APPH E3100 : Intro to Quantum Notes

Xiao xy2437

September 27, 2021

Contents

Reading: Chapter 1

Theorem 0.1: Schrodinger's Equation

The Schrodinger's equation (dd) $\Psi(x,t)$ is in complex:

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

Theorem 0.2: Born's Statistical Interpretation

To use the **complex** Schrodinger's equation, the probability of finding a particle is **proportional to**:

$$|\Psi|^2$$

So, the probability of finding a particle between $x = a$ and $x = b$ at time t is:

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

where:

- $\frac{1}{\int_{-\infty}^{\infty}|\Psi(x,t)|^2\,dx}$ is the **normalizing factor** for the probability

Note:

But for most cases, we will **assume** that Ψ itself is normalized, so that $\int_{-\infty}^{\infty}|\Psi|^2\,dx = 1$

1 Psi with Classical Measurements

Reminder:

Classically, we defined average of a quantity to be:

$$\langle Q\rangle = \int_{-\infty}^{\infty} Q\cdot P(x,t)\,dx$$

where:

- *Q is a function*
- *$P(x,t)$ is normalized*

However, in quantum mechanics, we would expect to have:

$$\langle Q\rangle = \int_{-\infty}^{\infty}\hat{Q}|\Psi|^2\,dx$$

where:

- we have $\hat{Q}$ being the QM operator associated with the quantity Q.
- but $\langle Q \rangle$ means **differently** in quantum mechanics:
  - it is the **expectation value of** Q for a range of measurements all **started** with the same $\Psi(x,t)$
  - this also means that our equation of simply integrating is wrong (in fact, sometimes it is correct)

Now, we need to remember to have the aim of:

- how we want to figure out the expected value equation correctly
- how QM connects to classical mechanics

Derivation: Velocity and Momentum

We want to know how v connects to classical mechanics.
First, assuming this is correct (it is actually correct):

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi|^2 \, dx$$

where:

- x here is not a function, it is just displacement

then we have:

$$\frac{d}{dt}\langle x \rangle = \int_{-\infty}^{\infty} x \frac{d}{dt}|\Psi|^2 \, dx \tag{1}$$

this means:

$$\frac{d}{dt}\left(\Psi^* \cdot \Psi\right) = \Psi * \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \tag{2}$$

but we know from Schrodinger's equation:

$$\begin{cases} \frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi \\ \frac{\partial \Psi^*}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} - \frac{i}{\hbar}V\Psi^* \end{cases}$$

where:

- remember that $V = V^*$ because potentials are real.

So substituting into (2), we have:

$$\begin{aligned} \frac{\partial}{\partial t}\left(|\Psi|^2\right) &= \Psi^*\left(\frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{h}V\Psi\right) + \Psi\left(-\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar}V\Psi^*\right) \\ &= \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial^2 \Psi}{\partial x^2} - \Psi\frac{\partial^2 \Psi^*}{\partial x^2}\right) \\ &= \frac{\partial}{\partial x}\left(\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial \Psi}{\partial x} - \Psi\frac{\partial \Psi^*}{\partial x}\right)\right) \end{aligned} \tag{3}$$

Now, substituting into (1), we have:

$$\frac{d}{dt}\langle x\rangle = i\frac{\hbar}{2m}\int_{-\infty}^{\infty} x\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)dx$$

Using integration by parts, taking $u = x$ and $dv = \frac{\partial}{\partial x}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)dx$, we have

$$\begin{aligned}\frac{d}{dt}\langle x\rangle &= \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)\Bigg|_{-\infty}^{\infty} - \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)dx \\ &= -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)dx \\ &= -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\Psi^*\frac{\partial\Psi}{\partial x}\,dx + \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\Psi\frac{\partial\Psi^*}{\partial x}\,dx\end{aligned} \tag{4}$$

where:

- remember that $\Psi = 0$ when $x = -\infty, \infty$

Now, taking the part $\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\Psi\frac{\partial\Psi^*}{\partial x}\,dx$ and integrating by parts with $u = \Psi$, we have:

$$\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\Psi\frac{\partial\Psi^*}{\partial x}\,dx = 0 - \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\Psi^*\frac{\partial\Psi}{\partial x}\,dx \tag{5}$$

Therefore, finishing up by substituting (5) into (4), we have:

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

Finishing up, the expected momentum becomes:

$$\langle p\rangle = m\langle v\rangle = \int_{-\infty}^{\infty}\Psi^*\hat{p}\Psi\,dx$$

where:

- we have $\hat{p} = \left(-i\hbar\frac{\partial}{\partial x}\right)$ as an operator

Theorem 1.1: QM Expected Value

Hence the more correct version is:

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

where we see:

- if $\hat{Q}$ is not a derivative, then the previous version of $Q|\Psi|^2$ is also correct

Note:

> The general rule of operators are that: **operators operate to everything on the right**

This also means that, in general, if you have a function $Q(x,p)$ of position and momentum, then:

$$\hat{Q} = \hat{Q}(x, \hat{p})$$

***Example*: Operator for Kinetic Energy and Potential Energy**

This means that, if we have $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$, then to convert that to operators:

$$\begin{aligned}\hat{T} &= \frac{1}{2m}\hat{p}\hat{p} \\ &= \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}.\end{aligned}$$

Simiarly, if we need $\hat{T} + \hat{V}$, we have:

$$\hat{V} = \hat{V}(\hat{x}) = V(x)$$

since $\hat{x} = x$.
As a result:

$$\left(\hat{T} + \hat{V}\right)\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V(x)\Psi$$

Theorem 1.2: Hamiltonian and General Schrodinger's Equation

Looking at the example, realize that this is basically the 1D schrodinger's equation:

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

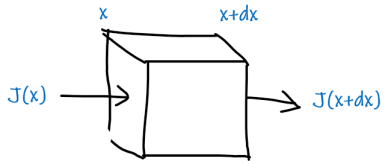
and we can define the Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$:

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

which is basically the **the General Schrodinger's equation**.

1.1 Probability Current/Flux

Consider a small cube with density flux $J(x)$ entering and $J(x+dx)$ exiting:



Then, we can have the number of particles inside the volume $V = dx^3$ to be:

$$\int_V P\, d^3r = \text{total number of particles inside } V$$

where:

- P is the probability of finding a particle in the volume as a function of the coordinate (**consider P as the normalized density distribution** n).

Therefore, connecting with the flow:

$$\frac{d}{dt}\int_V P\, d^3r = J_{into}A - J_{out}A \tag{6}$$

where:

- here, we have $J_{into} = J(x)$, and $J_{out} = J(x+dx)$

Now, notice that the quantity $V = dV = dx^3$:

$$\int_V P\, d^3r = PdV$$

Therefore, (6) becomes:

$$\frac{d}{dt}\int_V P\, d^3r = \frac{d}{dt}|\Psi|^2 dV$$

Substituting 3 we have:

$$\frac{\partial}{\partial x}\left(\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)\right)dV = J(x)A - J(x+dx)A = -\frac{dJ}{dx}Adx$$

Theorem 1.3: Current Density/Probability Flux

From the above, we have derived J as the probability flux/density flux (imagine as the rate of flow of this fluid):

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

where:

- then to get electrical current density, we just need $q \cdot J$, and etc.

Note:

You might remember that classically:

$$J = n \cdot v$$

where:

- n is density and v is velocity

but, as you see above, the analogy would be wrong in QM:

$$J_{QM} \neq |\Psi|^2 \frac{\hat{p}}{m} = \Psi^* \Psi \left(-\frac{i\hbar}{m} \frac{\partial}{\partial x} \right)$$

or no matter where you put the operator

***Example*: Using QM Current Density**

Consider an ideal wave function:

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

If we substitute that in and compute J:

$$\begin{aligned} J &= \frac{i\hbar}{2m} \left(\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right) \\ &= \frac{i\hbar}{2m} |A|^2 \left(-ik - ik \right) \\ &= |A|^2 \frac{\hbar k}{m}. \end{aligned}$$

However, remember that $p = \hbar k$, and that $|A|^2 = |\Psi|^2$ in this setup.

So we basically have:

$$J = v|A|^2 = v\left(\Psi^* \Psi\right) = v \cdot P$$

where:

- P would be the probability density = **normalized** density distribution
- constrast this with the classical $J = v \cdot n$

1.2 Ehrenfest's Principle

Theorem 1.4: Ehrenfest's Principle

This principle basically shows that **the following expected values have a clear analogy to the classical world** (such that *if we repeat the measurement for a very large number of times, the result will become classical*):

$$\frac{d}{dt}\langle x\rangle = \langle v\rangle = \frac{\langle p\rangle}{m} \tag{7}$$

which is proven in the section 1.1, under the derivation of Velocity and Momentum.

$$\frac{d}{dt}\langle p\rangle = \left\langle -\frac{dV}{dx}\right\rangle \tag{8}$$

where:

- V signifies the potential function

Note:

Notice the analogy of equation (7) and (8) with the classical mechanics:

$$\frac{d}{dt}x = v = \frac{p}{m}$$
$$\frac{d}{dt}p = -\frac{dV}{dx} = F$$

Derivation: Derivation for Ehrefest's Principle

I have already derived equation (7) in section 1.1, and here I derive equation (8).

Recall that:

$$\langle p\rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi \, dx$$

Then computing the LHS of equation (8):

$$\begin{aligned}\frac{d}{dx}\langle p\rangle &= -i\hbar \int_{-\infty}^{\infty} \frac{d}{dt}\left(\Psi^* \frac{\partial \Psi}{\partial x}\right) dx \\ &= -i\hbar \int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial t}\frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial^2 \Psi}{\partial t \partial x}\, dt.\end{aligned}$$

Now, for the time derivatives of Ψ, Ψ^*, we can substitute in the Schrodinger's

equation:

$$\begin{aligned}
\frac{d}{dt}\langle p\rangle &= -i\hbar\left(\int_{-\infty}^{\infty} -\frac{1}{i}\frac{d}{dt}\langle p\rangle\right) \\
&= -i\hbar[\int_{-\infty}^{\infty} -\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + V(x)\Psi^*\frac{\partial\Psi}{\partial x}\right)dx \\
&\quad + \int_{-\infty}^{\infty}\frac{1}{i\hbar}\left(\Psi^*\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\right)\right)dx] \\
&= \int_{-\infty}^{\infty} -\frac{\hbar}{2m}\left(\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x} - \Psi^*\frac{\partial^3\Psi}{\partial x^3}\right)dx \\
&\quad + \int_{-\infty}^{\infty} V(x)\Psi^*\frac{\partial\Psi}{\partial x} - \Psi^*\left(\frac{\partial V}{\partial x}\Psi + V\frac{\partial\Psi}{\partial x}\right)dx \\
&= \int_{-\infty}^{\infty} -\frac{\hbar}{2m}\left(\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x} - \Psi^*\frac{\partial^3\Psi}{\partial x^3}\right)dx + \int_{-\infty}^{\infty} -\Psi^*\frac{\partial V}{\partial x}\Psi\,dx.
\end{aligned}$$

Now, I claim the following term cancels:

$$\int_{-\infty}^{\infty}\left(\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x} - \Psi^*\frac{\partial^3\Psi}{\partial x^3}\right)dx = 0$$

Proof. Integrating this by parts:

$$\int_{-\infty}^{\infty}\left(\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x}\right)dx = \frac{\partial\Psi}{\partial x}\,\frac{\partial\Psi^*}{\partial x}\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\frac{\partial\Psi^*}{\partial x}\frac{\partial^2\Psi}{\partial x^2}\,dx$$

Integrating this by parts again, we have

$$RHS = \frac{\partial\Psi}{\partial x}\,\frac{\partial\Psi^*}{\partial x}\Big|_{-\infty}^{\infty} - \frac{\partial^2\Psi}{\partial x^2}\Psi^*\Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\Psi^*\frac{\partial^3\Psi}{\partial x^3}\,dx$$

Now, remember that $\Psi, \Psi^* = 0$ for $x = \pm\infty$, so that their derivatives are also 0. Hence, we have:

$$\int_{-\infty}^{\infty}\left(\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x}\right)dx = \int_{-\infty}^{\infty}\Psi^*\frac{\partial^3\Psi}{\partial x^3}\,dx$$

Hence:

$$\int_{-\infty}^{\infty}\left(\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x} - \Psi^*\frac{\partial^3\Psi}{\partial x^3}\right)dx = 0$$

□

Returning back to the derivation:

$$\frac{d}{dt}\langle p\rangle = 0 + \int_{-\infty}^{\infty}\Psi^*\left(-\frac{dV}{dx}\right)\Psi\,dx = \left\langle -\frac{dV}{dx}\right\rangle$$

which completes the derivation.

Note:

The take away message here is that: **for large amount of measurements, or for large systems, the expectation value $\langle p \rangle$ tends to the real life classical mechanmics**

1.3 Uncertainty Principle

The uncertainty principle in exact quantum mechanics definition is the following:

Theorem 1.5: Uncertainty Principle

$$\sigma_x \sigma_{p_x} \geq \frac{\hbar}{2} \tag{9}$$

$$\sigma_E \sigma_t \geq \frac{\hbar}{2} \tag{10}$$

where:

- $\sigma_x = \Delta x$, but it is a better notation because **uncertainty in QM is defined to be:**

  $$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\left\langle (x - \langle x \rangle)^2 \right\rangle}$$

  where $\langle x \rangle$ is the expectation value of x in quantum mechanics

Note:

The above also means that:

- the below would be correct:

  $$\begin{cases} \sigma_y \sigma_{p_y} \geq \frac{\hbar}{2} \\ \sigma_z \sigma_{p_z} \geq \hbar/2 \end{cases}$$

- and that:

  $$\sigma_x \sigma_{p_y} \geq 0$$

  because **the uncertainty principle implicitly says that x is unrelated to other momentum such as p_y, p_z**

2 Time Independent Schrodinger's Equation

Now, back from showing all the connections with classical mechanics/real life observations, we go on and study the quantum's world.

Theorem 2.1: Time Independent Schrodinger's Equation

Suppose, for the Schrodinger's equation:

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

we have:

- $V(x,t) = V(x)$

then this **condition alone** usually makes the wave function separable, such that:

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

which will in turn leads to the Time Independent Schrodinger's Equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi$$

or equivalently:

$$\hat{H}\psi(x) = E\psi(x) \tag{11}$$

which is time independent.

Derivation: Time Independent Schrodinfer's Equation

Suppose $V(x,t) = V(t)$, and assuming the solution is separable, we want to show that it leads to the time-independent Schrodinger's equation.

Substituting the wave function $\Psi(x,t) = \psi(x)\phi(t)$ into the Schrodinger's equation, we have:

$$i\hbar\psi(x)\frac{\partial\phi(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\phi(t) + V(x)\psi(x)\phi(t)$$

assuming a non-trvial wave function Ψ, we divide both sides by $\psi\phi$:

$$i\hbar\frac{1}{\phi}\frac{\partial\phi}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\partial^2\psi}{\partial x^2} + V(x)$$

and realize that:

- LHS only has time dependent, and RHS only has position dependence.

This means that both sides are **equal to a constant!**

Therefore, it leads to the two equations:

$$\begin{cases} i\hbar\frac{\partial\phi}{\partial t} = \phi E, & \phi(t) = Ae^{-i\frac{E}{\hbar}t} \\ -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi \end{cases}$$

where:

- E is a constant, which later you will see why it is named E.

And this completes the derivation.

Note:

The above solved the equation:

$$i\hbar\frac{\partial\phi}{\partial t} = E\phi$$

which is trivial since $\phi = \phi(t)$. But the **non-trivial part** is that you should always use $-i\frac{E}{t}$ instead of the other ones:

$$\phi(t) = Ae^{-i\frac{E}{\hbar}t} = Ae^{-i\omega t}$$

(remember that $E = \hbar\omega$)

- also, for most of the cases, you can assume ϕ is also "normalized" so that $A = 1$

Therefore, for the time-independent schrodinger's equation, the wave function will be in the form:

$$\Psi(x,t) = \psi(x)\phi(t) = \psi(x)e^{-i\frac{E}{\hbar}t}$$

assuming that $\phi = Ae^{-i\frac{E}{\hbar}t} = e^{-i\frac{E}{\hbar}t}$. However, since E and ϕ satisfy the system:

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

We have the following corollary:

Corollary 2.1

If we have a separable wave equation:

1. the solution of Ψ can **always** be written as a **superposition of the eigenstates** :

$$\Psi(x,t) = \sum_{n=1}^{k} c_k\psi_k(x)e^{-i\frac{E_k}{\hbar}t} \tag{12}$$

where ψ_k is the kth eigenfunction, and E_k is the k th eigenvalue, and c_k can be obtained using the initial configuration:

$$\Psi(x,0) = \sum_{n=1}^{k} c_k\psi_k(x)$$

2. the below holds for a **wave function of a single state** (single pair of eigenvalue and eigenfunction) :

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

which is **independent of time**

3. Each **single** state is a **stationary state with definitive *total energy*** E :

$$\begin{aligned}\langle E_{KE+P}\rangle = \langle H\rangle &= \int_{\infty}^{\infty} \Psi^* \bar{H}\Psi \, dx \\ &= \int_{-\infty}^{\infty} \psi^* \bar{H}\psi \, dt \\ &= \int_{-\infty}^{\infty} \psi^* E\psi \, dx \\ &= E\int_{-\infty}^{\infty} \psi^*\psi \, dx \\ &= E.\end{aligned}$$

this is only true for a single pair of eigenvalue and eigenfunction such that $\Psi = \psi_1\phi_1$, then $E = E_1$. If you have a superposition of the states, the step from $\Psi^*\hat{H}\Psi$ to $\psi^*\hat{H}\psi$ will not hold.

4. The uncertainty of measuring the total energy $\hat{H}$ is zero:

$$\sigma_H^2 = \left\langle H^2\right\rangle - \langle H\rangle^2 = \left\langle H^2\right\rangle - E^2$$

Now, computing $\left\langle H^2\right\rangle$, and assuming a **single state for the wave function**:

$$\begin{aligned}\int_{-\infty}^{\infty} \Psi^*\hat{H}^2\Psi \, dx &= \int_{-\infty}^{\infty} \psi^*\hat{H}^2\psi \, dx \\ &= E\int_{-\infty}^{\infty} \psi^*\hat{H}\psi \, dx \\ &= E^2.\end{aligned}$$

substituting back in, we get:

$$\sigma_H^2 = 0 \tag{13}$$

for a **separable wave function of a single state**

notice that the above talks a lot about wave function only of a single eigenstate.

What happens when you have a linear combination of two states?

***Example*: Separable Wave Function of Two EigenStates**

First and foremost, you will see that the second rule of $|\Psi|^2 = |\psi(x)|^2$ which is independent of time **does not hold any more**:

Consider the following wave function of two states combined:

$$\Psi(x,t) = c_1\phi_1(x)e^{-i\frac{E_1}{\hbar}t} + c_2\phi_2(x)e^{-i\frac{E_2}{\hbar}t}$$

Computing:

$$\begin{aligned}|\Psi^2| &= \Psi^*\Psi \\ &= \left(c_1^*\psi_1^* e^{i\frac{E_1}{\hbar}t} + c_2^*\psi_2^* e^{i\frac{E_2}{\hbar}t}\right)\left(c_1\psi_1 e^{-i\frac{E_1}{\hbar}t} + c_2\psi_2 e^{-i\frac{E_2}{\hbar}t}\right) \\ &= |c_1|^2|\psi_1|^2 + |c_2|^2|\psi_2|^2 + c_1^*c_2\psi_1^*\psi_2 e^{i\frac{E_1-E_2}{\hbar}t} + c_1c_2^*\psi_1^*{}_2 e^{-i\frac{E_1-E_2}{\hbar}t}.\end{aligned}$$

Now, remember that $|\Psi(x,t)|^2$ is real. However, unless under extreme coincidence that the latter two cancels terms out, the latter two term will emit a $\cos ...t$ and $\sin ...t$. This means now $|\Psi|^*$ is **dependent of time** again (as compared to the case of a single eigenstate).

Similarly, the third rule of definitive energy does not hold either when we have more than one eigenstate. In fact, in general:

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

so here we have (assuming $\hat{Q} = \hat{Q}(x,\hat{p})$, so it **does not deal with time**):

$$\begin{aligned}\langle Q\rangle &= \int_{-\infty}^{\infty}\left(c_1^*\psi_1^* e^{i\frac{E_1}{\hbar}t} + c_2^*\psi_2^* e^{i\frac{E_2}{\hbar}t}\right)\hat{Q}\left(c_1\psi_1 e^{-i\frac{E_1}{\hbar}t} + c_2\psi_2 e^{-i\frac{E_2}{\hbar}t}\right)dx \\ &= |c_1|^2\int_{-\infty}^{\infty}\psi_1^*\hat{Q}\psi_1\, dx + |c_2|^2\int_{-\infty}^{\infty}\psi_2^*\hat{Q}\psi_2\, dx \\ &\quad + c_1^*c_2 e^{i\frac{E_1-E_2}{\hbar}t}\int_{-\infty}^{\infty}\psi_1^*\hat{Q}\psi_2\, dx + c_1c_2^* e^{i\frac{E_2-E_1}{\hbar}t}\int_{-\infty}^{\infty}\psi_2^*\hat{Q}\psi_1\, dx.\end{aligned}$$

since the integrals only involve x, they essentially become a number. We have:

$$\langle Q\rangle = |c_1|^2Q_{11} + |c_2|^2Q_{22} + c_1^*c_2e^{i\frac{E_1-E_2}{\hbar}t}Q_{12} + c_1c_2^*e^{i\frac{E_2-E_1}{\hbar}t}Q_{21}$$

and notice we have oscillatory times for time

Note:

The above could be further simplified, if:

1. $\hat{Q}$ is a Hermitian (making $Q_{12} = Q_{21}^*$)

2. c_1, c_2, Q_{ij} are real

then, we would have:

$$Q_{12} = Q_{21}$$

then the above becomes:

$$\langle Q \rangle = c_1^2 Q_{11} + c_2^2 Q_{22} + 2c_1 c_1 Q_{12} \cos\left(\frac{E_1 - E_2}{\hbar} t\right)$$

which is still *not a stationary state*

This large section goes back to deal with various solutions for **time independent** Schrodinger's equation.

One important observation of Schrodinger's equation is that, for a state:

$$\Psi = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t}$$

with $\psi_n(x)$ being **normalized** (e.g. $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$.)

- **once you measured this wave function, it will *collapse to a single state, say n', and will stay in that state***
- If you set up the system and measure again, it might collapse into another state, say n''
- the **probability of collapsing to a state** n' in this case is defined by the **normalized coefficient**:

  $$|c_{n'}|^2, \quad \text{where} \sum_n |c_n|^2 = 1$$

  for example, if you used normalized ψ_n for calculating c_n, then c_n is **automatically normalized**.

2.1 Overview of Solutions of TISE

Here, we generally discuss the time independent solutions, and they can be:

- solved exactly
- solved piecewise exactly
- solved using approximate methods
- solved using perturbation theory

and they can be in:

- 1-D
- 2-D
- 3-D

with:

- 1 particle
- many particles
  - for this course, we *assume particles are not interacting with each other*
- spin

2.2 General Types of TISE

In general, we are dealing with ψ (since ϕ is basically solved already):

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi$$

And consider the region where $V(x) = V_0$, then:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = (E - V_0)\,\psi$$

and you will get two types of solutions.

Theorem 2.2

For a TISE in a region with $V(x) = V_0$:

1. When $E > V_0$, we have:

$$\frac{d^2\psi}{dx^2} = -K^2\psi, \quad K^2 = \frac{2m}{\hbar^2}(E - V_0) > 0$$

then solution becomes in the form:

$$\begin{aligned}\psi(x) &= Ae^{iKx} + Be^{-ikx} \\ &= C\sin(Kx) + D\cos(Kx) \\ &= F\sin(Kx + \delta).\end{aligned} \tag{14}$$

Note:

> **In general,** if $E > V(x,t)$ for a QM system, it will have **oscillations** in a similar manner like this one

2. When $E < V_0$, we have:

$$\frac{d^2\psi}{dx^2} = \mathcal{K}^2\psi, \quad \mathcal{K}^2 = \frac{2m}{\hbar^2}(V_0 - E) > 0$$

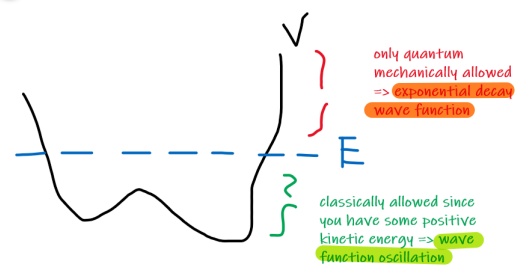
then solutions become:

$$\begin{aligned}\psi(x) &= A'e^{\mathcal{K}x} + B'e^{-\mathcal{K}x} \\ &= C'\sinh(\mathcal{K}x) + D'\cosh(\mathcal{K}x).\end{aligned} \tag{15}$$

Note:

> Here, usually the exponential growth term is ignored for large x since ψ exploding is classically and quantum mechanically forbidden. **Therefore, often we will have the exponential decay term in this case**

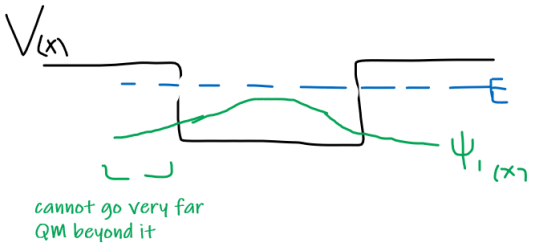
The classically forbidden region mentioned above can be understood like this:



3 Bound and Unbound States

Another category of TISE is **bound states v.s. unbound states**:

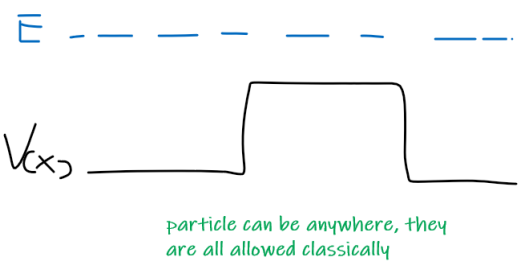
1. **bound states:**



where:

- at sometime point, the **potential of the particle becomes higher than total energy, making it classical forbidden but QM with decaying wavefunction**

2. **unbound states**:



where:

- everywhere, the **total energy is higher than potential energy, making classical kinetic energy possible. Hence, it becomes a *free particle***

Note:

> - A **bound state just means the particle cannot go very far outside the boundary**
> - An **unbound state means the particle can go to anywhere it wants**

Some examples of bound states include:

1. infinite square well
2. finite square well
3. simple harmonic oscillation

Some examples of unbound states include:

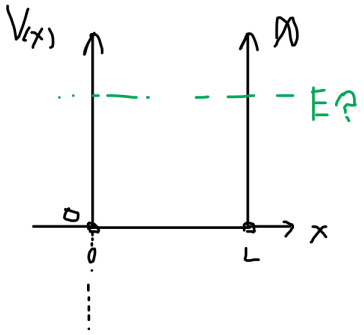
1. free particles
2. scattering

And of course, there could be **mixed bound and unbounded** case as well.

3.1 Bound States

3.1.1 Infinite Square Well

Consider the TISE with the setup of:



and, for most of the cases, we want the wave function to have:

1. **continuous** ψ
2. **continuous** $\frac{d\psi}{dx}$

Considering the equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V(x)\psi=E\psi$$

Then, we have:

$$\begin{cases}-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}=E\psi, & 0<x<L\\ \psi(x)=0, & x\geq L, x\leq 0\end{cases}$$

because if V explodes, you need $\psi=0$ so the TISE does not explode.

