau = \frac{md^2}{\hbar}$$

This shows that as time goes on, our wave-packet slowly flattens out, i.e. it **delocalizes**. But the time scale is important. Let's consider the typical delocalization time. For an electron, whose $m \approx 10^{-27}$ g, and $d \approx 10^{-8}$ cm, we get $\tau \approx 10^{-16}$ s, whereas if we take a human being, whose $m \approx 50$ kg, and $d \approx 1$ cm, we get $\tau \approx 10^{30}$ s, which is longer than the lifetime of the Universe. Hence we see that quantum mechanical effects only start appearing in microscopic scales.

Solution derivation How do we get this solution? Start by decomposing the wave-packet into plane-waves:

$$\Psi(x, 0) = A \exp\left(-\frac{x^2}{2d^2}\right) = \int \frac{dp}{2\pi\hbar} \phi_p e^{\frac{i}{\hbar}px}$$

Why do we want to do something like this? Well, we derived the S.Eq. from plane-waves, and so we hope this will simplify thing a little. Note that the above equation follows from the **Gaussian integral**, which we will be using in this derivation a few times:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2 + \beta x}\, dx = \sqrt{\frac{\pi}{\alpha}} e^{\frac{\beta^2}{4\alpha}}$$

The Fourier coefficients are commonly called the **wave-function in the momentum space**, and are

$$\phi_p = \int dx\, \Psi(x, 0) e^{-\frac{i}{\hbar}px} \propto e^{-\frac{p^2 d^2}{2\hbar^2}}$$

We will now interpret this Fourier transform in an interesting way. The uncertainty of our wave packet is $\Delta x \approx d$, and $\Delta p \approx \hbar/d$, and we see that these two are inverses of each other in our exponential, which is a particular manifestation of the **Heisenberg uncertainty principle**. Now we are in a position to solve the S.Eq. with our initial condition:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \frac{\hat{p}^2}{2m} \Psi(x, t)$$
$$\Psi(x, 0) \propto \int dp\, e^{-\frac{p^2 d^2}{2\hbar^2}} e^{\frac{i}{\hbar}px}$$

Observe that the S.Eq. is a linear equation, hence if $\Psi_1, ...$ are solutions, their sum is also a solution, with initial condition $\Psi(x, 0) = \sum_n \Psi_n(x, 0)$. Also, recall that a plane wave $e^{(i/\hbar)(px - \epsilon(p)t)}$ where $\epsilon(p) = p^2/2m$ satisfies the S.Eq. So the wave-packet time-evolves as

$$\Psi(x, t) \propto \int dp\, e^{-\frac{p^2 d^2}{2\hbar^2}} \exp\left(\frac{i}{\hbar}\left(px - \frac{p^2 t}{2m}\right)\right)$$

This follows from the linearity of the S.Eq. But this is just a Gaussian integral, so we get

$$\Psi(x, t) \propto \exp\left(-\frac{x^2}{2d^2}\left(1 + \frac{i\hbar t}{md^2}\right)^{-1}\right)$$

It turns out that we only care about $|\Psi|^2$ (we will cover this later). Squaring, we get the desired result.

Chapter 2

A Physical Interpretation of Quantum Theory

2.1 Meaning of the wave function; the Born rule

What is the meaning of the wave function? We introduced it in an abstract fashion, but never talked about its physical interpretation. Recall the S.Eq.:

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

It turns out that Schrödinger came up with this equation by formalizing some of de Broglie's earlier work on wave-particle duality. In Schrödinger's original paper introducing the wave function, he used his equation to solve a very important problem regarding a charged particle in a Coulomb potential, and found the energy level structure consistent with Bohr's atom, indicating that he was on the right track. But it turns out that Schrödinger's original paper did not contain much insight into the physical interpretation of his own work; whether he actually understood it is debated. Later on, though, Born gave a physical interpretation consistent with experimental data.

Born interpretation Before we begin, let's consider a classical system. If we know everything about this syteem, i.e. all the coordinates and velocities of every particle in the system, classical physics predicts with absolute certainty the result of every experiment that will happen in the future. But with a quantum system, even if we know everything possible about the system, we still cannot possibly predict with certainty the outcome of well-posed experiments. For example, if we have a detector to detect electrons emitted from the system, even if we know everything we cannot predict which detector will pick up what electron at what time. Born found a way to quantify this **uncertainty** using the S.Eq: $|\Psi(x,y,z;t)|^2\,dx\,dy\,dz$ gives the probability of finding the quantum particle (described by $\Psi(\vec{r},t)$) in the volume element $dV = dx\,dy\,dz$ at time t.

2.2 Continuity Equation

We need to derive the continuity equation for the probability in Born's interpretation of quantum theory. It also serves as a sanity check for Born's interpretation, because it guarantees **"conservation of probability"**, i.e. we shouldn't have a particle with negative probability of being somewhere at some time, nor should it exceed one, and probability rules should generally be obeyed if we take Born's interpretation. *Note: this derivation is technical.*

Continuity equation We have

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0$$

where $\rho(\vec{r}, t) = |\Psi(\vec{r}, t)|^2$. To see that this indeed gives a conservation law, let's consider an arbitrary volume V in space, with boundary area ∂V. We are interested in the probability of finding our quantum particle inside this volume:

$$p_V = \int_V \rho \, d^3\vec{r}$$

To look at the dynamics of this probability with time, let's integrate both sides of the continuity equation over V:

$$\frac{\partial p_V}{\partial t} + \int_V d^3\,\vec{r}\,\nabla \cdot \vec{j} = 0$$

Now we can use Gauss's law simplify the integral of the divergence:

$$\frac{\partial p_V}{\partial t} = -\oint_{\partial V} \vec{j} \cdot d\vec{s} = 0$$

Then to prove the continuity equation, we need to calculate the probability of finding the particle in V using the Born rule:

$$\frac{\partial p_V}{\partial t} = \frac{\partial}{\partial t} \int_V \Psi^* \Psi \, d^3\vec{r} = \int_V \left(\frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t} \right) d^3\vec{r}$$

But now we can use the S.Eq., which gives us that

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{h} \hat{H} \Psi \quad \frac{\partial \Psi^*}{\partial t} = \frac{i}{h} \hat{H} \Psi^*$$

So plugging this into the equation earlier, we get

$$\frac{\partial p_V}{\partial t} = \int_V \left(\frac{i}{h} (\hat{H} \Psi^*) \Psi - \frac{i}{h} \Psi^* (\hat{H} \Psi) \right) d^3\vec{r}$$

Note that since $\hat{H} = \hat{K} + u$, the potential u cancels out but the $\hat{K}$ does not necessarily. But we know that

$$\hat{K} = \frac{\hat{\vec{p}}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2$$

Hence plugging this in, we get

$$\frac{\partial p_V}{\partial t} = -\frac{i\hbar}{2m} \int_V \left((\nabla^2 \Psi^*) \Psi - \Psi^* (\nabla^2 \Psi) \right) d^3\vec{r}$$

The last step is to pull out a gradient from the Laplacian, which gives

$$\frac{\partial p_V}{\partial t} = -\frac{i\hbar}{2m} \int_V \nabla \cdot \left((\nabla \Psi^*) \Psi - \Psi^* (\nabla \Psi) \right) d^3\vec{r} = -\oint \vec{j} \cdot d\vec{s}$$

But this is exactly the current $\vec{j}$ we were looking for. Writing $\vec{j}$ out fully, it is

$$\vec{j} = \frac{1}{2} \left(\Psi^* \frac{\hat{\vec{p}}}{m} \Psi + \Psi \frac{\hat{\vec{p}}}{m} \Psi^* \right)$$

2.3 Observables, operators, and expectation values

Our derivation of the continuity equation involved operators, which play an important role in the mathematical formalism of quantum mechanics. Recall that we "derived" the Schrödinger equation by assuming that quantum electrons may exhibit wave-like properties, which led us to assume that the electron can be described by a plane-wave function $\Psi(\vec{r},t) = e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r}-Et)}$. Reconciling this with $E = \hat{p}^2/2m$ gave us the free Schrödinger equation. But we abstracted the right hand side as a Hamiltonian, i.e. as an **operator**. In other words, we were forced to take classical properties and turn them into operators acting on the wave-function:

- **momentum** became $\hat{\vec{p}} = -i\hbar\nabla$.
- **coordinate** became $\hat{\vec{r}} = \vec{r}$ (multiplication operator).
- **kinetic energy** became $\hat{K} = -(\hbar^2\nabla^2)/(2m)$.

As another example, angular momentum in classical physics is $\vec{L} = \vec{r}\times\vec{p}$, and to make it into an operator we simply put a hat on top of everything:

$$\hat{\vec{L}} = \hat{\vec{r}}\times\hat{\vec{p}} = -i\hbar\vec{r}\times\nabla$$

Expectation values What is the physical significance of these operators? We can directly measure their classical counterparts, but what do we do with operators? Well, let's first answer the question in a special case and then generalize. Consider the measurement of the coordinate of a particle, which from the Born rule is probabilistically described by $|\Psi(\vec{r})|^2$. From statistics, we know that given a **probability density function (PDF)** $F(x)$, we can find the average value of x by

$$\langle x\rangle = \int dx\, xF(x)$$

In full analogy with this, we define the **mean value** of a 3D coordinate by

$$\langle\vec{r}\rangle = \int dV\, \vec{r}|\Psi(\vec{r})|^2 = \int dV\, \Psi^*(\vec{r})\vec{r}\Psi(\vec{r})$$

Now we generalize this to an arbitrary quantum operator, as an educated guess. Suppose we have some observable X, and its corresponding operator $\hat{X}$. Define the **expectation value** of X as

$$\langle X\rangle = \int dV\, \Psi^*(\vec{r})\hat{X}\Psi(\vec{r})$$

For example, if $\hat{X} = \hat{p} = -i\hbar\nabla$, then

$$\langle p\rangle = \int dV\, \Psi^*(\vec{r})(-i\hbar\nabla)\Psi(\vec{r})$$

It turns out that this guess works out and is consistent with the experimental data. It is a basic principle of quantum mechanics: physical observables are associated with (self-adjoint) operators acting on the wave function with the expectation values defined above.

2.4 Time-independent Schrödinger Eq. eigenvalue problems

In this section, we will discuss a very important class of problems that appear throughout quantum mechanics, i.e. **eigenvalue problems**. Let's start with the time-dependent S.Eq. with a time-independent Hamiltonian:

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

We can "factor out" the time-dependence by performing separation of variables. Suppose the wave-function is

$$\Psi(\vec{r}, t) = \psi(\vec{r})e^{-\frac{i}{\hbar}Et}$$

Plugging this into the time-dependent S.Eq., we get the time independent S.Eq.

$$i\hbar\frac{\partial}{\partial t}\left(\psi(\vec{r}e^{-\frac{iEt}{\hbar}}\right) = E\psi(\vec{r})e^{-\frac{iEt}{\hbar}} = \left(\hat{H}\psi(\vec{r})\right)e^{-\frac{iEt}{\hbar}} \implies \hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

But we can interpret E as an **eigenvalue**, and $\psi(\vec{r})$ as an **eigenvector**! In fact, these eigenvalues are precisely the possible outcomes of measurements.

Hermitian operators For any operator $\hat{A}$, acting in a space of functions $\psi(\vec{r})$, we define its **Hermitian-adjoint operator** $A^\dagger$ by the relation

$$\int \psi^*(\vec{r})\left(\hat{A}\psi(\vec{r})\right)d^3r = \int \left(\hat{A}^\dagger\psi^*(\vec{r})\right)\psi(\vec{r})\,d^3r$$

An operator is called **Hermitian** if $\hat{A}^\dagger = \hat{A}$.

Physical measurement Let $\hat{A}$ be Hermitian, then:

- If $\hat{A}\psi_a(\vec{r}) = a\psi_a(\vec{r})$, then a is real, i.e. the eigenvalues of $\hat{A}$ are all real. This makes what we stated earlier make sense: the physically measurable quantities are guaranteed to be real.
- Its eigenvectors $\psi_a(\vec{r})$ form a basis, i.e. any function in our function space can be written as

  $$\psi(\vec{r}) = \sum_a = c_a\psi_a(\vec{r})$$

  It turns out that the probability of a measurement collapsing the state to $\psi_a(\vec{r})$ is precisely $|c_a|^2$.

2.5 Superposition principle, Dirac notation, and representations

An important component of putting together a new physical theory is coming up with convenient and elegant notation. But before we proceed with introducing Dirac notation, let's go through the superposition principle first.

Superposition principle If $\Psi_1(\vec{r}, t)$ and $\Psi_2(\vec{r}, t)$ are solutions to the S.Eq., then $\Psi(\vec{r}, t) = c_1\Psi_1(\vec{r}, t) + c_2\Psi_2(\vec{r}, t)$ is also a solution, since the S.Eq. is a linear DE. This motivates the notion of a **Hilbert space** where quantum states live. The wave-function $\Psi(\vec{r})$ is a specific representation of a quantum state, much like the coordinates of a vector, i.e. $\vec{a} = (a_x, a_y)$ has coordinates that depend on the choice of coordinate system, but the vector itself remains the same across any coordinate system.

Reminder from linear algebra Consider a 2D planar vector $\vec{a}$ in a coordinate system $\vec{e}_x, \vec{e}_y$. Written in these specific coordinates, we have

$$\vec{a} = \begin{pmatrix} a_x \\ a_y \end{pmatrix} \qquad \vec{a}^\dagger = (a_x, a_y)$$

Note also that for any orthonormal basis, including $\vec{e}_x, \vec{e}_y$, we have

$$\vec{e}_x\vec{e}_x^\dagger + \vec{e}_y\vec{e}_y^\dagger = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Dirac notation There are circumstances in which we don't want to specify a representation for a wave-function. Dirac suggested notations for the "vectors" of quantum states:

$$\langle\Psi| \text{ (bra)} \qquad |\Psi\rangle \text{ (ket)}$$

The Hilbert space is more complicated than a simple Euclidean space, and is usually infinite-dimensional, but most properties from linear algebra remain the same. The property of orthonormal bases expressed above in matrix notation becomes, for a basis $\{|q\rangle\}$,

$$\sum_q |q\rangle\langle q| = 1 \quad \text{or} \quad \int_q |q\rangle\langle q| = 1$$

A quantum state $|\Psi\rangle$ can be expanded in a basis $\{|q\rangle\}$:

$$|\Psi\rangle = \sum_q |q\rangle\langle q|\Psi\rangle \quad \text{or} \quad |\Psi\rangle = \sum_q |q\rangle\langle q|\Psi\rangle$$

We actually write $\Psi(q) = \langle q|\Psi\rangle$, just as we would write $a_x = \vec{e}_x^{\dagger}\vec{a}$ in the 2D example above.

Choosing basis/representation There are natural choices for bases. We know that physical observables are associated with linear, self-adjoint operators. Then for a generic operator $\hat{A}$, the eigenvalue problem gives us a basis of eigenvectors in our Hilbert space. So standard choices may be the coordinate representation $\Psi(x) = \langle x|\Psi\rangle$, or momentum representation $\Psi(p) = \langle p|\Psi\rangle$. Note that these two bases are completely different.

Chapter 3

Feynman Path Integral

3.1 Introduction

In the past sections, we introduced the S.Eq., which is the most popular formulation of quantum mechanics. However, an alternate formulation uses the **Feynmann path integral**, which is a bit more complicated than the S.Eq.

Rough summary Feynmann's original paper stated "non-relativistic quantum mechanics is formulated here in a different way," and technically it is quite involved. Consider a quantum particle localized at time $t = 0$ within the vicinity of some point $\vec{R}_i$. We're going to look at the probability this particle reaches a point $\vec{R}_f$ in a time t. A classical particle follows some unique, well-defined trajectory. Feynmann's paper considers that the particle goes over all possible trajectories at the same time, but there is a complex **weight** associated with each trajectory that looks like

$$e^{i\frac{S}{\hbar}} \qquad \text{where } S = \int_0^T [K - V]\, dt$$

Then in some sense, the probability can be represented as

$$w_{i\to f} = \left| \sum_l e^{i\frac{S_l}{\hbar}} \right|^2$$

3.2 Propagator

We are going to consider an object called a **propagator**. We can view it as an attempt to make quantum mechanics as close as possible to the concepts that we understand intuitively in classical physics, e.g. particles, and trajectories.

Trajectories in QM Let's assume at $t = 0$, our quantum particle is localized at a point $\vec{R}_i$:

$$|\Psi(0)\rangle = |\vec{R}_i\rangle$$

That is, our wavefunction is a very narrow wavepacket centered at $\vec{R}_i$. This initial state is going to evolve under the S.Eq.

$$i\hbar\partial_t|\Psi\rangle = \left(\frac{\hat{\vec{p}}^2}{2m} + V(\vec{R})\right)|\Psi\rangle$$

We know from previously that this wavepacket will slowly spread out. But what portion of it will propagate to the final point $\vec{R}_f$? Mathematically, we want to calculate

$$\langle \vec{R}_f | \Psi(t) \rangle = ?$$

Note that the particle is actually not propagating in a classical sense; we are looking at the spreading/propagation of the wavefunction.

Evolution operator How do we solve the general S.Eq. to find $\langle \vec{R}_f | \Psi(t) \rangle$? The general equation we have, the S.Eq., is

$$i\hbar \partial_t |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \qquad |\Psi(0)\rangle = |\Psi_0\rangle = |\vec{R}_i\rangle$$

The **evolution operator** is defined as

$$|\Psi(t)\rangle = \hat{U}(t) |\Psi(0)\rangle$$

It is a "rotation" in the sense that we should have $\Psi^2(t) = 1$, and geometrically in our vector space the only thing we can imagine $\hat{U}$ doing to our wavefunction vector while preserving its length is rotating it. It turns out that we can write the S.Eq. for the evolution operator:

$$i\hbar \partial_t \hat{U}(t) = \hat{H} \hat{U}(t) \qquad \hat{U}(0) = 1$$

Note that we can pick a $\hat{U}$ that satisfies for the S.Eq. and the initial condition, by

$$\hat{U}(t) = e^{-\frac{i}{\hbar} \hat{H} t}$$

So this evolution operator solves the S.Eq. with all initial conditions in one go, since it actually does not depend on the initial conditions of Ψ. Then we get

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar} \hat{H} t} |\vec{R}_i\rangle$$

Propagator Now let's return to the original question: what is $\langle \vec{R}_f | \Psi(t) \rangle$? But now we have a formal, exact expression for $\Psi(t)$, and we can plug this in directly to get the **propagator**

$$G(\vec{R}_i, \vec{R}_f; t) = \langle \vec{R}_f | e^{-\frac{i}{\hbar} \hat{H} t} | \vec{R}_i \rangle$$

The **Feynmann path integral** is actually just another representation of this. A motivation for another representation for this is that even though the expression looks simple, it is not actually. Calculating the exponential of an operator ($\hat{H}$ in this case) is difficult.

3.3 Deriving the Path Integral

In this section, we're going to do most of the calculations in 1D, for the sake of simplicity, though the calculation works out the same way in arbitrary dimensions. On a side note, a **propagator** is also called a **Green function**. Before we begin, let's go over a few facts:

- **Resolution of the identity operator**: $\hat{1} = \int |x\rangle\langle x| \, dx$
- **Splitting the time interval**: $|\Psi(t)\rangle = \hat{U}(t) \langle \Psi(0) \rangle = \hat{U}(t - t_1) |\Psi(t_1)\rangle = \hat{U}(t - t_1) \hat{U}(t_1) |\Psi(0)\rangle$.

Derivation Let's rewrite the evolution operator $\hat{U}(t) = e^{-i\hat{H}t/\hbar}$ as

$$\hat{U}(t) = \hat{U}\left(\frac{t}{2}\right) + \hat{U}\left(\frac{t}{2}\right)$$

We can split the propagator using the resolution of the identity as

$$\langle x_f|\hat{U}(t)|x_i\rangle = \int dx\, \langle x_f|\hat{U}\left(\frac{t}{2}\right)|x\rangle\langle x|\hat{U}\left(\frac{t}{2}\right)|x_i\rangle$$

This allows a useful and intuitive presentation. Consider a plot of x vs t. We are interested in the propagator going from x_i to x_f on this plot. This equation says we can take a point in the middle of the line, and consider all possible paths from x_i to this point, and from this point to x_f. The obvious thing is to continue doing this infinitely. Let's formalize this:

$$\hat{U}(t) = \hat{U}\left(\frac{t}{N}\right) \times \hat{U}\left(\frac{t}{N}\right) \times \ldots \times \hat{U}\left(\frac{t}{N}\right) \qquad N \to \infty$$

So we have $\delta t = t/N$, and we can truncate the Taylor expansion of the evolution operator as

$$e^{-\frac{i}{\hbar N}\hat{H}t} \approx 1 - \frac{i}{h}\hat{H}\delta t$$

Putting this back into the time interval splitting, we get a big mess:

$$\langle x_f|\hat{U}(t)|x_i\rangle = \int dx_1 \ldots x_{N-1} \prod_{k=0}^{N} \langle x_{k+1}|1 - \frac{i}{\hbar N}\hat{H}t|x_k\rangle$$

Note that in here, we have let $x_0 = x_i$ and $x_N = x_f$. But now we don't need to deal with a complicated exponential, since only a linear Hamiltonian is left as a matrix element.

Calculating the matrix elements Before we try to do this, note that $|\Psi\rangle$ is not $\Psi(x)$, but rather $|\Psi\rangle = \langle x|\Psi\rangle$. So we have something like

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px}$$

However, what about $\langle x|x'\rangle$? How do we get a wavefunction given the coordinates? It turns out that we need the **Dirac delta function**.

Dirac δ-function Recall the orthonormality condition for the standard basis vectors $\{\vec{e}_i\}$:

$$\vec{e}_i \cdot \vec{e}_j = \delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases}$$

For a continuum basis $\{|x\rangle\}$, however, we analogously want something like

$$\langle x|x'\rangle = \delta(x - x') = \begin{cases} 0 & \text{if } x \neq x' \\ ? & \text{if } x = x' \end{cases}$$

By analogy with the standard basis, the value ? needs to somehow satisfy

$$\int_{-\infty}^{\infty} dx\, \delta(x - x') = 1$$

This is rather silly, but that is how the definition goes.

Fourier transform of Dirac δ An important property of the Dirac delta is that the Fourier transform looks like

$$\delta(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx}$$

Calculating the matrix elements We actually calculated $\langle x_{k+1}|x_k\rangle$ already, it is $\delta(x_{k+1}-x_k)$. Similarly, we have

$$\langle x_{k+1}|V(\hat{x})|x_k\rangle = V(x_k)\delta(x_{k+1}-x_k)$$

This is because $|x_k\rangle$ is an eigenstate of the coordinate, $V(\vec{x})$ acting on x_k just gives some eigenvalue $V(x_k)$. However, kinetic energy is less trivial, since x_k is not an eigenfunction of the momentum $\hat{p}$. To calculate it, we again use the resolution of the identity:

$$\langle x_{k+1}|\frac{\hat{p}^2}{2m}|x_k\rangle = \int dp_k \, \langle x_{k+1}|\frac{p^2}{2m}|p_k\rangle\langle p_k|x_k\rangle$$

Now $\hat{p}$ is acting on its eigenstate, so we can factor a constant out to get

$$\langle x_{k+1}|\frac{\hat{p}^2}{2m}|x_k\rangle = \int \frac{dp_k}{2\pi\hbar}\frac{p_k^2}{2m} e^{i\frac{p_k}{\hbar}(x_{k+1}-x_k)}$$

But this looks like the Fourier transform of δ, and it turns out that in fact all three of our matrix element calculations can be written in terms of it.

Putting everything together So now we have something along the lines of

$$\langle x_{k+1}|1-\frac{i}{\hbar}\hat{H}\delta t|x_k\rangle \propto \int dp_k \, e^{\frac{i}{\hbar}p_k\delta x_k}\left(1-\frac{i}{\hbar}\left(\frac{p_k^2}{2m}+V(x_k)\right)\delta t\right)$$

The good thing about this expression is that there are no operators anymore, and we can simplify. Recall that for some infinitesimal ϵ, we have $e^{\epsilon} = 1+\epsilon+\ldots$, and we can use this backward to get the "equivalent" integral

$$\int dp_k \, e^{\frac{i}{\hbar}p_k\delta x_k} \exp\left(\frac{i}{\hbar}\left(\frac{p_k^2}{2m}+V(x_k)\right)\delta t\right)$$

But this is just a Gaussian integral, which evaluates to

$$\exp\left(\frac{i}{\hbar}\left(\frac{m}{2}\frac{\delta x_k^2}{\delta t^2}-V(x_k)\right)\delta t\right)$$

We can interpret this a little to simplify it. Note that $(\delta x_k)/(\delta t)$ is just the velocity of the particle, so we have

$$\exp\left(\frac{i}{\hbar}\left(\frac{mv_k^2}{2}-V(x_k)\right)\delta t\right)$$

In classical physics, this is just the **Lagrangian**, written $\mathcal{L}_k$. So we can rewrite our matrix element very compactly as

$$\langle x_{k+1}|\hat{U}(\delta t)|x_k\rangle \propto e^{\frac{i}{\hbar}\mathcal{L}_k\delta t}$$

Finally, plugging this back into our original propagator expression, we have

$$\langle x_f|\hat{U}(t)|x_i\rangle = \int dx_1\, dx_2 \ldots e^{\frac{i}{\hbar}\mathcal{L}_1\Delta t}e^{\frac{i}{\hbar}\mathcal{L}_2\Delta t}\ldots = e^{\frac{i}{\hbar}\sum_k \mathcal{L}_k\Delta t} = e^{\frac{i}{\hbar}\int_0^t \mathcal{L}\,dt} = e^{\frac{iS}{\hbar}}$$

Recalling, from classical mechanics, that we denote

$$S = \int_0^t \mathcal{L}\,dt$$

and call it the **classical action**. To simplify the sequence of dx_k's, we will write

$$\int \mathcal{D}x(t) e^{\frac{i}{\hbar} \int_0^t \mathcal{L}\, dt}$$

This is our final result of this very long derivation. It turns out that this will allow us to study some very deep things later.

Chapter 4

Using the Feynmann Path Integral

4.1 From Feynmann to Newton: classical limit

In this section, we will look at how the Feynmann path integral give us classical equations of motion such as **Newton's second law** in the **classical limit**, which we will clarify soon. We'll need some machinery before we do this though.

Laplace's method (saddle-point approximation) This is a mathematical trick that allows us to calculate certain integrals that cannot be calculated directly in the usual way. For example, we know the **Gaussian integral** is

$$\int_{-\infty}^{\infty} e^{-x^2}\, dx = \sqrt{\pi}$$

Since this Gaussian function e^{-x^2} decays very fast, this area is bounded. But there is no **closed analytical expression** for the antiderivative of $e^{-f(x)}$. However, if there is a small parameter in the exponential, i.e. $e^{-(1/\epsilon)f(x)}$, we can simplify things. Consider the example

$$\int_{-\infty}^{\infty} e^{-\frac{1}{\epsilon}(x^2+1/x^2)}\, dx$$

Note that the graph of $f(x)$ has a minimum at $x = 1$, which corresponds to a maximum in the integrand. As $\epsilon \to 0$, the tail of the integrand becomes less and less relevant as this maximum peak of the integrand increases higher and higher, and the integrand will slowly start looking like the Gaussian integral. Since the Taylor series of $f(x)$ at $x = 1$ is

$$f(x \approx 1) \approx f(1) + f'(1)(x-1) + \frac{f''(1)}{2}(x-1)^2$$

But since $x = 1$ is a minimum, $f'(1) = 0$, and so $f(x \approx 1) = f(1) + f''(1)/2(x-1)^2$. It turns out that doing the algebra gives

$$I = \int_{-\infty}^{\infty} e^{-\frac{1}{\epsilon}f(x)}\, dx \approx e^{-\frac{1}{\epsilon}f_{min}} \sqrt{\frac{2\pi\epsilon}{|f''(x_0)|}}$$

In this case, we get the estimation as $\sqrt{-2/\epsilon}\sqrt{\pi\epsilon}/2$. Note that even if the exponential is complex, we can use the same method.

Principle of Least Action Now we return to quantum physics. What does it mean to take the **classical limit** of a quantum theory? Recall that the most interesting quantum phenomenon is **interference** between

waves; suppressing this interference implies making the wavelength $\lambda = 2\pi\hbar/p$ as small as possible, i.e. we take $\hbar \to 0$. The **Planck constant** "controls" the quantum effects.

Now consider the Feynmann path integral as we take $\hbar \to 0$:

$$\int \mathcal{D}\vec{r}(t) e^{iS/\hbar \to 0}$$

This is rather similar to the functions we were just considering with Laplace's method, where $\hbar$ takes on the role of ϵ. Furthermore, as $\hbar \to 0$, we only "focus" on the trajectories for which the action S is minimal. This implies that

$$\hbar = 0 \Leftrightarrow \text{Principle of least action}$$

Of course, remember that $\hbar$ is actually a physical constant and we can't just set it to zero. What we actually mean here is that there are two length scales that we are considering: one on the scale of our quantum particles, and another on the scale of our typical system, which is usually much much larger than the quantum particles.

Finding the special trajectory Those familiar with the **Lagrangian** from classical mechanics should see that the principle of least action already implies Newton's law. How do we find the trajectory that minimizes action? Well, if we have a function $f(x)$ and we want to find a minimum point x_0, we demand that in the Fourier expansion,

$$f(x_0 + \delta x) = f(x_0) + f'(x_0)\delta x + \frac{1}{2} f''(x_0)\delta x^2 + \dots$$

we must have $f'(x_0)\delta x = 0$. So if we want a trajectory $x_{cl}(t)$ on which the functional of action $S(x)$ is minimal, we want in the expansion

$$S[x_{cl}(t) - \delta x(t)] = S[x_{cl}(t)] + \delta S + \dots$$

to have $\delta S = 0$. This is the calculation of the action in the vicinity of the classical trajectory. Note that in some sense, all of classical physics is contained in the equation $\delta S = 0$.

Recovering Newton's second law Recall that action is

$$S[\vec{r}(t)] = \int_0^t \left(\frac{m\vec{v}^2}{2} - V(\vec{r}) \right) dt$$

Let's calculate its first variation, i.e. the action of paths very close to $\vec{r}_{cl}(t)$. Plugging stuff in gives

$$S[\vec{r}_{cl}(t) + \delta\vec{r}(t)] = \int_0^t \left(\frac{m}{2} \left(\frac{d}{dt}(\vec{r}_{cl} + \delta\vec{r}) \right)^2 - V(\vec{r}_{cl} + \delta\vec{r}) \right) dt$$

Next, we are going to expand this, while only keeping track of the linear terms since $\delta\vec{r}$ is really small:

$$S[\vec{r}_{cl}(t) + \delta\vec{r}(t)] = \int_0^t \left(\frac{m}{2} \frac{d\vec{r}_{cl}^2}{dt} + m \frac{d\vec{r}_{cl}}{dt} \delta \frac{d\vec{r}}{dt} - V\vec{r}_{cl} - \frac{\partial V}{\partial \vec{r}} \cdot \delta\vec{r} \right) dt$$

But this can be rearranged and simplified using **integration by parts** on the second term. Since the variation in the trajectory does not change the endpoints, the full derivative term in the integration by parts vanishes, so we actually just flip the sign and move the differentiation from $\vec{r}$ to $\vec{r}_{cl}$.

$$S[\vec{r}_{cl}(t) + \delta\vec{r}(t)] = S_{cl} - \int_0^t \left(m \frac{d^2\vec{r}_{cl}}{dt^2} + \frac{\partial V}{\partial \vec{r}} \right) \cdot \delta\vec{r}\, dt$$

The integral is exactly δS, and we want to set this to zero for all trajectories. Hence the integrand must be identically zero, which gives

$$m \frac{d^2\vec{r}_{cl}}{dt^2} = -\frac{\partial V}{\partial \vec{r}} \implies m\vec{a} = \vec{F}_r$$

4.2 Quantum Corrections to Diffusion: Localization

We have been studying mostly quantum theories and physical phenomena that were discovered a relatively long time ago, e.g. the latest development we discussed, the path integral, comes from the 1940s. Let's consider a more recent theoretical development, called **weak localization**, using the main ideas of the Feynmann path integral. The full theory is complicated, but some basic ideas behind the phenomenon can be understood using the basic concepts that we know already.

In solid state physics, materials are roughly either **insulators** or **metals**. Insulators have electrons that cannot move: they don't conduct current. On the other hand, metallic systems conduct current in response to an electric field. However, in any real material, there are imperfections, which in metals lead to a finite resistance. It turns out that the classical theory of **transport** for metals needs to be modified at lower temperatures, where quantum effects come into play. For example, metals could potentially become insulators. Before this, though, let's review the classical theory behind conductivity.

Classical conductivity theory Consider some impurities in a metal as a fixed particles. An electron traveling through it get scattered by the impurities, i.e. it takes a random walk. But the application of an electric field cause electrons to tend to walk in one direction. This is the **Drude model**, which assumes we can view the electron as a classical particle that satisfies classical mechanics, so

$$m\vec{a} = q\vec{E} + \vec{F}_{fr}$$

where $\vec{F}_{fr}$ represents the impurities in the sense of a "friction" force which is proportional to the velocity of the electron:

$$\vec{F}_{fr} = -\gamma\vec{v} = -\frac{\vec{p}}{\tau}$$

We can think of τ as the average time between collisions with impurities for an electron. So when $\vec{a} = 0$, i.e. the steady-state equilibrium, we will have

$$\frac{d\vec{p}}{dt} = q\vec{E} - \frac{\vec{p}}{\tau} = 0$$

Solving for $\vec{p}$ gives $q\vec{E}\tau$, and $\vec{v} = \vec{p}/m$. Putting this together, the current $\vec{J}$ is simply

$$\vec{J} = qn\vec{v} = \frac{nq^2\tau}{m}\vec{E}$$

We call the coefficient on $\vec{E}$ the **conductivity** σ, which, in general, is the coefficient of proportionality between $\vec{J}$ and $\vec{E}$. It is a purely classical entity. Most theories of metals today rely on this Drude model derivation for the coefficient, and in most cases it actually works fine. However, at lower temperatures, the situation becomes trickier: quantum mechanics comes into play. In the Drude picture, we can see the quantum effects as electrons being waves interfering with each other, instead of classical particles with fixed trajectories.

Path-integral view of electron motion So let's view electron paths from a very different perspective. The probability of an electron diffusing through the impurities from an initial point $\vec{r}_i$ to a final point $\vec{r}_f$ according to Feynmann is

$$w_{i\to f} = \left|\sum_l e^{\frac{i}{\hbar}S_l}\right|^2$$

In some sense, the terms of the form $e^{iS_j/\hbar}e^{-iS_k/\hbar}$ plus their complex conjugates produces a cosine interference term, and the terms without a product of two different trajectories are the terms responsible for the Drude model. The quantum corrections boil down to figuring out what exactly these cosine terms are:

$$2\cos\left(\frac{S_1 - S_2}{\hbar}\right)$$

At high temperatures, there is a lot of motion around the electrons, and this "shaking" of the electron disturbs the phases. This is sometimes called **dephasing**. To determine the actions S_l, we will actually assume that quantum phase remains unperturbed. However, it turns out that even if we assume this, the interference terms tend to cancel each other out, and it is hard to find a situation in which they are dominant. In order to see this, let's estimate the total action appearing in the equation:

$$S_l \approx \int \frac{m\vec{v}^2}{2}\, dt \approx pL$$

Note that pL comes from approximating $m\vec{v}^2/2$ as $m\vec{v}\vec{v}\, dt$ and noting the typical momentum $p = m\vec{v}$ and L, the typical length of the trajectory, is $\vec{v}\, dt$. We can also approximate the quantum (interference) terms:

$$w_{i\to f}^{\text{quantum}} \propto \sum_{l_1 \neq l_2} e^{\frac{i}{\hbar} p_F (L_1 - L_2)} + c.c. = 2 \sum_{l_1 \neq l_2} \cos\left(\frac{p_F \Delta L}{\hbar}\right)$$

Note that here we have written $\Delta L = L_1 - L_2$, and the typical momentum as p_F, since it is typically called the **Fermi momentum**. It turns out that the argument of the cosine in a typical metal is very large, since the typical velocity is very small, and so the typical wavelength is less than a nanometer, much smaller than the distance between impurities. Fundamentally, then, the interference terms will not be very important. Roughly, if we have random phases, the average value of the cosine will actually be zero, and the canceling makes the interference terms disappear. However, this is not always the case: there is a very special class of trajectories where they don't cancel, i.e. **self-intersecting trajectories**. For these trajectories, the electron can move in a clockwise loop, or a counterclockwise loop, and so we have two paths with phase difference zero, and the cosines become significant.

Intuition The easier it is for an electron to move from $\vec{r}_i$ to $\vec{r}_f$, the easier the metal conducts, but the easier it is for an electron to move from $\vec{r}_i$ to $\vec{r}_i$, the worse the conductivity of the metal. So the probability of having these self-intersecting paths should in general reduce the conductivity, which is what happens in most cases, and therefore it called **weak localization**. Before continuing, however, let's look at classical diffusion.

Diffusion equation If we put a droplet of dye in water, the time-evolution of the droplet is described by the **diffusion equation**

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho$$

In fact, this equation describes the average density of many particles experiencing a random walk, where we interpret ρ as a function of position and time. In a conducting metal, the impurities act as scatterers, so the electrons experience a random walk. Hence the diffusion equation can also describe the density of the electrons. We can interpret the ρ as the probability of finding a certain electron at a certain time at a certain position in space. We can also note that this equation looks similar to the S.Eq.

Self-intersecting trajectories Basically, we return to the problem of the probability that a path is self-intersecting. If we set the density ρ at $t = 0$ to be a delta function, i.e. $\rho(\vec{r}, t = 0) = \delta(\vec{r})$, then it turns out we can solve the diffusion equation with this initial condition. The general solution is

$$\rho(\vec{r}, t) = \frac{1}{(2\pi D t)^{d/2}} \exp\left(-\frac{\vec{r}^2}{4Dt}\right)$$

Note that d here represents the dimensionality of the space.

Probability of self-intersection So we want the probability that $\vec{r} = 0$. Setting this in the above equation, we get

$$\rho(\vec{0}, t) = \frac{1}{(2\pi Dt)^{d/2}}$$

This gives the probability a random walking particle will return to its starting-point in time t. Then the total probability p_{total} of any self-intersection whatsoever is the integral of this expression over time from some t_{min} to t_{max}:

$$P_{total} \propto \int_{t_{min}}^{t_{max}} \frac{dt}{t^{d/2}}$$

Note that if there is no disturbance of the quantum phase, then $t_{max} \to \infty$. What is crucial is that this integral is finite for $d = 3$ but is infinite for $d = 1, 2$. Physically, this means it is easy to get lost in 3D, but not 2D. From the point of view of the electron, in 1D or 2D, the quantum interference terms will actually matter a lot at low temperatures.

Interpretation From an experimental point of view, if we plot the resistance $R(T)$ as a function of temperature T, we will actually get a minimum somewhere as T decreases in one or two dimensions, after which the metal becomes an insulator at lower temperatures. However, in three dimensions, this does not happen. There actually do exist quasi-1D or 2D materials such as nanowires to which this theory applies.

Chapter 5

Bound States in Quantum Potential Wells

5.1 Electron in a Box

Recall the canonical S.Eq:

$$i\hbar\frac{d\Psi}{dt} = \left(\frac{\hat{\vec{p}}^2}{2m} + V(\vec{r})\right)\Psi$$

Note that if the potential does not depend on time, we don't really need to look at the time-dependent S.Eq. The first term in the Hamiltonian is kinetic energy, and the potential term depends on the single-particle problem we are considering. So the variety of all single-particle problems are encoded in here, differing only by a choice in $V(\vec{r})$.

Roughly, we can classify our potential by whether they are attractive or repulsive, i.e. whether they are **potential wells** or **potential barriers**. In this section, we will look at potential wells, and the quantization of energy of particles in these potential wells.

Hard wall boundary Consider "boxing in" the particle with a potential that is infinity outside some range, and zero within the range. We will be solving this problem, known as the **electron in a box**.

Quantization in a guitar string In order to understand quantization, we don't need to look at quantum mechanics. The wavelengths that an oscillating string fixed on both ends, like on a guitar, can take on are $2L/n$. The fixing of the string on both ends corresponds roughly with the hard boundary of our quantum box, and the available wavelengths might depend on the length of the string L. Recall that the **fundamental wavelength** is $\lambda = 2L$, since otherwise we violate our boundary condition of the string being fixed its ends. Smaller wavelengths simply "fix" a point somewhere in the middle. In general, the string behaves according to

$$u_n(x) = A_n \sin\left(\frac{2\pi x}{\lambda_n}\right)$$

Note that these solutions for the string obey the boundary conditions $u_n(0) = u_n(L) = 0$.

Quantization in a quantum well It turns out that quantization in a quantum well is almost entirely analogous, but instead of a guitar string we have an electron wave. Our boundary conditions are simply $|\Psi|^2 = 0$ at $x = 0, L$. Interestingly, the wavefunction we get in our solution will look exactly like the equation describing the strings:

$$\psi_n(x) = A_n \sin\left(\frac{2\pi x}{\lambda_n}\right)$$

Recall that $E = p^2/2m$ and $p = 2\pi\hbar/\lambda$, so if λ is quantized, the energy E is also quantized, by $E = \pi^2\hbar^2 n^2/L^2$. Interestingly, we solved the S.Eq. without even writing it down; we used an analogy and observation of the boundary conditions, though it can be solved formally, which we will do later.

5.2 Finite Potential Well

Let's formalize our solution to the S.Eq. we found earlier. We will take the potential

$$U(x) = \begin{cases} U_0 & |x| > a/2 \\ 0 & |x| < a/2 \end{cases}$$

Note that the energy of any states we get inside this well must be smaller than U_0 but greater than 0. Then the S.Eq. is

$$\begin{cases} -\frac{\hbar^2}{2m}\psi''(x) + U_0\psi(x) = E\psi(x) & |x| > a/2 \\ -\frac{\hbar^2}{2m}\psi''(x) = E\psi(x) & |x| < a/2 \end{cases}$$

But we need to match the solutions to the two regions: we will demand that ψ and ψ' are continuous everywhere, in particular at $\pm a/2$. It doesn't make sense for ψ or ψ' to be discontinuous, since that would introduce an infinity in ψ'', and there will essentially be a delta, but there is no delta in the problem. It turns out that this condition, and the following, are enough to begin solving.

$$\psi(x \to \pm\infty) \to 0$$

This condition simply means that the particle can't exist at "infinity", i.e. the particle should be localized in some vicinity of our well.

Some preliminary simplification Before we begin solving, let's do some simplification and introduce a parameter γ, as

$$\gamma^2 = \frac{2m}{\hbar^2}(U_0 - E)$$

This allows us to rewrite the S.Eq. outside the well as $\psi'' - \gamma^2\psi = 0$. We can also introduce another parameter k, as

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

This simplifies the S.Eq. inside the well as $\psi'' + k^2\psi = 0$. Note that we can easily solve these second-order DE's as $e^{\pm\gamma x}$ and $e^{\pm ikx}$, but we can explore the symmetry of the problem to introduce some symmetry concepts in quantum mechanics.

Using the symmetry In general, if the Hamiltonian commutes with an operator $\hat{A}$ as follows,

$$\left[\hat{H}, \hat{A}\right] = \hat{H}\hat{A} - \hat{A}\hat{H} = 0$$

we can always chose solution to the S.Eq. to have definite a and E, denoted $\psi_{aE}(x)$. In other words, consider the eigenvalue problems

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

The solutions for the second will be solutions for the first. If the two operators were not commutative, then we won't necessarily be able to find a class of wavefunctions $\psi_{aE}(x)$ that have both a and E definite.

Our potential is **inversion symmetric**, i.e. $\hat{I}U(x) = U(-x) = U(x)$, but the eigenvalues of $\hat{I}$ are $p = \pm 1$. Basically, the eigenstates of the S.Eq. are either odd or even functions, and instead of finding a general solution of $(d^2/dx^2 + k^2)\psi = 0$ of the form

$$\psi(x) = C_1 e^{ikx} + C_2 e^{-ikx}$$

we can instead choose solutions with a **definite parity**, i.e.

$$\psi_+(x) = C\cos(kx) \qquad \psi_-(x) = \tilde{C}\sin(kx)$$

We will specifically consider the even solution only, for simplicity. Now we just have to find the solution in one of the infinite potential regions, since by symmetry the two are the same.

Using the constraints at infinities The S.Eq. in the infinite potential is $(d^2/dx^2 - \gamma^2)\psi = 0$, which has general solution

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

However, recall that we required ψ to remain finite when $x \to \infty$, otherwise the probability diverges toward infinity, which does not make physical sense. Hence we drop the divergent B term to get

$$\psi(x) = Ae^{-\gamma x} \qquad x > \frac{a}{2}$$

Using the matching conditions at $a/2$ Summarizing, we have

$$\psi_+(x) = \begin{cases} Ae^{\gamma x} & x < -\frac{a}{2} \\ C\cos(kx) & |x| < \frac{a}{2} \\ Ae^{-\gamma x} & x > \frac{a}{2} \end{cases}$$

We need to match the solutions at $x = \pm a/2$, i.e. we need the functions and their derivatives to match:

$$C\cos\left(\frac{ka}{2}\right) = Ae^{-\frac{\gamma a}{2}}$$
$$-Ck\sin\left(\frac{ka}{2}\right) = -A\gamma e^{-\frac{\gamma a}{2}}$$

Dividing the second equation by the first, we get $k\tan(ka/2) = \gamma$.