Now, the solution basically becomes:

$$\begin{cases}\psi(x)=A\sin(Kx)+B\cos(Kx), & 0<x<L\\ \psi(x)=0, & x\geq L, x\leq 0\end{cases}$$

for $K^2=\frac{2mE}{\hbar^2}$

Solving for E, we use the continuity of ψ as *boundary condition*:

$$\psi(0)=\psi(L)=0$$

then, we obtain:

$$\begin{cases}\psi(0)=B=0\\ \psi(L)=A\sin(Kx)=0, \quad K=\frac{n\pi}{L}, n>0\end{cases}$$

Hence, we get:

$$K_n=\frac{n\pi}{L}=\sqrt{\frac{2mE}{\hbar^2}}$$
$$E_n=\frac{n^2\pi^2\hbar^2}{2mL^2}.$$

Note:

> At this point, notice that the **continuity of $\frac{\partial\psi}{\partial x}$ does not hold. This is because this system is nonphysical, and will be covered during the discussion of finite well**

Now, solving for the unknown A_n, we can use:

$$\int_0^L \psi^*\psi\,dx=\int_0^L A_n^2\sin^2(K_nx)\,dx=1$$

So, in the end, the solution looks like:

Theorem 3.1: Solution for Infinite Square Well

In the end, for a well of width L, we have:

- the solution of the n-th stationary state:

$$\Psi_n(x,t)=\sqrt{\frac{2}{L}}\sin\left(n\pi\frac{x}{L}\right)e^{-i\frac{E_n}{\hbar}t}$$

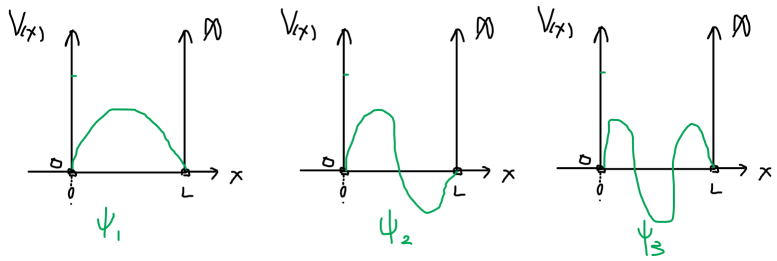
- the general solution:

$$\Psi(x,t) = \sqrt{\frac{2}{L}} \sum_{n=1}^{\infty} B_n \sin\left(n\pi \frac{x}{L}\right) e^{-i\frac{E_n}{\hbar}t}$$

for B_n being computed using the Fourier series with the **initial condition** $\Psi(x,0) = f(x)$:

$$B_n = \int_{-\infty}^{\infty} \psi_n^*(x) f(x)\, dx$$

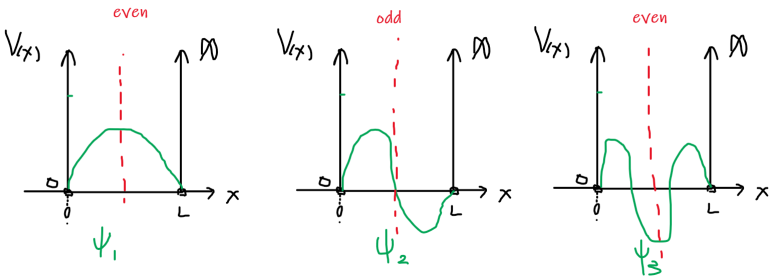
Graphically, the solutions look like:



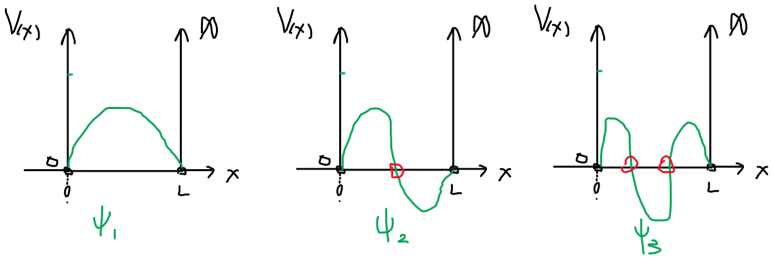
3.1.2 Properties of Infinite Square Well

Some useful properties you should see:

1. **When the potential function V is symmetric**, the eigenfunctions of ψ alternates is odd/even shape



2. increasing n by 1 increases the number of nodes by 1
   - **in general**, increasing eigenfunctions increases the number of nodes
3. different eigenfunctions (different n) are mutually orthogonal (and can be normalized to be orthornomal).
   - this is also **generally true for QM systems**



$$\int_{-\infty}^{\infty} \psi_k(x)\psi_l(x)\,dx = \begin{cases} 0, & k \neq l \\ 1, & k = l \text{ if normalized} \end{cases}$$

4. $\psi_n(x)$ gives a **complete set of states in QM**

   - **this is also generally true for QM systems**

   this means that, **any valid wave function** $f(x)$ of the system can be written as:

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

   and then, you can use orthogonality of eigenfunctions ψ to solve for c_n

5. **In general** the c_n values solved above **will be normalized automatically if Ψ or equivalently ψ is normalized**:

   $$\begin{aligned} 1 &= \int_{-\infty}^{\infty} |\Psi(x,0)|^2\,dx \\ &= \int_{-\infty}^{\infty} \left(\sum_{m=1}^{\infty} c_m \psi_m\right)^* \left(\sum_{n=1}^{\infty} c_n \psi_n\right) dx \\ &= \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n^* \int_{-\infty}^{\infty} \psi_m^* \psi_n^*\,dx \\ &= \sum_{n=1}^{\infty} c_n^* c_n. \end{aligned}$$

   since $\int_{-\infty}^{\infty} \psi_m^* \psi_n\,dx = \delta_{m,n}$ (1 if $m = n$, 0 otherwise) when they are normalized already

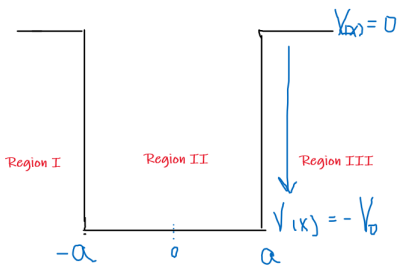
6. **In general for TISE**, the **expected value for energy** will be station-

ary:

$$\begin{aligned}
\langle H \rangle &= \int_{-\infty}^{\infty} \Psi^* \hat{H} \Psi \, dx \\
&= \int_{-\infty}^{\infty} \left(\sum_{m=1}^{\infty} c_m^* \psi_m^* e^{i \frac{E_m}{\hbar} t} \right) \hat{H} \left(\sum_{n=1}^{\infty} c_n \psi_n e^{-i \frac{E_n}{\hbar} t} \right) dt \\
&= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n e^{i \frac{(E_m - E_n)}{\hbar} t} \int_{-\infty}^{\infty} \psi_m^* \hat{H} \psi_n \, dx \\
&= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n e^{i \frac{(E_m - E_n)}{\hbar} t} E_n \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx \\
&= \sum_{n=1}^{\infty} c_n^* c_n E_n.
\end{aligned}$$

3.1.3 Finite Square Well

Now, consider this setup:



where:

- **bound energy will be below the** 0
- similar to the infinite square well, only **bound stats are of concern here**

Note:

> The procedure for solving these types of questions will be **mostly the same:**
>
> 1. Obtain the *form* of the solution in the given setup
> 2. Use the QM **constraint** of $\psi(-\infty) = \psi(\infty) = 0$ to simplify the coefficients
> 3. Use the **continuity** of ψ and $\frac{d\psi}{dx}$ to **solve** the coefficients of the solutions and especially the *energy eigenvalues*

For this problem, we solve it in piece wise:

1. In **Region I**, $V(x) = 0$:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} &= E\psi \\ \frac{d^2\psi}{dx^2} &= K^2\psi \\ \psi_I(x) &= Ae^{-Kx} + Be^{Kx}. \end{aligned}$$

for $K = \sqrt{-\frac{2mE}{\hbar^2}}$ (remember $E < 0$ here for bound states)

In **Region II**:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx} - V_0\psi &= E\psi \\ \frac{d^2\psi}{dx^2} &= -l^2\psi \\ \psi_{II}(x) &= C\sin(lx) + D\cos(lx). \end{aligned}$$

for $l = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$ with $V_0 > 0$

In **Region III** (basically the $-x$ of Region I):

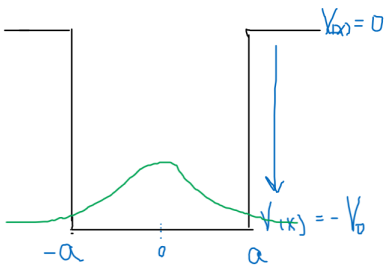
$$\psi_{III}(x) = Fe^{-kx} + Ge^{kx}.$$

2. Since we know $\psi(-\infty) = \psi(\infty) = 0$, I get for Region I and Region III:

$$\begin{aligned} \psi_I(x) &= Be^{Kx} \\ \psi_{III}(x) &= Fe^{-Kx}. \end{aligned}$$

3. Now, to **match the continuity constraint**, we consider here the **even and odd parity solutions:**

   - for even parity:



we expect $\psi(a) = \psi(-a)$, therefor a $\cos(...)$ solution:

$$\psi(x) = \begin{cases} Be^{Kx} = Fe^{Kx}, & x < -a \\ D\cos(lx), & |x| \leq a \\ Fe^{-Kx}, & x > a \end{cases}$$

then the contiuity at $x = a$ for ψ and $\frac{d\psi}{dx}$leads to:

$$\begin{cases} Fe^{-Ka} = D\cos(la) \\ -KFe^{-Ka} = -Dl\sin(la) \end{cases}$$

finally, we solved:

$$K = \sqrt{-\frac{2mE}{\hbar^2}} = l\tan(la)$$

for $l = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$

Though you can technically solve E from the above, there is a good trick to know for this:

Let $z = la$, and $z_0 = \frac{a}{\hbar}\sqrt{2mV_0}$, such that $\frac{z_0^2}{a^2} = K^2 + l^2$:

$$\begin{aligned} \frac{z_0^2}{z^2} &= \frac{K^2 + l^2}{l^2} \\ &= 1 + \frac{K^2}{l^2} \\ \frac{K}{l} &= \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}. \end{aligned}$$

since $K = l \cdot tan(la)$:

$$tan(z) = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$$

now, it only involves z, and solving for z solves for l, which solved E for *even parity solutions* :

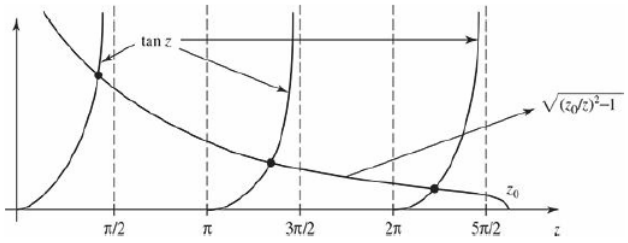
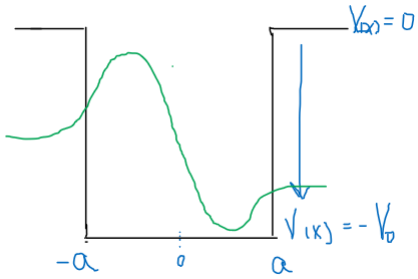


Figure 2.17: Graphical solution to Equation 2.159, for $z_0 = 8$ (*even* states).

- for odd parity:
  we expect $\psi(a) = -\psi(a)$, therefore a $\sin(...)$ solution, and the procedure is skipped here (since it is analogous with the previous one).



Theorem 3.2: Solution for Finite Square Well

For a finite square well with height of V_0 below 0, the **bound states solutions** look like:

- even parity:

$$\psi(x) = \begin{cases} Be^{Kx}, & x < -a \\ D\cos(lx), & |x| \leq a \\ Be^{-Kx}, & x > a \end{cases}$$

- odd parity:

$$\psi(x) = \begin{cases} -Be^{Kx}, & x < -a \\ D\sin(lx), & |x| \leq a \\ Be^{Kx}, & x > a \end{cases}$$

with

$$K = \sqrt{-\frac{2mE}{\hbar^2}} = l\tan(la)$$

for $l = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$

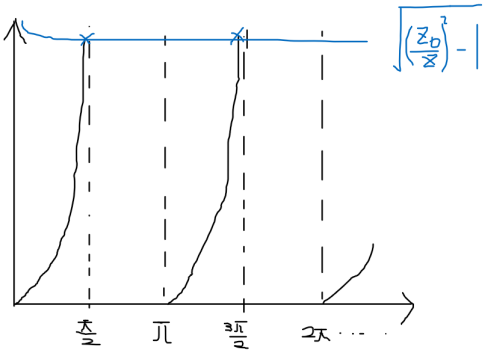
Interestingly, consider the following two cases for finite square well:

1. the V_0 **becomes infinity large**, such that z_0 becomes infinitely large. Then the graphically solution for *even parity* looks like:
   explicitly:

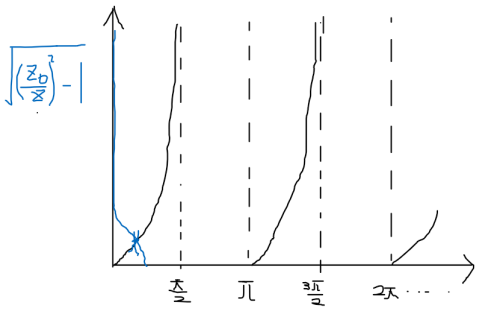
$$z_n = la = a\sqrt{\frac{2m(E+V_0)}{\hbar^2}} = n\frac{\pi}{2}, \quad n = 1, 3, 5, 7...$$
$$n\frac{\pi}{2a} = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$
$$\frac{n^2\pi^2\hbar^2}{2m(2a)^2} = E_n + V_0.$$

   for width of $2a$ and energy relative to V_0 being $E_n' = E_n + V_0$

2. the V_0 **becomes infinitely small/shallow**, such that z_0 becomes very small. Then, there will be no solution for odd parity, but **always a**



solution for even parity:



which means that, **no matter how shallow the potential well is, there is always a BOUND STATE**

3.1.4 Delta Function Potential

Reminder:

There are in general two commonly used delta functions:

- ***Kronecker Delta***

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

- ***Dirac Delta****:*

$$\delta(x) = \begin{cases} \infty, & x = 0 \\ 0, & x \neq 0 \end{cases}$$

and that:

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1, \quad \int_{-\infty}^{\infty} f(x)\delta(x)\, dx = f(0) \tag{16}$$

Consider a dirac delta potential function:

$$V(x) = -\alpha\delta(x),\ \alpha > 0$$

For bound states:

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

but for $x > 0$ or $x < 0$, we have the same case as finite square well (see theorem **??**), hence:

$$\psi(x) = \begin{cases} Be^{Kx}, & x < 0 \\ Fe^{-Kx}, & x > 0 \end{cases}$$

for $K = \sqrt{\frac{-2mE}{\hbar^2}}$, where $E < 0$ for bound states.

Now, will we have essentially **solved the wavefunction**, we need to solve K, which is **done by boundary conditions:**

- continuity of ψ
- continuity of $\frac{d\psi}{dx}$

Reminder:

> *The procedure for solving these types of questions will be* ***mostly the same:***
>
> 1. *Obtain the* form *of the solution in the given setup*
> 2. *Use the QM* ***constraint*** *of $\psi(-\infty) = \psi(\infty) = 0$ to simplify the coefficients*
> 3. *Use the* ***continuity*** *of ψ and $\frac{d\psi}{dx}$ to* ***solve*** *the coefficients of the solutions and especially the* energy eigenvalues

So we basically jumps to *step 3* and have:

$$\psi_<(0) = \psi_>(0), \quad B = F$$

but for continuity of $\frac{d\psi}{dx}$, there is a problem of infinity. Therefore, we need to find a way to do that while **using the dirac delta function**.

Consider a small positive number $\epsilon > 0$, and integrating Schrodinger's TISE:

$$\lim_{\epsilon\to 0}\left\{-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon}\frac{d^2\psi}{dx^2}\,dx + \int_{-\epsilon}^{\epsilon}\left(-\alpha\delta(x)\right)\psi(x)\,dx\right\} = \lim_{\epsilon\to\infty} E\int_{-\epsilon}^{\epsilon}\psi(x)\,dx \quad (17)$$

using the property of delta function, we get:

$$\begin{aligned} \lim_{\epsilon\to 0} -\frac{\hbar^2}{2m}\left[\left.\frac{d\psi}{dx}\right|_{\epsilon} - \left.\frac{d\psi}{dx}\right|_{-\epsilon}\right] - \alpha B &= 0 \\ -\frac{\hbar^2}{2m}(-2KB) &= \alpha B \\ K &= \frac{\alpha m}{\hbar^2}. \end{aligned}$$

Therefore, we get the eigen energy of:

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

Lastly, normalizing to find B, as now we have solved the wave function:

$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 2\int_{-\infty}^{0} |B|^2 e^{2Kx}\,dx = 1$$

so we get:

$$B = \sqrt{K} = \frac{\sqrt{m\alpha}}{\hbar}$$

Note:

1. the above means that in this case, there is **always only one state**, that is $E = -\frac{m\alpha^2}{2\hbar^2}$
2. the **continuity of $\frac{d\psi}{dx}$ did not work again, due to the infinity**. However, we see the continuity manifest when:

   $$\int_{-\epsilon}^{\epsilon} (-\alpha\delta(x))\,\psi(x)\,dx = 0$$

   then equation (17) will yield that:

   $$\left.\frac{d\psi}{dx}\right|_{<} = \left.\frac{d\psi}{dx}\right|_{>}$$

Theorem 3.3: Solution for Bound Dirac Delta Potential

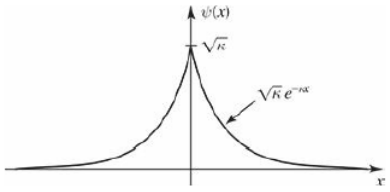
For a bound state with potential:

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

the wave function is:

$$\Psi(x,t) = \frac{\sqrt{m\alpha}}{\hbar} e^{-\frac{m\alpha}{\hbar^2}|x|} e^{-i\frac{E}{\hbar}t},\ E = -\frac{m\alpha^2}{2\hbar^2}$$

Graphically:



3.2 Unbound States

This basically have $E > V$, so that the wave function can practically extend to infinity.

3.2.1 Free Particle

This is covered well in chapter 2.4.

Consider a situation of $V(x) = 0$ everywhere. Then we have:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx} = E\psi$$

and the eigenfunctions are:

$$\frac{d^2\psi}{dx^2} = -K^2\psi, \quad \psi(x) = Ae^{iKx} + Be^{-iKx}$$

for **unbound energy** $E > 0$**,** $K = \sqrt{\frac{2mE}{\hbar^2}}$. This means that:

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

with no restriction on K **(i.e. no distinct eigenvalues of** K**), so that we have a continuous possibility of** K **and** E**!**

The wave function is therefore:

$$\Psi(x,t) = Ae^{i(Kx-\omega t)} + Be^{-i(Kx+\omega t)} = Ae^{i\left(Kx-\frac{\hbar K^2}{2m}t\right)}$$

for newly defining $K = \pm\sqrt{\frac{2mE}{\hbar^2}}$, and since:

- the wave traveling to the right ($Ae^{i(kx-\omega t)}$) is symmetric to the wave traveling to the left
  - the expression $Ae^{i(kx-\omega t)}$ travels to the right because, as t increases, x moves to the right for the same peak/phase

Now, there is an issue for us to figure out coefficient A : the above wave function extending to infinity is **not normalizable**!

- Asnwer: In the case of the free particle, then, the separable solutions **do not represent physically realizable states**. A free particle cannot exist in a stationary state.

So the **correct idea for superposition of** ψ **is**:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(K)e^{i\left(Kx-\frac{\hbar K^2}{2m}t\right)}\,dK$$

where we have K representing wave vector (related to energy) ranging for **all possible continuous values (also called a wave packet).**

Therefore, we need to consider $\phi(K)$ with:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(K)e^{iKx}\,dK$$

Theorem 3.4: Plancherel's Theorem

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} (K) e^{iKx}\, dK \iff F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-iKx}\, dx$$

which essentially is **Fourier's transform**.

Therefore, $\phi(x)$ becomes:

$$\phi(K) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-iKx}\, dx$$

Theorem 3.5: Solutoin for Free Particle

For a free particle with $E > 0$ at $V(x) = 0$, the wave function is:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(K) e^{i\left(Kx - \frac{\hbar K^2}{2m} t\right)}\, dK \tag{18}$$

for:

$$\phi(K) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-iKx}\, dx, \quad K = \pm\sqrt{\frac{2mE}{\hbar^2}}$$

***Example*: Textbook Example 2.6**

Consider a **free particle** with initial condition:

$$\Psi(x,0) = \begin{cases} A, & -a < x < a \\ 0, & |x| > a \end{cases}$$

First, since the **initial condition is bounded, we normalized and find out**:

$$A = \frac{1}{\sqrt{2a}}$$

then, we know:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(K) e^{i\left(Kx - \frac{\hbar K^2}{2m} t\right)} \, dK$$

for $K = \pm\sqrt{\frac{2mE}{\hbar^2}}$. Hence all we need to do is calculate $\phi(K)$:

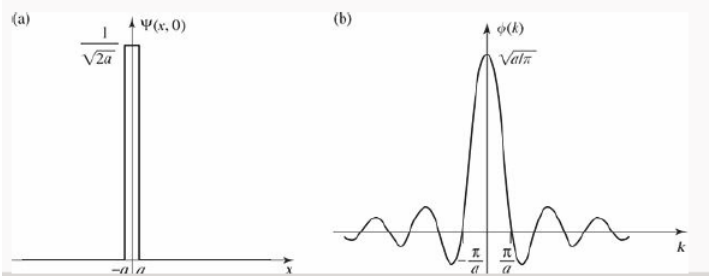
$$\begin{aligned} \phi(K) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-iKx} \, dx \\ &= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^{a} e^{iKx} \, dx \\ &= \frac{1}{\sqrt{\pi a}} \frac{\sin(Ka)}{K}. \end{aligned}$$

which completes the wave function:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{1}{\sqrt{\pi a}} \frac{\sin(Ka)}{K} e^{i\left(Kx - \frac{\hbar K^2}{2m}t\right)} \, dK$$

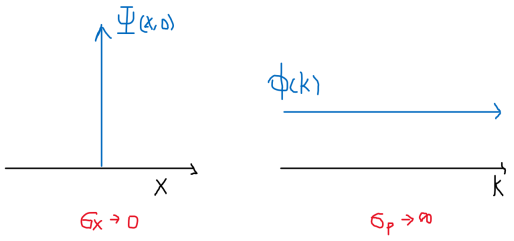
for $K = \pm\sqrt{\frac{2mE}{\hbar^2}}$

the above basically have transformed between Ψ and ϕ:

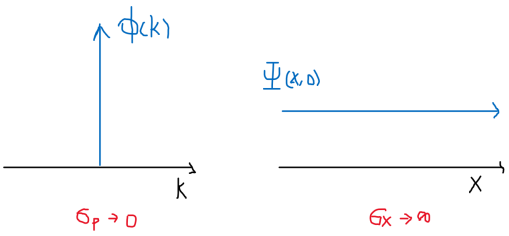


This hints at the **uncertainty principle**:

1. If $a \to 0$, meaning the position is very precise and localized



2. if $a \to \infty$, meaning the momentum vector K is very precise and localized:



3.2.2 Group Velocity of Free Particle

Recall that for the wave function ψ above, we had:

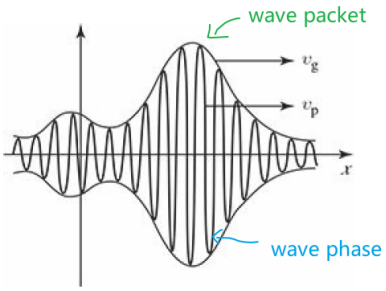
$$K = \sqrt{\frac{2mE}{\hbar^2}}, \quad E = \frac{\hbar^2 K^2}{2m}$$

this means that, for **each stationary state**, the **phase velocity is determined by**:

$$v_{phase} = \frac{p}{2m}$$

However, I will soon show that:

$$v_{particle} = v_{group} = \frac{p}{m}$$



Reminder:

> *Since we have already talked about that, for a particle, it only makes sense that it exist in a wave packet/super-positioned state, but not in individual stationary state, hence the actual velocity we care about should be the velocity of:*
>
> $$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(K) e^{i\left(Kx - \frac{\hbar K^2}{2m} t\right)} \, dK$$

Therefore, we need to find out the **velocity** corresponding to wave from the above equation.

Consider a narrowly packed wave such that $\phi(k)$ is *narrowly peaked at some value* k_0. This makes the calculation easier:

$$\begin{aligned} \omega(k) = \frac{\hbar k^2}{2m} &\approx w_0 + \left.\frac{d\omega}{dk}\right|_{k_0} (k - k_0) \\ &= w_0 + w_0'(k - k_0). \end{aligned}$$

Changing variable $s = k - k_0$, $dk = ds$, we have:

$$\begin{aligned}\Psi(x,t) &\approx \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k_0+s)e^{i\left((k_0+s)x-\left(w_0+w_0's\right)t\right)}\,ds \\ &= \frac{1}{\sqrt{2\pi}}e^{-iw_0t}e^{i(k_0w_0')t}\int_{-\infty}^{\infty}\phi(k_0+s)e^{i(k_0+s)x}e^{-ik_0w_0't}e^{-iw_0'st}\,ds \\ &= \frac{1}{\sqrt{2\pi}}e^{-i(\omega_0-k_0\omega_0')t}\int_{-\infty}^{\infty}\phi(k_0+s)e^{i(k_0+s)\left(x-w_0't\right)}\,ds.\end{aligned}$$

however, notice that:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k_0+s)e^{i(k_0+s)x}\,dk$$

hence, we see that the **wave packet as a whole** moves at speed w_0', which is:

$$v_{group} = w_0' = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m}$$

Theorem 3.6: Group Velocity and Dispersion Relation

For a dispersion relation of wave being (in this case):

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

the **group velocity is defined by the dispersion relation**:

$$v_{group} = \frac{d\omega}{dk} = \frac{\hbar k}{m} \tag{19}$$

and the *phase velocity is in this case*:

$$v_{phase} = \frac{\hbar k}{2m} = \frac{v_{group}}{2}$$

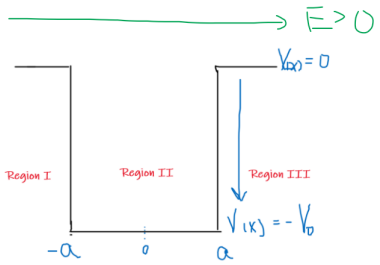
Note:

This also means that if the dispersion relation has $\omega \propto k$, then we will have:

$$v_{phase} = v_{group}$$

3.2.3 Scattering for Finite Square Well

Consider the finite square well again, but this time, with $E > 0$:



then we again, follow the conventional step of:

1. solve for the form of the solutions:

   - in region I and III, we have solved it before to be the same as free particle:
   $$\psi_I = Ae^{ikx} + Be^{-ikx}$$
   and
   $$\psi_{III} = Fe^{ikx} + Ge^{-ikx}$$
   with $k = \sqrt{\frac{2mE}{\hbar^2}}$.