Non-dimensionalizing the self-consistency equation Rewritten, this consistency equation is

$$\tan\left(\frac{ka}{2}\right) = \frac{\gamma}{k} = \sqrt{\frac{U_0}{E} - 1} \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

It turns out that we can't solve for the energy E analytically. We can introduce **dimensionless parameters** $x = ka/2$ and $\xi^2 = mU_0a^2/2\hbar^2$ to get

$$\tan x = \sqrt{\frac{\xi^2}{x^2} - 1}$$

Dealing with dimension-less quantities are simpler since we can talk about them being large or small, but for dimensional quantities it doesn't make sense to talk about large or small unless we set some reference. We will split this into two cases:

$$\xi^2 \gg 1 \text{ (deep well)} \qquad \xi^2 \ll 1 \text{ (shallow well)}$$

We cannot solve exactly for an arbitrary ξ, but we can do two separate analyses for these two cases. Note that after $x > \xi$, there are no real solutions. When we plot these two curves, each intersection, i.e. each solution, corresponds to an allowed energy level. For a plot of a deep potential ($\xi = 20$), for example, there are many intersections, while for a shallow potential ($\xi = 1$), there are few.

5.3 Bound state in a shallow (delta-) potential

We are going to solve the S.Eq. for a particle in a shallow quantum well, i.e. a delta potential, in 1D, 2D, or 3D. The outcome of this calculation will be that any weak attractive potential gives rise to a bound state of the particle. However, in 3D, a very weak potential is not enough to localize the particle. This difference has important consequences in many fields of physics. Before proceeding with the calculation, we need to review some mathematical machinery.

Fourier Transform Given any reasonable function $g(x)$, in our case the wavefunction and various derivatives of it, we can take the Fourier transform and inverse Fourier transform as:

$$F[g(x)] = \tilde{g}(k) = \int_{-\infty}^{\infty} g(x)e^{ikx}\,dx \qquad g(x) = \int_{-\infty}^{\infty} \tilde{g}(k)e^{-ikx}\frac{dk}{2\pi}$$

The 2π term appears in the inverse transform by convention; of course, it could appear anywhere in either the forward or inverse transform, or both. In quantum mechanics, the convention is that it appears in the inverse. A specific example of the Fourier transform is the transform of the Dirac δ:

$$F[\delta(x)] = \int_{-\infty}^{\infty} \delta(x)e^{ikx}\,dx = 1 \qquad \delta(x) = \int_{-\infty}^{\infty} e^{-ikx}\frac{dk}{2\pi}$$

Shallow levels in delta-well We'll use these identities to solve the time-independent S.Eq. for ψ, where the full solution for the wavefunction is $\Psi = \psi e^{-iEt/\hbar}$:

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

Our goal is to determine the values of E. Let's write ψ as the Fourier transform of the wavefunction, in the momentum representation:

$$\psi(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi}\tilde{\psi}_k e^{-ikx}$$

If we differentiate this Fourier transform twice over the coordinate, we'll be pulling out $(-ik)^2$, so we can write

$$\psi''(x) = \int_{-\infty}^{\infty} \tilde{\psi}_k(-ik)^2 e^{-ikx}\frac{dk}{2\pi}$$

Finally, we also have $\delta(x)\psi(x)$, but since δ is only relevant at 0, we have

$$\delta(x)\psi(x) = \delta(x)\psi(0) = \psi(0)\int_{-\infty}^{\infty} e^{-ikx}\,\frac{dk}{2\pi}$$

Writing this out fully, we have

$$\left(-\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} \tilde{\psi}_k(-ik)^2 e^{-ikx}\,\frac{dk}{2\pi} - \alpha\psi(0)\int_{-\infty}^{\infty} e^{-ikx}\,\frac{dk}{2\pi}\right) = E\int_{-\infty}^{\infty} \tilde{\psi}_k e^{-ikx}\,\frac{dk}{2\pi}$$

In all three terms, we have the integrals and exponentials, so let's focus on the coefficients to get the S.Eq. in the momentum space. This gives

$$\left(\frac{\hbar^2 k^2}{2m}\tilde{\psi}_k - \alpha\psi(0)\right) = E\tilde{\psi}_k$$

Hence we have reduced the second-order DE into solving a simple equation, to get

$$\left(\frac{\hbar^2 k^2}{2m} - E\right)\tilde{\psi}_k = \alpha\psi(0) \implies \tilde{\psi}_k = \frac{\alpha\psi(0)}{\frac{\hbar^2 k^2}{2m} - E}$$

This is already in some sense a solution to our problem: it determines the wavefunction in momentum space, which determines the wavefunction in real space via an inverse Fourier transform. But we want to know whether there are bound states in this potential, so let's look at E. Recall that

$$\psi(x) = \int_{-\infty}^{\infty} \tilde{\psi}_k e^{-ikx} \frac{dk}{2\pi}$$

So we can write

$$\psi(0) = \int_{-\infty}^{\infty} \tilde{\psi}_k \frac{dk}{2\pi}$$

Let's integrate both parts of the expression we have for $\tilde{\psi}_k$:

$$\int_{-\infty}^{\infty} \tilde{\psi}_k \frac{dk}{2\pi} = \psi(0) = \alpha\psi(0) \int_{-\infty}^{\infty} \frac{1}{\frac{\hbar^2 k^2}{2m} - E} \frac{dk}{2\pi}$$

Canceling and simplifying gives us an equation without the wavefunction, and only one unknown: the energy E. Note that we can replace the $-E$ in the denominator above by $+|E|$. Evaluating the integral gives

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

Hence there only is one solution for the energy in a shallow well in one dimension. Since α is the controlling coefficient for the strength of the delta potential, in a sense, the energy level scales proportional to the strength of the potential.

5.4 Bound states in a delta-potential (higher dimensions)

We will now look at the same problem in 2D and 3D. As an aside, there are actually few problems in quantum mechanics that allow relatively simple analytical solutions in higher dimensions; usually we resort to numerical analysis or technically complicated calculations. It turns out, however, that for this problem we can follow mostly the same procedure we did for 1D, but it will give us a different result.

Result In 1D, the bound state always exists, and the energy scales with how powerful the potential is. In 2D, the level also always exists, but the energy is extremely small and scales exponentially with the strength of the potential. In 3D, there is no level at all; weak attractions do not induce a bound state.

Derivation Again, we begin with the S.Eq in D dimensions:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \alpha\delta(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r})$$

Note that in 3D, the δ we have is simply $\delta(\vec{r}) = \delta(x)\delta(y)\delta(z)$. Now we go from real space to momentum space; the only difference in the transform is that we have to do a transform for each dimension:

$$\tilde{\psi}_{\vec{k}} = \underbrace{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}}_{D \text{ times}} d^D r \psi(\vec{r}) e^{-i\vec{k}\cdot\vec{r}}$$

Examining the coefficients as we did earlier, we get essentially the same equation that we got earlier:

$$\frac{\hbar^2 k^2}{2m}\tilde{\psi}_{\vec{k}} - \alpha\psi(0) = E\tilde{\psi}_{\vec{k}}$$

We can solve this equation for $\tilde{\psi}_{\vec{k}}$ to get

$$\tilde{\psi}_{\vec{k}} = \frac{\alpha\psi(0)}{\frac{\hbar^2 k^2}{2m} + |E|}$$

We use the exact same trick as before, integrating this entire equation over D dimensional space. This gives us the self-consistency equation.

$$1 = \alpha \int_{-\infty}^{\infty} \frac{d^D k}{(2\pi)^D} \frac{1}{\frac{\hbar^2 k^2}{2m} + |E|}$$

However, there is a difference now: this integral is over D dimensions, and it turns out that this difference in dimensionality has important consequences. In the 1D case, no matter how small α is, there is a solution for E. For higher dimensions, that doesn't happen.

Calculating the integral To understand this, let's calculate the integral. To do this calculation, note that the integrand doesn't care about the direction of the wave vector, only its absolute value. For example, in 2D, we can write $d^2k = dk\, k d\phi_{\vec{k}}$. So in 2D, we can write this integral as

$$1 = \alpha \int \frac{d^2 k}{(2\pi)^2} \ldots = \frac{\alpha}{(2\pi)^2} \int_0^{\infty} dk\, k \ldots \int_0^{2\pi} d\phi_k$$

But nothing depends on the angle, so the angle integral just comes out to 2π. In general, in D dimensions, we can also do the same thing:

$$1 = \frac{\alpha S_{D-1}}{(2\pi)^D} \int \frac{dk\, k^{D-1}}{\frac{\hbar^2 k^2}{2m} + |E|}$$

The S_{D-1} is the value that comes out of the angle integrals, e.g. in two dimensions we integrate over a circle, in three dimensions it is over the solid angles that cover the entire sphere. So $S_1 = 2\pi$, and $S_2 = 4\pi$ (formally, $S_0 = 2$), etc. Now let's look at the remaining integral. It is divergent for large k; the larger k is, the "more" divergent it becomes, and the integral is actually infinity. Why does this happen? Recall that $V(\vec{r}) = \alpha\delta(\vec{r})$, and δ is very artificial, we created/used it just to model a shallow potential which in reality has a finite width and finite depth. So we can limit the divergence by integrating from 0 to some parameter $1/a$.

In other words, if we redid everything with a real potential instead of $\alpha\delta(\vec{r})$, then this issue does not actually occur in our calculations.

Critical dimension (D=2) So let's look at $D = 2$, the 2D case.

$$\frac{1}{\alpha} = \frac{S_{D-1}}{(2\pi)^D} \int_0^{1/a} dk \frac{k^{D-1}}{\frac{\hbar^2 k^2}{2m} + |E|}$$

We want to know if there is a bound state as $\alpha \to 0$, or, rephrased, whether we can make the integral arbitrarily large by choosing E (we don't really care about the constants in front, since they are, well, constant for a fixed dimension). Upon inspection, we note that the larger E is, the smaller the integral, so the integral is largest when $E = 0$. Setting E to 0 and pulling out constants again, the question becomes whether the following integral can diverge:

$$\int_0^{1/a} dk\, k^{D-3}$$

Clearly if $D = 3$, there is no divergence, and so in $3D$ there is no bound state. However, at a lower dimension, $D = 2$, this integral becomes

$$\int_0^{1/a} \frac{dk}{k} = \ln \frac{1}{0} = \infty$$

So if $D \leq 2$, there is divergence, and in $1D$ and $2D$ there is a bound state.

Very shallow level in 2D quantum well Finally, let's estimate the energy of the bound state by estimating the integral

$$\frac{1}{\alpha} = \frac{1}{2\pi}\int_0^{1/a} dk \frac{k}{\frac{\hbar^2 k^2}{2m} + |E|} = \frac{m}{\pi\hbar^2}\int_0^{1/a} \frac{dk\, k}{k^2 + \left(\frac{\sqrt{2m|E|}}{\hbar}\right)^2}$$

If we set $|E| = 0$, then we get divergence, which allows the existence of the bound state. We can use the method of **logarithmic accuracy** to bring the squared term from the denominator into the integration bounds to get a reasonable estimate:

$$\approx \frac{m}{\pi\hbar^2}\int_{\frac{\sqrt{2m|E|}}{\hbar}} \frac{dk}{k} = \frac{m}{\pi\hbar^2}\ln\left(\frac{\hbar}{a\sqrt{2m|E|}}\right)$$

Finally, we can solve for $|E|$ by exponentiating and rearranging, to get

$$|E| \approx \frac{\hbar^2}{ma^2}\exp\left(-\frac{2\pi\hbar^2}{\alpha}\right)$$

This result is very interesting and strange. Recall that α controls the strength of the potential, and we are looking at the case $\alpha \to 0$. But $e^{-x/\alpha}$ when does not have a Taylor expansion around $\alpha \to 0$. This would actually have been an issue if we tried to solve the problem using **perturbation theory**, which often gives solutions to problems that other methods cannot solve.

Chapter 6

Cooper Pairing in Superconductors

6.1 The Phenomenon of Superconductivity

Superconductors have a number of interesting properties, e.g. levitation through expulsion of magnetic flux, which is unique to superconductors.

Zero-resistance state The main property of superconductors is that they have **zero resistance**. An early example is of mercury, whose resistance drops to zero (not close to zero, *exactly* zero) below a certain critical temperature $T_c = 4.2$ K. This is actually very surprising; consider what we discussed in chapter 4.

Magnetic flux expulsion Magnetic flux generally passes through materials, and they do not disrupt the flux. But in a superconducting phase, the magnetic field tries to "avoid" the superconductor. The magnetic field lines try to go around the conductor. This is also known as the **Meissner effect**, and is responsible for the levitation of superconductors on magnets. However, this description is a little simplified; there are actually **vortices** of magnetic flux in the conductor that "pins" the conductor with respect to the field lines. Interestingly, the Meissner effect is theoretically equivalent, to some degree, to the **Higgs mechanism**, in that while the Higgs gives mass to elementary particles, the Meissner effect gives "mass" to the magnetic field, making it energetically unfavorable for it to be in the conductor.

Race to increase transition temperatures Since the early 1900s, upon the discovery of the superconductivity of mercury, there have been continuous efforts to find superconductors with high critical temperature T_c. The goal is a room-temperature superconductor, which remove resistive losses from wires.

Bernd Matthias' rules Most of the recent progress in finding superconducting materials, however, is mostly experimental: pick a material, test it. In fact, a guy at Bell Labs who was really good at finding new superconductors, Bernd Matthias, put together a set of rules to help discover superconductors: high symmetry is good, cubic symmetry is best, stay away from oxygen, magnesium, and insulators. Apparently the most important rule was to stay away from theorists (since for many years there was no theory of superconductivity).

6.2 Quantum Statistics: Bosons and Fermions

Superconductivity is a many-particle (electrons) phenomenon, and doesn't really have a single-particle counterpart, so it can't be well understood with the single-particle S.Eq. The first step is to understand the concept of **quantum statistics**, which is an intrinsically quantum interaction between identical particles;

this, obviously, doesn't have a classical counterpart. We will be looking at **bosons** and **fermions**, two fundamental classes of particles with respect to their quantum statistics. Their lowest energy states, i.e. **ground states**, are very different, and it turns out that it is the transition between fermion-like to boson-like behavior that explains superconductivity.

Particle braiding and spin-statistics theorem Consider two identical particles at $\vec{r}_1, \vec{r}_2$, so every intrinsic property are the same. What happens if we "braid" the two particles, i.e. they exchange places? Note that the wavefunction requires a phase factor when we exchange the locations of the two particles:

$$\psi(\vec{r}_1, \vec{r}_2) \to e^{i\phi}\psi(\vec{r}_2, \vec{r}_1)$$

So even though from our perspective nothing has changed, we in principle get an extra quantum mechanical phase. What are the possible values of this quantum statistical phase ϕ? **Pauli** proved a one-to-one correspondence between the **internal angular momentum**, or **spin**, of a particle and its quantum statistics: for particles with integer (including 0) spin, $\phi = 0$ (these are bosons), but for half-integer spin, $\phi = \pi$ (these are fermions).

Remark This classification of fermions and bosons is actually unique to the 3D space that we inhabit; in a 2D space, there are many more possibilities for ϕ, implying many other classes of particles.

Pauli exclusion principle for fermions Consider the case $\phi = \pi$. What are the consequences of the minus sign we pick up in front of the wavefunction? An important consequence is for $\vec{r}_1 = \vec{r}_2$, for which we get

$$\psi(\vec{r}_1, \vec{r}_1) = -\psi(\vec{r}_1, \vec{r}_1) = 0$$

Hence the probability of finding two identical fermions at the same location is $|\psi(\vec{r}_1, \vec{r}_1)|^2 = 0$. More generally, no two fermions can occupy the **same quantum state**, but there is no such restriction for bosons. This is the **Pauli exclusion principle**, and has important consequences. Given a single state $|i\rangle$, the possible occupation number is $n_i^{(f)} = 0, 1$ for fermions, but $n_i^{(b)} = 0, 1, \ldots, \infty$ for bosons.

Ground state of many-boson system Suppose we have many energy levels that are initially empty. What happens if we "pour" identical bosons into these single-particle states $|i\rangle$ with energies E_i? What is the ground state the system forms at low temperature? Since any number of bosons can occupy any state, all the bosons are sitting at the lowest possible level. This lowest possible state is called a **Bose-Einstein condensate (BEC)**.

Superfluidity in a BEC A condensate of bosons can form a quantum liquid that has no viscocity and flows without resistance. When we talk about superconductivity, we somewhat want a "superfluid of electrons", only the problem is that electrons are not bosons, they are fermions.

Ground state of many-fermion system Consider the same setup as the many-boson system, except now we are pouring identical fermions into a prescribed landscape of energy levels. Due to the Pauli exclusion principle, each state can only contain one fermion, so we have to stack them one by one from lowest energy level upward. For a 3D metal, we will have some threshold momentum, called the **Fermi surface** below which every state is occupied, and above which no state is occupied, and this occurs because

$$E(\vec{p}) = \frac{\vec{p}^2}{2m}$$

It turns out that this implies a typical **Fermi temperature** of around $10,000$ K, calculated by converging the Fermi energy to temperature by dividing by the Boltzmann constant:

$$T_F = \frac{1}{k_B}\frac{p_F^2}{2m} \approx 10,000 \text{ K}$$

How do we reconcile this idea of a metal with superconductivity? A key to solving the mystery was to ask whether it was possible to convert "electron liquid" into a bosonic superfluid. For example, the electrons could "pair up" to get integer spin per pair, so perhaps each pair would behave as a boson. It turns out that this is actually what happens, and the pairs of electrons are called **Cooper pairs**. A superconductor is simply a Bose-Einstein condensate of Cooper pairs. But why do Cooper pairs form?

6.3 A Step Back: Two-Particle Schrödinger Equation

In this section, we are going to see how Cooper pairs form. In the previous section, we looked at a single particle in a potential; now, we will look at the two-particle problem (i.e. the two electrons near the Fermi surface). It turns out that two-particle problems often reduce to single-particle problems.

Two-particle S.Eq For the sake of generality, we're going to deal with two particles of (potentially) different masses m_1 and m_2, interacting in the potential $V(\vec{r})$:

$$\left(-\frac{\hbar^2\nabla_1^2}{2m_1} - \frac{\hbar^2\nabla_2^2}{2m_1} + V(\vec{r}_1 - \vec{r}_2)\right)\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

The goal of this section is to show that instead of solving this complicated DE, we can reduce it into two single-particle S.Eq's. First of all, let's do a change of variables:

$$(\vec{r}_1, \vec{r}_2) \to (\vec{R}, \vec{r}) = \left(\frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2},\ \vec{r}_2 - \vec{r}_1\right)$$

Note that the first coordinate $\vec{R}$ is the **center of mass**, and the second coordinate is the **distance** between the particles. The potential function under this coordinate transform is trivial, but what about the Laplacian?

Calculating the Laplacians Let's just focus on one (x) component of the Laplacian, with

$$X = \frac{m_1x_1 + m_2x_2}{m_1 + m_2} \qquad x = x_2 - x_1$$

We want to calculate $\nabla_1^2/m_1 + \nabla_2^2/m_2$ for the x-component, so we do a change of variables in the derivatives:

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} = \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

Similarly, $\partial/\partial x_2$ becomes:

$$\frac{\partial}{\partial x_2} = \frac{m_2}{m_1 + m_2}\frac{\partial}{\partial X} + \frac{\partial}{\partial x}$$

Plugging this in, we get the following expression for the Laplacian:

$$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \frac{1}{m_1}\left(\frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial x}\right)^2 + \frac{1}{m_2}\left(\frac{m_2}{m_1 + m_2}\frac{\partial}{\partial X} + \frac{\partial}{\partial x}\right)^2$$

If we expand the squares of these terms, we will get the squares of the derivatives themselves, but also the cross term $\partial/\partial X\partial x$. However, note that the coordinates were chosen in such a way that the cross terms of the two squared expressions cancel out (due to the $+$ and the $-$). We can verify this by expanding and simplifying to get

$$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \frac{1}{m_1 + m_2}\frac{\partial^2}{\partial X^2} + \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2}$$

Note that the coefficient of the second term $\partial^2/\partial x^2$ is often called the **reduced mass** $\mu = m_1m_2/(m_1+m_2)$.

Back to single-particle So now we have actually shown that

$$-\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 = -\frac{\hbar^2}{2(m_1+m_2)}\Delta_R - \frac{\hbar^2}{2\mu}\Delta_r$$

Plugging this into the S.Eq, we get

$$\left(-\frac{\hbar^2}{2}\left(\frac{\Delta_R}{m_1+m_2} + \frac{\Delta_r}{\mu}\right) + V(\vec{r})\right)\tilde{\Psi}(\vec{R},\vec{r}) = E\Psi(\vec{R},\vec{r})$$

We can group the terms in the left hand side: $\Delta_r/\mu + V(\vec{r})$ is the part that depends on the relative coordinate $\vec{r}$ and which involves interaction, and the other part is simply a **free S.Eq** for a particle with combined mass $m_1 + m_2$. So to extract the behavior of the bound pair $m_1 + m_2$, we simply look for a solution to the free S.Eq.:

$$\tilde{\Psi}(\vec{R},\vec{r}) = e^{\frac{i\vec{P}\cdot\vec{R}}{\hbar}}\psi(\vec{r})$$

where the energy of this motion is simply $\vec{P}^2/(m_1+m_2)$. The reduced mass term will give us

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\vec{r}^2} + V(\vec{r})\right)\psi(\vec{r}) = E'\psi(\vec{r})$$

where $E' = E - \vec{P}^2/(m_1+m_2)$. This is a **single-particle S.Eq**, which we can apply our earlier results to!

Remark Note that in the context of the electron-pairs problem we're going to be looking at, we have $m_1 = m_2 = m$, which gives us $\mu = m^2/2m = m/2$, so in this single-particle S.Eq, we will have 2μ simply as the electron mass.

6.4 The Cooper Problem

Finally, we will solve the **Cooper problem**, which is a problem of weakly attractive electrons near the **Fermi surface** that form pairs that, at low temperatures, act as a **Bose-Einstein condensate**. It turns out that this derivation isn't too technically involved at all.

Isotope effect Before we begin, let's investigate the origin of the **attractive potential** between electrons. Consider a **lattice** of particles, which is rigid but may oscillate. It turns out that the transition temperature of a superconductor depends strongly on the mass of the particles in this lattice, indicating that superconductivity has something to do with interactions between the ions and the crystal lattice. Later on we will see that whenever electrons pass through a region of the lattice, it will polarize the lattice (locally), and if a second electron passes through the same region, it is attracted to this region. Hence we have a **phonon**-mediated attraction between electrons. We will see this later.

Spherical-cow model of phonon-mediated attraction The actual full model is rather complicated, so let's use a slightly simplified version that works just as well. Note that when electrons interact by exchanging waves, called **phonons**, we must conserve both energy and momentum. Recall that the **Fermi temperature** is

$$T_K \approx 10,000 \text{ K}$$

It turns out that the **phonon energies**, when converged to a temperature, is

$$T_D \approx 400 \text{ K}$$

So the phonons exchanged by the electrons have much lower energies than the electrons themselves. This puts constraints on the possible momenta and energies of the electrons that can experience this sort of process. The exact interaction is complicated, but we can use a simple model:

$$V(\vec{p}) = \begin{cases} -V_0 & \text{if } \frac{p^2}{2m} - E_F < \hbar\omega \\ 0 & \text{otherwise} \end{cases}$$

This describes a momentum-dependent interaction between two electrons, and tells us that two electrons attract each other if they are located within a certain range of the Fermi surface, with the range proportional to the phonon energy: this is described by $-V_0$, some constant. This is rather similar to the delta potential wells we saw earlier, except with two particles. However, we also know that the two-particle S.Eq. can be reduced to the single-particle case.

Cooper pairing problem Recall the two-particle S.Eq, but with $m_1 = m_2 = m$, so we get

$$\left(-\frac{\hbar^2\nabla^2}{m} - V_0\delta(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r})$$

Using the same technique as we did when we first encountered delta potentials, we find the **momentum-space** version of this S.Eq. by taking the Fourier transform:

$$\frac{\hbar^2}{m}\vec{p}^2\psi(\vec{p}) - V_0\underbrace{\int\frac{d^3p}{(2\pi)^3}\psi(\vec{p})}_{\psi(0)} = E\psi(\vec{p})$$

Interestingly, recall that we discovered that weak attractions in 3D actually do not produce bound states; however, we are expecting bound states to arise here. Note that since electrons experiencing the attraction are close to the Fermi surface, we achieve a "reduction" of dimensionality into 2D. This actually gives rise to the appearance of a bound state in a surprising way.

Derivation We repeat the same procedure that we did for delta potentials, except now E consists of two parts:

$$E = 2E_F + \Delta$$

where E_F is the energy already possessed by the electrons at the Fermi surface, and Δ is the negative attractive potential. This difference is actually the mathematical reason that we get a bound state. The final result of this calculation, which is completely analogous to our earlier work, is

$$\Delta \propto -\hbar\omega_D \exp\left(-\frac{1}{N_0V_0}\right) \qquad N_0 = \frac{mp_F}{4\pi^2\hbar^3}$$

Note that the existence of such a solution indicates that indeed, the electrons can achieve lower energies. Furthermore, note that since V_0 is in the denominator of the exponential, we get exponentially small energies of the bound state. We can directly see the result of the reduction in dimensionality: we have already seen a result of this form in the 2D solutions to a particle in a delta potential. As before, the expression is very strange, in that it has no Taylor expansion, and so again, there is no way to approach it using perturbation theory. Finally, if we did not have the exponential in the expression, we would get superconductivity at very high temperatures.

Chapter 7

Quantum Harmonic Oscillator

A quantum harmonic oscillator is relevant to many experimental systems, ranging from cold atoms to molecules whose low-energy oscillations are described by a harmonic oscillator, and the quantization of light, and the oscillations of crystals (called phonons), and many other things. On the other hand, the solution to the problem, from a theoretic point of view, gives us many useful tools, e.g. **creation** and **annihilation** operators, that are useful in a variety of contexts.

7.1 Reminder From Classical Physics

Before we begin with a quantum oscillator, let's look at the classical harmonic oscillator of a mass on a spring. **Hooke's law** gives an expression for the force on the mass relative to its displacement:

$$F = -kx = -\frac{d}{dx}\left(\frac{kx^2}{2}\right)$$

We can write the force in terms of the gradient of the potential (here, in 1D, a simple derivative), which we find to be $V(x) = kx^2/2$. Using this, we can use Newton's second law to solve for x:

$$m\frac{d^2x}{dt^2} = F = -kx$$

Rewriting this as $d^2x/dt^2 + \omega^2 x = 0$ with $\omega = \sqrt{k/m}$, we get the solutions

$$A\sin(\omega t + \phi_0) \qquad A\cos(\omega t + \phi_0)$$

So here we have two free parameters A, ϕ_0 that determine initial conditions. To move further, let's say $x(0) = 0$. Then we get the solution

$$x(t) = x_0 \sin(\omega t)$$

If we want to find the velocity of the oscillator, differentiating the position gives us

$$v(t) = \frac{dx}{dt} = x_0\omega\cos(\omega t)$$

Now we can write the energy of the system, noting that the potential energy can be written as $V(x) = kx^2/2 = m\omega^2x^2/2$:

$$E = \frac{mv^2}{2} + \frac{1}{2}m\omega^2x^2$$

Note that this is the form in which this particular equation appears in the literature, particularly quantum mechanical literature. Plugging in $v(t)$ and $x(t)$, we find

$$E = \frac{m}{2}x_0^2\omega^2\cos^2(\omega t) + \frac{m}{2}x_0^2\omega^2\sin^2(\omega t) = \frac{m}{2}x_0^2\omega^2$$

This shows that energy is **conserved**, in accordance with energy conservation. Furthermore, note that if we plot $m\omega x$ vs mv (kinetic vs potential), we get a circle whose radius depends on the energy of the system.

Making the oscillator quantum If we have a molecule, we would like to talk about its oscillations. Or if we have a quantum particle in an arbitrary potential $V(x)$, we are interested in its low-energy behavior. In any case, quantizing the classical oscillator is well-motivated. To begin, let's take classical energy:

$$E = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$$

Doing the standard replacements E with $\hat{H}$ and p with $\hat{p} = -i\hbar d/dx$ and x with $\hat{x} = x$ gives us

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

The problem we want to solve now is to find solutions to the **eigenvalue problem**:

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

When solving this, we should keep in mind that the potential has localized, discrete states, i.e. the energies will be quantized. Determining these energy levels is the main problem we will be looking at.

7.2 Creation/Annihilation Operators

There are many equivalent ways to solve this eigenvalue problem, but we will look at a purely algebraic method of solving it using **creation/annihilation** operators. We will see that the oscillator spectrum and its wavefunction follows just from an analysis of these operators and their commutation relations. Actually, we will not even write down the S.Eq. or boundary conditions: these operators are sufficient for us.

Taking the square root of the Hamiltonian There are only three dimensional constants $m, \omega, \hbar$ in our problem. It turns out that we can construct one parameter out of these three that has units of energy, as

$$[\hbar\omega] = [E]$$

So whatever our spectrum looks like, it must be proportional to $\hbar\omega$. So let's divide our Hamiltonian by $\hbar\omega$:

$$\frac{\hat{H}}{\hbar\omega} = \frac{m\omega\hat{x}^2}{2\hbar} + \frac{\hat{p}^2}{2m\omega\hbar}$$

We will now write this expression as

$$\frac{\hat{H}}{\hbar\omega} = \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x}\right)^2 + \left(\frac{\hat{p}}{\sqrt{2m\omega\hbar}}\right)^2$$

This is so we can use difference of squares, $A^2 + B^2 = (A - iB)(A + iB)$:

$$\frac{\hat{H}}{\hbar\omega} = \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}\right)\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}\right)$$

However, this isn't correct. Note that $\hat{x}$ and $\hat{p}$ are **operators**, so they do not necessarily commute, i.e. $\hat{x}\hat{p} \neq \hat{p}\hat{x}$. So difference of squares does not actually hold, and we must add extra terms:

$$\frac{\hat{H}}{\hbar\omega} = \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}\right)\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}\right) - \frac{i}{2\hbar}[\hat{x}, \hat{p}]$$

where $[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x}$ is the **commutator** of $\hat{x}$ and $\hat{p}$. We can verify that this term is indeed correct by expanding term by term to make sure we actually get the Hamiltonian.

Creation/annihilation operators Note that the first factor is the **Hermitian conjugate** of the second factor, since $\hat{x}$ and $\hat{p}$ are physical operators, which means they are Hermitian (i.e. $\hat{x}^\dagger = \hat{x}$ and $\hat{p}^\dagger = \hat{p}$). Based on this observation, let's introduce a new operator $\hat{a}$ that is exactly the second factor, and then $\hat{a}^\dagger$ will be the first factor. Then $\hat{a}^\dagger$ is the **creation operator** and $\hat{a}$ is the **annihilation operator**.

Nomenclature The main result, as we will see later, is that the spectrum is a series of equidistant energy levels, separated by $\hbar\omega$, and the energy of the ground state is $\hbar\omega/2$, which comes from the commutator term in the identity for the Hamiltonian. Suppose we prepare our quantum oscillator in the ground state. Applying the creation operator $\hat{a}^\dagger$ "creates" a quanta of energy by promoting the oscillator to the first excited state. Analogously, the annihilation operator "removes" a quanta of energy by dropping the oscillator by one energy level. We will see a proof of these statements in the next section, using various commutation properties between the operators we have just seen.

7.3 Commutators; Generating the Energy Spectrum

Rewriting what we just proved, we have the oscillator Hamiltonian

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

where $\hat{a}^\dagger$ and $\hat{a}$ are the creation and annihilation operators

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}$$
$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}$$

Commutation relations The commutator $[\hat{x},\hat{p}]$ is one of the canonical commutation relations in quantum mechanics. It is proportional to $i\hbar\hat{I}$, i.e. this is actually not an operator at all, it is just a constant. To see this, let's look at

$$(\hat{x}\hat{p})\psi(x) = x\left(-i\hbar\frac{d}{dx}\right)\psi = -i\hbar x\psi'$$
$$(\hat{p}\hat{x})\psi(x) = -i\hbar\frac{d}{dx}(x\psi) = -i\hbar\psi - i\hbar x\psi'$$

Putting these two together, the commutator turns out to be

$$([\hat{x},\hat{p}])\psi(x) = (\hat{x}\hat{p} - \hat{p}\hat{x})\psi = i\hbar\psi = (i\hbar\hat{I})\psi$$

So the action of the commutator $[\hat{x},\hat{p}]$ is simply multiplication by $i\hbar$.

Another commutation relation In the same manner, let's calculate $[\hat{a},\hat{a}^\dagger]$:

$$[\hat{a},\hat{a}^\dagger] = \left[\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}, \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}\right]$$

However, the commutator of an operator with itself cancels, so the only relevant terms are the cross terms. So

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

But we know that $[\hat{x}, \hat{p}] = i\hbar$, so this expression completely simplifies to

$$[\hat{a}, \hat{a}^\dagger] = 1$$

These two commutation relations means that we can rewrite the expression of the Hamiltonian as

$$\hat{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \qquad [\hat{a}, \hat{a}^\dagger] = 1$$

Since the constant 1/2 will not affect the solutions to the eigenvalue problem, we will focus on the eigenvalue problem for $\hat{a}^\dagger \hat{a}$.

Generating the spectrum Assume we already know one eigenstate of $\hat{a}^\dagger \hat{a}$:

$$\hat{a}^\dagger \hat{a} |n\rangle = n|n\rangle$$

This implies that $|n\rangle$ is also an eigenstate of the Hamiltonian, as $\hat{H}|n\rangle = \hbar\omega(n + 1/2)|n\rangle$. Now let's act on $|n\rangle$ with $\hat{a}^\dagger$, and see how it behaves with regards to $\hat{a}^\dagger \hat{a}$ using the commutation relation:

$$\hat{a}^\dagger \hat{a}(\hat{a}^\dagger |n\rangle) = \hat{a}(1 + \hat{a}^\dagger \hat{a})|n\rangle = \hat{a}^\dagger (1 + n)|n\rangle = (n + 1)\hat{a}|n\rangle$$

So if $|n\rangle$ is an eigenfunction of the operator $\hat{a}^\dagger \hat{a}$, then $\hat{a}^\dagger |n\rangle$ is also an eigenfunction, but it raises the energy by 1. Similarly, if $|n\rangle$ is an eigenfunction, then so is $\hat{a}|n\rangle$, which lowers the energy by 1:

$$\hat{a}^\dagger \hat{a}(\hat{a}|n\rangle) = (n - 1)(\hat{a}|n\rangle)$$

Hence knowing one eigenfunction of the Hamiltonian gives us a seemingly infinite number of other eigenfunctions. But what can n be? It turns out that n must be an integer: since we are trying to find energy levels in a quadratic potential, if we know a certain eigenfunction with energy E_n, we can lower its energy by 1, seemingly indefinitely. But we can't go below 0, which implies that there must exist a ground state where

$$\hat{a}|0\rangle = 0 \implies \hat{a}^\dagger \hat{a}|0\rangle = 0 \implies E_0 = \frac{\hbar\omega}{2}$$

So our energy levels are

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

But this was constructed under the assumption that an eigenstate exists. We still need to show this.

7.4 Harmonic Oscillator Wavefunctions

Let's summarize what we have so far. We know the Hamiltonian of the oscillator:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right)$$

We know the energy spectrum:

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

We also know action on eigenfunctions by the creation and annihilation operators $\hat{a}^\dagger$ and $\hat{a}$:

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

However, we don't know the explicit form of an eigenfunction, i.e. a wavefunction.

Deriving the ground-state wavefunction So let's focus on the ground state, with wavefunction $\psi_0(x)$. We know that $\hat{a}^\dagger \hat{a}|0\rangle = 0$, or, explicitly,

$$\hat{a}\psi_0(x) = \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\omega\hbar}}\right)\psi_0(x) = 0$$

Expanding this using the definitions of $\hat{x}$ and $\hat{p}$ gives

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

Simplifying a little, and introducing the constant $x_0 = \sqrt{\hbar/m\omega}$ (which has a physical dimension of length), we see that

$$\left(\frac{x}{x_0} + x_0\frac{d}{dx}\right)\psi_0(x) = 0$$

Rewriting, we get the differential equation

$$\psi_0' = -\frac{x}{x_0^2}\psi_0$$

It is not hard to solve this differential equation (or, by inspection) to find the Gaussian wavefunction

$$\psi_0(x) = C\exp\left(-\frac{x^2}{2x_0^2}\right)$$

Note that C is the normalization constant, i.e. it must be chosen so that the integral over $(-\infty, \infty)$ is 1. This gives

$$\int_{-\infty}^{\infty}\psi_0^2(x)\,dx = 1 \implies C = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$$

So we did not need to solve the S.Eq.: we solved a much easier differential equation instead.

Excited states But this is just the ground state: the wavefunction of the lowest energy state. What about higher-energy excited states? We can use the creation operator. Recall that

$$\frac{\hat{a}^\dagger}{\sqrt{n+1}}|n\rangle = |n+1\rangle$$

So we can repeatedly apply this to the ground state $|0\rangle$. The polynomial factors that will appear in the wavefunctions of these higher-energy eigenstates are called **Hermite polynomials**.

Chapter 8

Phonons in Crystals

8.1 Preliminary Discussion

The quantum oscillator problem and its solution can be applied to situations other than the generalization of a mass on a spring from classical physics, e.g. electromagnetic radiation is an oscillation of photons, and complex structures in quantum mechanics sometimes are built from these oscillating building blocks. We will now explore how the quantum oscillator appears in a fundamental problem in **solid-state** or **condensed matter** physics: excitations in crystals called **phonons**.

Normal modes Let's go back to classical physics. Consider a spring-mass. We know the frequency of the oscillation is

$$\omega = \sqrt{\frac{k}{m}}$$

Now let's make the system more complicated. Consider a spring-mass-spring-mass-spring system, and now this system has two different oscillation frequencies: one when the two masses are in phase ($\omega_1 = \omega$), and the other out of phase ($\omega_2 = \omega\sqrt{3}$). We can keep making things complicated, e.g. six masses attached to springs, which will give us six different oscillation frequencies. These frequencies are called **normal modes** in classical physics. However, they do have quantum analogs. For example, in the two mass spring problem, just by knowing the classical modes, we can already write down the spectrum of the corresponding quantum problem:

$$E_{n_1,n_2} = \hbar\omega_1\left(n_1 + \frac{1}{2}\right) + \hbar\omega_2\left(n_2 + \frac{1}{2}\right)$$

"Spherical cow" model of crystals An interesting example of a many-particle quantum system is a crystal lattice. Ions arrange themselves into a unique pattern, e.g. a cubic pattern. However, the ions are not static: they have preferential/equilibrium positions, but they do move around, oscillating around the equilibrium. A good model of a lattice is simply atoms (masses) tied together in a lattice by springs with some stiffness. So the lattice will have many complex normal modes. In the limit, the discrete normal modes merge into a continuous curve, corresponding to elastic waves running through the system. Mathematically, the waves can be described by the displacement of an atom with respect to time:

$$\delta\vec{r}_n(t) \propto e^{i(\vec{k}\cdot\vec{r}_n - \omega_{\vec{k}}t)}$$

The main question in this model is how to determine $\omega_{\vec{k}}$, the **phonon dispersion**. Of particular interest are the **low-energy modes** of the system. Do we need to overcome any threshold in order to excite the crystal? We will see later that it doesn't matter how weak the perturbation is, there is always a low-energy mode that we can excite in the crystal, called an **acoustic mode**. It turns out that the appearance of

these modes has a profound explanation going as far as relativistic quantum physics, where **Goldstone's theorem** guarantees the existence of these modes.

Goldstone's theorem Suppose we have a quantum system invariant with respect to a class of transformations, i.e. if $\hat{U}$ is a transformation, it commutes with the Hamiltonian of our system ($\hat{U}\hat{H}\hat{U}^{-1} = \hat{H}$), but now we have a whole family of transformations. Examples include translational or rotational symmetry. Formally, we postulate the existence of a **symmetry group** of $\hat{H}$. It turns out that even though the model is invariant with respect to these transformations, the ground state is not necessarily invariant. So the system be in a state $|\psi_0\rangle$ such that

$$\hat{U}|\psi_0\rangle \neq |\psi_0\rangle$$

In this case, we say the symmetry is **spontaneously broken**. But the key statement here is that when this happens, then to each broken symmetry, there corresponds a low-energy mode.

Goldstone's theorem example Consider a crystal lattice described by some complex wavefunction $|\psi_0\rangle$ satisfying a Hamiltonian of the form

$$\hat{H} = \sum_n \frac{\vec{p}_n^2}{2m} + \sum_{n,m} V(\vec{r}_n - \vec{r}_m)$$

where the potential between two particles is dependent only on the distance between them. Note that, because of this, the Hamiltonian is invariant under any translation

$$\vec{r} \to \vec{r} + \vec{\alpha}$$

However, the crystalline structure is not invariant under this translation: if we move the particles by a fraction of the lattice constant, we don't get the same crystal. So here we have spontaneously broken three symmetries, in the x, y, z directions, and there must exist three low-energy modes in this structure. These modes are precisely the phonons we're going to find.

8.2 Classical Oscillator Chain

In this section, we will look at an infinite chain of classical oscillators (in 1D) and determine the normal modes of this system. We can do the same thing in 2D or 3D, and the key features of the solution pretty much stay the same, but the case in 1D is simpler.

The model We will have an infinite chain of two alternating types of "atoms" m (lighter) and M (heavier), with positions x_n and y_n respectively (i.e. we will group atoms into "cells" of a light and heavy atom). For further simplicity, we will measure distance with respect to this elementary cell size, denoting a has the equilibrium length of the spring connecting two atoms, and setting $2a = 1$. The energy of this system is very easy to write down:

$$H = \sum_n \left(\underbrace{\frac{p_n^2}{2m} + \frac{P_n^2}{2M}}_{\text{kinetic energy}} + \underbrace{\frac{k}{2}(x_n - Y_n)^2 + \frac{k}{2}(x_{n+1} - Y_n)^2}_{\text{potential energy } V} \right)$$

Note that the potential energy comes from Hooke's law. Now we need to write down the equations of motion for all the particles involved, which follow from Newton's equations:

$$\frac{dp_n}{dt} = -\frac{\partial V}{\partial x_n} \qquad \frac{dP_n}{dt} = -\frac{\partial V}{\partial Y_n}$$

Here we use that the time-derivative of the momentum is the force, which is the gradient of the potential, but we are in 1D so a partial suffices. Formally differentiating, we get

$$\frac{dp_n}{dt} = k(Y_n - x_n) + k(Y_{n-1} - x_n)$$
$$\frac{dP_n}{dt} = k(x_n - Y_n) + k(x_{n+1} - Y_n)$$

The presence of two terms in each equation is indicative of two springs being attached to each atom.

Wave solutions to Newton's Eqs. So we have an infinite system of coupled differential equations (rewritten version of the above):

$$m\frac{d^2x_n}{dt^2} = k(Y_n + Y_{n-1} - 2x_n)$$
$$M\frac{d^2Y_n}{dt^2} = k(x_n + x_{n+1} - 2Y_n)$$

However, it turns out we can use the Fourier transform along with a reasonable physical guess to solve the problem in a few relatively straightforward steps. The method involves representing the time-dependent coordinates of our particles as linear combinations of plane waves using a Fourier transform:

$$x_n(t) = \int \frac{dq}{2\pi} x_q e^{iqn - i\omega t}$$
$$Y_n(t) = \int \frac{dq}{2\pi} Y_q e^{iq(n+1/2) - i\omega t}$$

Note that in the plane wave parameters we use n because of our artificial length scale $2a = 1$. Essentially, we are assuming that whatever solution we get, it represents waves running through the crystal. Plugging this into the Newton Eqs., it turns out that we can find a self-consistent solution that relates ω and q, i.e. between the frequency of the wave and the wave vector. This is the dispersion of the waves, and solving the equations in this context basically means to find ω as a function of q. Anyhow, plugging things in, we find

$$\begin{aligned}
\frac{d^2x_n}{dt^2} &= \int_q x_q(-i\omega)^2 e^{iqn - i\omega t} \\
Y_n + Y_{n+1} &= \int_q Y_q \left(e^{iq(n+1/2)} + e^{iq(n-1/2)}\right) e^{-i\omega t} \\
&= \int_q Y_q \left(2\cos\frac{q}{2}\right) e^{iqn - i\omega t}
\end{aligned}$$

So in the Fourier space (equating the integrands), we get

$$-m\omega^2 x_q = k\left(2Y_q \cos\frac{q}{2} - 2x_q\right)$$

Repeating the same procedure for the second equation, we get

$$-M\omega^2 Y_q = k\left(2x_q \cos\frac{q}{2} - 2Y_q\right)$$

So now instead of an infinite chain of coupled equations, we have a system of two coupled equations (the coupling between neighboring q's is now gone), and now we just have a non-differential equation. Writing it in matrix form, we have

$$\begin{pmatrix} m\omega^2 - 2k & 2k\cos(q/2) \\ 2k\cos(q/2) & M\omega^2 - 2k \end{pmatrix} \begin{pmatrix} x_q \\ Y_q \end{pmatrix} = 0$$

From linear algebra, we know that in order to have a non-trivial solution, the determinant of the left matrix must be zero:

$$\det \begin{pmatrix} m\omega^2 - 2k & 2k\cos(q/2) \\ 2k\cos(q/2) & M\omega^2 - 2k \end{pmatrix} = \omega^4 - 2k(m+M)\omega^2 + 4k^2\left(1 - \cos^2\left(\frac{q}{2}\right)\right) = 0$$

This equation is for the dependence of the frequency ω on the wave vector q. It is known as a **dispersion relation**. We have already seen many dispersion relations already, actually, e.g. when we talk about the energy of a free particle $E(p) = p^2/2m$ being proportional to p^2. So here we have an equation determining the dispersion relation for elastic waves, i.e. phonons. Also, before we solve this equation, let's restore the usual physical units by $1 = 2a$. Solving, we get

$$\omega_\pm^2(q) = \frac{k}{\mu}\left(1 \pm \sqrt{1 - \frac{4\mu^2}{mM}\sin^2(qa)}\right)$$

where $\mu = mM/(m+M)$ is the reduced mass. Note that this is a non-trivial non-linear solution. The ω_- is called **acoustic phonons** and the ω_+ is called **optical phonons**. Plotting the solutions, we see a gap separating the optical phonons from zero-energy. So small perturbations will only excite acoustic modes in the vicinity of zero-energy. Note furthermore that as $q \to 0$, we have a linear dispersion with coefficient of proportionality as the speed of sound c. Also, the existence of the optical phonons turns out to be due to the existence of two types of atoms in our crystal: if we had just one type of atom, then we actually would not have the optical phonons.