   Additionally, **for an incident wave from the left, A is known; for no incoming wave from the right, $G = 0$**
   - in the middle, we have the Schrodinger's equation:
   $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx} - V_0\psi = E\psi$$
   hence:
   $$\psi_{II} = C\sin(lx) + D\cos(lx)$$
   for $l = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$

2. Now, we need to solve the coefficients B, F, C, D, with the *four* boundary conditions:
   $$\begin{cases} \psi_I(-a) = \psi_{II}(-a) \\ \frac{d\psi_I}{dx}(-a) = \frac{d\psi_{II}}{dx}(-a) \\ \psi_{II}(a) = \psi_{III}(a) \\ \frac{d\psi_{II}}{dx}(a) = \frac{d\psi_{III}}{dx}(a) \end{cases}$$
   this algebraic part is skipped, please see book section 2.6

   ending up with:
   $$B = i\frac{\sin(2la)}{2kl}\left(l^2 - k^2\right)$$
   $$F = \frac{e^{-2ika}A}{\cos(2la) - i\frac{k^2+l^2}{2kl}\sin(2la)}$$

Now, instead of combing to solve the wave function, I want to know the **reflection and transmission coefficient.**

Theorem 3.7: Reflection and Transmission Coefficient

In quantum mechanics, the definitions are simple:

$$\begin{aligned} T &= \frac{J_{trans}}{J_{inci}} \\ R &= \frac{J_{refl}}{J_{inci}}. \end{aligned} \tag{20}$$

usually, **if you have the below setup**:

$$\begin{cases} \psi_{incidient} = Ae^{ik_{inc}x} \\ \psi_{reflection} = Be^{-ik_{ref}x} \\ \psi_{transmission} = Fe^{ik_{trans}x} \end{cases}$$

the transmission coefficient is defined as:

$$T = \frac{J_{trans}}{J_{inci}} = \frac{v_{trans}|\psi_{trans}|^2}{v_{inci}|\psi_{inci}|^2} = \frac{|F|^2}{|A|^2}\frac{k_{trans}}{k_{inci}}$$

and the reflection coefficient becomes:

$$R = \frac{J_{refl}}{J_{inci}} = \frac{v_r|\psi_r|^2}{v_{inci}|\psi_{inci}|^2} = \frac{|B|^2}{|A|^2}\frac{k_r}{k_{inci}}$$

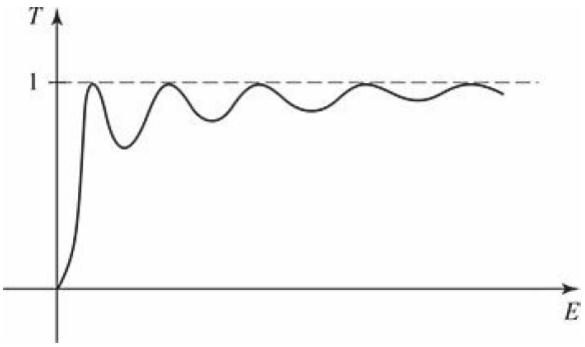
Therefore, continuing the above work, we get:

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

meaning that:

- $T = 1$ when the $\sin(...) = 0$ or $E \to \infty$
- $T = 0$ when $E \to 0$
- in other case, it oscillates btween $\frac{1}{2} \sim 1$

graphically:



additioanlly, notice that for $T = 1$, i.e. we have a *resonance between the wave and the material* :

$$\sin\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right) = 0$$

then we just get:

$$E + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \quad n = 1, 2, 3...$$

which is the same as the solution for infinite square well, but this represents the **energy states at which resonance occurs**

3.3 Operator Mathematics

Before talking about *Simple Harmonic Oscillation*, some technical things you need to know about operators:

1. in general, operators are **not commutative**

   $$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

   or equivalently:

   $$\hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$$

2. the **commutator symbol** is defined as follows:

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

3. many algebraic manipulations on operators do not work, as *they are operators and order matters*:

   $$\hat{A}^2 + \hat{B}^2 \neq \left(\hat{A} + i\hat{B}\right)\left(\hat{A} - i\hat{B}\right)$$

   because:

   $$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

Example

Consider the operator $x, \hat{p}$, computing the *commutator*:

$$\begin{aligned}[x,\hat{p}]f(x) &= x(\hat{p}f(x)) - \hat{p}(xf(x)) \\ &= x\left(-i\hbar\frac{d}{dx}f(x)\right) + i\hbar\frac{d}{dx}(xf(x)) \\ &= i\hbar f(x).\end{aligned}$$

therefore, we often *can simplify the commutators* :

$$[x,\hat{p}] = i\hbar$$

Theorem 3.8: Some Common Commutators

From the above, we get:

$$\begin{aligned}[x,\hat{p}_x] &= i\hbar \\ [y,\hat{p}_y] &= i\hbar \\ [z,\hat{p}_z] &= i\hbar.\end{aligned}$$

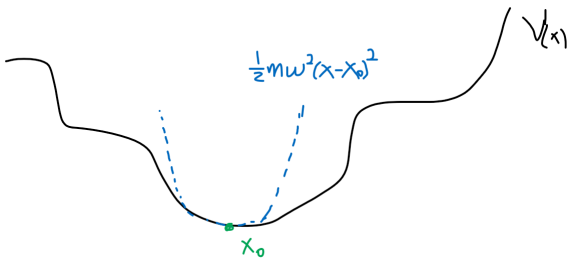
which has **everything to do with Heisenberg's Uncertainty principle**, and that:

$$[x,\hat{p}_y] = 0$$

3.4 Simple Harmonic Oscillation

In general, this problem is *special in that:*

- good approximation for lots of problems, as you can localize/series expand a point to fit a parabola
- a problem that can be *solved exactly*



The harmonic oscillation has the following function:

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

therefore, the Schrodinger's Equation for TISE is:

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

In general, there are two ways to solve this problem:

1. Operator Algebra
2. Brute Force

3.4.1 Operator Algebra for SHO

Reformatting the Simple Harmonic Oscillator, we have:

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

for:

$$\begin{aligned}\hat{H}&=\hat{T}+\hat{V}\\&=\frac{\hat{p}}{2m}+\frac{1}{2}m\omega^2x^2\\&=\frac{1}{2m}\left(\hat{p}^2+(m\omega x)^2\right).\end{aligned}$$

now consider two operators:

$$\begin{aligned}\hat{a}_+&=\frac{1}{\sqrt{2\hbar m\omega}}\left(-i\hat{p}+m\omega\hat{x}\right)\\\hat{a}_-&=\frac{1}{\sqrt{2\hbar m\omega}}\left(+i\hat{p}+m\omega\hat{x}\right).\end{aligned}$$

Definition 3.1: Ladder Operators

The operators above are also called Ladder operators:

$$\begin{aligned}\hat{a}_+&=\frac{1}{\sqrt{2\hbar m\omega}}\left(-i\hat{p}+m\omega\hat{x}\right),\quad\left(=\hat{a}^+\right)\\\hat{a}_-&=\frac{1}{\sqrt{2\hbar m\omega}}\left(+i\hat{p}+m\omega\hat{x}\right),\quad\left(=\hat{a}\right).\end{aligned}\tag{21}$$

where:

- $\hat{a}^+$ is often used and called $\hat{a}$ **dagger**
- they are called ladder operators because, for **SHO**:
  - $\hat{a}_+\psi$ will raise the eigenenergy of ψ by $\hbar\omega$
  - $\hat{a}_-\psi$ will lower the eigenenergy of ψ by $\hbar\omega$

Theorem 3.9: Commutator of Ladder Operators

Another useful commutator in this case is:

$$\begin{aligned}\hat{a}_-\hat{a}_+ &= \frac{1}{2m\hbar\omega}\left(-i\hat{p}+m\omega\hat{x}\right)\left(+i\hat{p}+m\omega\hat{x}\right)\\ &= \frac{1}{2m\hbar\omega}\left(\hat{p}^2+(m\omega x)^2\right)+\frac{1}{2}.\end{aligned}$$

and that you will see:

$$[\hat{a}_-,\hat{a}_+] = \hat{a}_-\hat{a}_+ - \hat{a}_+\hat{a}_- = 1 \tag{22}$$

so that :

$$\begin{aligned}\hat{H} &= \frac{1}{2m}\left(\hat{p}^2+(m\omega x)^2\right)\\ &= \hbar\omega\left(\hat{a}_-\hat{a}_+-\frac{1}{2}\right)\\ &= \hbar\omega\left(\hat{a}_+\hat{a}_-+\frac{1}{2}\right).\end{aligned} \tag{23}$$

Now, using theorem **??**, we have for the SHO:

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

the general idea of using ladder operators will be as follows:

1. **Suppose that ψ solved the above equation**. Consider the *quantity* $\hat{a}_+\psi$. Is this also a solution?
2. solving for the **eigenenergy of $\hat{a}_+\psi$** :

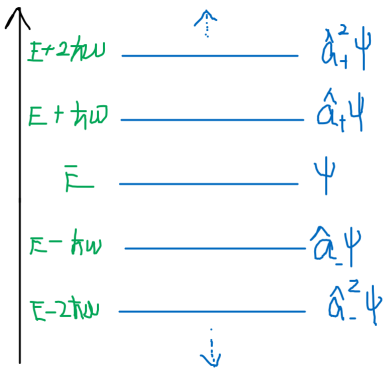
$$\begin{aligned}\hat{H}\left(\hat{a}_+\psi\right) &= \hbar\omega\left(\hat{a}_+\hat{a}_-+\frac{1}{2}\right)\left(\hat{a}_+\psi\right)\\ &= \hbar\omega\left(\hat{a}_+\hat{a}_-\hat{a}_+ + \frac{1}{2}\hat{a}_+\right)\psi\\ &= \hbar\omega\hat{a}_+\left(\hat{a}_-\hat{a}_+ + \frac{1}{2}\right)\psi\\ &= \hbar\omega\hat{a}_+\left(\hat{a}_+\hat{a}_- + \frac{1}{2}+1\right)\psi\\ &= \hat{a}_+\left(\hbar\omega\left(\hat{a}_+\hat{a}_-+\frac{1}{2}\right)\psi+\hbar\omega\psi\right)\\ &= \hat{a}_+\left(\hat{H}\psi+\hbar\omega\psi\right)\\ &= \left(E+\hbar\omega\right)\left(\hat{a}_+\psi\right).\end{aligned}$$

this means that **the eigen energy for $\hat{a}_+\psi$ is $E+\hbar\omega$!**

Simiarily, for the $\hat{a}_-$, you will get:

$$\hat{H}(\hat{a}_-\psi) = \left(E-\hbar\omega\right)\left(\hat{a}_-\psi\right)$$

3. now, all we need to do is to **solve one of the ψ**:



because for this question, we are *considering unbounded states*, we have $E \geq V(x) \geq 0$. However, notice that $\psi = 0$**, then it is not normalizable!**. Therefore, we want to have $E_0 > 0$ for the **lowest ψ in energy**.

Let the lowest one be ψ_0 with energy E_0. Because it is the lowest, it **must be that**:

$$\hat{a}_-\psi_0 = 0$$

(*if it is not 0, then that non-zero state will be the lowest eigenstate ψ_0*)

Therefore, solving for ψ_0, I have:

$$\begin{aligned}\hat{a}_-\psi_0 &= \frac{1}{\sqrt{2\hbar m\omega}}\left(-i\hat{p} + m\omega\hat{x}\right)\psi_0 \\ &= \frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{d}{dx}\psi_0 + m\omega x\psi_0\right) \\ &= 0.\end{aligned}$$

meaning that:

$$\begin{aligned}\hbar\frac{d}{dx}\psi_0 + m\omega x\psi_0 &= 0 \\ \frac{d}{dx}\psi_0 &= -\frac{m\omega x}{\hbar}\psi_0 \\ \psi_0 &= A_0 e^{-\frac{m\omega}{2\hbar}x^2}.\end{aligned}$$

normalizing the ψ_0 solution to solve for A_0, we get:

$$\begin{aligned}\int_{-\infty}^{\infty}\psi_0^*\psi_0\,dx &= 1 \\ A_0^2 &= \sqrt{\frac{m\omega}{\pi\hbar}}.\end{aligned}$$

4. now, going back and **solve for the eigen energy corresponding to**

the state using the TISE:

$$\begin{aligned}\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi_0 &= E_0\psi_0\\ 0 + \frac{\hbar\omega}{2}\psi_0 &= E_0\psi_0\\ E_0 &= \frac{\hbar\omega}{2}.\end{aligned}$$

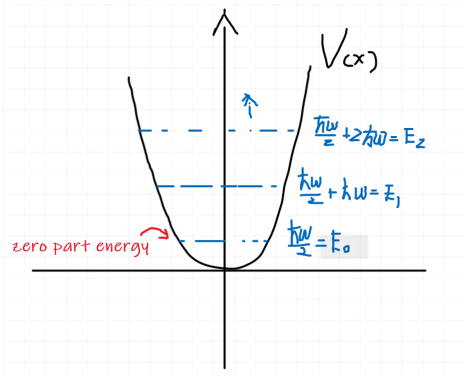
5. once we get **one solution, we can use the ladder operator to get the others**:

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}, \quad E_0 = \frac{\hbar\omega}{2}$$

then:

$$\psi_n = A_n\left(\hat{a}_+\right)^n\psi_0, \quad E_n = \frac{\hbar\omega}{2} + n\hbar\omega$$

Graphically, this is what happened to the *unbound states of SHO*:



where $E_0 \neq 0$ for the lowest energy state **even when** $V = 0$.

***Example*: Calculating ψ_1**

For example, computing ψ_1 using the ladder operator:

$$\begin{aligned}\psi_1 &= A_1\hat{a}_+\psi_0\\ &= A_1\frac{1}{\sqrt{2\hbar m\omega}}\left(-\hbar\frac{d}{dx} + m\omega x\right)\left[\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}\right]\\ &= \frac{A_1}{\sqrt{2m\hbar\omega}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}(2m\omega)\,xe^{-\frac{m\omega}{2\hbar}x^2}.\end{aligned}$$

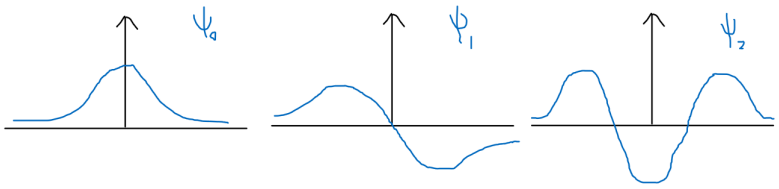
normalizing this, I get:

$$A_1 = 1$$

Hence the solution becomes:

$$\psi_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\sqrt{\frac{2m\omega}{\hbar}}xe^{-\frac{m\omega}{2\hbar}x^2}$$

Interestingly, for solutions of SHO, they look like:



where:

- as n increases, the *number of nodes increases*
- *alternate in odd and even parity*

3.4.2 Manipulating Operators for SHO

This section deals with *tricks of calculating quantities such as:*

$$\int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n \, dx$$

using **operators to simplify math**.

First, **if we have a SHO**, the *operators* $\hat{a}_+, \hat{a}_-$ for solution ψ will satisfy some **additional properties**:

Corollary 3.1: SHO with Operators

For **SHO**, we know:

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

and:

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

then:

$$\begin{aligned} \hat{a}_+\hat{a}_- &= n \\ \hat{a}_-\hat{a}_+ &= n+1. \end{aligned} \tag{24}$$

Additionally:

Definition 3.2: Hermitian Operator/Self-Adjoint

An operator $\hat{O}$ is a **Hermitian** or is self-adjoint if it satisfies the following condition:

$$\hat{O}^\dagger = \hat{O}$$

$$\int_{-\infty}^{\infty} f^*(x)\hat{O}g(x)\,dx = \int_{-\infty}^{\infty} \left(\hat{O}^\dagger f(x)\right)^* g(x)\,dx.$$

for some function $f(x), g(x)$.

Corollary 3.2: Hermitian for SHO

In general, ladder operators are "hermitian", such that:

$$\int_{-\infty}^{\infty} f^*(x)\hat{a}_+ g(x)\,dx = \int_{-\infty}^{\infty} \left(\hat{a}_- f(x)\right)^* g(x)\,dx$$
$$\hat{a}_+^\dagger = \hat{a}_-.$$

and that:

$$\int_{-\infty}^{\infty} f^*(x)\hat{a}_- g(x)\,dx = \int_{-\infty}^{\infty} \left(\hat{a}_+ f(x)\right)^* g(x)\,dx$$
$$\hat{a}_-^\dagger = \hat{a}_+.$$

this will be very useful for calculating integrals with cross terms.

Proof. For corollary 3.2, the proof can be done by explicit calculation:

$$\begin{aligned}
\int_{-\infty}^{\infty} f^*(x)\hat{a}_\pm g(x)\,dx &= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\hbar m\omega}} f^*(x)\left(\mp\hbar\frac{d}{dx} + m\omega x\right) g(x)\,dx \\
&= \frac{\mp\hbar}{\sqrt{2\hbar m\omega}}\left(\int_{-\infty}^{\infty} f^*(x)\frac{d}{dx}g(x)\,dx\right) \\
&\quad + \frac{1}{\sqrt{2\hbar m\omega}}\int_{-\infty}^{\infty} f^*(x)m\omega x g(x)\,dx \\
&= \frac{\mp\hbar}{\sqrt{2\hbar m\omega}}\left(0 - \int_{-\infty}^{\infty}\left(\frac{d}{dx}f\right)^* g(x)\,dx\right) \\
&\quad + \frac{1}{\sqrt{2\hbar m\omega}} m\omega \int_{-\infty}^{\infty} \left(xf(x)\right)^* g(x)\,dx \\
&= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\hbar m\omega}}\left(\pm\hbar\frac{d}{dx} + m\omega x\right) f^*(x)g(x)\,dx \\
&= \int_{-\infty}^{\infty} \hat{a}_\mp f^*(x)g(x)\,dx \\
&= \int_{-\infty}^{\infty} \left(\hat{a}_\mp f(x)\right)^* g(x)\,dx.
\end{aligned}$$

which works because $\hat{a}_\pm$ *is real.* □

Now, we can consider the below quantities, which *will be used often when we are calculating intergrals with* Ψ:

Corollary 3.3: Ladder Operators with SHO Solution

Applying the ladder operator to a SHO:

$$\begin{aligned}\hat{a}_+\psi_n &= \sqrt{n+1}\psi_{n+1}\\ \hat{a}_-\psi_n &= \sqrt{n}\psi_{n-1}.\end{aligned} \tag{25}$$

Proof. For corollary 3.3, I first define $\hat{a}_+\psi_n = c_n\psi_{n+1}$, and $\hat{a}_-\psi = d_n\psi_{n-1}$. Then, consider:

$$\begin{aligned}\int_{\infty}^{-\infty} (\hat{a}_+\psi_n)^* (\hat{a}_+\psi_n)\, dx &= |c_n|^2\\ \text{Using corollary 3.2} &= \int_{-\infty}^{\infty} (\hat{a}_-\hat{a}_+\psi_n)^* \psi_n\, dx\\ \text{Using corollary 3.1} &= \int_{-\infty}^{\infty} ((n+1)\psi_n)^* \psi_n\, dx\\ &= n+1.\end{aligned}$$

therefore $c_n = \sqrt{n+1}$, and the similar is done for $d_n = \sqrt{n}$. □

Additionally, a property that is *not very useful yet but is interesting is:*

Corollary 3.4

For **SHO**:

$$\begin{aligned}\psi_1 &= \hat{a}_+\psi_0\\ \psi_2 &= \frac{1}{\sqrt{2}}\hat{a}_+^2\psi_0\\ \psi_3 &= \frac{1}{\sqrt{3\cdot 2}}\hat{a}_+^3\psi_0\\ &\dots\\ \psi_n &= \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0.\end{aligned}$$

Last but not least, going to *calculating the cross term:*

Corollary 3.5: Cross Terms with Operators

For **SHO**:

$$\begin{aligned}\int_{-\infty}^{\infty} \psi_m^* (\hat{a}_+\hat{a}_-)\psi_n\, dx &= \int_{\infty}^{\infty} (\hat{a}_+\hat{a}_-\psi_m)^* \psi_n\, dx\\ n\int_{-\infty}^{\infty} \psi_m^*\psi_n\, dx &= m\int_{-\infty}^{\infty} \psi_m^*\psi_n\, dx.\end{aligned} \tag{26}$$

this gives the **orthogonality of stationary states for SHO**:

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = \delta_{m,n} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases}$$

and that ψ_n **spans the complete set of states for** Ψ.

Finally, we can go to introduce the topic of concern, *computing the expected value (e.g. $\langle x \rangle, \langle V \rangle$) for a stationary state*.

Theorem 3.10: Expected Value for SHO

Consider first the $\langle x \rangle$ for the *n-th eigenstate of a SHO*:

First, *transforming into using operators:*

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

then, we compute:

$$\begin{aligned} \langle x \rangle = \int_{-\infty}^{\infty} \psi_n^* x \psi_n \, dx &= \int_{-\infty}^{\infty} \psi_m^* \sqrt{\frac{\hbar}{2m\omega}} \left(\hat{a}_+ + \hat{a}_- \right) \psi_n \, dx \\ &= \sqrt{\frac{\hbar}{2m\omega}} \left(\int_{-\infty}^{\infty} \psi_n^* \hat{a}_+ \psi_n \, dx + \int_{-\infty}^{\infty} \psi_n^* \hat{a}_- \psi_n \, dx \right) \\ &= \left(\sqrt{n+1} \int_{-\infty}^{\infty} \psi_n^* \psi_{n+1} \, dx + \sqrt{n} \int_{-\infty}^{\infty} \psi_n^* \psi_{n-1} \, dx \right) \\ &= 0. \end{aligned}$$

similarly, calculating the expected potential for the *n-th eigenstate* :

$$\langle V_n \rangle = \frac{1}{2} m\omega^2 \left\langle x^2 \right\rangle = \frac{1}{2} m\omega^2 \int_{-\infty}^{\infty} \psi_m^* \frac{\hbar}{2m\omega} \left(\hat{a}_+ + \hat{a}_- \right)^2 \psi_n \, dx$$

we will get:

$$\langle V_n \rangle = \frac{1}{2} \hbar\omega (n + \frac{1}{2}) = \frac{1}{2} E_n$$

which makes sense as the other *half will be kinetic energy*.

Theorem 3.11: Cross Terms for SHO

Sometimes, if you need to calculate $\int_{-\infty}^{\infty} \Psi^* x \Psi \, dx$, as $\Psi = \sum_{n=0}^{\infty} \psi_n e^{-i \frac{E_n}{\hbar} t}$,

we need to deal with terms such as:

$$\int_{-\infty}^{\infty} \psi_m^* x \psi_n \, dx.$$

for $m \neq n$. In this case using $\langle x \rangle$ in theorem 3.10 :

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m^* x \psi_n \, dx &= \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n+1} \int_{-\infty}^{\infty} \psi_m^* \psi_{n+1} \, dx \right. \\ &\quad \left. + \sqrt{n} \int_{-\infty}^{\infty} \psi_m^* \psi_{n-1} \, dx \right) \\ &= \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n+1}\, \delta_{m,n+1} + \sqrt{n}\, \delta_{m,n-1} \right). \end{aligned} \tag{27}$$

for $m \neq n$.

3.4.3 Analytic/Exact Solution for SHO

First, we need to **redefine a few variables**:

$$\xi = \sqrt{\frac{m\omega}{\hbar}} x$$

then we get the central equation to deal with:

$$\frac{d^2\psi}{d\xi^2} = \left(\xi^2 - k\right)\psi, \quad k = \frac{2E}{\hbar\omega} \tag{28}$$

Ansatz: the solution of the above equation takes the form:

$$\psi(\xi) = h(\xi) e^{-\frac{\xi^2}{2}}$$

then computing the derivatives:

$$\begin{aligned} \frac{d\psi}{d\xi} &= \frac{dh}{d\xi} e^{-\frac{\xi^2}{2}} - \xi h e^{-\frac{\xi^2}{2}} \\ \frac{d^2\psi}{d\xi^2} &= \frac{d^2h}{d\xi^2} e^{-\frac{\xi^2}{2}} - 2\xi \frac{dh}{d\xi} e^{-\frac{\xi^2}{2}} - h e^{-\frac{\xi^2}{2}} + \xi^2 e^{-\frac{\xi^2}{2}}. \end{aligned}$$

inserting it back into equation (28), we get:

$$\begin{aligned} 0 &= \frac{d^2\psi}{d\xi^2} - \xi^2\psi + k\psi \\ &= \frac{d^2h}{d\xi^2} e^{-\frac{\xi^2}{2}} - 2\xi \frac{dh}{d\xi} e^{-\frac{\xi^2}{2}} - h e^{-\frac{\xi^2}{2}} + k h e^{-\frac{\xi^2}{2}} \\ 0 &= \frac{d^2h}{d\xi^2} - 2\xi \frac{dh}{d\xi} + h(k-1). \end{aligned} \tag{29}$$

and now we *end up with a second order ODE with $h(\xi)$*.

Suppose that (ansatz again) $h(\xi)$ is a **power series** :

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + ... = \sum_{j=0}^{\infty} a_j \xi^j$$

then to solve the *second order ODE for $h(\xi)$*, compute:

$$\frac{dh}{d\xi} = a_1 + 2a_2\xi + ... = \sum_{j=0}^{\infty} j a_j \xi^{j-1}$$
$$\frac{d^2h}{d\xi^2} = 2a_2 + 3\cdot 2a_3\xi + ... = \sum_{j=0}^{\infty} j(j-1)a_j\xi^{j-2} \equiv \sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}\xi^j.$$

plugging this *back into equation (29)*:

$$\sum_{j=0}^{\infty}\left[(j+1)(j+2)a_{j+2} - 2ja_j + (k-1)a_j\right]\xi^j = 0$$

since this must be **true for any $\xi = \sqrt{\frac{m\omega}{\hbar}}x$** , this means the inside is 0. Therefore:

$$\begin{aligned}(j+1)(j+2)a_{j+2} - 2ja_j + (k-1)a_j &= 0\\ (j+1)(j+2)a_{j+2} &= (2j+1-k)a_j\\ a_{j+2} &= \frac{2j+1-k}{(j+1)(j+2)}a_j.\end{aligned}$$

which we see is a recursion formula, and that this **separates into even and odd series** (i.e. we have $\{a_0, a_2, a_4, ...\}, \{a_1, a_3, a_5, ...\}$).

However, there is an **additional constraint that we need ψ to be finite as $\xi \to \pm\infty$**. This means that:

$$\psi(\xi) = h(\xi)e^{\frac{\xi^2}{2}} \quad \text{cannot blow up}$$

Theorem 3.12: Constraint on $h(\xi)$

For $\psi(\xi)$ to not blow up with $h(\xi) = \sum_{j=0}^{\infty} a_n\xi^j$, $h(\xi)$ **must be truncated**, with the top coefficient being:

$$2j_{top} + 1 = k = \frac{2E}{\hbar\omega}$$

such that any $a_{j>j_{top}} = 0$. Therefore, we recover the correct solution:

$$\begin{aligned} 2j_t + 1 &= \frac{2E}{\hbar\omega} \\ E &= \hbar\omega\left(j_t + \frac{1}{2}\right) \\ E_n &= \hbar\omega\left(n + \frac{1}{2}\right). \end{aligned}$$

Proof. Consider the limiting case for $j \to \infty$, we have:

$$\begin{aligned} a_{j+2} &= \frac{2j+1-k}{(j+1)(j+2)}a_j \\ a_{j+2} &\sim \frac{2}{j}a_j. \end{aligned}$$

and consider the series expansion for e^{ξ^2} :

$$\begin{aligned} e^{\xi^2} &= \sum_{n=0}^{\infty}\frac{\xi^{2n}}{n} \\ &= \sum_{j=even}^{\infty}\left(\frac{1}{(\frac{j}{2})!}\right)\xi^j \\ &\equiv \sum_{j=even}^{\infty} a_j\xi^j. \end{aligned}$$

with $a_j = \frac{1}{(\frac{j}{2})!}$, which means:

$$a_{j+2} = \frac{2}{j}a_j$$

Therefore, the *the original series would converge to:*

$$h(\xi) = e^{\xi^2}$$

which blows up $\psi(\xi) = h(\xi)e^{-\frac{\xi^2}{2}} = e^{\frac{\xi^2}{2}}$. Therefore, there *exists a last term* $j_{top} = j_t$, such that:

$$0 = a_{j_t+2} = \frac{2j_t+1-k}{(j_t+1)(j_t-2)}a_{j_t}$$

which gives:

$$2j_t + 1 - k = 0$$

□

Once we have solved $h(\xi)$ (*up to the coefficients inside, which can be obtained from normalization*), we obtain the solution for SHO.

Theorem 3.13: Solution for SHO

For a single state $j_t = n$, we have:

$$\psi_n = h_n(\xi)e^{-\frac{\xi^2}{2}}$$

so that $h_n(\xi)$ is **either an even or an odd series**:

$$h_n(\xi) = \sum_{j=even/odd}^{j_t=n} a_j \xi^j$$

since the relation relates $a_j \to a_{j_t}$, the other series is unconstraint. Hence, the other series (even/odd) will be 0s.

The solution also has age instate energies of:

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

In fact, the more *exact format* of the solution looks like:

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\xi)e^{-\frac{\xi^2}{2}}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}}x \tag{30}$$

where $H_n(\xi)$ is the **Hermite Polynomial** (which also separates to *even and odd series*).

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$

or

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2H_{n-1}(\xi)$$

- for example: $H(\xi) = \{H_0 = 1, H_1 = 2\xi, H_3 = 4\xi^2 - 2, ...\}$

***Example*: Computing Solutions with Equation (30)**

Using the above theorem, we can compute:

$$\psi_0 = a_0 e^{-\frac{\xi^2}{2}}$$
$$\psi_1 = a_1 \xi e^{-\frac{\xi^2}{2}}$$
$$\psi_2 = \left(a_0 - 2a_0\xi^2\right) e^{-\frac{\xi^2}{2}}$$
$$....$$

then, to compute the coefficients, just normalize them.

4 Separable Problems in Multi-dimension

This section not only discusses separable wave functions, but also **separable operators in different coordinates.**

4.1 Separable Problems in Cartesian Coordinates

Consider the simple case of a $2-D$ system, so that their position and momentum is related *separately* :

$$\begin{cases} x_1 \iff p_1 \\ x_2 \iff p_2 \end{cases}$$

Theorem 4.1: Principle for Multi-dimension/particle Problems

Suppose the particles do not interact with each other (decoupled system), and that **assuming the following is true**:

$$\begin{aligned} \hat{H}(x_1, x_2) &= \hat{H}_1(x_1) + \hat{H}_2(x_2) \\ \psi(x_1, x_2) &= \psi_1(x_1)\psi_2(x_2). \end{aligned}$$

then the Schrodinger's Equation becomes:

$$\begin{aligned} \left(\hat{H}_1(x_1) + \hat{H}_2(x_2)\right)\psi_1(x_1)\psi_2(x_2) &= E\psi_1(x_1)\psi_2(x_2) \\ \psi_2\hat{H}_1(x_1)\psi_1 + \psi_1\hat{H}_2(x_2)\psi_2 &= E\psi_1\psi_2 \\ \psi_2 E_1\psi_1 + \psi_1 E_2\psi_2 &= E\psi_1\psi_2 \\ (E_1 + E_2)\,\psi_1\psi_2 &= E\psi_1\psi_2. \end{aligned}$$

so we get that the **energy state of the system is the sum of the individual decoupled system:** $E = E_1 + E_2$.

Note:

Again, the **addition properties holds only when** $\hat{H}$ **and** ψ **is separable**.

As a result, we can easily *induce solutions from 1-D to 3-D* if they are decoupled:

***Example*: Free Particle in 3D**

Since in 1-D we have:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad E = \frac{\hbar^2 k^2}{2m}$$

then in 3-D, *separable*:

$$\psi(x, y, z) = \left(Ae^{ik_x x} + Be^{-ik_x x}\right)\left(Ae^{ik_y y} + Be^{-ik_y y}\right)\left(Ae^{ik_z z} + Be^{-ik_z z}\right)$$

***Example*: 3D Infinite Cube Well**

The *separable solution* for an infinite cube well with length a looks like:

$$\psi(x,y,z) = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{a}}\sqrt{\frac{2}{a}} \sin\left(n_x\pi\frac{x}{a}\right)\sin\left(n_y\pi\frac{y}{a}\right)\sin\left(n_z\pi\frac{z}{a}\right)$$

with:

$$E = \frac{n_x^2\pi^2\hbar^2}{2ma^2} + \frac{n_y^2\pi^2\hbar^2}{2ma^2} + \frac{n_z^2\pi^2\hbar^2}{2ma^2}$$

and since the x, y, z are separable, the coefficients n_x, n_y, n_z are *decoupled*.

Therefore, this implies the existence of some **degenerate level**. For example, the following (macro)states share the *same energy*:

$$\begin{cases} n_x = 2,\ n_y = 1,\ n_z = 1 \\ n_x = 1,\ n_y = 2,\ n_z = 1 \\ n_x = 1,\ n_y = 1,\ n_z = 2 \end{cases}$$

***Example*: 2-Particles in 1D**

Again, assuming that they are *not interacting:*

$$\psi(x_1,x_2) = \left(A_1e^{ik_1x_1} + B_1e^{-ik_1x_1}\right)\left(A_2e^{ik_2x_2} + B_2e^{-ik_2x_2}\right)$$

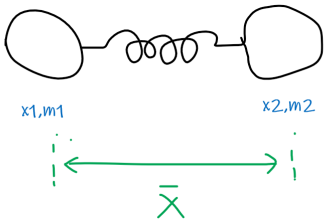
with:

$$E = \frac{\hbar^2}{2m}k_1^2 + \frac{\hbar}{2m}k_2^2$$

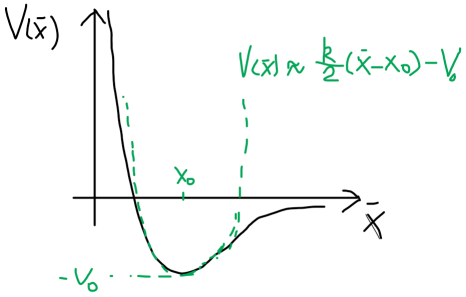
for k being continuous since it is a free particle.

4.2 Diatomic Molecule

In short, we would think of a *diatomic molecule in 1-D* as the follows:



its potential looks like this, which can be *fitted with a SHO*:



where the spring constant would represent the curvature k.

Now, if we write out the Schrodinger's Equation (Hamiltonian):

$$\hat{H} = \frac{\hat{p}_1}{2m_1} + \frac{\hat{p}_2}{2m_2} + \frac{1}{2}k\left(\bar{x} - x_0\right)^2 \neq \hat{H}(p_1, x_1) + \hat{H}(p_2, x_2)$$

Note:

> Whenever we are dealing with *coupled systems like the above*, the first thing would be to **de-couple it**.

1. consider the idea of **diagonalization**:

$$\hat{H} = [...] \begin{bmatrix} x_1 \\ x_2 \\ p_1 \\ p_2 \end{bmatrix}$$

$$\hat{H} = [A]\,[diagonal...]\,[B] \begin{bmatrix} x_1 \\ x_2 \\ p_1 \\ p_2 \end{bmatrix}$$

$$[A]^{-1}\,\hat{H} = [diagonal...]\,[B] \begin{bmatrix} x_1 \\ x_2 \\ p_1 \\ p_2 \end{bmatrix}.$$

   where you see that:

$$[B] \begin{bmatrix} x_1 \\ x_2 \\ p_1 \\ p_2 \end{bmatrix}$$

   basically **transformed the original coordinate into normal modes,** which then decouples so that you have only *diagonal matrix* left.

2. Substitute the decoupled coordinates into the equation, and **group them to the analogous form of the equations we have solved before**

3. use the solutions we know for each normal mode, and combine them to form the final solution

Therefore:

Step 1 : Transforming the coordinates (Diagonalization Skipped):

$$\begin{cases} u = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} & \text{Center of Mass} \\ P = p_1 + p_2 & \text{Center of Mass} \\ \bar{x} = x_2 - x_1 & \text{Relative} \\ p = \mu \left(\frac{p_2}{m_2} - \frac{p_1}{m_1} \right) & \mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass} \end{cases}$$

Step 2: Insert the changed coordinates back to decouple them:

$$\begin{aligned} \hat{H} &= \frac{\hat{P}}{2M} + \left(\frac{\hat{p}}{2\mu} + \frac{1}{2}\bar{k}\left(\bar{x} - x_0\right)^2 \right) \\ &= \frac{\hat{P}}{2M} + \left(\frac{\hat{p}}{2\mu} + \frac{1}{2}\bar{k}\left(x\right)^2 \right). \end{aligned}$$

where $M = m_1 + m_2, x = \bar{x} - x_0$.

Then we have basically decoupled into the pair of coordinates specified above, so we basically have a *free particle term* and a *simple harmonic oscillation term*.

Step 3: Now, we just use the solution we already know:

$$\psi = \psi_{plane-wave} \cdot \psi_{SHO}$$

and that:

$$E = \frac{1}{2}\frac{K^2}{M} + \hbar\omega\left(n + \frac{1}{2}\right)$$

where K is continous since it is free particle, and $\omega = \sqrt{\frac{\bar{k}}{\mu}}$, and that $\bar{k}$ is the curvature of the potential.

4.2.1 Vibration of Diatomic Molecule

Continuing from the above, I now only look at the *oscillation/vibration term*:

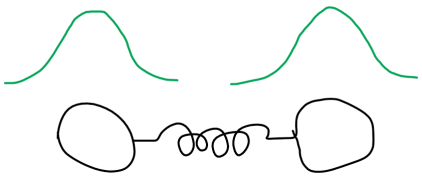
$$\hat{H}_{relative} = \frac{\hat{p}}{2\mu} + \frac{1}{2}\bar{k}x^2$$

and I know that:

$$E_{vibration_n} = \hbar\sqrt{\frac{\bar{k}}{\mu}}\left(n + \frac{1}{2}\right)$$

since $\omega = \sqrt{\frac{\bar{k}}{\mu}}$.

Now, recall that the *zero-point state of a SHO is a Gaussian*. Since this was the solution to the *transformed coordinate*, what happens in this:



Additionally:

Theorem 4.2: Excitation of Diatomic Molecule

Since the energy gap in the above equation is *still* $\hbar\omega$, we could calculate the *wave length of photon absorbed that would excite this one level*.

$$E_{photon} = \hbar\omega = h\nu = h\frac{c}{\lambda}$$

then, for example ($3\mu m \leq \lambda \leq 20\mu m$ is in *infrared range*):

- N_2 has $\hbar\omega = 0.29eV$, $\lambda = 4.3\mu m$
- H_2 has $\hbar\omega = 0.19eV$, $\lambda = 6.4\mu m$
- O_2 has $\hbar\omega = 0.52eV$, $\lambda = 2.4\mu m$

- CO has $\hbar\omega = 0.27eV$, $\lambda = 4.6\mu m$

which essentially explains why we have **green house gases causing global warming**.

Theorem 4.3: Dissociation Rate of Isotopes

For isotopes, since the *potential function* is the same, we have the same $\bar{k}$. However, their mass are different, so we have a different $\omega = \sqrt{\frac{\bar{k}}{\mu}}$. This means:

- the *zero-point energy* E_0 is slightly different, however, the dissociation energy until $E = 0$ is the same
- Hence, isotopes at a *lower zero-point energy will dissociate slower* than isotopes with a higher zero-point energy (closer to $E = 0$)

4.3 2-D Harmonic Oscillator

Consider a 2-D SHO:

$$\hat{H}(x,y) = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}k_1x^2 + \frac{1}{2}k_2y^2$$

since the above is *already decoupled*, we get the solution from using theorem 4.1:

$$\begin{aligned}
\psi_{n_1}(\xi) &= A_{n_1}H_{n_1}(\xi)\,e^{-\frac{\xi^2}{2}}, \quad \xi^2 = \frac{m\omega_1}{\hbar}x^2 \equiv \beta_1^2x^2 \\
\psi_{n_2}(\eta) &= A_{n_2}H_{n_2}(\eta)\,e^{-\frac{\eta^2}{2}}, \quad \eta^2 = \frac{m\omega_2}{\hbar}y^2 \equiv \beta_2^2y^2 \\
\psi &= \psi_{n_1}\psi_{n_2}.
\end{aligned}$$

therefore, the energy gives:

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

where $\omega_1 = \sqrt{\frac{k_1}{m}}, \omega_2 = \sqrt{\frac{k_2}{m}}$

Note:

Here, we thought about the *same particle in 2-D*, hence we have the same m. The solution is basically the same if you use m_1, m_2 instead.

Corollary 4.1: Degeneracy of 2D Harmonic Oscillator

Since again we have n_1, n_2, degeneracy happens **if $\omega_1 = \omega_2 = \omega$, and that masses are the same** (which we already have). Then:

$$E = \hbar\omega\,(n_1 + n_2 + 1)$$

and we see:

1. degeneracy occurs, for example the following configuration has the same energy:
    - $n_1 = 1, n_2 = 0$ and $n_1 = 0, n_2 = 1$
2. the zero-point energy *starts at $\hbar\omega$ instead of $\hbar\frac{\omega}{2}$* for 1-D SHO. Additionally, each consecutive energy level is **offset by $\hbar\frac{\omega}{2}$** as compared to the 1-D SHO.

4.4 Multi-Mode Vibrational Molecule

Reminder:

The procedure for essentially solving coupled system was:

1. *consider the idea of **diagonalization** to **de-couple the system** :*

$$[A]^{-1}\hat{H} = [diagonal...]\,[B]\begin{bmatrix} x_1 \\ x_2 \\ p_1 \\ p_2 \end{bmatrix}.$$

where you see that:

$$[B]\begin{bmatrix} x_1 \\ x_2 \\ p_1 \\ p_2 \end{bmatrix}$$

*basically **transformed the original coordinate into normal modes,** which then decouples so that you have only* diagonal matrix *left.*

2. *Substitute the decoupled coordinates into the equation, and **group them to the analogous form of the equations we have solved before***
3. *use the solutions we know for each normal mode, and combine them to form the final solution*

In general, we will see that:

Theorem 4.4: General Multi-Particle in Multi-Dimension

If you have a **separable Hamiltonian**, then you will have:

1. the total wave function of the system be:

$$\psi = \Pi_i \psi_i$$

for each i being an eigenfunction for either *vibration/translation/rotation*

2. the total energy of the system be:

$$E = \sum_i E_i$$

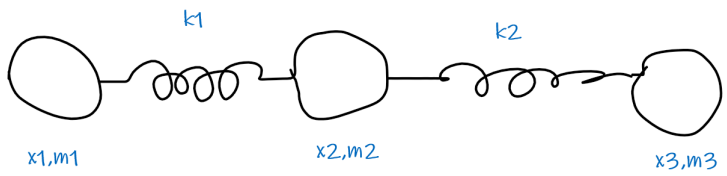
for each i being an eigenenergy for either *vibration/translation/rotation*, and that *for vibration/SHO:*

$$E_{vib} = \sum_i^{\text{modes}} \hbar\omega_i \left(n_i + \frac{1}{2}\right)$$

where ω_i is the *frequency of each normal mode*

4.4.1 Tri-Atomic Molecule in 1D

Now, we basically have **two modes of vibration**:



For simplicity, assume that:

$$\begin{cases} k_1 = k_2 = \bar{k} \\ m_1 = m_2 = m_3 = \bar{m} \end{cases}$$

then we are dealing with the Schrodinger's Equation:

$$\hat{H} = \frac{\hat{p}_1}{2\bar{m}} + \frac{\hat{p}_2}{2\bar{m}} + \frac{\hat{p}_3}{2\bar{m}} + \frac{1}{2}\bar{k}\left(x_2 - x_1\right)^2 + \frac{1}{2}\bar{k}\left(x_3 - x_2\right)^2$$

since this is coupled, we follow our conventional step:

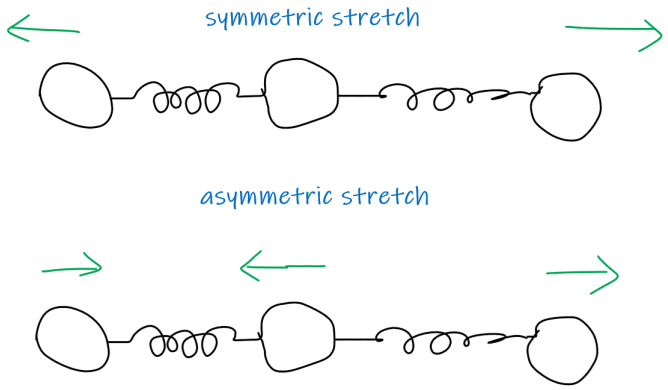
Step 1: find the normal mode (coordinate) and decouple the system (step skipped):

$$\begin{cases} u_0 = \frac{x_1+x_2+x_3}{3} & \text{Center of Mass} \\ u_1 = x_3 + x_1 - 2x_2 & \text{Asymmetric Stretch} \\ u_2 = x_3 - x_1 & \text{Symmetric Stretch} \end{cases}$$

where:

Step 2: Insert this back and compute. Now, we should remember that the $\hat{p}_i$ involved $\frac{\partial}{\partial x_i}$, which becomes:

$$\frac{\partial}{\partial x_i} = \frac{\partial u_0}{\partial x_i}\frac{d}{du_0} + \frac{\partial u_1}{\partial x_i}\frac{d}{du_1} + \frac{\partial u_2}{\partial x_i}\frac{d}{du_2}$$



hence I get:

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\bar{m}}\left(\frac{1}{3}\frac{\partial^2}{\partial u_0^2}+6\frac{\partial^2}{\partial u_1^2}+\frac{\partial^2}{\partial u_2^2}\right)+\frac{1}{2}\left(\frac{\bar{k}}{2}\right)u_1^2+\frac{1}{2}\left(\frac{\bar{k}}{2}\right)u_2^2 \\ &= \left(-\frac{\hbar^2}{2\bar{m}}\frac{1}{3}\frac{\partial^2}{\partial u_0^2}\right)+\left(-\frac{\hbar^2}{2(\bar{m}/6)}\frac{\partial^2}{\partial u_1^2}+\frac{1}{2}\frac{\bar{k}}{2}u_1^2\right)+\left(-\frac{\hbar^2}{2(\bar{m}/2)}\frac{\partial^2}{\partial u_2^2}+\frac{1}{2}\frac{\bar{k}}{2}u_2^2\right).\end{aligned}$$

which is one free particle term, and 2 vibrational term.

Step 3: Putting them back, I get for *vibrational energy*:

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

using the known quantity: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2}kx^2 \to \omega = \sqrt{\frac{k}{m}}$, we get:

$$\begin{cases}\omega_1 = \sqrt{\frac{\bar{k}/2}{\bar{m}/6}} = \sqrt{3\frac{\bar{k}}{\bar{m}}} \\ \omega_2 = \sqrt{\frac{\bar{k}/2}{\bar{m}/2}} = \sqrt{\frac{\bar{k}}{\bar{m}}} = \sqrt{3}\omega_1\end{cases}$$

and then the wave function becomes:

$$\psi_{total} = \psi_{free}\psi_{SHO_1}\psi_{SHO_2}$$

4.4.2 Molecule with N Atom in 3D

Theorem 4.5: Degrees of Freedom in 3-D

If we have a *molecule with N-atoms in 3-D*, then there are in total **3N** Degree of Freedom:

$$\begin{cases}3 & \text{DOF for center of mass translation} \\ 3 & \text{DOF for center of mass rotation} \\ 3N-6 & \text{DOF for vibrational modes}\end{cases}$$

therefore, in this case:

$$E_{vib} = \sum_{i=1}^{3N-6} \hbar\omega_i \left(n_i + \frac{1}{2}\right)$$

where $\omega_i = \sqrt{k_i/\mu_i}$ with **reduced mass of μ_i if we are transforming coordinates**, and that the **quantized energy difference between to level** is called a **phonon**.

Note:

If we are dealing a *linear particle in 1-D*, for example in the subsubsection 4.4.1, we will have 3 DOF in total:

$$\begin{cases} 1 & \text{DOF for center of mass translation in 1-D} \\ 0 & \text{DOF for center of mass rotation in 1-D} \\ 2 & \text{DOF for vibrational modes} \end{cases}$$

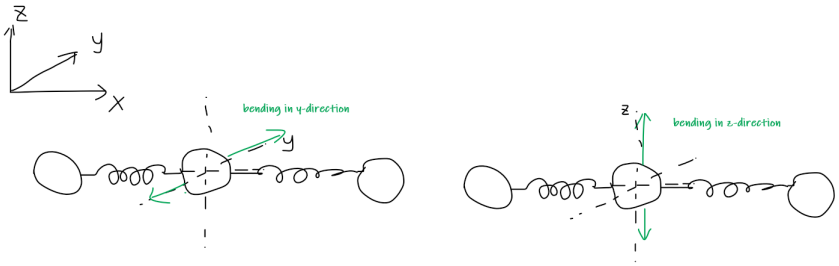
For Example: Consider the linear molecule of CO_2 *in 3-D*:

1. then there are $3 \times 3 = 9$ DOF in total:

$$\begin{cases} 3 & \text{DOF for center of mass translation} \\ 2 & \text{DOF for center of mass rotation due to linear molecule} \\ 4 & \text{DOF for vibrational modes} \end{cases}$$

Therefore we have:

$$\begin{cases} \hbar\omega_1 = 1366\ cm^{-1}, & \text{Symmetric Stretch} \\ \hbar\omega_2 = 667\ cm^{-1}, & \text{Bending in y-Direction} \\ \hbar\omega_3 = 667\ cm^{-1}, & \text{Bending in z-direction} \\ \hbar\omega_4 = 2349\ cm^{-1}, & \text{Asymmetric Stretch} \end{cases}$$



2. *Extension:* the CO_2 is built on the principle of (combining ω_2, ω_3 into one mode):

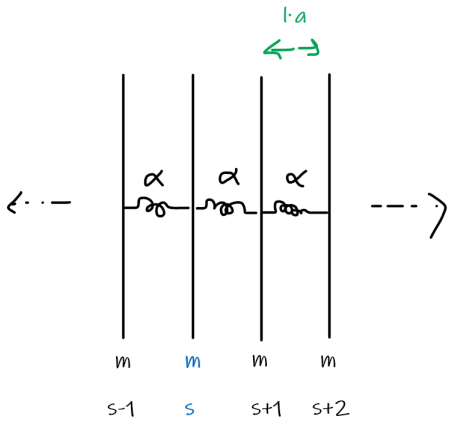
- photon emitted going from state $(0,0,1) \to (1,0,0)$, which gives off $\lambda \approx 9.6\mu m$
- photon emitted going from state $(0,0,1) \to (0,2,0)$, which gives off $\lambda \approx 10.6\mu m$

4.4.3 Overview of N-Atom Lattice

In short, you will have a very large number of atoms, such that there are:

1. $3N - 6 \approx 3N$ *vibrational modes*
2. vibrational energy sum of those E_i

Consider the lattice structure as *planes of molecules connected by spring*:



where:

- the separation between to sheets is $l \cdot a$, for some random *integer* l, so that a is the smallest unit of separation here
- α is the spring constant
- m is the total mass of the atoms in the sheet
- s is the index referring to each sheet

Considering the sheet s, we have the *displacement from equilibrium* u_s being:

$$m\frac{d^2u_s}{dt^2} = \alpha\left((u_{s+1} - u_s) + u_{s-1} - u_s\right)$$

then we will end up solving u_s with:

$$u_s = u_0 e^{i(k(s\cdot a)-\omega t)}$$

for $s \cdot a$ being the equilibrium distance. Correspondingly:

$$\omega = \sqrt{\frac{4\alpha}{m}} \sin\left(\frac{k \cdot a}{2}\right)$$

being the *dispersion relation between* ω, k for some discrete k.

Now, it turns out that $0 < k < \frac{\pi}{a}$. Therefore we have the graph:

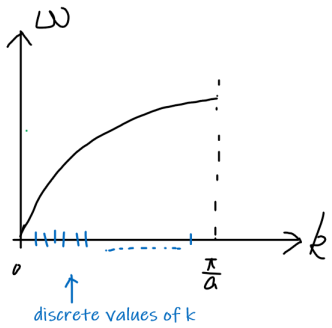


Figure 1: Acoustic Mode for a Large N-Atom Structure

Therefore, we will end up with *a number of normal modes due to the discrete k*:

$$E_k = \hbar\omega_k \left(n_k + \frac{1}{2}\right)$$

with the total vibrational energy being the sum of those E_k

Last but not least, if we consider $k \to 0$, we get:

$$\omega = \left(\sqrt{\frac{4\alpha}{m}}\frac{a}{2}\right) k$$

where the $\sqrt{\frac{4\alpha}{m}}\frac{a}{2}$ would be *speed of sound in this medium*.

4.5 Overview of Photons in EM

Reminder:

The vector potential $\vec{A}$ of a magnetic field $\vec{B}$ is:

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

so that we have:

$$\nabla \times \vec{B} = \vec{\nabla} \times \vec{\nabla} \times \vec{A} = 4\pi \frac{\vec{J}}{c}$$

for CGS units.

Consider the vector potential for EM Wave:

$$\vec{A} = \sum_{\epsilon,\vec{k}} \vec{e}_\epsilon \left(\vec{a}_{\epsilon,\vec{k}} e^{-i\omega_{\epsilon,\vec{k}} t} e^{i\vec{k}\cdot\vec{r}} + \vec{a}^*_{\epsilon,\vec{k}} e^{i\omega_{\epsilon,\vec{k}} t} e^{-i\vec{k}\cdot\vec{r}}\right)$$

where we have:

- a *sum of plane waves*

- $\vec{k}$ indicates the wave vector, which can have *different magnitude and direction*
- $\vec{e}_\epsilon$ is the *polarization of EM Wave*
- ω is different on each $\epsilon, \vec{k}$ set, but its magnitude is defined with $\omega = c|\vec{k}|$

then, computing $\vec{B} = \vec{\nabla} \times \vec{A}$, and then getting $\vec{E}$ from $\vec{J}$, I get:

$$\vec{E} = \sum_{\epsilon,\vec{k}} \frac{i\omega}{c} \vec{e}_\epsilon \left(\vec{a}_{\epsilon,\vec{k}} e^{-i\omega_{\epsilon,\vec{k}} t} e^{i\vec{k}\cdot\vec{r}} + \vec{a}^*_{\epsilon,\vec{k}} e^{i\omega_{\epsilon,\vec{k}} t} e^{-i\vec{k}\cdot\vec{r}} \right)$$

Reminder:

> *In CGS, if we want to calculate the* energy density from EM field*:*
>
> $$\frac{u}{V} = \frac{1}{8\pi} (E^* E + B^* B)$$

Therefore, calculating the energy density and calculating the energy using integral, you will find that the *cross terms cancel* and you have:

$$E_{\epsilon,\vec{k}} = \frac{V}{4\pi} \frac{\omega^2_{\epsilon,\vec{k}}}{c^2} \left(\vec{a}_{\epsilon,\vec{k}} \vec{a}^*_{\epsilon,\vec{k}} + \vec{a}^*_{\epsilon,\vec{k}} \vec{a}_{\epsilon,\vec{k}} \right)$$

for each mode of , $\vec{k}$.