Speed of sound Let's calculate the coefficient of proportionality in the dispersion of acoustic waves as q goes to zero. We can expand the $\sin^2(qa)$ term up to first-order, and the same for the square root, as $q \to 0$:

$$\sqrt{1 - \frac{4\mu^2}{mM}\sin^2(qa)} \approx \sqrt{1 - \frac{4\mu^2}{mM}(qa)^2} \approx 1 - \frac{2\mu^2}{mM}(qa)^2$$

So we find that

$$\omega_-^2(q \to 0) \approx \frac{k}{\mu}\frac{2\mu^2}{mM}(qa)^2 = \frac{2k}{m+M}(qa)^2$$

Taking the square root, we get

$$\omega_- \approx \sqrt{\frac{2ka^2}{m+M}}q$$

This is our constant of proportionality: the speed of sound c.

8.3 Quantum Oscillator Chain

Now we will look at the same oscillator chain, except in a quantum setting. The results will turn out to be very similar to those in the classical case.

Quantizing the classical model Let's just study an oscillator chain consisting of the same type of atoms, with mass m, and quantum springs of stiffness k, in the 1D case. The classical Hamiltonian is

$$H = \sum_n \left(\frac{p_n^2}{2m} + \frac{k}{2}(x_n - x_{n+1})^2\right)$$

We quantize this Hamiltonian by putting everything in their operator forms:

$$\hat{H} = \sum_n \left(\frac{\hat{p}_n^2}{2m} + \frac{k}{2}(\hat{x}_n - \hat{x}_{n+1})^2\right)$$

Note that $\hat{x}_n$ and $\hat{p}_n$ satisfy the canonical commutation relation $[\hat{x}_n, \hat{p}_n] = i\hbar$. Furthermore, if $\hat{x}_n$ and $\hat{p}_m$ are for different particles, their commutator is zero. We can unify these two by writing

$$[\hat{x}_n, \hat{p}_m] = i\hbar\delta_{nm}$$

Now we will represent each $\hat{x}_n$ with the corresponding creation/annihilation operators:

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

Of course, the creation/annihilation operators satisfy the canonical commutation relation $[\hat{a}_n, \hat{a}_m^\dagger] = \delta_{nm}$.

Rewriting in terms of $\hat{a}_n^\dagger$ and $\hat{a}_n$ Plugging these in, we get the Hamiltonian as

$$\hat{H} = \frac{\hbar\omega}{4}\sum_n \left(-\left(\hat{a}_n^\dagger - \hat{a}_n\right)^2 + \left(\hat{a}_n^\dagger + \hat{a}_n - \hat{a}_{n+1}^\dagger - \hat{a}_{n+1}\right)^2\right)$$

Here, of course, we still would like to solve the S.Eq $\hat{H}|\psi\rangle = E|\psi\rangle$, but we don't really care right now about the wavefunction ψ; we just care about the energy spectrum. Instead of working with wavefunctions, we will work with the operators themselves, to go from the operators $(\hat{a}_n, \hat{a}_n^\dagger)$ to some new operators $(\hat{B}_q, \hat{B}_q^\dagger)$ such that the form of the Hamiltonian will be simpler under these operators. The challenge is to find such a linear transformation of the original creation/annihilation operators into these new operators. To do this, we begin by expanding everything in the Hamiltonian.

$\hat{a}_n^\dagger, \hat{a}_n$ in q-space Now we Fourier-transform the operators

$$\hat{a}_n = \int_q \hat{a}_q e^{iqn} \qquad \hat{a}_n^\dagger = \int_q \hat{a}_q^\dagger e^{-iqn}$$

where we have written

$$\int_q = \int_{-\pi}^{\pi} \frac{dq}{2\pi}$$

Note that the integral is not on $(-\infty, \infty)$ because we have a periodic array of oscillators, not a continuum of operators (so it is actually more like a Fourier series rather than a transform that we are examining). Also, we have the fairly straightforward identities

$$\sum_n e^{iqn} = 2\pi\delta(q)$$
$$\int_q e^{iqn} = \delta_{n,0}$$

Our goal is to rewrite the Hamiltonian in terms of these creation/annihilation operators in q-space $\hat{a}_q$ and $\hat{a}_q^\dagger$. We refer to them as creation/annihilation operators, but haven't formally shown them to be so; let's derive a commutation relation for them that resembles the canonical commutation relation for the corresponding real-space operators by performing an inverse Fourier transform:

$$[\hat{a}_q, \hat{a}_q^\dagger] = \left[\sum_{n_1} \hat{a}_{n_1} e^{-iq_1 n_1}, \sum_{n_2} \hat{a}_{n_2}^\dagger e^{iq_2 n_2}\right]$$

Since the commutator only cares about the operators, we can factor out the coefficients and sums and use the identities we have:

$$[\hat{a}_q, \hat{a}_q^\dagger] = \sum_{n_1, n_2} e^{i(q_2 n_2 - q_1 n - 1)}[\hat{a}_{n_1}, \hat{a}_{n_2}^\dagger] = \sum_n e^{i(q_2 - q_1)n} = 2\pi\delta(q_2 - q_1)$$

We see that this commutation relation is essentially a continuous version of the canonical commutation relation, so $\hat{a}_q$ and $\hat{a}_q^\dagger$ indeed are creation/annihilation operators. But what do they create or destroy? Unlike $\hat{a}_n$ and $\hat{a}_n^\dagger$, which create/destroy oscillations in position in space, $\hat{a}_q$ and $\hat{a}_q^\dagger$ create/destroy waves propagating through the oscillator chain, i.e. they create waves with a certain wave vector, which is basically q.

Hamiltonian in q-space Plugging these new operators into the Hamiltonian, we get after some algebraic manipulation that

$$\hat{H} = \int_q \left(A(q)\hat{a}_q^\dagger \hat{a}_q + B(q)\hat{a}_q \hat{a}_{-q} + \text{H.c.}\right)$$

where H.c. stands for Hermitian conjugate (of the terms preceding it), and

$$A(q) = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{2}(1 - \cos q)$$
$$B(q) = -\frac{\hbar\omega}{4} + \frac{\hbar\omega}{2}(1 - \cos q)$$

8.4 Bogoliubov Transformations; Quantum Phonons

We will now complete the derivation of the dispersion relation of quantum phonons

Where we are and where we're going Recall that we started with a classical oscillator chain, and then we quantized the Hamiltonian. Then we expressed the position and momentum operators using the creation/annihilation operators, and Fourier transformed these operators to express them in q-space (the wave vector space), to get the Hamiltonian in the previous equation. Now we have to work with these new creation/annihilation operators and this new Hamiltonian.

Imagine that in our Hamiltonian, we do not have the $B(q)$ term, i.e. it looks like

$$\hat{H} = \int_q \left(A(q)\hat{a}_q^\dagger \hat{a}_q + \text{H.c.}\right)$$

If this were the case, we would already have solved the problem: the integral is linear, and each $\hat{a}_q^\dagger \hat{a}_q$ corresponds to a quantum oscillator, the spectrum of which we know, so we know the result: $2A(q)$ would have been the spectrum of our quantum phonons. But since we do indeed have the $B(q)$ term, the spectrum of the Hamiltonian is not obvious. The solution is actually to construct new operators $\hat{b}_q$ and $\hat{b}_q^\dagger$ such that they are linear combinations of $\hat{a}_q$ and $\hat{a}_q^\dagger$ such that we remove the bad term, to get

$$\hat{H} = \int_q \left(\tilde{A}(q)\hat{b}_q^\dagger \hat{b}_q + \text{H.c.}\right)$$

for which the spectrum is known. It turns out that the operators $\hat{b}_q$ and $\hat{b}_q^\dagger$ we will create correspond to creation/annihilation operators for quantum phonons: they will be quantized normal modes in our quantum oscillator chain. This transformation of operators is known as the **Bogoliubov transformation**.

Bogoliubov transformation Let's consider the q-space Hamiltonian:

$$\hat{H} = \int_q \left(A(q)\hat{a}_q^\dagger \hat{a}_q + B(q)\hat{a}_q \hat{a}_{-q} + \text{H.c.}\right)$$

We will assume we can create the new operators $\hat{b}_q$ and $\hat{b}_q^\dagger$ as

$$\hat{a}_q = u_q \hat{b}_q + v_q \hat{b}_{-q}^\dagger$$
$$\hat{a}_q^\dagger = u_q \hat{b}_q^\dagger + v_q \hat{b}_{-q}$$

Note that the second definition is redundant: we could have just taken the Hermitian conjugate of the first equation. We need to make sure these $\hat{b}_q$ and $\hat{b}_q^\dagger$ are indeed creation/annihilation operators, i.e. we want to constrain

$$[\hat{b}_q, \hat{b}_p^\dagger] = 2\pi\delta(q-p) = [\hat{a}_q, \hat{a}_p^\dagger]$$

This calculation results in a constraint on the coefficients u_q and v_q:

$$\begin{aligned}
[\hat{a}_q, \hat{a}_p^\dagger] &= [u_q\hat{b}_q + v_q\hat{b}_{-q}^\dagger, u_p\hat{b}_p^\dagger + v_p\hat{b}_{-p}] \\
&= u_q u_p \underbrace{[\hat{b}_q, \hat{b}_p^\dagger]}_{2\pi\delta(q-p)} + u_q v_p \underbrace{[\hat{b}_q, \hat{b}_{-p}]}_{=0} + v_q u_p \underbrace{[\hat{b}_{-q}^\dagger, \hat{b}_p^\dagger]}_{=0} + \underbrace{v_q v_p [\hat{b}_{-q}^\dagger \hat{b}_{-p}]}_{-2\pi\delta(q-p)} \\
&= 2\pi(u_q^2 - v_q^2)\delta(q-p)
\end{aligned}$$

But this is supposed to equal $2\pi\delta(q-p)$, because we want these new operators to be creation/annihilation operators, so we get the constraint on the coefficients u_q and v_q as

$$u_q^2 - v_q^2 = 1$$

We can parameterize u_q and v_q with regard to some parameter λ_q to resolve this constraint, by

$$\begin{aligned}
u_q = \cosh\lambda_q &= \frac{e^{\lambda_q} + e^{-\lambda_q}}{2} \\
v_q = \sinh\lambda_q &= \frac{e^{\lambda_q} - e^{-\lambda_q}}{2}
\end{aligned}$$

This gives us the following expression for the creation/annihilation operators $\hat{a}_q$ and $\hat{a}_q^\dagger$:

$$\begin{aligned}
\hat{a}_q &= \cosh(\lambda_q)\hat{b}_q + \sinh(\lambda_q)\hat{b}_{-q}^\dagger \\
\hat{a}_q^\dagger &= \cosh(\lambda_q)\hat{b}_q^\dagger + \sinh(\lambda_q)\hat{b}_{-q}
\end{aligned}$$

Now we can plug this into the Hamiltonian. This tedious exercise results in the following form of $\hat{H}$:

$$\hat{H} = \int_q \left(\tilde{A}(q)\hat{b}_q^\dagger\hat{b}_q + \tilde{B}(q)\hat{b}_q\hat{b}_{-q} + \text{H.c.}\right)$$

where the coefficients $\tilde{A}(q)$ and $\tilde{B}(q)$ are

$$\begin{aligned}
\tilde{A}(q) &= \cosh(2\lambda_q)A(q) + \sinh(2\lambda_q)B(q) \\
\tilde{B}(q) &= \cosh(2\lambda_q)B(q) + \sinh(2\lambda_q)A(q)
\end{aligned}$$

Why does this help? Well, λ_q is a free parameter: we can choose it in any way we want. In particular, we can choose it so that the "bad" $\tilde{B}(q)$ term disappears, i.e. we want λ_q such that

$$\tilde{B}(q) = \cosh(2\lambda_q)B(q) + \sinh(2\lambda_q)A(q) = 0$$

Solving, we get that λ_q satisfies

$$\tanh(2\lambda_q) = -\frac{B(q)}{A(q)} = \frac{\frac{\hbar\omega}{2}(1-\cos(qa)) - \frac{\hbar\omega}{4}}{\frac{\hbar\omega}{2}(1-\cos(qa)) + \frac{\hbar\omega}{4}}$$

which simplifies. Furthermore, by plugging this λ_q into the expression for $\tilde{A}(q)$, we find the explicit form

$$\tilde{A}(q) = \hbar\omega\left|\sin\left(\frac{qa}{2}\right)\right|$$

Final results So after all this work, we have

$$\hat{H} = \int_q \left(\tilde{A}(q) \hat{b}_q^\dagger \hat{b}_q + \text{H.c.} \right)$$

This is sometimes called the **diagonal form** of the Hamiltonian, which essentially means expressing it as a linear combination of quantum oscillators or other particles whose behaviors we know well. Note that there is a constant term in the Hamiltonian that correspond to zero-point motion (it is actually just $1/2$ added on, exactly analogous to the simple quantum oscillator). In this form, we can see the spectrum of the quantum phonons:

$$\omega_q = 2\omega \left| \sin\left(\frac{qa}{2}\right) \right|$$

The remarkable thing is that this spectrum is **identical** to the spectrum for classical phonons: they have identical dispersion relations. Recall that our classical phonon model consisted of two different atoms chained together, though, while our quantum phonon model consisted only of one type of atom. So we could have quantized our solution at any stage, even though in our solution we quantized at the very beginning. Instead of doing this, a second version of the solution could have quantized the classical normal modes after solving everything classically. It turns out that this quantum to classical correspondence holds as long as our theory is non-interacting. In the language of our creation/annihilation operators, the theory must be bilinear in $\hat{b}_q$ and $\hat{b}_q^\dagger$.

As a final note, if quartic terms such as $\hat{b}_q^\dagger \hat{b}_q^\dagger \hat{b}_q \hat{b}_q$ had appeared, they would have indicated the interaction of phonons with one another, i.e. the scattering of waves off each other. This is still an ongoing theoretical challenge.

Chapter 9

Atomic Structure and Spectra

9.1 Introduction to Optical Spectra

White light entering a prism gives a band of colors from red to blue. This can be called a **demultiplexing** system. Newton demonstrated that white light is a mix of these colors by separating off one color and putting it through a second prism, which induced no further splitting of colors. Today, we know that color is an index of the **wavelength**, or the **frequency**. We can also **multiplex** red, green, and blue to get white.

Spectrum of the sun Interestingly, when seen under high resolution, the spectrum of the sun gives numerous dark lines. When this phenomenon was discovered, it was unexplained: there was no good reason why the smooth spectrum of the sun's light would be disrupted by so many imperfections.

9.2 Cracking the Hydrogen Code

The dim spots in the spectrum can be interpreted as **absorption** features. There is a complementary feature that we often see in neon signs, due to the sharp **emission lines** in certain low-density gases. For example, the emission spectrum of hydrogen is very sparse, and neon is less sparse, but still consists of distinct, sharp lines. It turns out that the emission spectra of low-density gases often correspond to the dim features in the spectrum of the sun. So it became understood that the same mechanism that caused the sharp emission lines also caused the absorption in the spectrum of the sun.

Invariable properties of atoms How do we account for this? In classical mechanics, a set of interacting particles can have any position and velocities, and there's nothing to single out particular configurations. There were some interesting theories in the late 19th century, but none bore fruit.

Rutherford's discovery In 1911, **Rutherford** showed that virtually all of the mass of an atom is concentrated in 10^{-15} of its volume. This caused some trouble with continuum models, since the discovery of electrons and nuclei indicated they behaved as particles.

Bohr's model of the atom In 1913, **Bohr** postulated that certain orbits of electrons would be stable, and correspond to the stationary states of atoms. By solving the classical equations of motion, he postulated that the spectral emission lines were caused by electrons changing from one orbit to another.

Classical equations of motion for hydrogen-like systems Let's try to model the atom using classical mechanics. Let the position, mass, and electric charge of the nucleus be $\vec{r}_n, M, +Ze$ respectively, and let the same for the electron be $\vec{r}_e, m, -e$. Here, Z is the atomic number, and e is the **specific charge**, the

absolute value of the charge of the electron. Newton's equations give us, using Coulomb's law for electrostatic attraction,

$$M\frac{d^2\vec{r}_n}{dt^2} = -\frac{Ze^2\vec{r}}{r^3}$$
$$m\frac{d^2\vec{r}_e}{dt^2} = +\frac{Ze^2\vec{r}}{r^3}$$

Note that we use r to denote the separation distance between electron and nucleus. Rearranging,

$$\frac{d^2\vec{r}}{dt^2} = -\left(\frac{1}{M}+\frac{1}{m}\right)\frac{Ze^2\vec{r}}{r^3}$$

We can rewrite using the **reduced mass** $\mu = Mm/(M+m)$, and the momentum $\vec{p} = \mu d\vec{r}/dt$, to get a pair of coupled first-order differential equations:

$$\frac{d\vec{p}}{dt} = -\frac{Ze^2\vec{r}}{r^3}$$
$$\frac{d\vec{r}}{dt} = \frac{1}{\mu}\vec{p}$$

Motivation Why did we reduce this to two first-order equations? To understand the dynamics of a system means that if we know the state of S at the time t_0, then we can do a linear approximation at $t_0 + \delta t$, for some small δ. This is why the S.Eq. must be first-order in time, so that we can write

$$\Psi(t_0+\delta t) \approx \left(1 - \frac{i\delta t\hat{H}}{h}\right)\Psi(t)$$

The primary objection is that other wave equations are second-order. This is simply because they are packaged that way; they can be rewritten as a system of first-order equations.

9.3 Classical Hydrogen Atom: Angular Momentum

Since we have equations of motion for the two vector quantities $\vec{p}$ and $\vec{r}$, it makes sense to try and find constants of motion from their products. For example, the total kinetic energy is

$$T = \frac{\vec{p}\cdot\vec{p}}{2\mu} = \frac{p^2}{2\mu}$$

Note that this T is in the frame of reference of the nucleus. Also, we can write

$$\frac{dT}{dt} = \frac{\vec{p}\cdot\vec{p}}{\mu} = -\frac{Ze^2\vec{r}\cdot\vec{r}}{r^3} = -\frac{\partial}{\partial t}\left(-\frac{Ze^2}{r}\right) = -\frac{\partial V(r)}{\partial t}$$

So we have the total energy $E = T + V(r)$. However, we need one more constraint in order to solve the system. What about $\vec{r}\cdot\vec{r}$ or $\vec{r}\cdot\vec{p}$? Consider the **angular momentum** $\vec{L} = \vec{r}\times\vec{p}$. We can verify that this is indeed a constant in our system. Recall that $\vec{v}\times\vec{v} = 0$ for any vector $\vec{v}$, so

$$\frac{d\vec{L}}{dt} = \frac{d\vec{r}}{dt}\times\vec{p} + \vec{r}\times\frac{d\vec{p}}{dt} = \frac{1}{\mu}\vec{p}\times\vec{p} - \frac{Ze^2}{r^3}\vec{r}\times\vec{r} = 0$$

The angular momentum is actually always conserved when the force is the gradient of a radial function, i.e. there is no dependence of the force on the relative angle. Note that this implies

$$\vec{r}\cdot\vec{L} = 0$$

since the cross product produces a vector perpendicular to both vectors.

9.4 Classical Hydrogen Atom: Runge-Lenz Vector

It is not difficult to see via the same reasoning that $\vec{r}\times\vec{L}$ and $\vec{p}\times\vec{L}$ lie in the same plane as $\vec{p}$ and $\vec{r}$. Because of this, we are interested in seeing whether there is some relation between them. We have

$$\vec{r}\times\vec{L}=\vec{r}\times(\vec{r}\times\vec{p})=\mu\vec{r}\times\left(\vec{r}\times\frac{d\vec{r}}{dt}\right)$$

Now we can invoke the identity

$$\vec{A}\times(\vec{B}\times\vec{C})=\vec{B}\left(\vec{A}\cdot\vec{C}\right)-\vec{C}\left(\vec{A}\cdot\vec{B}\right)$$

to simplify the previous equation, to get

$$\vec{r}\times\left(\vec{r}\times\frac{d\vec{r}}{dt}\right)=\vec{r}(\vec{r}\cdot\vec{r})-\frac{d\vec{r}}{dt}(\vec{r}\cdot\vec{r})=\vec{r}r\frac{dr}{dt}-\frac{d\vec{r}}{dt}r^2=-r^3\frac{d\hat{r}}{dt}$$

where $\hat{r}=\vec{r}/r$ is the unit vector of $\vec{r}$. Similarly, we can find

$$\frac{d}{dt}\left(\vec{p}\times\vec{L}\right)=\frac{d\vec{p}}{dt}\times\vec{L}=-\frac{Ze^2}{r^3}\vec{r}\times\vec{L}$$

Putting these two together, we find that the following vector is a constant:

$$\vec{A}=\vec{p}\times\vec{L}-Ze^2\mu\hat{r}$$

This is called the **Runge-Lenz vector**. Remarkably, this solves the problem for us. Consider

$$\vec{r}\cdot\vec{A}=rA\cos\phi=\vec{r}\cdot\left(\vec{p}\times\vec{L}\right)-rZe^2\mu$$

Again, using the following vector identity,

$$\vec{A}\cdot(\vec{B}\times\vec{C})=\vec{C}\cdot(\vec{A}\times\vec{B})=\vec{B}\cdot(\vec{C}\times\vec{A})$$

we can find that

$$\vec{r}\cdot\vec{A}=L^2-rZe^2\mu$$

Rearranging, we get an explicit expression for r, the radius of the orbit:

$$r=\frac{L^2}{Ze^2\mu+A\cos\phi}$$

Note, however, that this orbit may be an ellipse, circle, or hyperbola, and the distinguishing feature between the three is the energy. We must calculate A^2, to get

$$A^2=\vec{A}\cdot\vec{A}=2\mu EL^2+Z^2e^4\mu^2$$

Or, rearranging,

$$E=\frac{A^2-Z^2e^4\mu^2}{2\mu L^2}$$

Summary We can conclude that the energy of this system,

$$E=\frac{p^2}{2\mu}-\frac{Ze^2}{r}$$

can be anything! Furthermore, note that for $E<0$, the orbits are **elliptical**, which correspond to bound states of atoms that produce strong emission/absorption lines. On the other hand, if $E>0$, then the orbits are **hyperbolic**, which correspond to unbounded states produced the photoelectric effect, or in the ionization of gases.

Chapter 10

Quantum Theory: Old and New

10.1 Bohr Model of the Atom

In Niels Bohr's breakthrough paper, he found that the series of circular orbits that are stationary states have angular momentum that is some integral factor of the reduced Planck constant $\hbar/2\pi$. So the hydrogen atom has stationary states for $A = 0$ and $L = n\hbar$, for $n = 1, 2, \ldots$. We can plug this into our equation earlier to get

$$E(n) = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2} = -\frac{(Z\alpha)^2}{2n^2}\mu c^2$$

where we've used α to denote the **fine-structure constant**,

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137.036}$$

If we take $Z = 1$ and $\mu = m_e$, the mass of the electron, we get

$$E(n) = -\frac{1}{n^2}\frac{e^4 m_e}{2\hbar^2} = -\frac{1}{n^2}R_\infty hc$$

where $R_\infty \approx 10973731 m^{-1}$ is the **Rydberg constant**. Note that

$$R_\infty hc \approx 13.606 \text{ eV (electron volts)}$$

Furthermore, we can find the relationship between the radius of the orbit r and n, called the **principle quantum number**:

$$r(n) = n^2 \frac{\hbar^2}{m_e e^2} = n^2 a_0$$

where $a_0 \approx 5.292 \cdot 10^{-11}$ m is the **Bohr radius**. In particular, we may note that Bohr's model lets us compute the energy differences between different stationary states, giving the emission lines of the hydrogen atom!

10.2 Applications of the Bohr Model

Using Bohr's energy expression, we can find

$$E(n_2) - E(n_1) = hv = \frac{hc}{\lambda}$$

This describes the "disturbance" of an electron from a stationary state to a different stationary state, through electromagnetic interaction, e.g. excitation by or absorption of light. It turns out that

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

for infinite nuclear mass. For a finite nuclear mass, we get

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \frac{\mu}{m_e}$$

This correctly predicts the wavelengths for the emission lines for the **Balmer series** ($n_1 = 2$, $Z = 1$), the **Paschen series** ($n_1 = 3$, $Z = 1$), and the **Pickering series** for He^+, and so on.

Bohr Model for Large Bound Atoms In 2007, it was found that the absorption lines for carbon-like atoms in space at radio-frequency are still accurate. The atoms are associated with principle quantum number up to $n = 1009$, i.e. atoms over a million times larger than hydrogen. So the Bohr transition frequencies are accurate over a range spanning $2.5 \cdot 10^{15}$ to $2.6 \cdot 10^7$ Hz. However, as we will see, Bohr only used the classical properties of an atom in order to derive his model, neglecting any quantum effects.

Heavy isotope of hydrogen In 1931, the neutron was not discovered, but it was known that there were several varieties of many elements that had different nuclear masses, i.e. **isotopes**. However, all the isotopes that had been discovered up until then were via **mass spectrometry**, which could not distinguish between the ion H_2^+ and the heavy isotope of hydrogen. **Urey** had the idea that the heavy isotope of hydrogen could be distinguished via its spectrum. He decided to evaporate liquid hydrogen, in the hopes that the heavier isotope would be less volatile and the residue from evaporation could be spectroscopically analyzed. This worked.

Chapter 11

Solving the Schrödinger Equation

11.1 Simple Constructive Techniques

Recall the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

The precept of quantum mechanics is that all accessible information about the state is contained within the wavefunction. We can look at this as an initial value problem: given $\Psi(t)$, we can integrate this equation to find $\Psi(t+\tau)$. For simple systems, solutions to the S.Eq. are easy to find. However, for real systems, we encounter problems involving, say, Ytterbium, with 70 electrons. If we represent these electrons on a $10 \times 10 \times 10$ grid, we will get Ψ as a vector of dimension $100^{70} = 10^{210}$. This is completely infeasible. Sometimes we do need to solve the full time-dependent S.Eq., but often we can take approximations.

Stationary states There are many interesting things, however, that can be described by stationary states. The time-independent problem is:

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

The real-life problem is some setup involving electrons or simple atoms or molecules, and as such as usually know the potential V in the Hamiltonian, and we want to solve for Ψ and E. What we will do now is pick a Ψ that we like, and find V and E such that Ψ satisfies a S.Eq. involving V and E.

Constructive approach We can write out the S.Eq. in full by

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

A simple algebraic manipulation shows us that if we can differentiate Ψ, we can find E and V:

$$-\frac{1}{\Psi(x,y,z)}\left(\frac{\hbar^2}{2M}\nabla^2\Psi(x,y,z)\right) = E - V(x,y,z)$$

So technically, any function will solve an S.Eq., but we want those that solve it for an interesting potential. Furthermore, there are constraints on what allowable solutions are, e.g.

$$\int d^3\vec{r}\,\Psi^*\Psi = 1$$

We will see next that for a given E and V, there are actually infinitely many solutions to the S.Eq.

11.2 Gaussians and the Variational Theorem

One of the most widely-used functions in quantum mechanics is the **Gaussian**

$$\Psi(x,y,z) = \frac{1}{\pi^{3/4}d^{3/2}} \exp\left(-\frac{x^2+y^2+z^2}{2d^2}\right)$$

We will use 1D case of this, and the notation

$$\Psi(x,y,z) = \frac{1}{\pi^{3/4}d^{3/2}} \exp\left(-\frac{x^2}{2d^2}\right) \qquad d = \sqrt{\frac{\hbar}{m\omega}}$$

This notation serves to illustrate that if x is much greater than d, Ψ goes rapidly to 0. Furthermore, since d appears in the exponent, it must have dimensions of length L. In fact, this indicates that the wavefunction has dimension $1/\sqrt{L}$. This makes sense because the square of the wavefunction is the probability density, which has dimension $1/L$.

Variational Theorem For any Hamiltonian $\hat{H}$ and any function Ψ for which $\langle\Psi|\Psi\rangle = 1$, then the **expectation value** of the Hamiltonian satisfies

$$\langle\Psi|\hat{H}|\Psi\rangle \geq E_0$$

where E_0 is the ground state energy of the system. So we can use convenient sets of "trial functions" to estimate the ground-state energy of the system: we take a large set of functions that we can systematically expand and start varying them, to try to lower the energy of the system. With luck, this approaches the ground-state energy.

Proof Suppose we know all the eigenfunctions of the Hamiltonian, which we write

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

We start by writing Ψ as a linear combination of these eigenfunctions

$$\sum_n |\Phi_n\rangle\langle\Phi_n|\Psi\rangle$$

So we can expand $\langle\Psi|\hat{H}|\Psi\rangle$ to get

$$\begin{aligned}
\langle\Psi|\hat{H}|\Psi\rangle &= \sum_{n,m}\langle\Psi|\Phi_m\rangle\langle\Phi_m|\hat{H}|\Phi_n\rangle\langle\Phi_n|\Psi\rangle \\
&= \sum_n \langle\Psi|\Phi_n\rangle E_n \langle\Phi_n|\Psi\rangle \\
&\geq \sum_n \langle\Psi|\Phi_n\rangle E_0 \langle\Phi_n|\Psi\rangle \\
&= E_0
\end{aligned}$$

In fact, from this, we can see that equality holds if and only if $\hat{H}|\Psi\rangle = E_0|\Psi\rangle$.

Why this is important Electrons move much faster than nuclei, so they adjust "instantaneously" to the motion of the nuclei. If we can minimize the total energy of the system for fixed internuclear coordinates, we can get a good approximation of E_0 by varying those coordinates. This was made conceptually much easier by **Kohn**, whose density-functional theory is one of the theoretical underpinnings upon which a Gaussian trial approximation is used.

11.3 Variational Estimates and Applications

Now we can use the variational method to make estimates of properties of quantum mechanical systems. We will be working with our canonical one-dimensional Gaussian function:

$$\Psi(x) = \frac{1}{\pi^{1/4} d^{1/2}} \exp\left(-\frac{x^2}{2d^2}\right)$$

Since d has the units of length (the **characteristic length scale** of the function), the wavefunction Ψ has units of $1/\sqrt{L}$. When we interpret the wavefunction as the ground state of a harmonic oscillator, then d is actually

$$d = \sqrt{\frac{\hbar}{m\omega}}$$

Furthermore, we are interested in looking at

$$\langle \Psi | T | \Psi \rangle = \langle \Psi | -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} | \Psi \rangle$$

It turns out we can do this without evaluating any integrals.

Virial Theorem Recall that for the harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2m^2}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 = T + V(x)$$

the Virial theorem states that

$$\langle \Psi | T | \Psi \rangle = \langle \Psi | V | \Psi \rangle$$

So on average, the kinetic and potential energies make an equal contribution to the total energy. Hence we have that

$$\langle \Psi | T | \Psi \rangle = \frac{1}{2}\langle \Psi | \hat{H} | \Psi \rangle$$

In the ground state, this is equal to $\hbar\omega/4$. It turns out that the Virial theorem applies to any state, including a time-dependent wavepacket (however, for this case, we need to time-average the expectation value). It is also valid in any number of dimensions: if we have an N dimensional harmonic oscillator, we can just count the contribution of each individual coordinate to the kinetic energy. Virial theorems exist for other potentials too, but the harmonic oscillator is very special, since the kinetic and potential energies are equal.

Universal average energy of Gaussian So if we take our canonical one-dimensional Gaussian,

$$\langle \Psi | T | \Psi \rangle = \frac{1}{2}\langle \Psi | \hat{H} | \Psi \rangle = \frac{1}{2}\frac{\hbar\omega}{2} = \frac{1}{2}\frac{\hbar^2}{2md^2}$$

So if we just remember the correspondence of this Gaussian with the harmonic oscillator ground state, we don't need to do the integral anymore.

Variational estimate of energy of attractive Dirac delta The Dirac delta is widely used as a **pseudo-potential** to represent interactions between atoms in terms of a single parameter. For example, given that

$$\int_{-\infty}^{\infty} dx\, V(x) = -V_0 a$$

we can simply write $V(x) \approx -V_0 a \delta(x)$. We will find the expectation value of the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V_0 a \delta(x)$$

We already know the expectation value for the kinetic energy:

$$\langle\Psi|T|\Psi\rangle = \frac{1}{2}\frac{\hbar^2}{2md^2}$$

Furthermore, we can integrate over the potential to get the expectation value for the potential energy:

$$\langle\Psi|V|\Psi\rangle = -V_0 a|\Psi|^2_{x=0} = -\frac{V_0 a}{d\sqrt{\pi}}$$

So at small d, $\langle T\rangle$ is positive and decreasing proportional to the square of the potential, and $\langle V\rangle$ is negative and increasing proportionally to the inverse of the potential. The sum of the two is therefore positive at short distances, but becomes negatives at large distances. The minimum point gives the best choice of the scale parameter to estimate the energy. It turns out that this is the same minimization condition for the hydrogen atom in three dimensions.

11.4 Estimating the Ground State Energy of Hydrogen

We will use the variational technique to approximate the ground-state energy of the hydrogen atom. Recall that we made up a 3D wavefunction earlier,

$$\Psi(x,y,z) = \frac{1}{\pi^{3/4}d^{3/2}}\exp\left(-\frac{x^2+y^2+z^2}{2d}\right)$$

Note that this is just three separate 1D Gaussians multiplied together. It is also the ground state of an isotropic harmonic oscillator when $d = \sqrt{\hbar/m\omega}$. Thus we can use this to find the expectation value of

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{r}$$

Again, we already know $\langle\Psi|T|\Psi\rangle = (3/4)\hbar^2/md^2$: we have equal contributions from all three coordinates. We move to spherical polar coordinates to find the expectation value of V, since the potential energy is spherically symmetric:

$$\langle\Psi|V|\Psi\rangle = -\frac{Ze^2}{\pi^{3/2}d^3}4\pi\int_0^\infty dr\, r^2\frac{1}{r}\exp\left(-\frac{r^2}{d^2}\right) = -\frac{Ze^2}{d}\frac{2}{\sqrt{\pi}}$$

So the expectation value of V is inversely proportional to d, and the scaling is correct. If we now minimize the expectation value of $\hat{H}$ with respect to d, we find

$$\langle\Psi|\hat{H}|\Psi\rangle = -\frac{4}{3\pi}\frac{mZ^2e^4}{\hbar^2} = -0.85R_\infty$$

Which is a 15% error, but the scaling is correct and the procedure was simple.

Displaced Gaussians If we add the potential for an electric field $V_{\text{Electric}} = -q\vec{\mathcal{E}}\cdot\vec{r}$ to the harmonic oscillator potential (for convenience, direct this field along the x axix), we find

$$\frac{m\omega^2}{2}r^2 + V_{\text{Electric}} = \frac{m\omega^2}{2}\left(x^2 - \frac{q\mathcal{E}}{m\omega^2/2}x + y^2 + z^2\right) = \frac{m\omega^2}{2}r'^2 - \frac{q^2\mathcal{E}^2}{2m\omega^2}$$

where we have defined a new shifted coordinate system which is simply the old one shifted:

$$x' = x - \frac{q\mathcal{E}}{m\omega^2} \qquad y' = y \qquad z' = z$$

The levels in the energy spectrum are therefore still the same, just shifted down.

Another made-up function Consider the nicely localized (normalized) function

$$\Psi_H(r) = \frac{4\sqrt{\pi}}{d^{3/2}} \exp\left(-\frac{r}{d}\right)$$

Is it the solution of an S.Eq.?

11.5 Use of Special Functions

We are now going to start to apply more modern mathematical tools to solving problems in quantum mechanics. Schrödinger used **special functions** to solve the equations for the harmonic oscillator and hydrogen atom.

Three one dimensional examples Consider

$$\begin{aligned} V(x) &= V_0 \\ V(x) &= V_0 + V_1 x \\ V(x) &= V_0 + V_1 x + V_2 x^2 \end{aligned}$$

It turns out that the solutions to the S.Eq for these are the exponential, Airy, and parabolic cylinder functions respectively.

Linear potential Let $V = V_0$. Then

$$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + V_0\right)\Psi(x) = E\Psi(x)$$

We want solutions for all E so that we can find particular solutions satisfying boundary equations. This can be rewritten in non-dimensionalized form

$$\frac{\partial^2}{\partial \rho^2}\psi(\rho) \pm \psi(\rho) = 0$$

where $\rho = kx$ and $\hbar^2 k^2/2m = |E - V_0|$. Note that since energy can be any real number, we need the $\pm$. If $E > V_0$, we have the oscillatory solutions $\sin(\rho)$ and $\cos(\rho)$. Otherwise, we have the divergent solutions $\exp(\rho)$ and $\exp(-\rho)$. Furthermore, we can simulate a general $V(x)$ by constant segments on which we can solve the S.Eq. exactly, so this solution is general.

11.6 The Bouncing Ball

Now let's look at a linear potential $V(x) = V_0 + V_1 x$. We get

$$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + V_0 + V_1 x\right)\Psi(x) = E\Psi(x)$$

The non-dimensionalized form is

$$\frac{\partial^2}{\partial \rho^2}\psi(\rho) = \rho\psi(\rho)$$

with the pair of universal solutions $\mathrm{Ai}(\rho), \mathrm{Bi}(\rho)$, which are the **Airy functions**. They are both oscillatory for $\rho < 0$. For $\rho > 0$, the Bi diverges while Ai converges.

Quantum mechanical bouncing ball Consider a neutron bouncing off a mirror in the Earth's gravitational field. We have $V(x) = Mgx$, so

$$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + Mgx\right)\Psi(x) = E\Psi(x)$$

where $M \approx 1.67 \cdot 10^{-27} kg$ is the mass of the neutron, and we take $g \approx 9.8 m/s^2$. The boundary condition is $\Psi(x) = 0$ for $x = 0$, i.e. the wavefunction has to vanish at the mirror. We will define ρ by

$$x = \frac{\alpha\rho + E}{Mg} \qquad \alpha = \left(\frac{\hbar^2 M g^2}{2}\right)^{1/3}$$

Then $\rho = 0$ is the "classical turning point", where the velocity changes sign. Hence Ai is the relevant solution, since it dies off as $\rho \to \infty$. We can get an infinite family of solutions by shifting the Airy function so that the mirror is at one of its nodes, since we must satisfy $\Psi(x = 0) = 0$. Hence

$$\phi_n(\rho) = \mathrm{Ai}(\rho - \rho_n) \qquad E_n = -\alpha\rho_n$$

where $\{\rho_n\} = \{-2.34, -4.09, -5.52, \ldots\}$.

Quadratic potential We will look at the quadratic potential briefly. A quadratic oscillator with "impurities" is given by $V(x) = V_0 + V_1 x + (m\omega^2/2)x^2$. The non-dimensionalized form is

$$\frac{\partial^2}{\partial\rho^2}\psi(\rho) + \left(n + \frac{1}{2} - \frac{1}{4}\rho^2\right)\psi(\rho) = 0$$

We get two solutions: the parabolic cylinder functions $D_n(\rho)$ and $D_n(-\rho)$. Both of these diverge unless n is an integer, in which case we get bound eigenstates.

Chapter 12

Angular Momentum

12.1 Basic Properties of Angular Momentum Operators

"Everything revolves around angular momentum": it is a very important framework. We will try to understand the **conservation** of angular momentum in quantum systems and its **quantization**. To do so, we will review some standard conventions and procedures in **tensor calculus**, first used by Einstein in general relativity.

Notation For the sake of simplicity, we will use vector notation, but all the symbols denote **operators**. In the classical theory, we had the angular momentum

$$\vec{L} = \vec{r} \times \vec{p}$$

However, now we will interpret it as a quantum mechanical operator:

$$\vec{L} = \frac{\hbar}{i} \vec{r} \times \vec{\nabla}$$

We will also use x_1, x_2, x_3 for the coordinates x, y, z, and write $\hat{e}_1, \hat{e}_2, \hat{e}_3$ for the standard basis vectors. Furthermore, we will use **Einstein's summation convention**:

$$\vec{a} \dot{\vec{b}} = \sum_{i=1}^{3} a_i b_i \quad \text{we will write as} \quad a_i b_i$$

Also, recall the **Levi-Civita symbol**, written ϵ_{ijk}, which is defined as

$$\epsilon_{ijk} = \begin{cases} 1 & (ijk) = (123), (231), (312) \text{ cyclic} \\ -1 & (ijk) = (213), (132), (321) \text{ odd} \\ 0 & \text{otherwise} \end{cases}$$

Note that the "otherwise" case is when two or more of the indices i, j, k are equal.

Contraction identity We have the identity

$$\epsilon_{ijk} \epsilon_{ist} = \delta_{js} \delta_{kt} - \delta_{jt} \delta_{ks}$$

Here we have used Einstein's summation convention, since the subscript i is repeated.

Example Let's look at $\vec{A} \times (\vec{B} \times \vec{C})$. This is equal to

$$\epsilon_{ijk}\hat{e}_i A_j (B \times C)_k$$

by using the Levi-Civita symbol and Einstein's summation convention. Then we can expand out $(B \times C)_k$ to get

$$\epsilon_{ijk} A_j \epsilon_{kst} B_s C_t = \epsilon_{kij}\epsilon_{kst}\hat{e}_i A_j B_s C_t$$

By using the contraction identity on this, we get

$$(\delta_{is}\delta_{jt} - \delta_{it}\delta_{js})\hat{e}_i A_j B_s C_t$$

But by the filtering effect of δ (recall this whole thing is still a sum), we get

$$\hat{e}_i B_j A_j C_j - \hat{e}_i C_i A_j B_j$$

Which is equivalent to $\vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B})$.

12.2 Basic Commutation Relations

The definition of the angular momentum operator is

$$\vec{L} = \vec{r} \times \vec{p} = \frac{\hbar}{i}\vec{r} \times \vec{\nabla} = \hat{e}_i L_i = \frac{\hbar}{i}\epsilon_{uvw}\hat{e}_u x_v p_w$$

Everything we do now is based simply on the commutation relationship between position and momentum:

$$[p_j, x_k] = p_j x_k - x_k p_j = \frac{\hbar}{i}\delta_{jk}$$

For example, we have

$$[x_a p_j, x_k] = \frac{\hbar}{i}\delta_{jk} x_a$$

Now let's calculate $[L_a, x_b]$. We get

$$[L_a, x_b] = [\epsilon_{acd} x_c p_d, x_b] = \epsilon_{acd}\frac{\hbar}{i} x_c \delta_{bd} = i\hbar\epsilon_{abc} x_c$$

Hence we have $[L_a, x_b] = i\hbar\epsilon_{abc}x_c$. Writing this out fully, we get

$$\frac{1}{2}\left(\vec{L} \times \vec{x} + \vec{x} \times \vec{L}\right) = i\hbar\vec{x}$$

Note that in the classical sense, this would vanish, since $\vec{A} \times \vec{B} = -\vec{B} \times \vec{A}$. Furthermore, if we let $\hbar \to 0$, we get back the classical identity.

Similar identities Using the same procedure, we can show that

$$[L_a, L_b] = i\hbar\epsilon_{abc}L_c$$

This gives $\vec{L} \times \vec{L} = i\hbar\vec{L}$, which exhibits some more quantum funniness. Also, we can show

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

This shows that any component of the angular momentum commutes with the square magnitude of the angular momentum.

12.3 Angular Momentum as an Effective Potential

It seems that there should be a relationship between L^2 and the kinetic energy operator, since

$$L^2 = -\hbar^2\big(\vec{r} \times \vec{\nabla}^2\big) \cdot \big(\vec{r} \times \vec{\nabla}^2\big)$$

So there should be a p^2 somewhere in there. Using our notation from earlier, we can write

$$-\frac{L^2}{\hbar^2} = \epsilon_{ijk} x_j \partial_k \epsilon_{ipq} x_p \partial_q = (\delta_{jp}\delta_{kq} - \delta_{jq}\delta_{kp}) x_j \partial_k x_p \partial_q$$

Here we have used the contraction identity. Note that ∂_k denotes $\partial/\partial x_k$. By the filtering of the δ, we get this is equal to

$$x_j \partial_k x_j \partial_k - x_j \partial_k x_k \partial_j$$

We can further reduce this by using $\partial_k x_j = \delta_{jk} + x_j \partial_k$ in order to move the x_j in front of the ∂_k. Now, from this, we can get

$$r^2 \nabla^2 - r^2 \frac{\partial^2}{\partial r^2} - 2r \frac{\partial}{\partial r}$$

Thus the potential for the particle in a potential $V(x, y, z)$ is

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 + V(x, y, z) = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}\right) + V(x, y, z)$$

We didn't actually explicitly transform to spherical coordinates, but now the kinetic energy is now expressed naturally in spherical coordinates. It turns out that as long as we have a Laplacian, we have something that will turn out to be very similar to angular momentum. Interestingly, we can see from this that angular momentum presents an inverse square potential.