Last but not least, it can be shown that we can covert the above to:

$$\hat{H}_{\epsilon,\vec{k}} = \frac{V}{4\pi} \frac{\omega^2_{\epsilon,\vec{k}}}{c^2} \alpha^2_{\epsilon,\vec{k}} \left(\hat{a}_{\epsilon,k-} \hat{a}^*_{\epsilon,k+} + \hat{a}^*_{\epsilon,k+} \hat{a}_{\epsilon,k-} \right)$$

which means we get back *ladder operators!* Using the identity $\hat{a}_- \hat{a}_+ = \hat{a}_+ \hat{a}_- + 1$:

$$\hat{H}_{\epsilon,k} = \frac{V}{2\pi} \frac{\omega^2_{\epsilon,\vec{k}}}{c^2} \alpha^2_{\epsilon,\vec{k}} \left(\hat{a}^*_{\epsilon,k+} \hat{a}_{\epsilon,k-} + \frac{1}{2} \right)$$

which is again **simple harmonic oscillation**. Therefore, the *energy levels become*:

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

$$E_{\epsilon,k} = \hbar\omega_{\epsilon,k} \left(n_{\epsilon,k} + \frac{1}{2} \right), \qquad \hbar\omega_{\epsilon,k} = \frac{V}{2\pi} \frac{\omega^2_{\epsilon,\vec{k}}}{c^2} \alpha^2_{\epsilon,\vec{k}}.$$

and the **fixed energy difference between each level will be a photon**.

5 Formalism

This section introduces some *formal notation and analysis* on problems in QM. A lot will be using ideas from *linear algebra* and expanding them onto **(eigen) functions**.

Definition 5.1: Dirac Notation with Vectors

For *normal vectors and matrices:*

- A **ket** looks like:

$$|\alpha\rangle \iff \vec{\alpha} = \begin{bmatrix} a_1 \\ a_2 \\ ... \\ a_n \end{bmatrix}$$

  where here we are just looking at a simple vector.

- A **bra** looks like:

$$\langle\beta| \iff \vec{\beta}^T = \begin{bmatrix} b_1 & b_2 & ... & b_n \end{bmatrix}$$

  where here we are just looking at a simple vector.

- An inner product is a **bra-ket**:

$$\langle\beta|\alpha\rangle \iff \begin{bmatrix} b_1 & b_2 & ... & b_n \end{bmatrix}^* \begin{bmatrix} a_1 \\ a_2 \\ ... \\ a_n \end{bmatrix}$$

  notice that we needed to **also take the conjugate of the first**

- operator T will be like:

$$|\beta\rangle = T\,|\alpha\rangle \iff \vec{\beta} = T\vec{\alpha}$$

  where T is basically a **matrix**

5.1 Hilbert Space

Quantum theory is based on two constructs: wave functions and operators.

1. The **state** of a system is represented by its **wave function**
2. **observables** are represented by **operators**

So now, we want to consider the *analogy of*:

1. The **"vectors** we encounter in quantum mechanics are (for the most part) **functions**, and they live in infinite-dimensional spaces.

Definition 5.2: Dirac Notation for Functions

In short, we can define *each eigenfunction in its own dimension*, so that:

- A **ket** looks like:
$$|f\rangle \iff f(x)$$
- A **bra** looks like:
$$\langle g| \iff g^*(x)$$
- An inner product is a **bra-ket**:
$$\langle g|f\rangle \iff \int_a^b f^*(x)g(x)\,dx$$
notice that we needed to **also take the conjugate of the first**, and the bound of integral would be the *domain of the given problem*

  An additional example would be:
$$|f\rangle\langle g|h\rangle = f(x)\int_a^b g^*(x)h(x)\,dx$$
- **operator** $\hat{Q}$ will be used like:
$$\langle g|\hat{Q}f\rangle \equiv \langle g|\hat{Q}|f\rangle \iff \int_a^b f^*(x)\hat{Q}g(x)\,dx$$
so we can basically say:
$$\left\langle \hat{Q} \right\rangle = \text{Expected Value} = \langle \Psi|\hat{Q}\Psi\rangle \equiv \langle \Psi|\hat{Q}|\Psi\rangle$$

Additionally, in Hilbert Space, we have the additional benefit of:

Theorem 5.1: Square Integrable

Functions in Hilbert space are square integrable, such that:
$$f(x) \to \int_a^b |f(x)|^2\,dx < \infty$$
basically the function is **finite**.

Therefore, if $a, b \to \mp\infty$, then we know that:
$$\lim_{x\to\pm\infty} f(x) \to 0$$

Theorem 5.2: Schawrz Inequality

In Hilbert Space, we also have this property of:

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

which basically would be the *vector analogy of*:

$$\vec{A}\cdot\vec{B} \leq \sqrt{|\vec{A}|^2|\vec{B}|^2}$$

Theorem 5.3: Other Useful Properties

The following properties will be extremely useful as we have seen before:

1. we have:
$$\langle g|f\rangle = \langle f|g\rangle^*$$
so that we *usually cannot change order*

2. and that the *eigenfunctions* forming the basis would be **orthogonal** (also normalizable)
$$\langle f_m|f_n\rangle = \delta_{m,n}$$

3. the eigenfunctions $f_n(x)$ of the Hilbert space is *complete*, so that any function in the space $h(x)$ can be written as:
$$h(x) = \sum_{n=1}^{\infty} c_n f_n(x)$$
and that:
$$c_n = \langle f_n|h\rangle$$

Theorem 5.4: Wave Functions in Hilbert Space

Wave functions live in Hilbert space. Therefore, we can have the following:

1. wave functions as sum of eigenfunctions/eigenstates:
$$|\Psi\rangle = \sum_{n=1}^{\infty} c_n\,|f_n\rangle$$

2. we can also *interpret it as vectors*:

$$|\Psi\rangle = \begin{bmatrix} c_1 \\ c_2 \\ \dots \\ c_n \end{bmatrix}$$

for the basis being the eigenfunction/states of f_n, and then the observables $\hat{Q}$ would become:

$$|\hat{Q}\Psi\rangle = \hat{Q}\sum_{n=1}^{\infty} c_n f_n \to \begin{bmatrix} Q_{11} & \dots & Q_{1n} \\ \dots & \dots & \dots \\ Q_{n1} & \dots & Q_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ \dots \\ c_n \end{bmatrix}$$

5.2 Observables

Recall that an observable is defined to be the **expectation value of an operator** $\left\langle \hat{Q} \right\rangle$, and the *result must be real*.

Corollary 5.1: Observables in Hilbert Space

Since we know that observables are real:

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

This implies that **observable must be a Hermitian/Self-Adjoints**

$$\int_a^b \Psi^* \hat{Q}\Psi \, dx = \int_a^b \left(\hat{Q}^\dagger \Psi\right)^* \Psi \, dx$$

such that $\hat{Q}^\dagger = \hat{Q}$.

In general, if we have **Hermitian Operators**, then this would hold for any $f(x), g(x)$:

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$$

because $\hat{Q}$ is self-adjoint/hermitian

***Example*: Momentum Operator**

We knew that the operator $\hat{p}$ is hermitian. To prove it, we can consider to show that:

$$\langle f | \hat{p} g \rangle = \langle \hat{p} f | g \rangle$$

consider:

$$\begin{aligned}
\langle f|\hat{p}g\rangle &= \int_{-\infty}^{\infty} f^* \left(-i\hbar \frac{d}{dx} g\right) dx \\
&= -i\hbar \int_{-\infty}^{\infty} f^* \frac{dg}{dx}\, dx \\
&= -i\hbar \left[f^*\, g|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} g \frac{df^*}{dx}\, dx \right] \\
&= i\hbar \int_{-\infty}^{-\infty} g \frac{df^*}{dx}\, dx \\
&= \int_{-\infty}^{\infty} \left(-i\hbar \frac{d}{dx} f\right)^* g\, dx \\
&= \int_{-\infty}^{\infty} (\hat{p}f)^*\, g\, dx \\
&= \langle \hat{p}f|g\rangle\,.
\end{aligned}$$

Therefore, *$\hat{p}$ is observable such that $\langle\hat{p}\rangle$ corresponds to real quantity*

5.3 Determinant State

Definition 5.3: Determinate State of an Observable

The determinant state of an observable means that: *any measurement of an observable $\hat{Q}$ to a Ψ with the same initial state* would yield **the same result** q.

An example would be the *energy of the eigenstate/stationary state* ψ_n, which is always E_n

As a result, this means:

$$\sigma_Q = 0$$

Theorem 5.5: Definitive States and Eigenvalues

The determinant state of an observable $\hat{Q}$ will be its eigenvalue **if it has a definite state**, so that:

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

which is easy to prove since *if it has a definite state*:

$$\begin{aligned}
\sigma_Q^2 &= \left\langle \left(\hat{Q} - \left\langle \hat{Q} \right\rangle\right)^2 \right\rangle \\
&= \langle \Psi | \left(\hat{Q} - q\right)^2 \Psi \rangle \\
&= \langle \left(\hat{Q} - q\right) \Psi | \left(\hat{Q} - q\right) \Psi \rangle \\
&= 0.
\end{aligned}$$

which implies:

$$\begin{aligned}
\left(\hat{Q} - q\right) \Psi &= 0 \\
\hat{Q}\Psi &= q\Psi.
\end{aligned}$$

Definition 5.4: Spectrum of EigenValues

The collection of all the eigenvalues of an operator is called its **spectrum**.

Sometimes two (or more) linearly *independent eigenfunctions share the same eigenvalue*; in that case the spectrum is said to be **degenerate**

5.4 Eigenfunctions of Hermitian Operators

Our attention is thus directed to the **eigenfunctions of hermitian operators** (physically: determinate states of observables).

- e.g. the solution to things like $\hat{p}\Psi = p\Psi$

In general, we have two categories of solutions to deal with:

1. If the spectrum of **eigenvalues** is **discrete** (i.e. the eigenvalues are separated from one another) then the eigenfunctions lie in Hilbert space and they constitute physically realizable states (*can use the nice properties of Hilbert Space*).
2. f the spectrum is **continuous** (i.e. the eigenvalues fill out an entire range) then the eigenfunctions are not normalizable, and they do not represent possible wave functions

5.4.1 Discrete Spectra of Eigenvalues

In this case, we have the following properties:

Theorem 5.6: Eigenvalues are Real

The normalizable eigenfunctions of a *Hermitian operator* will have **real eigenvalues**. This can be seen by:

Suppose:

$$\hat{Q}f = qf$$

then for *Hermitian Operators* $\hat{Q}$:

$$\begin{aligned} \langle f|\hat{Q}f\rangle &= \langle \hat{Q}f|f\rangle \\ q\langle f|f\rangle &= q^*\langle f|f\rangle \\ q &= q^*. \end{aligned}$$

this means that if you *measure an observable on a particle in a determinate state, you will at least get a real number.*

Theorem 5.7: Orthogonal Eigenfunctions

Eigenfunctions of **distinct eigenvalues** are orthogonal.

Suppose we have:

$$\hat{Q}f = qf, \quad \hat{Q}g = q'g$$

and that $q \neq q'$ being distinct eigenvalues. Then, *since $\hat{Q}$ is Hermitian* :

$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$$

I have:

$$q'\langle f|g\rangle = q^*\langle f|g\rangle$$

which means that **if** $q \neq q'$, then:

$$\langle f|g\rangle = 0$$

Thats why the stationary states of the infinite square well, for example, or the harmonic oscillator, are orthogonal *they are eigenfunctions of the Hamiltonian with distinct eigenvalues.*

Note:

However, if two (or more) *eigenfunctions share the same eigenvalue*, any linear combination of them is itself an eigenfunction, with the same eigenvalue (Problem 3.7), and we can use the GramSchmidt orthogonalization procedure (Problem A.4) to **construct orthogonal eigenfunctions within each degenerate subspace.**

Theorem 5.8: Complete Set of Eigenfunctions

In a **finite-dimensional** vector space the eigenvectors of a *Hermitian Operator* spans the **entire space**.

- But for inifinite-dimensional space, we don't know. Therefore, we can take the folowing as an **axiom**: the eigenfunctions of an observable operator are **complete:** Any function (in Hilbert space) can be expressed as a linear combination of them

5.4.2 Continuous Spectra of Eigenvalues

In short, if the spectrum of a hermitian operator is continuous:

1. theorem 5.6 and theorem 5.7 fails, because the *inner product (integral) might not exist*
2. However, if we impose that en **eigenvalues must be real**, then we can **recover the three properties**

Theorem 5.9: Delta Function as Integral

This relation will be **very useful** in this chapter.

$$\delta(x-a) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ip(x-a)}\, dp$$

Example

Consider the eigenfunctions and eigenvalues of the momentum operator:

$$-i\hbar\frac{d}{dx}f_p(x) = pf_p(x)$$

which gives:

$$f_p(x) = Ae^{i\frac{px}{\hbar}}$$

This is *not square-integrable for any (complex) value of p*. This means that **the momentum operator has no eigenfunctions** in Hilbert

space.

However, if we let $p \in \mathbb{R}$, then:

$$\begin{aligned}\int_{-\infty}^{\infty} f_{p'}^{*}(x) f_p(x)\, dx &= |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')\frac{x}{\hbar}}\, dx \\ &= |A|^2 2\pi\hbar\delta(p-p').\end{aligned}$$

Therefore, we can *"normalize it" in the continuous fashion to give* $\delta(p-p')$:

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{px}{\hbar}}$$

so that:

$$\langle f_{p'} | f_p \rangle = \delta\left(p - p'\right)$$

Note:

> This is *in comparison to the discrete spectrum with*:
>
> $$\langle \varphi_m | \varphi_n \rangle = \delta_{m,n}$$

Now we have just **finished the first step** of making **eigenfunctions in continuous space**. We would want to see if there are **analogies of** the properties in discrete spectrum.

Theorem 5.10: Completeness of Continous Eigenfunction

Now functions $f_p(x)$ are *square integral for real* p, consider an **arbitrary function** $f(x)$:

$$f(x) = \int_{-\infty}^{\infty} c(p) f_p(x)\, dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p) e^{i\frac{px}{\hbar}}\, dp$$

basically *"summing" over all possible* $f_p(x)$.

Theorem 5.11: Fourier Series for Continous Eigenfunction

In summary, the coefficient $c(p)$ in theorem 5.9 can be **computed in reverse** :

$$c(p) = \langle f_p | f \rangle = \int_{-\infty}^{\infty} f_p^*(x) f(x)\, dx$$

in full, this basically looks like a *Fourier Transform* (it becomes this due to the exponential factor $e^{i\frac{px}{\hbar}}$):

$$c(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} f(x)\, e^{-i\frac{px}{\hbar}}\, dx$$
$$f(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p) e^{i\frac{px}{\hbar}}\, dx.$$

Proof. To show that computing $c(p)$ actually becomes the *Fourier Transform*, consider:

$$\begin{aligned}
\langle f'_p | f \rangle &= \int_{-\infty}^{\infty} f_{p'}^* f(x)\, dx \\
&= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_{p'}^*(x) c(p) f_p(x)\, dp\, dx \\
&= \int_{-\infty}^{\infty} \delta(p - p')\, c(p)\, dp \\
&= c(p').
\end{aligned}$$

if we have *normalized eigenfunction* f_p. □

5.5 Generalized Statistical Interpretation of QM

These are basically *generalized results* of what we have seen before.

Theorem 5.12: Generalized Statistical Interpretation

If you measure an **observable** $\hat{Q}(x,p)$ on a particle in the state $\psi(x,t)$, you are certain to get:

- if the spectrum of is **discrete**, **one of the eigenvalues** q_n of the **hermitian operator**, associated with eigenstate $f_n(x)$

  The probability of getting that q_n associated with $f_n(x)$ is:

  $$Prob(q_n) = |c_n|^2 = \langle f_n | \Psi \rangle$$

- If the spectrum is **continuous**, **real eigenvalues** $c(z)$ associated (Dirac-orthonormalized) **eigenfunctions** $f_p(z)$.

  The probability of getting a result in the **range** dz is:

  $$Prob(z \sim z + dz) = |c(z)|^2 dz = \langle f_z | \Psi \rangle$$

***Example*: Probability for Continous Momentum**

Using idea from theorem 5.11, I can do

1. the momentum is an observable, so it has:

$$\hat{p} = -i\hbar\frac{d}{dx}$$

2. now, by assuming that eigenvalues p are real, we have solved the equation:

$$\hat{p}\Psi = p\Psi$$

and we have *actually computed the form of* $f_p(x)$

3. We know that it forms a full set of basis:

$$\Psi = \int_{-\infty}^{\infty} c(p) f_p(x)\, dp$$

Therefore, probability of a particular state $f_p(x)$ is just **its contribution in** Ψ:

$$|c(p)|^2 dp = |\langle f_p|\Psi\rangle|^2 dp = \left|\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} f_p^*(x)\Psi(x,t)\, dx\right|^2 dp$$

if you want, you can also substitute in $f_p(x) = e^{i\frac{px}{\hbar}}$

***Example*: Probability for Continous Position**

Again, the same procedure.

1. Let y be the *eigenvalue* and $g_y(x)$ be the *eigenfunction associated with it* :

$$\hat{xg_y}(x) = xg_y(x) = yg_y(x)$$

for y being a **fixed number** and x a **continuous variable**

2. Actually solving for the eigenfunction, I get a *Dirac delta* function:

$$g_y(x) = A\delta(x-y)$$

for y being a number/eigenvalue. (**Again, the eigenfunctions are not square integrable, but again they admit Dirac orthonormality**) :

$$\begin{aligned}\int_{-\infty}^{\infty} g_y^{*\prime}(x) g_y(x)\, dx &= |A|^2 \int_{-\infty}^{\infty} \delta(x-y')\,\delta(x-y)\, dx \\ &= |A|^2\delta(y-y').\end{aligned}$$

which is easily *"normalized"* with $A = 1$.

3. Now, we get a full set of basis:

$$\psi = \int_{-\infty}^{\infty} c(y) g_y(x)\, dy$$

for *continuous eigenvalues* y. Then, the probability of getting a specific position is:

$$\begin{aligned} |c(y)|^2 dy &= |\langle g_y(x)|\Psi\rangle|^2 dy \\ &= \left| \int_{-\infty}^{\infty} \delta(x-y)\Psi(x,t)\, dx \right|^2 dy \\ &= |\Psi(y,t)|^2 dy. \end{aligned}$$

again, using **orthogonality of eigenfunctions**.

Corollary 5.2: Momentum-Space Wave Function

This basically comes from the result of a **free particle** with derived **continuous eigenvalue** $c(p)$ **and eigenstate** $f_p = \frac{1}{\sqrt{2\pi\hbar}} e^{-i\frac{px}{\hbar}}$:

$$c(p) = \langle f_p|\Psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-i\frac{px}{\hbar}} \Psi(x,t)\, dx$$

and it is **so useful such that**:

$$\Phi(p,t) \equiv c(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-i\frac{px}{\hbar}} \Psi(x,t)\, dx$$

therefore, we get the **Fourier Transform Pair**:

$$\begin{aligned} \Phi(p,t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-i\frac{px}{\hbar}} \Psi(x,t)\, dx \\ \Psi(x,t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{i\frac{px}{\hbar}} \Phi(x,t)\, dx. \end{aligned}$$

such that $\Phi(p,t)$ is called the **momentum space wave function**.

Then, the *probabilities of measuring position/momentum becomes*:

$$\begin{aligned} Prob(x \sim x + dx) &= |\Psi(x,t)|^2 dx \\ Prob\,(p \sim p + dp) &= |\Phi(p,t)|^2 dp. \end{aligned}$$

***Example*: Dirac Delta Well**

We had the potential well of:

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

so that for *any other place expect for origin, it is a* ***free particle*** :

$$\Psi(x,t) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\frac{\alpha|x|}{\hbar^2}} e^{-i\frac{E}{\hbar}t}$$

then, since we *essentially have same setup as above*, we know that the **eigenfunction for momentum is** $f_p = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{px}{\hbar}}$:

$$\begin{aligned}\Phi(p,t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-i\frac{px}{\hbar}} \Psi(x,t)\, dx \\ &= \sqrt{\frac{2}{\pi}} p_0^{\frac{3}{2}} \frac{e^{-i\frac{E}{\hbar}t}}{p^2 + p_0^2}, \quad p_0 \equiv \frac{m\alpha}{\hbar}.\end{aligned}$$

and this function is called **Lorantian**.

Theorem 5.13: General Probability

It will be generally true that *for an observable* $\hat{Q}$ and its eigenvalue c_n associated with eigenfunction f_n:

$$\Psi = \psi(x)\phi(t) = \sum_{n=1}^{\infty} c_n f_n(x)\phi(t)$$

such that **I have a complete set of basis**, and that:

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

if **eigenfunctions are normalized**. (The same for continuous case).

Proof. Just consider the fact that:

$$\begin{aligned}\langle\Psi|\Psi\rangle &= 1 \\ &= \langle \sum_{m=1}^{\infty} c_m f_m | \sum_{n=1}^{\infty} c_n f_n \rangle \\ &= \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n \langle f_m | f_n \rangle \\ &= \sum_{n=1}^{\infty} c_n^* c_n \\ &= 1.\end{aligned}$$

□

Theorem 5.14: General Expected Value

The same goes for expected value of an *observable* Q:

$$\langle Q \rangle = \sum_{n=1}^{\infty} q_n |c_n|^2$$

Proof. The idea is identical, start from:

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

using:

$$\Psi = \sum_{n=1}^{\infty} c_n f_n$$

and that:

$$\langle f_{n'} | \hat{Q} f_n \rangle = q_n \delta_{n',n}$$

and get:

$$\langle Q \rangle = \sum_{n=1}^{\infty} |c_n|^2 q_n$$

□

Theorem 5.15: Expected Value of Non-Hermitian

If we **have $\hat{Q}$ not being an observable**:

$$\langle Q \rangle = \sum_{n'=1}^{\infty} \sum_{n=1}^{\infty} c_{n'}^* Q_{n',n} c_n$$

which *looks like a vector-matrix multiplication*, where $Q_{n',n}$ will be like a matrix.

If we have Q being observable, such that:

$$\hat{Q} f_n = q_n f_n$$

with *eigenvalues/eigenfunction pairs*, then:

$$Q_{n',n} = q_n \delta_{n',n} = \text{diagonal matrix}$$

and we *recover the result of*:

$$\langle Q \rangle = \sum_{n=1}^{\infty} |c_n|^2 q_n$$

Proof. The same idea:

$$\begin{aligned}\langle Q\rangle &= \langle\Psi|\hat{Q}\Psi\rangle \\ &= \langle\sum_{n'}^{\infty} c_{n'} f_{n'}|\hat{Q}\sum_{n}^{\infty} c_n f_n\rangle \\ &= \sum_{n'}^{\infty}\sum_{n}^{\infty} c_{n'}^* c_n \langle f_{n'}^*|\hat{Q} f_n\rangle \\ &= \sum_{n'}^{\infty}\sum_{n}^{\infty} c_{n'}^* c_n \int_{-\infty}^{\infty} f_{n'}^*\hat{Q} f_n\, dx \\ &= \sum_{n'}^{\infty}\sum_{n}^{\infty} c_{n'}^* c_n Q_{n',n}.\end{aligned}$$

□

5.6 Generalized Uncertainty Principle

This basically talks about the foundation of:

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

Reminder:

The standard deviation/uncertainty of an observable looks like:

$$\sigma_A^2 = \langle\Psi|\left(\hat{A} - \left\langle\hat{A}\right\rangle\right)^2\Psi\rangle$$

Theorem 5.16: Generalized Uncertainty Principle

For any **two hermitian operator** $\hat{A}, \hat{B}$, by letting the quantity:

$$\begin{cases} f \equiv \left(\hat{A} - \left\langle\hat{A}\right\rangle\right)\Psi \\ g \equiv \left(\hat{B} - \left\langle\hat{B}\right\rangle\right)\Psi \end{cases}$$

and **using Schwartz Inequality** and the fact that $|z|^2 \geq Im(z)^2$:

$$\sigma_A^2\sigma_B^2 \geq |\langle f|g\rangle|^2 \geq \left(\frac{\langle f|g\rangle - \langle g|f\rangle}{2i}\right)^2.$$

it can be proven that the **uncertainty of the two hermitian is**:

$$\sigma_A^2\sigma_B^2 \geq \left(\frac{\left\langle[\hat{A},\hat{B}]\right\rangle}{2i}\right)^2 \tag{31}$$

where for the commutator of two hermitian operators **carries its own factor of** i, and the two cancel out the quantity in parentheses is real,

and its **square is positive**.

However, for other quantities where the i is *not canceled inside the bracket*, we would just have a *negative RHS and it becomes trivial*.

Note:

Notice that the uncertainty of two hermitian $\hat{A}, \hat{B}$ **depends on the commutator** $\left[\hat{A}, \hat{B}\right]$. This means that if:

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

then:

$$\sigma_A \sigma_B \geq 0$$

meaning arbitrary precision.

Definition 5.5: Incompatible Observables

Since we can have an uncertainty principle for every pair of observables whose operators *do not commute* we call them **incompatible observables**.

Incompatible observables **do not have a complete set of shared eigenfunctions** at least one of the eigenfunctions will be different for the hermitian operator.

- *on the contrary*, for compatible (commuting) observables do admit complete sets of simultaneous eigenfunctions (i.e. we can construct *eigenfunctions for both of them at the same time*)

Proof. Consider two **Hermitian** operators, $\hat{A}, \hat{B}$, associated with a wave function $|\Psi\rangle$:

$$\begin{cases} f \equiv \left(\hat{A} - \left\langle \hat{A} \right\rangle\right) |\Psi\rangle \\ g \equiv \left(\hat{B} - \left\langle \hat{B} \right\rangle\right) |\Psi\rangle \end{cases}$$

then, I have:

$$\begin{aligned} \sigma_A^2 &= \langle \Psi | \left(\hat{A} - \left\langle \hat{A} \right\rangle\right)^2 \Psi \rangle \\ &= \langle \left(\hat{A} - \left\langle \hat{A} \right\rangle\right) \Psi | \left(\hat{A} - \left\langle \hat{A} \right\rangle\right) \Psi \rangle \\ &= \langle f | f \rangle . \end{aligned}$$

same for σ_B^2.