12.4 Angular Momentum and the Runge-Lenz Vector

Recall that earlier we derived the Runge-Lenz vector, which is a constant, for the hydrogen atom:

$$\vec{A} = \vec{p} \times \vec{L} - Ze^2 \mu \hat{r}$$

However, this classical formulation is non-symmetric in $\vec{p}$ and $\vec{L}$. **Pauli** derived the symmetric form required for quantum mechanics:

$$\vec{M} = \frac{\vec{p} \times \vec{L} - \vec{L} \times \vec{p}}{2\mu} - Ze^2 \frac{\vec{r}}{r}$$

For this new Runge-Lenz vector $\vec{M}$, we have the following commutators:

$$[L_u, M_v] = i\hbar \epsilon_{uvw} M_w$$

$$[M_u, M_v] = i\hbar \left(-\frac{2H}{\mu}\right) \epsilon_{uvw} L_w$$

The first commutator comes from our work earlier with $[L_u, L_v]$. However, the derivation of the second commutator is lengthy and complicated. It turns out that using these commutators, we can find the bound state energies without solving the S.Eq.

Spectrum associated with $\vec{L}$ Since L_3 and L^2 commute, they have common eigenfunctions. Note that there is nothing special about L_3: L_1 and L_2 both commute with L^2 too. Let's call these eigenfunctions $|lm\rangle$, so we have

$$L_3|lm\rangle = m\hbar|lm\rangle$$

It will turn out that $l = 0, 1, 2, \ldots$ and $m = -l, -l+1, \ldots, l-1, l$. But for now the values of m are undetermined. In order to prove the spectral property

$$L^2|lm\rangle = \hbar^2 l(l+1)|lm\rangle \qquad l = 0, 1, 2, \ldots \qquad m = -l, -l+1, \ldots, l-1, l$$

we will define the operators

$$L_+ = L_1 + iL_2 \qquad L_- = L_1 - iL_2$$

These resemble the creation and annihilation operators of the harmonic oscillator. Indeed, we can verify the identity

$$[L_3, L_\pm] = \pm\hbar L_\pm$$

Furthermore, we can show that these operators do generate a sequence of eigenstates:

$$L_3 L_\pm|lm\rangle = L_\pm L_3|lm\rangle \pm \hbar L_\pm|lm\rangle = \hbar(m \pm 1)L_\pm|lm\rangle$$

Note that this sequence of eigenstates must terminate somewhere: since L^2 is a fixed value, there is a maximum value for any one of its components. A full analysis will show that

$$l = 0, 1, 2, \ldots \qquad m = -l, -l+1, \ldots, 0, \ldots, l-1, l$$

Eigenfunctions of angular momentum There is a widely used system for the corresponding eigenfunctions called **spherical harmonics**. We have

$$|lm\rangle = Y_{l,m}(\theta, \phi)$$

These eigenfunctions are functions of the angles only: they parameterize the angular dependence. It is useful to keep in mind that $Y_{l,m}$ is simply a polynomial of degree l over r^l.

Remarks It turns out that L and M together are the generators of the rotation group SO(4). So the hydrogen atom has an internal symmetry in four spacial dimensions. A creation/annihilation operator approach gives the spectrum

$$E(n, l) = -\frac{R_\infty hc(\mu/m_e)}{(n+l+1)^2}$$

So given a principle quantum number $N = n + l + 1$, there are N^2 states with the same energy.

Chapter 13

Angular Momentum: Applications

13.1 Rotation and Dipole Moments of Molecules

We know now angular momentum's contribution to kinetic energy:

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 + V(x,y,z) = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}\right) + V(x,y,z)$$

An instance of this, in a different context, is for a two-particle rigid rotator. Consider a mass M_1 attached to another mass M_2 separated by r_e. Then the kinetic energy is

$$\frac{\hat{L}^2}{2Mr^2} \to \frac{\hat{L}^2}{2\mu r_e^2} \qquad \mu = \frac{M_1 M_2}{M_1 + M_2}$$

It turns out that we can model diatomic molecules as rigid rotators, and this is fairly accurate. We will look at the rotational dynamics of a **potassium-rubidium** molecule in this section.

Spherical harmonics Recall that we introduced spherical harmonics in the previous section:

$$|lm\rangle = Y_{l,m}(\theta,\phi)$$

It turns out that for describing angular motion, this set of functions is universally applicable. However, the explicit expressions for spherical harmonics are complicated. But we can always think of them as generalized polynomials:

$$|lm\rangle = r^{-l}\sum_{a+b+c=l} U(a,b,c)x_1^a x_2^b x_3^c$$

It is immediate that this is dimensionless. Furthermore, the spherical harmonics all obey the relation

$$\nabla^2\left(\sum_{a+b+c=l} U(a,b,c)x_1^a x_2^b x_3^c\right) = 0$$

This enables us to test whether something is a spherical harmonic. This also lets us form our own spherical harmonics for low orders l. Note that under parity transformation (coordinate inversion), $x_k \to -x_k$ for all k, we have

$$|lm\rangle \to (-1)^l |lm\rangle$$

Potassium-Rubidium We know that $r_e = 4.0 \cdot 10^{-10}$ m, and for the isotopes K40 and Rb87, the reduced mass is $\mu = 4.6 \cdot 10^{-26}$ kg. Furthermore, KRb has a permanent electric dipole moment, $d = 0.24ea_0$, where e is elementary charge and a_0 is Bohr radius. When there's no electric field, the Hamiltonian describes the rotational dynamics

$$\frac{\hat{L}^2}{2\mu r_e^2} \to l(l+1)kT_{\text{equiv}}$$

where $T_{\text{equiv}} = 55$ millikelvin. Note that this is a translation to temperature. We use the dipole moment d to orient the molecular wavefunction in the ground state, where the spherical harmonic is just a constant:

$$\Psi(\theta, \phi) = |00\rangle = Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

So the ground state $l = 0$ is **isotropic**: there is no net dipole moment. How do we orient it?

13.2 Atomic and Molecular Polarizabilities: Perturbation Theory

To orient the molecule, we will apply an electric field. To see what happens quantum mechanically in the electric field, we will use a tool called **perturbation theory**.

Perturbation theory Originally developed by Schrödinger, perturbation theory is used mostly in its original form today. Suppose we're solving a very complex equation of motion, perhaps given by a Hamiltonian we don't know how to solve. The idea is to find an approximation

$$i\hbar\frac{\partial\Psi}{\partial t} = (H_0 + \lambda V)\Psi$$

such that we know how to solve H_0 and the equations of motion we're interested in can be reached to some degree by an expansion of the small parameter λ, as

$$\Psi = \sum_{n=0}^{\infty} \Psi_n \lambda^n$$

Very often, we often take only the first or second terms in this power series.

Example Let's apply this to the time-independent S.Eq. Let

$$(H_0 + \lambda V)\Psi = E\Psi$$

We expand both the wavefunction Ψ and the energy E as formal power series in λ:

$$\Psi = \sum_{n=0}^{\infty} \Psi_n \lambda^n \qquad E = \sum_{n=0}^{\infty} E_n \lambda^n$$

Now we plug these back in and match coefficients:

$$H_0\Psi_0 = E_0\Psi_0$$

$$H_0\Psi_1 + V\Psi_0 = E_0\Psi_1 + E_1\Psi_0$$

Applying $\langle\Psi_0|$ to both sides of the last equation gives

$$\langle\Psi_0|H_0|\Psi_1\rangle + \langle\Psi_0|V|\Psi_0\rangle = \langle\Psi_0|E_0|\Psi_1\rangle + \langle\Psi_0|E_1|\Psi_0\rangle$$

But from $H_0\Psi_0 = E_0\Psi_0$, we can drop two of the terms above, to get

$$\langle\Psi_0|V|\Psi_0\rangle = E_1$$

KRb molecule Now let's go to the real problem. We will apply an electric field F to a freely rotating KRb molecule:

$$\hat{H} = \frac{\hat{L}^2}{2\mu r_e^2} - \vec{F} \cdot \vec{d} = \frac{\hat{L}^2}{2\mu r_e^2} - Fd\cos\theta = \frac{\hat{L}^2}{\hbar^2} kT_{\text{equiv}} - \lambda k T_{\text{electric}} \cos\theta$$

Here we have rewritten the Hamiltonian first in polar, and then converted it to a temperature equivalent. It turns out that

$$\frac{T_{\text{electric}}}{T_{\text{equiv}}} = 3 \cdot 10^{-6}$$

We also introduced the dimensionless parameter

$$\lambda = \frac{F}{1\text{V/m}}$$

This is a sign that perturbation theory may be useful, since we are using it to treat something that is small compared to the underlying rotational motion of the molecule. From a physical standpoint, this makes perfect sense: if we have a freely rotating molecule and we only apply a small force to it, it's not going to be that effective.

Perturbation theoretic approach So we are going to do the approximation, where

$$\hat{H}_0 = \frac{\hat{L}^2}{\hbar^2} kT_{\text{equiv}} \qquad V = -kT_{\text{electric}} \cos\theta \qquad E = \sum_{n=0}^{\infty} E_n \lambda^n$$

It turns out that E_0 vanishes, and Ψ_0 is simply the lowest order spherical harmonic, the ground state of a rotating molecule. The first-order energy correction is

$$\langle \Psi_0 | V | \Psi_0 \rangle = E_1 = -kT_{\text{electric}} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, \sin\theta \frac{\cos\theta}{4\pi}$$

But this is simply zero, since we are integrating over the entire period of a cosine, and symmetry cancels things out. So $E_1 = 0$. This is actually quite a common occurrence. We continue to the next order:

$$H_0 \Psi_2 + V \Psi_1 = E_0 \Psi_2 + E_1 \Psi_1 + E_2 \Psi_0$$

Applying the bra $\langle \Psi_0 |$ to both sides again, we get

$$\langle \Psi_0 | H_0 | \Psi_2 \rangle + \langle \Psi_0 | V | \Psi_1 \rangle = \langle \Psi_0 | E_0 | \Psi_2 \rangle + \langle \Psi_0 | E_1 | \Psi_1 \rangle + \langle \Psi_0 | E_2 | \Psi_0 \rangle$$

After canceling the H_0 and E_0 terms, and noting that the E_1 term vanishes since $E_1 = 0$, we get

$$\langle \Psi_0 | V | \Psi_1 \rangle = E_2$$

Finding Ψ_1 To find E_2, we need Ψ_1. To find Ψ_1, we will rewrite the term-matching equation as

$$(H_0 - E_0)\Psi_1 = -V\Psi_0$$

Plugging everything in, we find that

$$\frac{\hat{L}^2}{\hbar^2} \Psi_1 = \frac{T_{\text{electric}}}{T_{\text{equiv}}} \frac{\cos\theta}{\sqrt{4\pi}}$$

Note, however, that $\cos\theta = x_3/r$, so it is a spherical harmonic of order $l = 1$. It then follows that

$$\frac{\hat{L}^2}{\hbar^2} \cos\theta = 2\cos\theta$$

So plugging in and canceling, we get

$$\Psi_1 = \frac{T_{\text{electric}}}{T_{\text{equiv}}} \frac{\cos\theta}{4\sqrt{\pi}}$$

Calculating E_2 Completing the calculation, we get

$$E_2 = -\frac{kT_{\text{electric}}}{6}\frac{T_{\text{electric}}}{T_{\text{equiv}}}$$

From the point of view of classical thermodynamics, this actually describes the **polarizability** of the molecule.

Polarizability Consider a conducting sphere of radius R in an electric field F: it acquires a dipole moment $d = \alpha_{\text{sphere}}F$. This was an empirical law understood before any theories of electrodynamics. For the sphere,

$$\alpha_{\text{sphere}} = R^3 \text{ (c.g.s units)}$$

It turns out that the relationship between polarizability and the second-order energy from perturbation theory is given by

$$\alpha = -2E_2$$

So this allows us to derive the polarizability of matter from first principles. Applying it to the KRb molecule, we find

$$\alpha = \frac{2}{3}\frac{\mu d^2 r_e^2}{\hbar^2} \approx (2.5 \cdot 10^{-7} \text{ cm})^3$$

It is interesting to note that the polarizability, which is a ratio of the dipole moment to the induced field strength, actually diverges as we take the classical limit $\hbar \to 0$! In a classical world, then, for a rotating molecule, the polarizability is infinite. We can see this since if there were no energy cost of localization, then the dipole moment would be localized instantly even by the smallest force. So the electrical polarizability of matter is a quantum effect.

13.3 Polarizability of the Hydrogen Atom

It turns out that we can apply these concepts not only to molecules, but also to atoms. In particular, we will look at the polarizability of the hydrogen atom. We will work in c.g.s units, with Ze denoting the ionic charge, r the electron-nucleus distance, μ the reduced mass, and F the electric field. For convenience, we will take $\lambda = F$, and write

$$(H_0 + FV)\Psi = E\Psi$$

So we have the ground state variables

$$H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$$

$$E_0 = -\frac{\mu Z^2 e^4}{2\hbar^2}$$

$$\Psi_0 = \frac{e^{-r/d}}{d^{3/2}\sqrt{\pi}} \qquad d = \frac{\hbar^2}{\mu Z e^2}$$

Now, as usual, we calculate the first-order energy

$$\langle \Psi_0 | V | \Psi_0 \rangle = E_1 = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \int_{-\infty}^{\infty} \frac{e^{-2r/d}}{\pi d^3} e\hat{F} \cdot \vec{r}$$

It is fairly obvious that by symmetry, this integral vanishes. Note that this is a generic features of odd-parity perturbations if Ψ_0 has definite symmetry. Now we need to find the first-order wavefunction, which is the most difficult part of the calculation. We want

$$(H_0 - E_0)\Psi_1 = -V\Psi_0 = -e\hat{F} \cdot \vec{r}\Psi_0 = -er\cos\theta \frac{e^{-r/d}}{\sqrt{\pi} d^{3/2}}$$

The issue is that we have two variables: the radius and the angle. This makes the equation much more complex. However, we can note that H_0 is symmetric in angle, so the asymmetry in the right hand side must be introduced by Ψ_1. The behavior near $r = 0$ is governed by the angular momentum. So

$$\Psi_1 = r \cos\theta f(r) e^{-r/d}$$

It is not difficult to show from this that $f(r) \propto 1 + r/2d$. The result that we get turns out to be

$$\alpha = \frac{9}{2Z^4} \frac{\hbar^6}{e^6 \mu^3}$$

We can sanity check this crazy expression by noting that it indeed has dimensions of volume. Note again that as we take the classical limit $\hbar \to 0$, we find $\alpha \to 0$. So in a classical world, atoms would not respond to electric fields.

Chapter 14

Symmetry in Quantum Physics

14.1 Angular Momentum – More Explicit Solutions

Previously, we found that any purely radial function $f(r)$ has zero angular momentum. This is obvious, almost by definition. Let's look among familiar things to find functions with non-trivial angular momentum. How about x_1, x_2, x_3? We have already seen a calculation of this type:

$$L_u x_a = \epsilon_{uvw} x_v p_w x_a = \epsilon_{uvw} x_v \frac{\hbar}{i} \delta_{wa} = \frac{\hbar}{i} \epsilon_{uva} x_v$$

So the angular momentum gives a linear combination of all the coordinates. Then we have

$$\begin{aligned} L^2 x_a &= L_u L_u x_a = \epsilon_{ust} x_s p_t L_u x_a = \epsilon_{ust} x_s p_t \frac{\hbar}{i} \epsilon_{uva} x_v \\ &= \epsilon_{ust} \epsilon_{uva} x_s \left(\frac{\hbar}{i}\right)^2 \delta_{tv} = \hbar^2 \epsilon_{usv} \epsilon_{uav} x_s = 2\hbar^2 x_a = \hbar^2 l(l+1) x_a \end{aligned}$$

with $l = 1$. Hence x_1, x_2, x_3 are eigenfunctions of L^2 with eigenvalues $l(l+1)\hbar^2$ with $l = 1$. If we multiply these by a spherical Gaussian $\exp(-r^2/2d^2)$, we get the orbitals p_1, p_2, p_3. These are commonly used by chemists to describe orbitals directed along specific axes.

Another possible choice of eigenfunctions is just a straightforward linear combination of x_1, x_2, x_3:

$$\begin{aligned} \chi_{1,1} &= -\frac{x_1 + i x_2}{\sqrt{2}} \\ \chi_{1,0} &= x_3 \\ \chi_{1,-1} &= \frac{x_1 - i x_2}{\sqrt{2}} \end{aligned}$$

These have a definite projection, satisfying

$$L_3 \chi_{1,m} = m\hbar \chi_{1,m}$$

$$(L_1 \pm i L_2)\chi_{1,m} \equiv L_\pm \chi_{1,m} = \sqrt{2 - m(m \pm 1)}\chi_{1,m\pm 1}$$

Another useful feature of these is that they satisfy

$$L_3 (\chi_{1,1})^l = l\hbar (\chi_{1,1})^l$$

$$L^2 (\chi_{1,1})^l = l(l+1)\hbar^2 (\chi_{1,1})^l$$

So taking successive powers of these eigenfunctions gives us higher and higher eigenfunctions to reach an extremal value of m. Then we can use a lowering function to systematically step down and find all the eigenfunctions. Explicitly, we construct $|l, m\rangle$ by first finding

$$|l, l\rangle = (\chi_{1,1})^l$$

Then we apply the lowering operator repeatedly, the first step being

$$L_-|l, l\rangle = \sqrt{l(l+1) - m(m-1)}|l, l-1\rangle \qquad m = l$$

We can see the lowering operator L_- as redistributing the powers of the coordinates in the huge polynomial that is $|l, l\rangle$.

14.2 Solution of Schrödinger Equations for Systems with Definite Angular Momentum

So far we have been making functions up and seeing that they have the properties we want. Now we will systematically and rigorously develop solutions to the S.Eq. We learned that when we have a spherical potential $V(r)$, we can choose eigenfunctions that are eigenfunctions of angular momentum, and these are of a general, universal form:

$$\Psi = \Psi(r)Y_{l,m}(\theta, \phi)$$

If we expand the S.Eq., taking the view that the solution will be an eigenfunction of angular momentum,

$$\left(-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right) + V(r)\right)\Psi(r) = E\Psi(r)$$

It helps to non-dimensionalize now. Let $r = a\rho$. We do the scaling

$$\frac{Ma^2}{\hbar^2}E = \epsilon \qquad U(\rho) = \frac{Ma^2}{\hbar^2}V(a\rho) \qquad \Psi(r) = a^{-3/2}\psi(r/a)$$

$$\left(\frac{1}{2}\left(\frac{\partial^2}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial}{\partial \rho} - \frac{l(l+1)}{\rho^2}\right) + \epsilon - U(\rho)\right)\psi(r) = 0$$

Near $\rho = 0$, this equation has a singularity. These singular points are where ψ and $d\psi/d\rho$ cannot be specified independently. However, there still always exists two solutions for a second-order DE. It turns out that if we pick a point near the singular point and specify the value and slope there, there is a unique solution that is regular at the singular point.

Provided the potential $U(\rho)$ is weaker than r^{-2} as $r \to 0$, the other terms in the S.Eq. dominate, and the leading-order behavior near $\rho = 0$ is independent of U. So we write

$$\psi(\rho) = \phi(\rho)\rho^\nu \qquad \nu = l, -(l+1)$$

Then we have, from this isolation of the singular points,

$$\left(\frac{1}{2}\frac{\partial^2}{\partial \rho^2} + \frac{l+1}{\rho}\frac{\partial}{\partial \rho} + \epsilon - U(\rho)\right)\phi(\rho) = 0$$

Now we will get specific and solve this for the hydrogen atom (with infinite nuclear mass, so $M = m_e$). We have, when $a = a_0$, the Bohr radius,

$$V(r) = -\frac{e^2}{r} \qquad U(\rho) = -\frac{1}{\rho}$$

Non-dimensionalizing, the S.Eq. is of the following form:

$$\left(\frac{1}{2}\frac{\partial^2}{\partial\rho^2} + \frac{l+1}{\rho}\frac{\partial}{\partial\rho} + \epsilon + \frac{1}{\rho}\right)\phi(\rho) = 0$$

If the energy is positive, the electron escapes from the nucleus completely; otherwise, it is bound. We're interested in the bound states, so we have $\varepsilon = -\kappa^2/2 < 0$. It is evident that as $\rho \to \infty$, every term that contains $1/\rho$ vanishes. So at large ρ, there is an exponentially decaying envelope, and we set

$$\phi(\rho) = f(\rho)\exp(-\kappa\rho)$$

Plugging this in to our S.Eq,

$$\frac{1}{2}\frac{\partial^2 f}{\partial\rho^2} + \frac{l+1}{\rho}\frac{\partial f}{\partial\rho} - \kappa\frac{\partial f}{\partial\rho} + \frac{1-\kappa(l+1)}{\rho}f = 0$$

The first two terms contribute a ρ^{-2} factor, and the last two ρ^{-1}. Hence if we use a power series for $f(\rho)$, this transformation leads us to a two-term recurrence. The series must terminate at some point: the two term relation implies that higher terms vanish at eigenvalues. It turns out that if n is the highest non-vanishing term in the series, then

$$E_{nl} = -\frac{\hbar^2}{2m_e a_0^2}\frac{1}{(n+l+1)^2} = -\frac{R_\infty hc}{(n+l+1)^2}$$

Chapter 15

Spins and Quantum Gases

15.1 The Dirac Equation – Basics

The S.Eq. for a free particle in one dimension, as ordinarily presented,

$$i\hbar\frac{\partial\Psi}{\partial t} = \frac{\hat{p}^2}{2m}\Psi \qquad E = \frac{p^2}{2m}$$

is of first-order in time but second-order in space. This is fundamentally unsatisfactory: it violates relativity, which says we have to make our models so that they are invariant under relativistic transformations. To satisfy this, we require an equation that is, at least, of equal order in space and time. Other equations, such as Maxwell's, always begin by being of the same order in space and time. We already know that the evolution equation for quantum mechanics must be first-order in time, because, well, it is a time-evolution equation. **Dirac** tried to find such an equation, satisfying

$$i\hbar\frac{\partial\Psi}{\partial t} = c\alpha\hat{p}\Psi + mc^2\beta\Psi \qquad E^2 = c^2p^2 + m^2c^4$$

Note that here, we require that the **dispersion relation** from relativity is satisfied. α and β are numbers to be determined. By dimensional analysis, they have to be unitless. We square the right hand side of the equality and note that in order to get the relativistic dispersion relation,

$$\alpha^2 = \beta^2 = 1 \qquad \alpha\beta + \beta\alpha = 0$$

We write $\{\alpha, \beta\} = \alpha\beta + \beta\alpha$.

Non-commuting "numbers" Of course, there are no actual numbers such that $\{\alpha, \beta\} = 0$. But there are simple mathematical objects that do exhibit non-commutativity, e.g. the matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We can interpret these geometrically as a reflection across $y = x$ and $y = 0$ respectively.

Antimatter In fact, these matrices work as α and β, and we can substitute them into the Dirac equation to get

$$\Psi(x) = A\exp\left(\frac{ipx}{\hbar}\right)$$

Note that now A is a 2D vector. Furthermore, note that while in non-relativistic quantum mechanics a negative energy indicates a diverging wavefunction, here the negative energy wavefunctions behave normally and indicate the existence of antimatter.