Then, using Schwartz Inequality:

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

Note:

For any complex number z, it is true that:

$$|z|^2 \geq Im(z)^2 = \left[\frac{1}{2i}(z - z^*)\right]^2$$

Therefore, *letting* $z = \langle f|g\rangle$ (**this is the central part of the proof**):

$$\sigma_A^2 \sigma_B^2 \geq |\langle f|g\rangle|^2 \geq \left(\frac{\langle f|g\rangle - \langle g|f\rangle}{2i}\right)^2$$

Now, computing $\langle f|g\rangle$ explicitly:

$$\begin{aligned}\langle f|g\rangle &= \langle\left(\hat{A} - \left\langle\hat{A}\right\rangle\right)\Psi| \left(\hat{B} - \left\langle\hat{B}\right\rangle\right)\Psi\rangle \\ &= \langle\Psi|\left(\hat{A}\hat{B} + \left\langle\hat{A}\right\rangle\left\langle\hat{B}\right\rangle - \hat{A}\left\langle\hat{B}\right\rangle - \left\langle\hat{A}\right\rangle\hat{B}\right)\Psi\rangle\,.\end{aligned}$$

since I know $\langle\Psi|\hat{A}\Psi\rangle = \langle A\rangle$:

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

then, by analogy:

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

This means the *quantity inside the inequality becomes* :

$$\langle f|g\rangle - \langle g|f\rangle = \left\langle\hat{A}\hat{B}\right\rangle\left\langle\hat{B}\hat{A}\right\rangle = \left\langle\left[\hat{A},\hat{B}\right]\right\rangle$$

Therefore, substituting into the inequality:

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

where we see that $\left[\hat{A},\hat{B}\right]$ is the **commutator**. □

***Example*: Heisenberg's Uncertainty Principle**

Using theorem 5.16, the uncertainty principle can be easily derived:

$$[\hat{x},\hat{p}] = i\hbar$$

therefore:

$$\sigma_x^2\sigma_p^2 \geq \left(\frac{i\hbar}{2i}\right)^2$$

so that:

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

5.6.1 Minimizing Uncertainty

Corollary 5.3: Minimizing Uncertainty

The uncertainty of two Herminia Operators are **minimized**:

$$\sigma_A^2 \sigma_B^2 = \left| \frac{\left\langle \left[\hat{A}, \hat{B} \right] \right\rangle}{2i} \right|^2$$

if we have:

$$\begin{cases} f \equiv \left(\hat{A} - \left\langle \hat{A} \right\rangle \right) \Psi \\ g \equiv \left(\hat{B} - \left\langle \hat{B} \right\rangle \right) \Psi \end{cases}$$

and **that**:

$$g(x) = cf(x)$$

for some **imaginary** c, then the uncertainty will be **minimized**.

Proof. The proof it simple, due to Schwartz Inequality:

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

for this *inequality to be equal* we get:

$$\begin{aligned} \langle f|f \rangle \langle g|g \rangle &= |c|^2 \langle f|f \rangle^2 \\ \langle f|g \rangle^2 &= |c|^2 \langle f|f \rangle^2 . \end{aligned}$$

then, for the inequality $|z|^2 \geq Im(z)^2$ to be equal such that this is *equal*

$$\sigma_A^2 \sigma_B^2 \geq |\langle f|g \rangle|^2 \geq \left(\frac{\langle f|g \rangle - \langle g|f \rangle}{2i} \right)^2$$

we just need $|z|^2 = Im(z)^2$, where $z = \langle f|g \rangle$.

Therefore, this means that:

$$c \langle f|f \rangle = \text{Imaginary}$$

so that c is *imaginary* □

***Example*: Minimum Uncertainty Wave Packet**

Suppose we want to *minimize the position-momentum uncertainty*:

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

then using the corollary 5.3, I have $\hat{A} = \hat{x}, \hat{B} = \hat{p}$:

$$\begin{aligned} g &= cf \\ (\hat{p} - \langle \hat{p} \rangle)\Psi &= ia \left(\hat{x} - \langle \hat{x} \rangle \right) \Psi . \end{aligned}$$

for a being real.

Then, we obtain the following equation:

$$\begin{aligned}\left(i\hbar\frac{\partial}{\partial x}-\langle\hat{p}\rangle\right)\Psi &= ia\left(x-\langle x\rangle\right)\Psi\\ \frac{d\Psi}{\Psi} &= \left(-\frac{a}{\hbar}\left(x-\langle x\rangle\right)+i\langle p\rangle\right)dx\\ \ln(\Psi) &= \left(-\frac{a}{2\hbar}\left(x^2-2\langle x\rangle x\right)+i\langle p\rangle x\right)+C\\ \Psi &= Ae^{-\frac{a}{2\hbar}(x-\langle x\rangle)^2}e^{i\langle p\rangle x}.\end{aligned}$$

since $\langle x\rangle, \langle p\rangle$ are *essentially constants,* we basically got a **Gaussian** $e^{-\frac{a}{2\hbar}(x-\langle x\rangle)^2}$ (times a *propagation term* $e^{i\langle p\rangle x}$). This means that **position-momentum uncertainty is minimized when Ψ is a Gaussian**.

5.6.2 Energy-Time Uncertainty Principle

After all, position, momentum, and energy are all *dynamical variables* measurable characteristics of the system, at any given time. But **time itself is not a dynamical variable** (not, at any rate, in a nonrelativistic theory).

Therefore, instead we should think about **the time it takes the system to change substantially**.

Theorem 5.17: Energy-Time Uncertainty Principle

The uncertainty principle:

$$\sigma_H\sigma_t \geq \frac{\hbar}{2}$$

holds if the **uncertainty of time is defined to be**:

$$\sigma_t = \Delta t \equiv \frac{\sigma_Q}{\left|d\langle Q\rangle/dt\right|}$$

for an **operator $\hat{Q}$ independent of time**.

Or, *intuitively:*

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

so that:

1. σ_t represents the **amount of time it takes the expectation value of $\hat{Q}$ to change by one standard deviation**.
2. In particular, the uncertainty also depends entirely on **what observable** you care to look at.

Proof. First consider a **observable $\hat{Q}$**, and we want to measure **how fast the system is changing:**

$$\begin{aligned}\frac{d}{dt}\langle Q\rangle &= \frac{d}{dt}\langle\Psi|\hat{Q}\Psi\rangle \\ &= \langle\frac{d}{dt}\Psi|\hat{Q}\Psi\rangle + \langle\Psi|\frac{d\hat{Q}}{dt}\Psi\rangle + \langle\Psi|\hat{Q}\frac{d}{dt}\Psi\rangle\,.\end{aligned}$$

Using **Schrodinger's Equation** (key step):

$$\hat{H}\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$
$$\frac{\partial}{\partial t}\Psi = \frac{1}{i\hbar}\hat{H}\Psi.$$

similarly, the term:

$$\frac{\partial}{\partial t}\Psi^* = \frac{1}{-i\hbar}\hat{H}\Psi^*$$

by substituting them into the first equation:

$$\begin{aligned}\frac{d}{dt}\langle Q\rangle &= -\frac{1}{i\hbar}\langle\hat{H}\Psi|\hat{Q}\Psi\rangle + \left\langle\frac{d\hat{Q}}{dt}\right\rangle + \frac{1}{i\hbar}\langle\Psi|\hat{Q}\hat{H}\Psi\rangle \\ &= \frac{i}{\hbar}\langle\Psi|\left(\hat{H}\hat{Q}-\hat{Q}\hat{H}\right)\Psi\rangle + \left\langle\frac{d\hat{Q}}{dt}\right\rangle \\ &= \frac{i}{\hbar}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle + \left\langle\frac{d\hat{Q}}{dt}\right\rangle.\end{aligned}$$

this is also known as the *Generalized Ehrenfest Principle*.

In the typical case where the operator **$\hat{Q}$ does not depend explicitly on time**, this tells us that:

$$\frac{d\left\langle\hat{Q}\right\rangle}{dx} = \frac{i}{\hbar}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle$$

then, using the **Generalized Uncertainty Principle** (theorem 5.16):

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

I get:

$$\sigma_H^2\sigma_Q^2 \geq \left(\frac{\hbar}{2}\left|\frac{d\left\langle\hat{Q}\right\rangle}{dt}\right|\right)^2.$$

Therefore, if we need:

$$\sigma_H^2\sigma_t^2 \geq \left(\frac{\hbar}{2}\right)^2$$

we need that:

$$\sigma_t \equiv \frac{\sigma_Q}{\left|d\langle Q\rangle/dt\right|}$$

and this finishes the proof. □

Theorem 5.18: Generalized Ehrenfest Theorem

Basically one **important result from the above** is the part for **any observable** $\hat{Q}$:

$$\frac{d\langle Q\rangle}{dt} = \frac{i}{\hbar}\left\langle\left[\hat{H},\hat{Q}\right]\right\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle \tag{32}$$

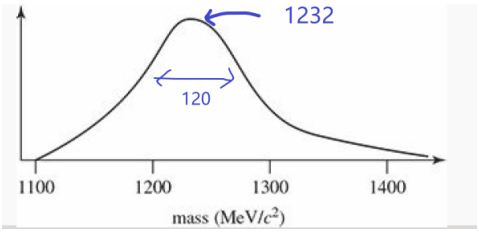
where using this, it can be easily proven the **Ehrenfest Principles** :

$$m\frac{d\langle x\rangle}{dt} = \langle p\rangle$$

and etc.

Now, we consider some examples using Δt

Figure 2: Measurement of Mass of Delta Particle



***Example*: Measurement of Delta Particle**

The particle Δ has a *life time of* 10^{-23} *s*, before spontaneously disintegrating.

If you make a histogram of all measurements of its mass, you get a kind of bell-shaped curve centered at $1232\,MeV/c^2$, with a **width of about** $120\,MeV/c^2$

Now, if we take Δt to be the *lifetime* of the Δ particle (certainly **one measure of how long it takes the system to change appreciably**):

$$\Delta E\delta t = \left(\frac{120}{2}\right)\left(10^{-23}\right) = 6\times 10^{-22}$$

which works since:

$$\Delta E\Delta t \geq \frac{\hbar}{2} = 3\times 10^{-22}$$

but since $E = mc^2$:

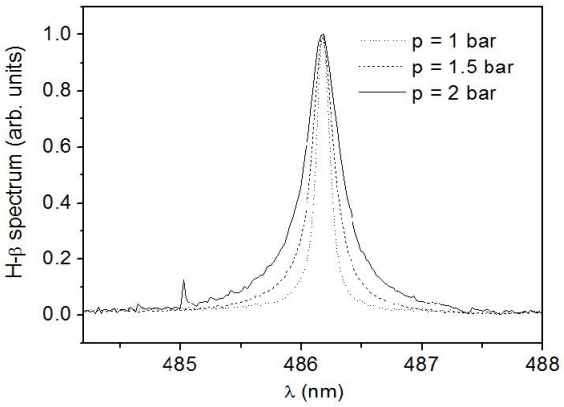
$$\Delta E\Delta t = (\Delta m)\,c^2\Delta t \geq \frac{\hbar}{2}$$

and inserting $\Delta t = 10^{-23}$, I obtain:

$$\Delta m \geq 30\, MeV/c^2$$

This is *one contribution to* $\Delta m = 60\, MeV/c^2$ in the graph above, due to the *uncertainty principle*

Figure 3: Spectral Line of Helium Discharge



***Example*: Helium Discharge**

Consider a discharge of helium leading to the *spectral lines* (see figure below). We see that there is an uncertainty **width of measured wavelength**.

As it turns out, for electrons in helium going from a higher energy level to a lower one γ_{rad}, or when photons are emitted due to collisions γ_1, we have:

$$\frac{1}{\Delta t} \sim \gamma_{rad} + \gamma_1$$

where Δt is the **time it takes for the jump/release of energy** (also a major change in the system).

For $E = 2.4eV$ for charging the helium, we will have a $\Delta t = 10^{-9}\, s$, then:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

$$\Delta E \geq_3 .3 \times 10^{-7}\, eV.$$

because:

$$E = h\nu = hc\frac{1}{\lambda}$$
$$dE = -\frac{\hbar c}{\lambda^2}d\lambda$$
$$\frac{d\lambda}{\lambda} = -\frac{dE}{E}$$
$$\left|\frac{d\lambda}{\lambda}\right| = \left|\frac{dE}{E}\right|.$$

hence we get:

$$d\lambda \geq 6.5 * 10^{-5}\, nm$$

which is *one contribution to the width of the measured discharge*.

5.7 Vectors and Operators

This section aims to *solve the Schrodinger's Equation using Linear Algebra*, due to the fact that we know **wave functions live in Hilbert Space**.

5.7.1 Bases in Hilbert Space

Theorem 5.19: General Wave Function

Now, we need to imagine having a **vector $|\mathcal{S}\rangle$ that lives in Hilbert Space**, and that it can be expressed with respect to any number of different bases in the Hilbert Space. (This turns out to be **true**).

Then we have the **wave function** being the **x-component** of the general wave function:

$$\Psi(x,t) = \langle x|\mathcal{S}(t)\rangle$$

similarly, the momentum space wave being the **p-component** of the general wave function:

$$\Phi(p,t) = \langle p|\mathcal{S}(t)\rangle$$

If we expand in the basis of energy eigenfunctions (supposing for simplicity that the spectrum is discrete) (*one valid basis for Hilbert Space, but there are also other basis such as the momentum eigenfunctions*):

$$c_n(t) = \langle n|\mathcal{S}(t)\rangle$$

where $\langle n|$ means the nth eigenfunction of $\hat{H}$, i.e. ψ_n.

Alternatively, this also means that the **general wave function can**

be expressed as:

$$\begin{aligned}\mathcal{S}(t) &= \int \Psi(y,t)\delta(x-y)dy \\ &= \frac{1}{\sqrt{2\pi\hbar}}\int \Phi(p,t)e^{ipx/\hbar}dp \\ &= \sum_{n=1}^{\infty} c_n e^{-iE_n t/\hbar}\psi_n(x).\end{aligned}$$

Now, we can also consider **Operators** as linear transformatino of vectors in Hilbert Space from one to another, i.e. they are **transformation Matrices**.

Theorem 5.20: Operators and Matricies

Consider *two vectors (i.e. states) in Hilbert Space* with respect to *orthonormal basis* $\{|e_n\rangle\}$:

$$\begin{aligned}|\alpha\rangle &= \sum_n a_n |e_n\rangle \\ |\beta\rangle &= \sum_n b_n |e_n\rangle .\end{aligned}$$

and notice that:

$$a_n = \langle e_n|\alpha\rangle$$

with the same for b_n.

Now, if we consider **an operator** $\hat{Q}$ (does not have to be Hermitian):

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

Then an **operator can be seen as a transformation matrix**:

$$\langle e_m|\hat{Q}|e_n\rangle \equiv Q_{mn}$$

Thus the matrix elements of tell you how the components transform.

Proof. Staring with the *transformation equation*:

$$\begin{aligned}|\beta\rangle &= \hat{Q}|\alpha\rangle \\ \sum_n b_n |e_n\rangle &= \hat{Q}\sum_n a_n |e_n\rangle .\end{aligned}$$

multiplying both sides by $|e_m\rangle$ (the *analogy of using orthogonality principle*) :

$$\sum_n b_n |e_n\rangle = \hat{Q} \sum_n a_n |e_n\rangle$$
$$\sum_n b_n \langle e_m|e_n\rangle = \sum_n a_n \langle e_m|\hat{Q}|e_n\rangle$$
$$\sum_n b_n \delta_{mn} = \sum_n a_n Q_{mn}$$
$$b_m = \sum_n Q_{mn} a_n.$$

□

Corollary 5.4: Solving Schrodinger's Equation with Linear Alg

Starting with a general wave function $|\mathcal{S}(t)\rangle$, and consider the Schrodinger's Equation:

$$i\hbar \frac{\partial}{\partial t} |\mathcal{S}\rangle = \hat{H} |\mathcal{S}\rangle$$

As always, we begin by solving the time-independent Schrödinger equation. For TISE, we look for the **eigenvectors and eigenvalues** of $\hat{H}$:

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

for $|s\rangle$ being an *eigenvector of the basis* $|e_n\rangle$:

$$|s\rangle = \sum_n c_n |e_n\rangle = \begin{bmatrix} c_1 \\ c_2 \\ \dots \end{bmatrix}$$

then, plugging into the TISE and *multiplying both sides with* $|e_m\rangle$:

$$\sum_n c_n \langle e_m|\hat{H}|e_n\rangle = \sum_n E \langle e_m|e_n\rangle$$
$$\sum_n c_n H_{mn} = E \sum_n c_n \delta_{mn}$$
$$\sum_n (H_{mn} - E\delta_{mn})\, c_n = 0.$$

this becomes a linear algebra problem:

$$\begin{bmatrix} H_{11} - E & H_{12} - 0 & \dots \\ H_{21} - 0 & H_{22} - E & \dots \\ \dots & \dots & \dots \end{bmatrix}$$

is not *full rank*, hence:

$$\det |H_{mn} - E\delta_{mn}| = 0$$

so then we can:

1. **solve for E eigenvalues**
2. substitute the eigenvalues back and **solve for eigenfunctions** (i.e. the c_n)

***Example*: Classical Two Level System**

Imagine a system in which there are just two linearly independent states:

$$|e_1\rangle = |1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$
$$|e_2\rangle = |2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

then, we are dealing with:

$$i\hbar \frac{\partial}{\partial t} |\mathcal{S}\rangle = \hat{H} |\mathcal{S}\rangle$$

and first consider the TISE:

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

for $|s\rangle = \begin{bmatrix} a \\ b \end{bmatrix}$ in this basis. Hence, as we know:

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

then the TISE becomes:

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = E \begin{bmatrix} a \\ b \end{bmatrix}$$

which is **the linear algebra problem of solving for eigenvalues and eigenvectors**.

If it happens that:

$$H = \begin{bmatrix} h & g \\ g & h \end{bmatrix}$$

for h, g being real, then we get:

$$\begin{bmatrix} h - E & g \\ g & h - E \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0$$

hence for non-trivial solution, we need a *non-full rank matrix*:

$$\det \begin{bmatrix} h - E & g \\ g & h - E \end{bmatrix} = (h - E)^2 - g^2 = 0$$

Therefore, we get **two eigenvalues** :

$$E_{\pm} = h \pm g$$

then to determine the eigenvectors,

$$\begin{bmatrix} h & g \\ g & h \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = E_{+} \begin{bmatrix} a \\ b \end{bmatrix}$$

and using the normalization that $a^2 + b^2 = 1$, then we get:

$$E_{+} = h + g, \quad |s_{+}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

and similarly:

$$E_{-} = h - g, \quad |s_{-}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

so we have found the **eigenvalue and eigenvector(eigenfunction) pairs**.

Now, we have essentially:

- **solved the for the eigenstates in terms of some basis eigenfunctions** $|1\rangle, |2\rangle$

we want to consider:

***Example*: Time Evolution of Two Level System**

Suppose the initial condition is:

$$|\mathcal{S}(0)\rangle = |1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

since we know from previous problem:

$$|s_{+}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad |s_{-}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

for our *specific Hamiltonian in the previous problem*. Then, we have the **wave function as a superposition of eigenstates** $|s_{+}\rangle\, m\, |s_{-}\rangle$:

$$|\mathcal{S}(0)\rangle = \frac{1}{\sqrt{2}} \left(|s_{+}\rangle + |s_{-}\rangle\right)$$

which we also see the **coefficient/contribution of each eigenstate**.

Then, since we **know the time dependence for Hamiltonian is**

$e^{-i\frac{E_n}{\hbar}t}$:

$$\begin{aligned}
|\mathcal{S}(t)\rangle &= \frac{1}{\sqrt{2}}\left(e^{-i\frac{(h+g)}{\hbar t}}|s_+\rangle + e^{-i\frac{(h-g)}{\hbar t}}|s_-\rangle\right) \\
&= \frac{1}{2}e^{-i\frac{h}{\hbar}t}\left(e^{-i\frac{g}{\hbar}t}\begin{bmatrix}1\\1\end{bmatrix} + e^{i\frac{g}{\hbar}t}\begin{bmatrix}1\\-1\end{bmatrix}\right) \\
&= e^{-i\frac{h}{\hbar}t}\begin{bmatrix}\frac{e^{-igt/\hbar}+e^{igt/\hbar}}{2}\\ \frac{e^{-igt/\hbar}-e^{igt/\hbar}}{2}\end{bmatrix} \\
&= e^{-i\frac{h}{\hbar}t}\begin{bmatrix}\cos\left(\frac{g}{\hbar}t\right)\\ -i\sin\left(\frac{g}{\hbar}t\right)\end{bmatrix}.
\end{aligned}$$

this solves the **time evolution of the two level system**.

Additionally, this means that the **probability of staying in the state of** $\begin{bmatrix}1\\0\end{bmatrix}$ (this is not an eigenstate):

$$\begin{aligned}
\text{Prob}\left(\begin{bmatrix}1\\0\end{bmatrix}\right) &= \left|e^{-i\frac{h}{\hbar}t}\cos\left(\frac{g}{\hbar}t\right)\right|^2 \\
&= \left|\cos\left(\frac{g}{\hbar}t\right)\right|^2.
\end{aligned}$$

and similarly:

$$\text{Prob}\left(\begin{bmatrix}0\\1\end{bmatrix}\right) = \left|\sin\left(\frac{g}{\hbar}t\right)\right|^2$$

notice that the probability **sum up to one because they are orthogonal to each other**, even though they are not eigenstates (but orthonormal basis).

***Example*: Different Hamiltonian**

Now, consider the same Schrodinger's Equation but with a different Hamiltonian:

$$H = \begin{bmatrix}h & ig\\ -ig & h\end{bmatrix}$$

for h, g being some real number.

Again, plugging in this into the TISE, you will end up solving:

$$\det\begin{bmatrix}h-E & ig\\ -ig & h-E\end{bmatrix} = 0$$

interestingly, you end up with the **same eigenvalues, but different**

eigenvector(eigenstates):

$$E_+ = h + g, \quad |s_+\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$$
$$E_- = h - g, \quad |s_+\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix}.$$

with respect to the *same basis in the previous problems*. So we see that the *eigenstates change if Hamiltonian change*.

5.7.2 Projection Operator

Now, we have considered:

- wave function/eigenstates as *vectors in Hilbert Space* with some orthornormal basis

We would like to think about **how to transform the same vector into different representations in the same Hilbert Space**, i.e. projection and change basis.

Reminder:

In a function space, the bra can be thought of as an instruction to integrate:

$$\langle f| = \int f^* [...] \, d\, x$$

*In a **finite-dimensional vector space**, with the kets expressed as columns:*

$$\langle \beta| = [b_1^*, \ b_2^*, \ ..., b_n^*]$$

so that in a sense, when we have a bra hitting a ket (e.g. a vector):

$$\langle \beta | \alpha \rangle$$

*it should yield a **complex number**.*

Theorem 5.21: Projection Operator

The operator:

$$\hat{P}_n = |e_n\rangle \langle e_n|$$

picks out the portion of any other vector that lies along the **orthornormal basis** $|e_n\rangle$.So that:

$$\hat{P}_n |\beta\rangle = (\langle e_n|\beta\rangle) |e_n\rangle$$

where $\langle e_n|\beta\rangle$ is the projection.

Then, the full **projection matrix** would be:

$$P = \sum_n |e_n\rangle \langle e_n| = \begin{bmatrix} \langle \bar{e}_1|e_1\rangle & \langle \bar{e}_1|e_2\rangle & ... \\ ... & ... & ... \\ ... & ... & ... \end{bmatrix}$$

so that if we consider $P = P_{\to \bar{m}}$ as projecting to a basis of $|\bar{e}_m\rangle$, and consider $\Psi = \sum_n a_n |e_n\rangle$ in the n-basis, then:

$$P_{\to \bar{m}} |\Psi\rangle = \sum_m \left(\sum_n a_n \langle \bar{e}_m|e_n\rangle \right) |\bar{e}_n\rangle = \sum_m \bar{a}_m |\bar{e}_m\rangle$$

for the *projected coefficients as "summing the contributions of each $|e_n\rangle$ onto a specific $|e_m\rangle$"*:

$$\bar{a}_m = \left(\sum_n a_n \langle \bar{e}_m|e_n\rangle \right)$$

in the end, we are just doing:

$$|\Psi_{\text{basis } m}\rangle = P |\Psi\rangle$$
$$\begin{bmatrix} \bar{a}_1 \\ \bar{a}_2 \\ ... \end{bmatrix} = \begin{bmatrix} \langle \bar{e}_1|e_1\rangle & \langle \bar{e}_1|e_2\rangle & ... \\ ... & ... & ... \\ ... & ... & ... \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ ... \end{bmatrix}.$$

so that we have **projected $|\Psi\rangle$ from $|e_n\rangle$ basis to $|\bar{e})_m\rangle$ basis**. Since we are just doing the projection, the **vector itself did not change since:**

$$P = \sum_n |e_n\rangle \langle e_n| = 1$$

which is an identity (see proof below).

In the **continuous space**, we have the analogous:

$$P = \int |e_z\rangle \langle e_z| \, dz$$

Proof. The idea stems from *ordinary Linear Algebra*. Consider an arbitrary vector $\vec{A}$ in the basis $\hat{x}_i$

$$\vec{A} = \sum_i \left(\vec{A} \cdot \hat{x}_i \right) \hat{x}_i.$$

as basically *summing each of its components*, but this is equivalent to:

$$\vec{A} = \sum_i \left(\vec{A} \cdot \hat{x}_i \right) \hat{x}_i$$
$$= \left(\vec{A} \cdot \sum_i \hat{x}_i \right) \hat{x}_i.$$

and we can see:

$$\sum_i \hat{x}_i \hat{x}_i$$

as the idea for an projection matrix. Now, going to the business, consider a vector:

$$|\alpha\rangle = \sum_n a_n |e_n\rangle$$

and getting its *contribution onto other basis*:

$$\langle e_m|\alpha\rangle = \sum_n a_n \langle e_m|e_n\rangle = a_m$$

$$\langle \alpha|e_m\rangle = \sum_n a_n^* \langle e_m|e_n\rangle = a_m^*$$

Therefore, we can **rewrite the vector as its components**:

$$|\alpha\rangle = \sum_n \langle e_n|\alpha\rangle |e_n\rangle$$

$$\langle \alpha| = \sum_{n'} \langle \alpha|e_{n'}\rangle |e_{n'}\rangle .$$

then since we know, if we have a **normalized vector** $|\alpha\rangle$, such that $\sum_n |a_n|^2 = 1$:

$$\begin{aligned}
\langle \alpha|\alpha\rangle &= 1 \\
\sum_n \langle e_n|\alpha\rangle |e_n\rangle \sum_{n'} \langle \alpha|e_{n'}\rangle |e_{n'}\rangle &= 1 \\
\sum_m \sum_n \langle \alpha|e_m\rangle \langle e_n|\alpha\rangle \langle e_m|e_n\rangle &= 1 \\
\sum_n \langle \alpha|e_n\rangle \langle e_n|\alpha\rangle &= 1 \\
\langle \alpha| \left(\sum_n |e_n\rangle \langle e_n| \right) |\alpha\rangle &= 1.
\end{aligned}$$

which shows the transformation matrix:

$$P = \left(\sum_n |e_n\rangle \langle e_n| \right)$$

and that it must be:

$$P = 1$$

meaning that it **does not change the vector, only its representation**. □

Note:

> The above proof basically used the fact that:
>
> $$\langle e_m|e_n\rangle = \delta_{mn}$$
>
> so, we can **generalize to the continuous space**:
>
> $$\langle e_{z'}|e_z\rangle = \delta(z - z')$$

and hence:

$$P = \int |e_z\rangle \langle e_z| \, d\, z$$

***Example*: Typical Projection**

Consider some *easy, orthonormal basis*:

$$\int |x\rangle \langle x| \, dx = 1$$
$$\int |p\rangle \langle p| = 1$$
$$\sum_n |n\rangle \langle n| = 1.$$

then **acting on the state vector $|\mathcal{S}(t)\rangle$**, we obtain the useful ones

$$|\mathcal{S}(t)\rangle = \int \langle x|\mathcal{S}(t)\rangle \, |x\rangle \, d\, x \equiv \int \Psi(x,t) \, |x\rangle \, d\, x$$
$$|\mathcal{S}(t)\rangle = \int \langle p|\mathcal{S}(t)\rangle \, |p\rangle \, d\, p \equiv \int \Phi(x,t) \, |p\rangle \, d\, p$$
$$|\mathcal{S}(t)\rangle = \sum_n \langle n|\mathcal{S}(t)\rangle \, |n\rangle \equiv \sum_n c_n(t) \, |n\rangle \, .$$

which is also the meaning of the *general wave function $\mathcal{S}(t)$*

5.7.3 Changing Basis

Now, we know how projections work, we can work on **change of coordinates back AND forth**.