Angular momentum Now consider the Dirac equation in 3D. It has the same general form:

$$H\Psi = c\left(\alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3\right)\Psi + mc^2\beta\Psi$$

where when we square the wavefunction, we have the relations

$$\{\alpha_j, \alpha_k\} = \alpha_j\alpha_k + \alpha_k\alpha_j = 2\delta_{jk} \qquad \{\alpha_j, \beta\} = 0 \qquad \beta^2 = 1$$

This produces a problem. It turns out that the angular momentum $\vec{l} = \vec{r} \times \vec{p}$ does not commute with H:

$$\left[\vec{l}, H\right] = \vec{l}H - H\vec{l} = i\hbar c\vec{\alpha} \times \vec{p}$$

15.2 The Dirac Equation – How it Exhibits Spin

It also turns out that this is a valuable feature, not an issue with our model. In earlier sections, we saw that we could try to construct constants of motion from natural types of entities, the most significant of which are the quadratic forms. So let's try that here. Consider the quadratic form

$$\vec{s} = \frac{\hbar}{4i}\alpha \times \alpha$$

We can extract something from this. Looking at s_1 and using the commutation relations, we find

$$s_1 = \frac{\hbar}{4i}(\alpha_2\alpha_3 - \alpha_3\alpha_2) = \frac{\hbar}{2i}\alpha_2\alpha_3$$

which looks suspiciously like a cross product. This works for the other components s_2 and s_3 as well. Then we look at

$$\begin{aligned}
[s_1, \beta] &= \frac{\hbar}{2i}(\alpha_2\alpha_3\beta - \beta\alpha_2\alpha_3) \\
&= \frac{\hbar}{2i}(\alpha_2(-1)\beta\alpha_3 - \beta\alpha_2\alpha_3) \\
&= \frac{\hbar}{2i}(\beta\alpha_2\alpha_3 - \beta\alpha_2\alpha_3) = 0
\end{aligned}$$

We can also look at the commutation relation

$$\begin{aligned}
[s_1, a_1] &= \frac{\hbar}{2i}(\alpha_2\alpha_3\alpha_1 - \alpha_1\alpha_2\alpha_3) \\
&= \frac{\hbar}{2i}(\alpha_2(-1)\alpha_1\alpha_3 - \alpha_1\alpha_2\alpha_3) \\
&= \frac{\hbar}{2i}(\alpha_1\alpha_2\alpha_3 - \alpha_1\alpha_2\alpha_3) = 0
\end{aligned}$$

Now we look at

$$\begin{aligned}
[s_1, \alpha_2] &= \frac{\hbar}{2i}(\alpha_2\alpha_3\alpha_2 - \alpha_2\alpha_2\alpha_3) \\
&= \frac{\hbar}{2i}(\alpha_2(-1)\alpha_2\alpha_3 - \alpha_3) \\
&= -2\frac{\hbar}{2i}\alpha_3 = i\hbar\alpha_3
\end{aligned}$$

This looks like the commutator of angular momentum with a vector. By now, we can see the general pattern, and it is easy to show that

$$[\vec{s}, H] = \vec{s}H - H\vec{s} = -i\hbar c\vec{\alpha} \times \vec{p}$$

Spin Now we can see that if we add up $\vec{l}$ and $\vec{s}$, we get something that commutes with the Hamiltonian:

$$[\vec{j}, H] = 0 \qquad \vec{j} = \vec{l} + \vec{s}$$

Furthermore, we can see that

$$\vec{s} \cdot \vec{s} = \frac{3\hbar^2}{4}$$

This implies that the additional spin part $\vec{s}$ of the angular momentum has magnitude $\hbar/2$, which is half the value of the increment of angular momentum for orbital motion.

Dirac equation Hence the Dirac equation gives us many consequences: antimatter, electron spin, magnetic moment of the electron, the "fine structure" of atomic spectra, and "zitterbewegung", which states that the instantaneous speed of the electron is always the speed of light. This last effect has not been observed in relativistic electrons directly.

15.3 Spin and Antimatter in Material Systems

We derived the existence of spin without putting it into a specific representation. It turns out there is a convenient representation by **Pauli matrices**:

$$\vec{s} = \frac{\hbar}{2}\vec{\sigma}$$

where σ is a Pauli matrix. We have seen two of them previously:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The Pauli matrices are also frequency encountered in treatments of two-state systems. In this matrix form, these matrices operate on vectors such as

$$\langle\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \langle\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

This is the most conventional framework for the treatment of spin.

Implications of spin All the important spin-1/2 particles (e.g. electron, proton, neutron, leptons, baryons) are **fermions**, which have to obey Pauli's **exclusion principle**, which says that the wavefunction of a many-particle system must change sign under the exchange of any two identical fermions. An important generic case that arises a lot in practice is when we separate the wavefunction as

$$\Psi(1,2) = \Psi_{\text{space}}(\vec{r}_1, \vec{r}_2)\Psi_{\text{spin}}(\vec{s}_1, \vec{s}_2)$$

For two particles of spin-1/2, the total $S = |\vec{s}_1 + \vec{s}_2|$ is either 0 or 1 (in units of $\hbar$). There is only one spin state of two spin-1/2 particles that has $S = 0$:

$$|00\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

We can easily show this by applying the angular momentum raising and lowering operators to the spin state. On the other hand, there are three states that have $S = 1$:

$$\begin{aligned} |11\rangle &= |\uparrow\uparrow\rangle \\ |10\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1{-1}\rangle &= |\downarrow\downarrow\rangle \end{aligned}$$

Spin in material systems Electron spins provide the "persistent currents" in magnetic materials. In effect, the electron spins and it never stops, creating a magnetic moment. It turns out that many of the strongest magnetic materials have many spin-parallel electrons.

Spintronics An emerging technology is spintronics. One example is **giant magnetoresistance**, where the resistance of a material can be affected by the presence of a magnetic field, which depresses certain spin states of electrons from passing through materials. It has been incorporated into magnetic storage devices. The idea is that instead of using the transport of charge to communicate information, we can transport spin instead. This has the potential for higher efficiency.

Applications of antimatter Before Dirac's paper in 1928, no one had any idea that antimatter should exist; the interpretation of Dirac's equation wasn't entirely agreed upon until **Anderson** discovered the anti-electron, or the **positron**. Today, it is widely used in **positron emission tomography**, or a PET scan.

15.4 Bose-Einstein Condensation

One of the iconic phenomena of modern atomic physics is Bose-Einstein condensation. In 1924, Einstein discovered that in the quantum theory of ideal gases, an ideal gas at constant temperature being compressed exhibits a saturation density such that the density above the saturation density consists of molecules that don't participate in the thermal agitation of the gas. This is the first example of a **quantum phase transition**: the occurrence of a new phase of matter. Somehow, if we compress a gas at finite temperature, eventually we reach a temperature at which a zero-temperature fluid is somehow created.

Circumstances for condensation For a classical ideal gas, the particles don't interact in any significant way. The one characteristic length scale is the mean distance between particles $d = \rho^{-1/3}$, where ρ is the number density. In a quantum gas, however, there is an additional length scale, the **de Broglie wavelength** $\lambda_{dB} = h/\sqrt{2\pi mkT}$. We observe the phase transition when $d \approx \lambda_{dB}$.

Impossibility It turns out that the de Broglie wavelength of room-temperature air is so much smaller than d that we would need an incredible density before it would exhibit Bose-Einstein condensation. However, 70 years after Einstein's prediction, a Bose-Einstein condensate was experimentally created.

Asymmetry in quantum gas expansion Interestingly, in the creation of the Bose-Einstein condensate, we can observe a signature property of a quantum gas. When released from a trap, a classical gas cloud eventually becomes spherical, independent of the initial shape of the trap. The expanding Bose-Einstein condensate cloud, however, eventually adopts the reverse aspect ratio of the originally trapped cloud, due to the uncertainty principle.

Coherent matter wave How do we perform a first-principles, theoretical simulation of the particles in a Bose-Einstein condensate? The workhorse of the field is the **Gross-Pitaevskii equation**. The basic idea is that N_0 atoms of mass M all occupy the same quantum state Ψ. The interaction between atoms is a dominant part of the total energy, but it can be well-approximated by a Dirac delta pseudo-potential characterized by scattering length a. An interesting feature of this equation is that all the parameters are determined by experiment; none are adjustable:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2M}\nabla^2\Psi + V_{\text{trap}}(\vec{r},t)\Psi + \frac{4\pi\hbar^2 a N_0}{M}|\Psi^2|\Psi$$

This looks very much like an S.Eq, with the exception of the non-linear last term, which makes our arguments about variational approaches and superposition of states are no longer valid. Equations of this type are known as **non-linear wave dynamics**, and support structures such as solitons, vortices, and rings.

Chapter 16

Time-Dependent Quantum Mechanics

16.1 General Remarks About the Time-Dependent Schrödinger Equation

Time-dependent quantum mechanics is very much an active field of research, with some open problems left unsolved: we still don't know all the answers. Recall that at the very beginning, we actually "derived" the full time-dependent S.Eq., but we have never used it, because all of our potentials were time-independent. Now, we will look at the full time-dependent S.Eq.:

$$i\hbar\partial_t|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle \qquad |\Psi(0)\rangle = |\Psi_0\rangle$$

Note that even if $\hat{H}$ is constant, we would actually still have a time-dependent wavefunction, as

$$|\Psi(t)\rangle = \exp\left(-\frac{i}{\hbar}\hat{H}t\right)|\Psi_0\rangle$$

Of course, this doesn't work if the Hamiltonian is a function of time. We would like to know either the wavefunction $|\Psi(t)\rangle$, or, even better, to find the **evolution operator** $\hat{U}(t)$, such that

$$|\Psi(t)\rangle = \hat{U}(t)|\Psi_0\rangle$$

In the case of a constant Hamiltonian, this evolution operator is simply $e^{-i\hat{H}t/\hbar}$, as we saw above. Interestingly, the evolution operator for a time-dependent Hamiltonian is independent of the initial conditions; we can think of it as a rotation operator on the wavefunction in the Hilbert space. We can see this from the fact that the wavefunction must still have norm 1:

$$\langle\Psi(t)|\Psi(t)\rangle = 1$$

This sounds nice, but it is usually very difficult to find the evolution operator. To see why, suppose $\hat{H}(t)$ is not an operator, and instead, it is just some function. Then we have a simple linear differential equation that can be solved easily:

$$i\hbar\frac{d\Psi}{dt} = H(t)\Psi \implies \Psi(t) = \exp\left(-\frac{i}{\hbar}\int_0^t H(u)\,du\right)\Psi(0)$$

The intuitive thing to do now is to just add a hat on the H and say we're done, but we cannot do that. The main reason for that is because the Hamiltonian doesn't necessarily commute with itself at different moments in time:

$$[\hat{H}(t_1), \hat{H}(t_2)] \neq 0$$

This is the major problem that makes almost all of time-dependent quantum mechanics difficult.

Examples of time-dependent problems Consider a particle in a non-equilibrium potential:

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

Even if the potential were constant, we already know it is a non-trivial problem to figure out the energy levels. In any moment in time, we can of course define a time-independent problem there and solve for energy levels, but the problem is that with a time-dependent Hamiltonian, energy is not necessarily conserved. So it is meaningless to talk about the energy levels of the time-dependent system. However, the probabilistic interpretation of the wavefunction is still valid: we can still talk about the probability of finding the particle in a certain region of space:

$$P(x_1, x_2) = \int_{x_1}^{x_2} |\Psi(x,t)|^2\, dx$$

where $P(x_1, x_2)$ is the probability of finding the particle in the interval $[x_1, x_2]$.

Another example is the spin of a particle in a time-dependent magnetic field:

$$i\hbar\begin{pmatrix}\partial_t\psi_\uparrow(t)\\ \partial_t\psi_\downarrow(t)\end{pmatrix} = -\mu\vec{B}(t)\cdot\hat{\vec{\sigma}}\begin{pmatrix}\psi_\uparrow(t)\\ \psi_\downarrow(t)\end{pmatrix}$$

Here, the spin of the particle is being rotated by the time-dependent magnetic field, e.g. such as in an MRI. This is essentially a first-order differential equation, and the problem here is to find $\psi(t)$, as usual. Here, $|\psi_\uparrow(t)|^2$ would give us the probability of finding the spin as up at the time t. Amazingly, this equation has no solution in elementary functions for a general $\hat{H}(t) = -\mu\vec{B}(t)$.

"Fast" and "slow" perturbations We will investigate these time-dependent problems involving perturbations. There are generally two cases: "fast" (**sudden**) and "slow" (**adiabatic**) perturbations. If the typical time scale of the perturbations is τ, we can compare it to the gap Δ between neighboring energy levels in the energy spectrum, because $\hbar/\Delta$ is a time scale. Hence

$$\tau \ll \frac{\hbar}{\Delta} \qquad \text{fast}$$
$$\tau \gg \frac{\hbar}{\Delta} \qquad \text{slow}$$

16.2 Sudden Perturbations; Shaking of an Atom

Now we will investigate one of the simplest problems in time-dependent quantum mechanics: fast perturbations in the potential. Another term for this is a **quantum quench**. This is when a potential changes sharply in time:

$$V(\vec{r},t) = \begin{cases} V_1(\vec{r}) & t < 0 \\ V_2(\vec{r}) & t > 0 \end{cases}$$

This can happen, for example, when we have a harmonic oscillator, but at $t = 0$, the frequency of the oscillator potential changes completely. A classical analog might be taking a guitar string oscillating at a harmonic, and then we suddenly change the length of the string. The main insight into this problem is that while the potential changes very rapidly, the wavefunction doesn't have enough time to change. So the state right after the quench is exactly the same as the one right before. However, it is no longer an eigenstate of the new Hamiltonian, i.e.

$$\hat{H}_2|\Psi_0^{(1)}\rangle \neq \hat{E}|\Psi_0^{(1)}\rangle$$

We can still expand the old eigenstate in the new eigenbasis, though:

$$|\Psi_0^{(1)}\rangle = \sum_{n=0}^{\infty} c_n|\Psi_n^{(2)}\rangle$$

But in general, these coefficients c_n are all non-zero. Note that each $|c_n|^2$ indicates the probability we will find the new state to be $|\Psi_n^{(2)}\rangle$.

Excitation of an atom Now let's consider a toy problem that is similar, which was a serious research problem 70 years or so ago. Suppose we have an atom. For the sake of simplicity, we'll consider the hydrogen atom, but this works for any atom in general. Imagine that the nucleus of the atom, which has its electron in the ground state, receives a sharp impulse that gives it a velocity $\vec{v}$. We are interested in the state of the electron after the "jolt". Since the atom is the potential that binds the electron, the potential starts moving due to the jolt, and therefore has suddenly changed.

To solve this problem, it turns out that looking at the frame of the reference of the atom is useful. In this frame of reference, the nucleus is static, and the electron is moving, and so we have the initial wavefunction as

$$\Psi_0(\vec{r}) = \underbrace{\frac{1}{\sqrt{\pi a_B^3}} e^{-r/a}}_{\text{standard ground state wavefunction}} \times \underbrace{\exp\left(-\frac{i}{\hbar} m\vec{v}\cdot\vec{r}\right)}_{\text{plane wave with velocity } \vec{v}}$$

Calculating the excitation probability Now we want to find the probability of the electron being excited to some higher energy state. But now we know the wavefunction $\Psi_0(\vec{r})$ after the jolt. If we want to know the probability of an excitation to $|\tilde{\Psi}_k\rangle$, the transition amplitude is

$$w_k = |\mathcal{A}_{0\to k}|^2 \qquad \mathcal{A}_{0\to k} = \int \Psi_0^* \tilde{\Psi}_k(\vec{r}\, d^3r$$

Note that here, $\tilde{\Psi}_k$ is moving together with the atom, while Ψ_0 is moving with velocity v relative to the atom, i.e. $\tilde{\Psi}_k$ does not have the plane wave component. To find the probability of excitation, then, we have to sum over all the w_k's. But since the electron must be in some state, we have

$$w_0 + \sum_k w_k = 1 \implies \sum_k w_k = w_* = 1 - w_0$$

Hence, writing w_0 explicitly and doing the integral,

$$\begin{aligned} w_* &= 1 - \left|\int \Psi_0^*(\vec{r})\tilde{\Psi}_0(\vec{r})\, d^3r\right|^2 \\ &= 1 - \frac{1}{\pi a_B^3}\left|\int \exp\left(-\frac{2r}{a_B} - \frac{i}{\hbar}\vec{p}\cdot\vec{r}\right) dV\right|^2 \\ &= 1 - \frac{1}{(1+\frac{1}{4}\frac{m^2v^2a_B^2}{\hbar^2})^4} \end{aligned}$$

We can run some sanity checks on this result. If $v = 0$, we don't have a jolt, and $w_* = 0$, which makes sense. If $v \to \infty$, then $w_* = 1$, and the electron will be left behind (of course, this doesn't take into account relativity).

16.3 Adiabatic Perturbations; Berry Phase

It turns out that when we have slow perturbations, we get a very interesting mathematical structure. Let's return to the original time-dependent S.Eq. setup:

$$i\hbar\partial_t|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle \qquad |\Psi(0)\rangle = |\Psi_0\rangle$$

Assume that $\hat{H}(0) = \hat{H}(T)$ for some T, i.e. that the Hamiltonian is periodic. We want to know what $|\Psi(\tau)\rangle$ is. It turns out this wavefunction has a very interesting topological contribution that is very counterintuitive.

Loops in parameter space Suppose the Hamiltonian depends on a parameter λ which changes in time:

$$i\hbar\partial_t|\Psi(t)\rangle = \hat{H}(\vec{\lambda}(t))|\Psi(t)\rangle$$

Now we suppose $\vec{\lambda}(0) = \vec{\lambda}(T)$. What happens to the wavefunction? Note that it does not necessarily return to itself.

Adiabaticity condition We also require that the Hamiltonian changes "slowly" with time. To define this formally, we define the instantaneous eigenstates

$$\hat{H}(\vec{\lambda}(t))|n;\, t\rangle = E_n(t)|n;\, t\rangle$$

For the sake of simplicity, let's assume the spectrum is discrete, and that the initial condition is the ground state of the Hamiltonian. This assumption is not necessary, but it makes things more concrete in the derivation to follow. Recall that in the previous section, we found that in the case of a sudden perturbation, the original wavefunction exists as a combination of the resulting eigenstates. Now, for a slow perturbation, we define it oppositely: the energy levels $E_n(t)$ are changing, but the state of the system remains in the instantaneous ground state of the Hamiltonian. Hence throughout the periodic evolution, the system remains in the original ground state. We take this as the definition of a slow perturbation. It turns out we can formally express this condition as

$$|\langle n;t|\frac{\partial}{\partial t}\hat{H}|0;t\rangle| \ll \frac{E_n(t) - E_0(t)}{\tau}$$

Geometric Berry phase Now we can derive the geometric Berry phase. By our adiabaticity condition, when we solve the time-dependent S.Eq., we require that $\Psi(t)$ remains proportional to the ground state, i.e. we only differ by a phase factor

$$|\Psi(t)\rangle = e^{i\psi(t)}|0,t\rangle$$

Under this assumption, what remains is to find the quantum phase. Plugging this back into the S.Eq., we get

$$i\hbar\partial_t|\Psi(t)\rangle = E_0(t)|\psi(t)\rangle$$

Note that E_0 is not an operator; it is just a function now. Naively, we want to write

$$\psi(t) = -\frac{1}{\hbar}\int_0^t E_0(u)\,du$$

However, this is not entirely correct. There is an additional contribution γ to $\psi(t)$, which is the **Berry phase**. This first term is usually called the **dynamical phase**, and commonly written as θ_d. Now, if we plug $\psi(t)$ into hte S.Eq.,

$$i\hbar\partial_t\left(e^{i\theta_d}e^{i\gamma}|0,t\rangle\right) = E_0|\psi(t)\rangle$$

Differentiating, we get, noting that $|0,t\rangle$ varies with time,

$$i\hbar(i\partial_t\theta_d)|\psi\rangle + i\hbar(i\partial_t\gamma)|\psi\rangle + i\hbar e^{i(\theta_d+\gamma)}\partial_t|0,t\rangle = E_0|\psi\rangle$$

Note also that by construction, the first term cancels the right hand side, and a lot of things cancel out afterward:

$$\frac{\partial}{\partial t}\gamma|0,t\rangle = i\frac{\partial}{\partial t}|0,t\rangle$$

We can also note that $\langle 0,t|0,t\rangle = 1$, so we multiply this entire equation by $\langle 0,t|$ to get

$$\gamma(T) = i\int_0^T \langle 0,t|\frac{\partial}{\partial t}|0,t\rangle\,dt$$

This term has a very interesting geometric interpretation.

Fictitious magnetic field and monopoles To see this geometric interpretation, we recall that the Hamiltonian depends only on time through the parameter $\vec{\lambda}$:

$$\hat{H}(\vec{\lambda})|0,\vec{\lambda}\rangle = E_0(\vec{\lambda})|0,\vec{\lambda}\rangle$$

We can transform the integral in the Berry phase from being over time to being over $\vec{\lambda}$. This change of variables can be done via

$$\frac{\partial}{\partial t} = \frac{\partial \vec{\lambda}}{\partial t}\frac{\partial}{\partial \vec{\lambda}}$$

Plugging this in to the expression for γ, we have

$$\gamma = i\oint_C \langle 0,\vec{\lambda}|\frac{\partial}{\partial \vec{\lambda}}|0,\vec{\lambda}\rangle\, d\vec{\lambda}$$

where C is the contour parameterized by $\vec{\lambda}$ that we are now integrating over. We introduce some new notation now:

$$\vec{\mathcal{A}} = i\langle 0,\vec{\lambda}|\frac{\partial}{\partial \vec{\lambda}}|0,\vec{\lambda}\rangle$$

Then we can see that γ is just the integral of this $\vec{\mathcal{A}}$ on the contour C. From electromagnetism, we know it is useful to introduce a vector potential such that the curl of the potential is simply the magnetic field in real space. So we can also define the curl of $\vec{\mathcal{A}}$ as

$$\nabla_{\vec{\lambda}} \times A(\vec{\lambda}) = \vec{B}(\vec{\lambda})$$

If we do this, we can rewrite the Berry phase as the flux of a fictitious magnetic field through the area enclosed by the contour C:

$$\gamma = \iint \vec{B}(\vec{\lambda})\cdot d\vec{\lambda}$$

So the quantum phase acquired by the wavefunction is the result of some fictitious magnetic field that exists in our model. Hence when we have a quantum system parameterized by a parameter $\vec{\lambda}$, there exists a fictitious magnetic field that becomes relevant when we perform quantum evolution with a periodic, time-dependent perturbatino, which gives our wavefunction a quantum phase that is simply the flux of the fictitious magnetic field through the area enclosed by C. This is why the Berry phase is called geometric.

However, unlike the magnetic field in real space, which doesn't have any sources and sinks, this fictitious magnetic field can have sources. These sources are "monopoles" in the parameter space that correspond to degeneracies in the spectrum of the problem. This means that if we have some special values of λ that we call λ_* such that there exists two wavefunctions with the same energy, then these points serve as "monopoles" of the fictitious magnetic field.