Theorem 5.22: Change of Coordinate Matrix

The projection/change of coordinate matrix $U = P_{\to m}$ from an **original basis n to a basis m** looks like:

$$U = \begin{bmatrix} \langle \bar{e}_1|e_1\rangle & \langle \bar{e}_1|e_2\rangle & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \end{bmatrix}$$

where the components are:

$$u_{mn} = \langle \bar{e}_m|e_n\rangle$$

and the **reverse transformation $U^{-1} = P_{\to n}$ from the new bass m to basis n looks like**:

$$U^{-1} = \begin{bmatrix} \langle e_1|\bar{e}_1\rangle & \langle e_1|\bar{e}_2\rangle & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \end{bmatrix}$$

where the components are:

$$u_{mn}^{-1} = \langle e_m | \bar{e}_n \rangle$$

and so we see that, for the **orthonormal basis**:

$$u_{mn}^{-1} = u_{nm}^{*} = u_{mn}^{\dagger}$$

Reminder:

> *The adjoint of a matrix A is the transpose of the cofactor matrix of A.*

Therefore, this means the change of basis matrix U is **unitary but not necessarily Hermitian**:

$$U^{\dagger} = U^{-1}$$

(i.e. not always $U^{-1} = U$, hence not always Herminia.)

Proof. The forward direction of $U = P_{\to m}$ is shown in the previous section. In the end, we are just doing:

$$P_{\to \bar{m}} |\Psi\rangle = \sum_m \left(\sum_n a_n \langle \bar{e}_m | e_n \rangle \right) |\bar{e}_n\rangle = \sum_m \bar{a}_m |\bar{e}_m\rangle$$

in analogy, we look at the reverse direction. If we have done the transformation, we can prove the U^{-1}, which is trivial hence skipped. □

Basically, we are just doing:

$$\begin{bmatrix} \bar{a}_1 \\ \bar{a}_2 \\ \dots \end{bmatrix} = \begin{bmatrix} \langle \bar{e}_1 | e_1 \rangle & \langle \bar{e}_1 | e_2 \rangle & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \dots \end{bmatrix}$$

$$\begin{bmatrix} a_1 \\ a_2 \\ \dots \end{bmatrix} = \begin{bmatrix} \langle e_1 | \bar{e}_1 \rangle & \langle e_1 | \bar{e}_2 \rangle & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} \bar{a}_1 \\ \bar{a}_2 \\ \dots \end{bmatrix}.$$

being the forward and reverse transformation. However, notice that this would also work **in combination of operators (which are also matrices)**.

Theorem 5.23: Operators with Change of Coordinates

Consider an operator $\hat{Q} = Q$ in matrix form, and suppose it operates on:

$$\hat{Q} |\Psi\rangle = Q \sum_n a_n |e_n\rangle$$

we can let Q **become Q_{new} operate on another basis** without changing the meaning of the operator:

$$Q_{new} = U Q_{old} U^{-1}$$

and the reverse transform:

$$Q_{old} = U^{-1} Q_{new} U$$

6 3D Quantum Mechanics

This would also correspond to the PDE lectures, on which we talked about solving:

- PDEs in **cylindrical coordinate**
- PDEs in **spherical coordinate**

and in the end, it comes down to the *same separating variables* but with some solutions as Bessel Functions.

6.1 Wave Function in Spherical Coordinate

Consider the same Schrodinger's Equation and TISE:

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

and recall that:

$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2m} + V(\vec{r}) \\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(\vec{r}) \\ &= -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}).\end{aligned}$$

Reminder:

In spherical coordinate, we have r, θ, φ, and that:

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

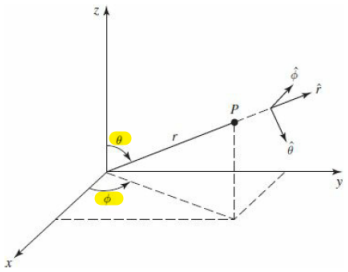


Figure 4.1: Spherical coordinates: radius r, polar angle θ, and azimuthal angle ϕ.

notice we are using $\varphi \in [0, 2\pi]$

Theorem 6.1: Solution in Spherical Symmetry

In fact, the above equations is only **exactly solvable if we are spherical symmetry** $V(\vec{r}) = V(r)$.

Then separating the variables $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$, we get:

$$Y_l^m(\theta,\varphi) = A_{l,m}e^{im\varphi}P_l^m(\cos(\theta))$$

where we have:

- $A_{l,m} = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}$ is the *normalization from*

$$\int_0^{2\pi}\int_0^{\pi}|Y(\theta,\varphi)|^2\sin(\theta)\,d\theta\,d\phi = 1$$

- $P_l^m(x), x = \cos(\theta)$ is the *Legendre Polynomial*.

and the $R(r)$ part without knowing $V(r)$ can be only solved until:

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

where we have:

- for $u(r) = rR(r)$
- the *effective potential being*:

$$V_{eff} = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

- and the *normalization in the end would be:*

$$\int_0^{\infty}|R|^2 r^2\,dr = 1$$

Proof. First, start with the TISE (since the time dependent part will just be $e^{i\frac{E}{\hbar}t}$), and let $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$:

$$\begin{aligned}
-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi &= E\psi \\
-\frac{\hbar^2}{2m}[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2}\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) & \\
+\frac{R}{r^2}\sin^2(\theta)\frac{\partial^2 Y}{\partial\varphi^2}] &= E\,RY \\
\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{Y}\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + & \\
\frac{1}{Y\sin^2(\theta)}\frac{\partial^2 Y}{\partial\varphi^2} - (V(r)-E)\frac{2mr^2}{\hbar^2} &= 0.
\end{aligned}$$

Then, splitting the equation into r **dependent parts and** θ, φ **part**, I get two ODEs:

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

The first one is the **radial equation**, and the second one is called the **angular equation** for the rest of this section. □

6.2 Angular Equation

Theorem 6.2: Solution of Angular Equation

The solution to this equation is well founded:

$$\frac{1}{Y}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\varphi^2}\right]=-\alpha$$
$$\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\varphi^2}=-\alpha\sin^2(\theta)Y.$$

then the solution is:

$$Y_l^m(\theta,\varphi)=A_{l,m}e^{im\varphi}P_l^m(\cos(\theta))$$

for $A_{l,m}$ being the *normalization constant such that*:

$$\int_0^{2\pi}\int_0^{\pi}|Y|^2\sin(\theta)\,d\theta\,d\varphi=1$$
$$A_{l,m}=\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)}}.$$

and for:

$$l=0,1,2,...;\quad m=0,\pm1,...,\pm l$$

Proof. So we need to solve this equation:

$$\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\varphi^2}=-\alpha\sin^2(\theta)Y$$

Let we *separate variables into* $Y=\Theta(\theta)\Phi(\varphi)$, then we will get two ODEs again:

$$\frac{1}{\Theta}\left[\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right)\right]+\alpha\sin^2(\theta)\equiv\mu$$
$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}\equiv-\mu.$$

solving the simple one first, we get:

$$\Phi(\varphi)=Ae^{\pm i\sqrt{\mu}\varphi}$$

due to symmetry, and the **boundary condition is the continuity one**:

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

henec we get:

$$\sqrt{\mu}=m,\quad m=0,1,2,3...$$

or, **equivalently**:

$$\Phi(\varphi)=Ae^{im\varphi},\quad m=0,\pm1,\pm2,...$$

now, to deal with the Θ equation, we have:

$$\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right)+\left(\alpha\sin^2(\theta)-m^2\right)\Theta=0$$
$$\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right)+\left[\alpha\sin(\theta)-\frac{m^2}{\sin(\theta)}\right]\Theta=0.$$

Reminder:

Recall that we had the same thing in PDE, where we needed to solve the Spherical Laplace's Equation in section 7.5, stated with $\nabla^2\omega+\lambda\omega=0$ *and reaching:*

$$\left(\sin(\varphi)g'\right)'+\left(R^2\lambda^2\sin(\varphi)-\frac{m^2}{\sin(\varphi)}\right)g=0$$

we can make it into a Spherical Bessel's Equation, by having $x=\cos(\varphi)$*, and using* $\sin^2(\varphi)=1-\cos^2(\varphi)=1-x^2$ *, we get:*

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{dg}{dx}\right]+\left(\lambda R-\frac{m}{1-x^2}\right)g=0$$

then this ***only has a bounded solution when*** *:*

- $\lambda R^2=n(n+1)$
- *when* $n\geq m$
- *the solution is* $g_{mn}=P_n^m(x)$ *being the* associate Legendre Polynomial of the First Kind

Therefore, here we are **also cantering the equation to the Spherical Bessel Equation** by using $x=\cos(\theta)$:

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{d\Theta}{dx}\right]-\frac{m}{1-x^2}\Theta+\alpha\Theta=0$$

and the solution is:

$$\Theta(\theta)=A_{l,m}P_l^m(\cos(\theta))$$

for a *bounded* Θ *at* $\theta=0$, and that we have:

$$\alpha=l(l+1)$$

and that:

$$l=0,1,2,3,...;\quad m=0,\pm1,\pm2,...\pm l$$

In general, those *associated Legendre Function* can be generated using **Rodriguez Formula**:

$$P_l^m(x)=(-1)^m\left(1-x^2\right)^{\frac{m}{2}}\left(\frac{d}{dx}\right)^m P_l(x)$$

for $P_l(x) = P_l^{m=0}(x)$ is also called the ***l*-th Legendre Polynomial**, which can be generated by:

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

Putting them together, we get the *final solution for Y*:

$$Y_l^m(\theta, \varphi) = A_{m,l} P_l^m\left(\cos\left(\theta\right)\right) e^{im\varphi}$$

for

$$l = 0, 1, 2, ...; \quad m = 0, \pm 1, \pm 2, ..., \pm l$$

and that $Y_l^m(\theta, \varphi)$ are also called the **Spherical Harmonics** being a complete set of functions. This would be *orthonormal after normalization, such that*:

$$\int_0^\pi \int_0^\pi Y_l^m Y_{l'}^{m'} \sin\left(\theta\right) d\theta \, d\varphi = \delta_{l,l'} \delta_{m,m'}$$

□

Corollary 6.1: l-th Legendre Polynomial

The l-th Legendre Polynomial can actually be solved directly. Since we have now $m = 0$, we have:

$$\frac{d}{dx}\left[\left(1 - x^2\right) \frac{d\Theta}{dx}\right] + \alpha\Theta = 0$$

$$\left(1 - x^2\right) \frac{d^2\Theta}{dx^2} - 2x \frac{d\Theta}{dx} + \alpha\Theta = 0.$$

Since we know that Θ *is a polynomial*:

$$\Theta = P(x) = \sum_{n=0}^{\infty} a_n x^n$$

then calculating the *derivative and substituting*:

$$\left(1 - x^2\right) \left[\sum_{n=0}^{\infty} a_n (n)(n-1) x^{n-2}\right] - 2x \sum_{n=0}^{\infty} a_n n x^{n-1} + \alpha \sum_{n=0}^{\infty} a_n x^n = 0$$

$$\sum_{n=0}^{\infty} \left[a_n n \left(n - 1\right) x^{n-2} - a_n n(n-1) x^n - 2n x^n + \alpha a_n x^n\right] = 0$$

$$\sum_{n=0}^{\infty} \left[a_{n+2} \left(n + 2\right) \left(n + 1\right) x^n - a_n n(n-1) x^n - 2 a_n n x^n + \alpha a_n x^n\right] = 0$$

$$\sum_{n=0}^{\infty} \left[a_{n+2}(n+1) - a_n \left(n(n-1) + 2n - \alpha\right)\right] x^n = 0.$$

this gives:

$$a_{n+2} = \left(\frac{n(n+1) - \alpha}{(n+2)(n+1)}\right) a_n$$

which has an *odd and even series*. However, since the ratio tend to 1 as $n \to \infty$, we would **want to terminate the series** ($x = \cos(\theta), |x| \leq 1$ still explodes at $x = \pm 1$) . Therefore, we needed:

$$\alpha = n(n+1) = l(l+1)$$

to **terminate the series at $n = l$-th term**, for $l = 0, 1, 2, 3, ...$

***Example*: Exmaples of Legendre Polynomials**

Using the generating formula:

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

we have some examples being

$$\begin{cases} P_0 = 1 \\ P_1 = x \\ P_2 = \frac{1}{2}(3x^2 - 1) \\ P_3 = \frac{1}{2}(5x^3 - 3x) \\ ... \end{cases}$$

recall that $x = \cos(\theta)$
For the *associated Legendre polynomials*, we have the Rodriguez's Formula:

$$P_l^m(x) = (-1)^m (1 - x^2)^{\frac{m}{2}} \left(\frac{d}{dx}\right)^m P_l(x)$$

with some examples of:

$$\begin{cases} P_0^0 = 1 & P_1^0 = \cos(\theta) \\ P_1^0 = x = \cos(\theta) & P_1^1 = -\sin(\theta) \\ P_2^0 = \frac{1}{2}(3x^2 - 1) = \frac{1}{2}(3\cos^2(\theta) - 1) & P_2^1 = 3\sin(\theta)\cos(\theta), ... \\ ... \end{cases}$$

for having $m = 0, \pm 1, \pm 2, ... \pm l$. As it basically alternates between all combinations of cosine and sine, $P_l^m(x)$ turns out to be a **complete set of functions**.

***Example*: Examples of Spherical Harmonics**

For a *normalized Spherical Harmonics*, we have:

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

some sample terms look like:

$$\begin{cases} Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} & \text{s-orbital, no angular dep.} \\ Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos(\theta) & \text{p-x orbital} \\ Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin(\theta) e^{\pm i\varphi} & \text{p-y and p-z orbital} \\ \dots \end{cases}$$

6.3 Radial Equation

Now, we have solved the angular part. We still needed:

$$\phi = R(r) Y_l^m(\theta, \varphi)$$

hence we needed the radial part:

$$\begin{aligned} \frac{1}{R}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] &= l(l+1) \\ \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] R &= l(l+1) R. \end{aligned}$$

since we know that $\alpha = l(l+1)$ from the angular part.

Theorem 6.3: Solution to the Radial Equation

In short, we cannot proceed far **without knowing the expression for $V(r)$**. We attempt to simplify the equation to:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] u &= Eu \\ -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + V_{\text{eff}} u &= Eu. \end{aligned}$$

for:

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

for the term in the equation:

- $-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}$ *changes as distance between particle changes*, which is the vibration term
- $\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$ changes as the *rotation term of $Y_l^m(\theta, \varphi)$ change*. Later, you will see that this gives the rotation term.

6.4 Infinite Spherical Well

One case that we can apply the previous eqaution would be this case, where:

$$\begin{cases} V(r) = 0, & r \leq a \\ V(r) = \infty, & r > a \end{cases}$$

and in this case, the **radial equation can be solved**, and we will obtain a full answer.

Reminder:

The Schrodinger Equation separeted into $R(r), Y(\theta\varphi)$ would look like

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

*and the **angular solution was completely general such that**:*

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

*. Only requiring contiguity of angles. So all we need to solve is the **radial equation**.*

Theorem 6.4: Solution to Infinite Spherical Well

The radial part has the solution:

$$R(r) = A_{n,l}\, j_l(k_{n,l}r)$$

for:

- j_l being the l-th spherical Bessel Function
- $k_{n,l}a = \beta_{n,l}$, for $\beta_{n,l}$ being the **n-th zero of the l-th Spherical Bessel Equation**.

Then, in total, we just have:

$$\psi_{n,l,m}(r,\theta,\varphi) = A_{nl}j_l(k_{nl}r)\,Y_l^m(\theta,\varphi)$$

for Y_l^m already contains the variable coefficient:

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

Proof. Consider the $R(r)$ ODE:

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

$$\frac{d^2u}{dr^2}=\left[\frac{l\left(l+1\right)}{r^2}-k^2\right]u.$$

for having:

- $u(r)=rR(r)$
- $V(r\leq a)=0$
- and $k=\sqrt{\frac{2mE}{\hbar^2}}$ for $E\geq 0$

Now, since we have infinite well outside, we need:

$$R(a)=0$$

When $l=0$, this equation is easy to solve:

$$\frac{d^2u}{dr^2}=-k^2u$$

then the solution is just:

$$u(r)=A\sin\left(kr\right)+B\cos\left(kr\right)$$

this means that we have:

$$R(r)=A\frac{\sin\left(kr\right)}{r}+B\frac{\cos\left(kr\right)}{r}$$

hence, **if we needed** $0\leq r\leq a$, then for the solution not to blow up *at origin*, we needed $B=0$ (if we only needed $0<r$, then both solutions are needed). The, using $R(a)=0$, we get that:

$$k_n=\frac{n\pi}{a},\quad n=1,2,3...$$

and so that:

$$R_{n,l=0}(r)=A_n\frac{\sin\left(k_nr\right)}{r},\quad E_{n,l=0}=\frac{\hbar^2}{2m}k^2=\frac{n^2\pi^2\hbar^2}{2ma^2}$$

Now, for a **general** l, we have:

$$\frac{d^2u}{dr^2}=\left[\frac{l\left(l+1\right)}{r^2}-k^2\right]u$$

then the solution is:

$$u(r)=Arj_l\left(kr\right)+Br\eta_l\left(kr\right)$$

for:

- $j_r(x)$ is the *spherical Bessel function of order l*

- $n_l(x)$ is the *spherical Neumman function of order l*

and the above two functions are related to **ordinary Bessel Functions** $J_n(x), Y_n(x)$ by:

$$j_n(x) = \sqrt{\frac{\pi}{2x}} J_{n+\frac{1}{2}}(x)$$
$$\eta_n(x) = \sqrt{\frac{\pi}{2x}} Y_{n+\frac{1}{2}}(x).$$

additionally, they can **also be generated using Rayleigh's Formula**:

$$j_n(x) = (-x)^n \left(\frac{1}{x}\frac{d}{dx}\right)^n \frac{\sin(x)}{x}$$
$$\eta_n(x) = -(-x)^n \left(\frac{1}{x}\frac{d}{dx}\right)^n \frac{\cos(x)}{x}.$$

However, we know that the **Neumann Spherical function blows up at** $r = 0$, therefore, since we had $0 \leq r \leq a$ to solve for, we have only the j_l term left, and that:

$$j_l(ka) = 0$$

so I get:

$$k = \frac{\beta_{nl}}{a}, \quad n = 1, 2, 3...$$

for β_{nl} being the **n-th zero of the l-th order**.

Finally, putting everything together:

$$\psi_{nlm} = A_{nl} j_l(k_{nl} r) Y_l^m(\theta, \varphi)$$

for Y_l^m already containing its *coefficient of depending on l, m* □

Note:

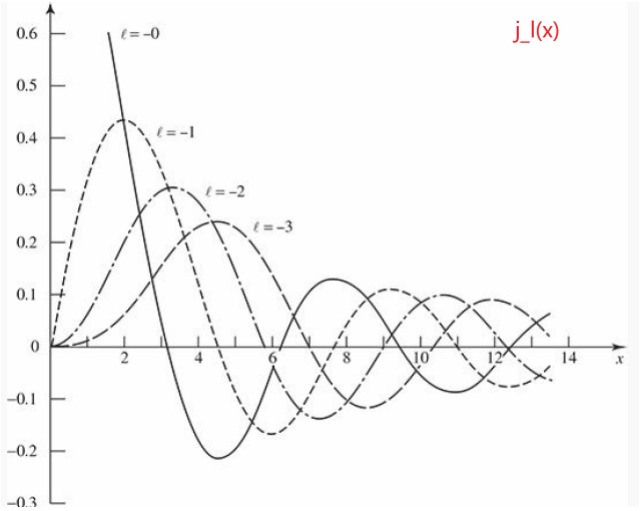
If we are solving for the region $0 < r \leq a$, then we would have also needed to have the η_l equation included as well.

***Example*: Examples of Using Rayleigh's Formulas**

Using the *Rayleigh's Formula*, we can compute some spherical Bessel functions for example:

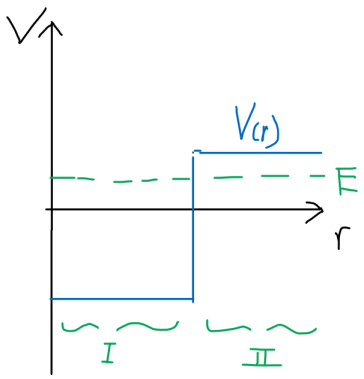
$$j_0(x) = \frac{\sin(x)}{x}$$
$$j_1(x) = (-x)\frac{1}{x}\frac{d}{dx}\left(\frac{\sin(x)}{x}\right) = \frac{\sin(x)}{x^2} - \frac{\cos(x)}{x}$$
$$j_2(x) = x^2\left(\frac{1}{x}\frac{d}{dx}\right)\left(\frac{x\cos(x) - \sin(x)}{x^3}\right)$$
$$= \frac{3\sin(x - 3x\cos(x) - x^2\sin(x))}{x^3}.$$

Graphically, those *Spherical Bessel Functions look like:*



which shows that they are also *oscillatory in nature*.

In general, if we have some more complicated situation like:



then the idea would be:

1. solve the radial equation in the **two regions separately**
2. match the boundary terms, being:

$$\psi_I(a) = \psi_{II}(a)$$
$$\frac{\partial \psi_I}{\partial r} = \frac{\partial \psi_{II}}{\partial r}.$$

6.5 Rotation of Diatomic Molecule

Now, consider the potential energy of a **diatomic molecule**:

$$V(r) = \frac{1}{2}\bar{k}\,(r - r_{eq})^2$$

Reminder:

The simple harmonic oscillation that we dealt with was:

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

and the solutions gave:

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

Now, we are considering the equation:

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

$$V(r) = \frac{1}{2}\bar{k}\,(r - r_{eq})^2\,.$$

You shall soon see that **the E_{rot} will come out from the l term**.

First, to simplify the problem, we consider a **rigid rotor**, by having:

$$r \to r_{eq}, \quad \bar{k} \to \infty$$

then we have essentially:

$$R(r) = R\,(r_{eq}) = \text{constant}$$

hence that:

$$\frac{\hbar^2}{2\mu r_{eq}^2}l\,(l+1)\,R\,(r_{eq}) = ER\,(r_{eq})$$

$$E_l = \frac{l\,(l+1)\,\hbar^2}{2\mu r_{eq}^2}.$$

notice that we are now using *reduced mass* μ because we have **shifted coordinate into** $V(r) = \frac{1}{2}\bar{k}\,(r - r_{eq})^2$.

Additionally, we know that:

$$\begin{cases} \mu r_{eq}^2 = I & \text{Moment of Inertia} \\ B = \frac{\hbar^2}{2\mu r_{eq}^2} \end{cases}$$

then we nicely obtain:

$$E_l = Bl\,(l+1)$$
$$E_J = BJ\,(J+1) \equiv E_{\text{rot}}.$$

for $l = J = 0, 1, 2, 3...$ being the **rotational modes w.r.t the term $Y_l^m = Y_J^m$ term**.

***Example*: HCl atom**

For HCL, you will have:

$$B = 10.6cm^{-1} \rightarrow E_{\text{rot}}$$

for vibrational energy, it is in a **much smaller order of magnitude**:

$$\omega = 2990cm^{-1} \rightarrow E_{\text{vib}}$$

Therefore, you will see that:

1. gap between E_{rot} is usually smaller than the gaps between E_{vib} for the first few $J = 0, 1, 2$
2. since E_{rot} increases by $J(J+1)$, the distance between two levels are also increasing

6.6 Hydrogen Atom

Here, we are considering the following:

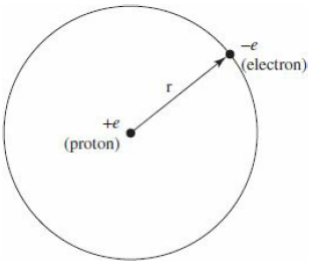


Figure 4.4: The hydrogen atom.

which has:

- nucleus of charge $Z_{\text{eff}} = +1e$
- electron *of interest* of charge $-e$

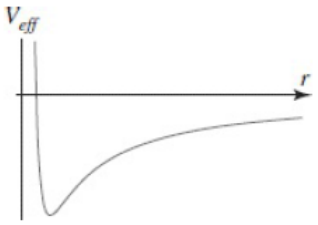
Here, we are **considering the wave function of the electron**, so we have the potential energy form the **Coulomb's Law**:

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

again, we just need to solve for the **radial equation**. In the end, we will see that the idea is similar to a *simple harmonic oscillator to some extent*:

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

so here the V_{eff} actually looks like:



Theorem 6.5: Solution to Hydrogen Atom

The overall solution *with normalization* looks like:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-l-1)!}{2n\,(n+l)!}}e^{-\frac{r}{na_0}}\left(\frac{2r}{na_0}\right)^l\left[L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)\right]Y_l^m\,(\theta,\varphi)$$

where the *spherical harmonics is basically untouched*, and the radial

part is solved to be:

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$$

and $v(\rho)$ being:

$$v(\rho) = L_{n-l-l}^{2l+1}(2\rho)$$

where:

$$\rho = \frac{r}{a_0 n}$$

as defined in corollary 6.2.

The hydrogen atom has the following **quantum numbers**:

1. the upper level is $n = 1, 2, 3...$
2. then, we have $l = 0, 1, 2, ...n-1$ because $j_{\min} = 0, j + l + 1 = n$
3. then finally $m = 0, \pm 1, \pm 2, ... \pm l_{\max}$

And the **eigen-energies** are as follows:

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \quad n = 1, 2, 3...$$

where if we take E_1, we can calculate it to be:

$$E_1 = -13.6\text{eV}$$

Proof. First, tidying up the equations:

$$k \equiv \frac{\sqrt{-2m_e E}}{\hbar}$$

since we are only looking at **bounded states**. Introducing also:

$$\rho \equiv kr, \rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 k}$$

then we get:

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right] u$$

Now, we examine the **asymptotic case**:

(*case 1*): Consider $\rho \to \infty$, i.e. we are very far form the nucleus, then:

$$\frac{d^2 u}{d\rho^2} = u$$

and the solution is:

$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

for **not blowing up**, we have $B = 0$. Hence:

$$u(\rho) = Ae^{-\rho}$$

(*case 2*): Consider $\rho \to 0$, which means we are going close to the nucleus, then:

$$\frac{d^2u}{d\rho^2} = \frac{l\,(l+1)}{\rho^2}u$$

then we get:

$$u(\rho) = C\rho^{l+1} + D\rho^{-l}$$

and for not blowing up at $\rho \to 0$, we have:

$$u(\rho) = C\rho^{l+1}$$

Now, we solve for the **general case**, with the Ansatz that:

$$u\,(\rho) = \rho^{l+1}e^{-\rho}P(\rho)$$

for a **polynomial $P(\rho)$ attached**. Then, the aim is to solve the equation

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l\,(l+1)}{\rho^2}\right]u$$

so we first **manually compute**:

$$\frac{du}{d\rho} = ...$$
$$\frac{d^2u}{d\rho^2} = ...$$

(detailed steps see textbook page 188)
Substituting them back in, I have:

$$\rho\frac{d^2P}{d\rho^2} + 2\,(l+1-\rho)\,\frac{dP}{d\rho} + [\rho_0 - 2\,(l+1)]\,P = 0. \tag{33}$$

since we said that $P(\rho)$ is a *polynomial*:

$$P(\rho) = v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$$

so this means we need to **determine the coefficients c_j**. To do this we need to first *compute the derivatives in equation (33) above*:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty}(j+1)\,c_{j+1}\rho^j$$
$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j\,(j+1)\,c_{j+1}\rho^{j-1}.$$

where in the second derivative I have renamed $j \to j+1$ so that this would be easier later. Then, **inserting in to equation (33)** and we will get:

$$j\,(j+1)\,c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]\,c_j = 0$$

then we obtained:

$$c_{j+1} = \left[\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right] c_j$$

this means that we have found the polynomial $v(\rho) = P(\rho)$, which means we have found the **radial equation** $u(\rho) = \rho^{l+1}e^{-\rho}P(\rho) = rR(r)$.

Now, notice the generating formula gives us an *infinite series*. Check if any term should be terminated by looking at j **large**:

- when j is large, we have:

  $$c_{j+1} \approx \frac{2}{j+1} c_j$$

  which means that:

  $$c_j \approx \frac{2^j}{j!} c_0$$

  therefore, the polynomial becomes:

  $$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

  this **causes the** $u(\rho)$ **term to be unbounded as** $\rho = kr \to \infty$:

  $$u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

Therefore, the **series must terminate**, and it happens at:

$$\begin{aligned} 2(j_{\max} + l + 1) - \rho_0 &= 0 \\ 2n - \rho_0 &= 0. \end{aligned}$$

for $n \equiv j_{\max} + l + 1$, and it goes from $1, 2, 3...$ since the minimum of $l = 0, 1, 2, 3..$ is 0 (and so is j).

Note:

It turns out that there is actually a *formula* for:

$$\begin{aligned} v(\rho) &= \sum_{j=0}^{j_{\max}} c_j \rho^j \\ c_{j+1} &= \left[\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right] c_j. \end{aligned}$$

which is called **Laguerre Polynomials** :

$$v(\rho) = L_{n-l-l}^{2l+1}(2\rho)$$

up to some *normalization constant*

Now, this essentially **decided the solution and all the quantum numbers because**:

1. the upper level is $n = 1, 2, 3...$
2. then, we have $l = 0, 1, 2, ...n-1$ because $j_{\min} = 0, j + l + 1 = n$
3. then finally $m = 0, \pm 1, \pm 2, ... \pm l_{\max}$

Lastly, **don't forget to solve for the eigen-energies**. Since we know ρ_0 contains the energy term k:

$$\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 k}$$

and we know that:

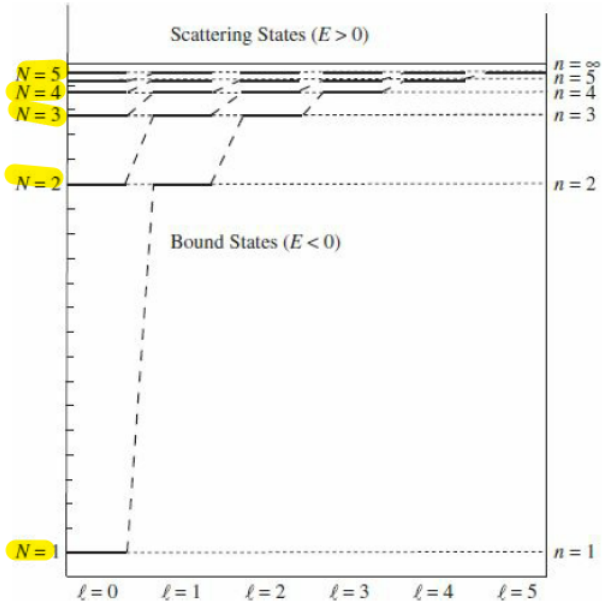
$$k = \sqrt{\frac{-2mE}{\hbar^2}}$$

so we arrive at the **Bohr Formula** :

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \quad n = 1, 2, 3...$$

where notice that E_n **does not depend on** l, m because we are dealing with single-electron system. For multi-electron, we will have $E_{n,l}$. □

Graphically, the energies will look like:



where the *degeneracy coming from l not affecting the E_n*

Corollary 6.2: Bohr Radius

Let us redefine:

$$k = \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}\right)\frac{1}{n} \equiv \frac{1}{a_0 n}$$

so that:

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10}\text{m}$$

which is known as the **Bohr Radius**, so that:

$$\rho = \frac{r}{a_0 n}$$

Corollary 6.3: Generalized Version

In general, if we have:

- single electron but nucleus of charge Z_{eff}, then we just get

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{Z_{\text{eff}}e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \quad n = 1, 2, 3...$$

  and probably we needed $m \to \mu$

- if we are in a different medium than vacuum, then we need to update ϵ_0

***Example*: First Few States of Hydrogen Atom**

First, we can consider the **ground state where $n = 1$**, then we have $l = 0, m = 0$ as the only possibility. We knew that:

$$v(\rho) = \sum_{j=0}^{j_{\max}} c_j \rho^j$$

$$c_{j+1} = \left[\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)}\right] c_j.$$

Therefore:

$$v(\rho) = c_0\rho^0 = c_0$$

then since:

$$R_{nl} = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho), \ \rho = \frac{r}{a_0 n}$$

we get:

$$R_{n=1,l=0}(r) = \frac{c_0}{a_0}e^{-r/a_0}$$

meanwhile, since $Y_0^0 = \frac{1}{4\pi}$, we have:

$$\Psi_{100}(r, \theta, \varphi) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

which basically looks like a **1s orbital**.

For the **second state**, we have $n = 2$, and now:

$$\begin{cases} l = 0, m = 0; & \text{2s orbital} \\ l = 1, m = -1, 0, 1; & \text{2p orbitals} \end{cases}$$

then we would need to compute:

$$v(\rho) = \sum_{j=0}^{j_{\max}} c_j \rho^j$$
$$c_{j+1} = \left[\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right] c_j.$$

1. first, look at $l = 0$, then we have:

$$\begin{cases} c_1 = -c_0 \\ c_2 = 0 \end{cases}$$

   then we get:

$$R_{20}(r) = \frac{c_0}{2a_0} \left(1 - \frac{r}{2a_0} \right) e^{-r/2a_0}$$

2. similarly, we can compute the other R with $n = 1, l = 1$:

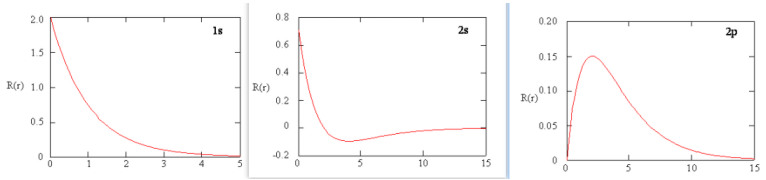
$$R_{21} = \frac{c_0}{4a_0^2} r e^{-r/2a_0}$$

   with the **states/orbitals being**:

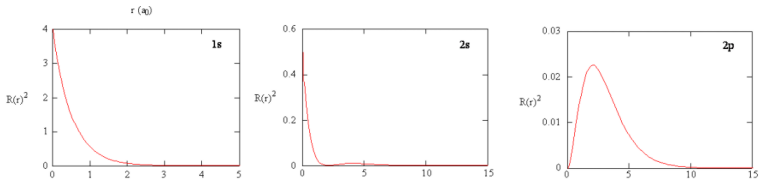
$$\Psi_{2p} = R_{21}(r) Y_1^{m=0,\pm 1}$$

   which means we have 3 orbitals.

Graphically, the **radial distribution** look like:

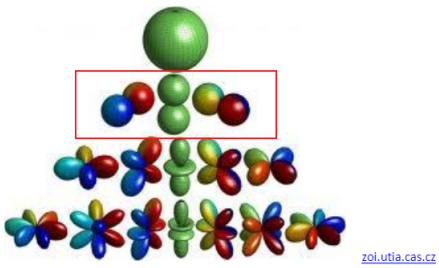


and the magnitude:

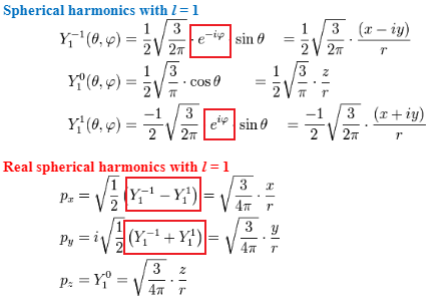


Last but not least, one other thing to note is that the **actual shapes of the**

three orbitals look like:



Yet some of them **actually comes from linear combination of the wave functions in the same** n, l



Corollary 6.4: Total Number of Orbitals

If we want to find out how many orbitals there are per n, we know that, **for each** n:

$$\begin{cases} \text{n values of } l \\ \text{each } l \text{ has } 2l+1 \text{ values of } m \end{cases}$$

So we have:

$$d(n) = \text{number of orbitals} = \sum_{l=0}^{l=n-1} (2l+1) = n^2$$

one way to compute the above is to consider:

$$d(n+1) = d(n) + 2n + 1$$

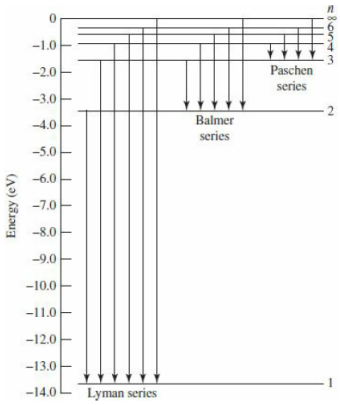
so the different is in n, hence let:

$$d(n) = an^2 + bn + c$$

and you will find out that $b = c = 0, a = 1$. So there are in total n^2 **number of orbitals/states per** n.

6.6.1 Spectrum of Hydrogen

Another related topic is the spectrum, which basically involves an electron **transitioning** from a higher state Ψ_{nlm} to a lower energy state, and emitting energy.



where **some series you need to know**:

1. Lyman Series is in UV
2. Balmer Series is in Visible
3. Pashen Series is in IR

Then we get:

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

for a **hydrogen atom**.
Using planks formula of $E_\gamma = h\nu$, we can get:

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

where we have the **Rydberg's Constant** :

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

6.7 Angular Momentum

Classically, we know that $\vec{L} = \vec{r} \times \vec{p}$. Specifically:

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x. \end{aligned}$$

In quantum mechanics, we need to think about **converting** $x \to \hat{x}$, and $p_x \to \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, and etc. So in **quantum mechanics**:

$$\begin{aligned} \hat{L}_x &= y\hat{p}_z - z\hat{p}_y \\ \hat{L}_y &= z\hat{p}_x - x\hat{p}_z \\ \hat{L}_z &= x\hat{p}_y - y\hat{p}_x. \end{aligned}$$

Then we have the **following results**.

Corollary 6.5: Angular Momentum Commutator

If we consider $\left[\hat{L}_x, \hat{L}_y\right]$, then we have:

$$\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= [y\hat{p}_z - z\hat{p}_y, z\hat{p}_x - x\hat{p}_z] \\ &= [y\hat{p}_z, z\hat{p}_x] - [y\hat{p}_z, x\hat{p}_z] - [z\hat{p}_y, z\hat{p}_x] + [z\hat{p}_y, x\hat{p}_z] \\ &= [y\hat{p}_z, z\hat{p}_x] + [z\hat{p}_y, x\hat{p}_z] \\ &= i\hbar\left(x\hat{p}_y - y\hat{p}_x\right) \\ &= i\hbar\hat{L}_z. \end{aligned}$$

And this can be **generalized** so that:

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar\hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar\hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar\hat{L}_y. \end{aligned}$$

which also means that there are **uncertainty principles for each two**, which can be easily computed as well:

$$\begin{aligned} \sigma_{L_x}^2\sigma_{L_y}^2 &\geq \left(\frac{1}{2i}\langle[L_x, L_y]\rangle\right) \\ &\geq \left(\frac{1}{2i}\langle i\hbar L_z\rangle\right) \\ \sigma_{L_x}\sigma_{L_y} &\geq \frac{\hbar}{2}\left|\langle L_z\rangle\right|. \end{aligned}$$

It would therefore be futile to look for states that are simultaneously eigenfunctions of L_x and L_y.

However, there is a way to do something with the total angular momentum:

$$\hat{L}^2 = L_x^2 + L_y^2 + L_z^2$$

Corollary 6.6: Total Angular Momentum Commutator

The total angular momentum does **commute with** $\hat{L}_x, \hat{L}_y, \hat{L}_z$:

$$\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}^2, \hat{L}_y\right] = \left[\hat{L}^2, \hat{L}_z\right] = 0.$$

So is $\hat{L}^2$ **compatible with each component of** L, and we can hope to find **simultaneous eigenstates of** $\hat{L}^2$ **and (say)** L_z

Proof for Corollary 6.6. Compute:

$$\begin{aligned}
\left[\hat{L}^2, \hat{L}_x\right] &= \left[\hat{L}_x^2, \hat{L}_x\right] + \left[\hat{L}_y^2, \hat{L}_x\right] + \left[\hat{L}_z^2, \hat{L}_x\right] \\
&= \hat{L}_y \left[\hat{L}_y, \hat{L}_x\right] + \left[\hat{L}_y, \hat{L}_x\right] \hat{L}_y + \hat{L}_z \left[\hat{L}_z, \hat{L}_x\right] + \left[\hat{L}_z, \hat{L}_x\right] \hat{L}_z \\
&= \hat{L}_y \left(-i\hbar \hat{L}_z\right) + \left(-i\hbar \hat{L}_z\right) \hat{L}_y + \hat{L}_z \left(i\hbar \hat{L}_y\right) + \left(i\hbar \hat{L}_y\right) \hat{L}_z \\
&= 0.
\end{aligned}$$

□

6.7.1 Eigenvalues of Angular Momentum

Since angular momentum are **real observables**, we expect (due to L^2, L_z commutes):

$$\hat{L}^2 f = \lambda f, \quad \hat{L}_z f = \mu f$$

where:

- because the **operators commute**, they have the same eigenfunction

We would like to find out the **eigenvalue and eigenfunction** (next section) of the equation.

Definition 6.1: Laddder Operators for Angular Momentum

Usually this approach would make algebra easier. Consider:

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y, \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

being the **ladder operators**.

Theorem 6.6: Eigenvalues for Angualar Momentum

By thinking of the *impact of ladder operators*

$$\hat{L}_+ f_t = 0, \quad \hat{L}_- f_b = 0$$

and that using the *original eigen-equation*

$$\hat{L}_z f_t \equiv l\hbar f_t, \quad \hat{L}^2 f_t = \lambda f_t$$

$$\hat{L}_z f_b \equiv \bar{l}\hbar f_b, \quad \hat{L}^2 f_b = \lambda f_b$$

We obtained:

$$\hat{L}^2 f_t = \hbar^2 l\,(l+1)\, f_t, \quad \hat{L}_z f_t = \hbar l f_t$$
$$\hat{L}^2 f_b = \hbar^2 \bar{l}\,(\bar{l}-1)\, f_b, \quad \hat{L}_z f_b = \hbar \bar{l} f_b$$

since eigenvalues λ **stays unchanged**, we get that $\bar{l} = -l$. In total, this means that the **eigenvalues/quantum number** for $\hat{L}_z$ would be:

$$\mu = -l\hbar, (-l+1)\,\hbar, ..., (l-1)\,\hbar, l\hbar$$

for l *either integer or half integer*. Therefore, in general, we just *substitute in the eigenvalues into the original equation*:

$$\hat{L}^2 f_l^m = \hbar^2 l\,(l+1)\, f_l^m$$
$$\hat{L}_z f_l^m = \hbar m f_l^m.$$

Proof. Let

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y, \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

Then some **useful quantities** will be:

$$\begin{aligned}\left[\hat{L}_z, \hat{L}_\pm\right] &= i\hbar\hat{L}_y \pm \hbar\hat{L}_x \\ &= \pm\hbar\left(\hat{L}_x \pm i\hat{L}_y\right) \\ &= \pm\hbar\hat{L}_\pm.\end{aligned}$$

and that:

$$\begin{aligned}\left[\hat{L}^2, \hat{L}_\pm\right] &= \left[\hat{L}^2, \hat{L}_x\right] \pm i\left[\hat{L}^2, \hat{L}_y\right] \\ &= 0.\end{aligned}$$

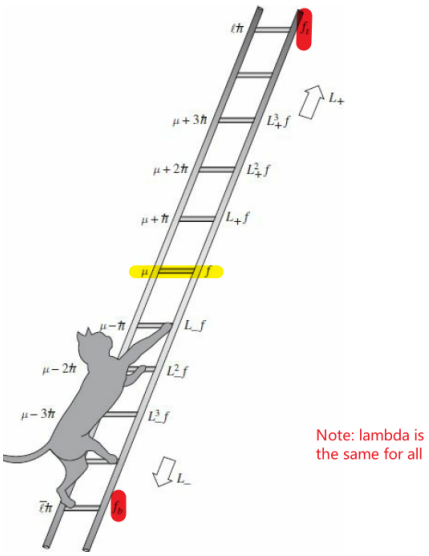
so that they *commute*.
now, going back to the equation can consider the *typical use of a ladder operator*:

$$\begin{aligned}\hat{L}^2\left(\hat{L}_\pm f\right) &= \hat{L}_\pm\left(\hat{L}^2 f\right) \\ &= \lambda\left(\hat{L}_\pm f\right).\end{aligned}$$

which means that **applying ladder operator to f does not change λ**.
However, consider:

$$\begin{aligned}\hat{L}_z\left(\hat{L}_\pm f\right) &= \left(\hat{L}_z\hat{L}_\pm - \hat{L}_\pm\hat{L}_z + \hat{L}_\pm\hat{L}_z\right) f \\ &= \left(\pm\hbar\hat{L}_\pm + \hat{L}_\pm\hat{L}_z\right) f \\ &= (\mu \pm \hbar)\left(\hat{L}_\pm f\right).\end{aligned}$$

which means that **applying ladder operator to f does change μ, up or down by $\hbar$**.



But this process of raising and lowering cannot go on forever: Eventually were

going to reach a state for which the *z-component exceeds the total*, and that cannot be.

Therefore, we propose that there is a **upper bound f_t and a lower bound f_b**, so that:

$$\hat{L}_+ f_t = 0, \quad \hat{L}_- f_b = 0$$

which means that:

- the next level of ladder will have *eigenvalue of* 0, meaning non-existent angular momentum

and that:

$$\hat{L}_z f_t \equiv l\hbar f_t, \quad \hat{L}^2 f_t = \lambda f_t$$

essentially $l\hbar = \mu$, l represents the **maximum number of ladders** we can climb.

Before computing what the lowest/highest eigenvalue is, some **helpful quantity**:

$$\begin{aligned}
\hat{L}_\pm \hat{L}_\mp &= \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x \mp \hat{L}_y\right) \\
&= \hat{L}_x^2 + \hat{L}_y^2 \pm i\hat{L}_x\hat{L}_y \mp \hat{L}_x\hat{L}_y \\
&= \hat{L}_x^2 + \hat{L}_y^2 \mp i\left(i\hbar\hat{L}_z\right) \\
&= \hat{L}_x^2\hat{L}_y^2 \pm \hbar\hat{L}_z.
\end{aligned}$$

so that:

$$\hat{L}^2 = \hat{L}_\pm \hat{L}_\mp \mp \hbar\hat{L}_z + \hat{L}_z^2$$

This is useful because, **now finding the top/bottom eigenvalues**:

$$\begin{aligned}
\hat{L}^2 f_t &= \left(\hat{L}_\pm \hat{L}_\mp + \hat{L}_z^2 \mp \hbar\hat{L}_z\right) f_t \\
&= \left(\hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar\hat{L}_z\right) f_t \\
&= \hbar^2\left(l^2 + l\right) f_t.
\end{aligned}$$

since we know that:

$$\begin{cases}
\hat{L}_z f_t = \hbar l f_t \\
\hat{L}_z^2 f_t = \hbar^2 l^2 f_t \\
\hat{L}_+ f_t = 0
\end{cases}$$

Therefore, we obtained that the **top rung has eigenvalue**:

$$\hat{L}^2 f_t = \hbar^2 l\left(l+1\right) f_t, \quad \hat{L}_z f_t = \hbar l f_t$$

so the **maximum eigenvalue/quantum number of $\hat{L}_z$ is $l = m_{max}$**, which is the same as what we knew before.

Similarly, compute the bottom rung:

$$\hat{L}_z f_b \equiv \bar{l}\hbar f_b, \quad \hat{L}_- f_b = 0$$

then, doing the same thing

$$\begin{aligned}\hat{L}^2 f_b &= \left(\hat{L}_{\pm}\hat{L}_{\mp} + \hat{L}_z^2 \mp \hbar \hat{L}_z\right) f_b \\ &= \left(\hat{L}_{+}\hat{L}_{-} + \hat{L}_z^2 - \hbar \hat{L}_z\right) f_b \\ &= \hbar^2 \bar{l}\left(\bar{l}-1\right) f_b.\end{aligned}$$

However, recall that *climbing the ladder does not change eigenvalue for* λ. Therefore, it means:

$$l\left(l+1\right) = \bar{l}\left(\bar{l}-1\right)$$

which means:

$$\begin{cases}\bar{l} = l+1 & \text{cannot be} \\ \bar{l} = -l\end{cases}$$

Therefore, this means that the **bottom ladder has quantum number** $-l$.

In total, this means that the **eigenvalues/quantum number** for $\hat{L}_z$ would be:

$$\mu = -l\hbar, \left(-l+1\right)\hbar, ..., \left(l-1\right)\hbar, l\hbar$$

and recall that the *quantum number for* m *was that:*

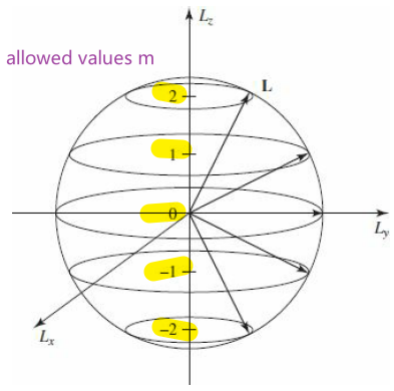
$$m = -l, -1+1, ..., 0, ...l-1, l$$

Since it goes from $-l$ to l in an **integer amount of** (N) **steps**, which means that:

$$l = -l + N, \;\; l = \frac{N}{2}$$

so this means that l **is either an integer or a half-integer**. □

If you want to interpret it **graphically**, you need to be cautious:



where we see:

- the **"magnitude"** would be $\left\langle L^2 \right\rangle = l\left(l+1\right)\hbar^2$, e.g. here $l = 2$
- the allowed values for L_z would have, e.g. $m = \{-2, -1, 0, 1, 2\}$

- the **"magnitude" for L_z** would be $\langle L_z \rangle = m\hbar$
- **magnitude of L is always larger than L_z**. This is because of the fact that *due to uncertainty principle, you cannot have a determinant angular momentum vector* (i.e. you cannot aim your vector to be exactly at the z-axis, otherwise you know all three components exactly).

Corollary 6.7: Hermitian of Ladder Operators

It turns out that:

$$\left(\hat{L}_+\right)^\dagger = \hat{L}_-$$
$$\left(\hat{L}_-\right)^\dagger = \hat{L}_+$$

since we can just compute:

$$\begin{aligned}\left(\hat{L}_+\right)^\dagger &= \left(\hat{L}_x + i\hat{L}_y\right)^\dagger \\ &= \hat{L}_x - i\hat{L}_y \\ &= \hat{L}_-.\end{aligned}$$

***Example*: Intermediate Levels for Ladder Operators**

Since ladder operators raise or lower the eigenvalue m by one unit, consider:

$$\hat{L}_+ f_l^m = \left(A_l^{(+)m}\right) f_l^m, \quad \hat{L}_- f_l^m = \left(A_l^{(-)m}\right) f_l^{m-1}$$

but since we *know*:

$$\hat{L}^2 f_l^m = \left(\hat{L}_\pm \hat{L}_\mp + \hat{L}_z^2 \mp \hbar \hat{L}_z\right) f_l^m.$$

trying different combinations give:

$$\begin{aligned}l\left(l+1\right)\hbar^2 &= A_l^{(+)m-1} A_l^{(-)m} + \left(m^2 - m\right)\hbar^2 \\ l\left(l+1\right)\hbar^2 &= A_l^{(-)m+1} A_l^{(+)m} + \left(m^2 + m\right)\hbar^2.\end{aligned}$$

and because **ladder operators are "each other hermitian"**, we know:

$$\begin{aligned}\langle f_l^{m+1} | \hat{L}_+ | f_l^m \rangle &= \langle \hat{L}_- f_l^{m+1} | f_l^m \rangle \\ A_l^{(+)m} &= \left(A_l^{(-)m+1}\right)^*.\end{aligned}$$

similarly, you will also get:

$$A_l^{(-)m} = \left(A_l^{(+)m-1}\right)^*$$

plugin in those back, we will get:

$$\left|A_l^{(-)m}\right| = \hbar\sqrt{l(l+1) - m(m-1)} = \hbar\sqrt{(l+m)\,(l-m+1)}$$
$$\left|A_l^{(+)m}\right| = \hbar\sqrt{l(l+1) - m(m+1)} = \hbar\sqrt{(l-m)\,(l+m+1)}$$

.

and **notice that**:

- at the top, we have $m = l$, so $\left|A_l^{(+)m}\right| = 0$
- at the bottom, we have $m = -l$, so $\left|A_l^{(-)m}\right| = 0$

6.7.2 Eigenfunctions of Angular Momentum

This part is skipped in class due to limited time, but the idea is as follows:

1. rewrite the angular momentum operators **spherical coordinates**:

$$\hat{L} = -i\hbar\left(r \times \nabla\right)$$

   and use the *spherical coordinate* to do the same thing with $\hat{L}_x, \hat{L}_y$

2. then, we compute $\hat{L}^2$ as well as the $\hat{L}_\pm$, and put it back into our eigenequation:

$$\hat{L}^2 f_l^m = -\hbar^2\left[\frac{1}{\sin\left(\theta\right)}\frac{\partial}{\partial\theta}\left(\sin\left(\theta\right)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\left(\theta\right)}\frac{\partial^2}{\partial\varphi^2}\right] f_l^m = \hbar^2 l\left(l+1\right) f_l^m$$

   with is precisely the **angular equation in spherical coordinate**:

$$\frac{1}{Y}\left[\frac{1}{\sin\left(\theta\right)}\frac{\partial}{\partial\theta}\left(\sin\left(\theta\right)\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\left(\theta\right)}\frac{\partial^2 Y}{\partial\varphi^2}\right] = -\alpha$$

   with the **same eigenvalues as well**.

3. Therefore, we conclude that:

$$f_l^m = Y_l^m, \quad \alpha = l\left(l+1\right)$$

   being the eigenfunctions for angular momentum.

Note:

Some critical formulas that you might find helpful are the **spherical coordinate version** for:

$$\begin{aligned}
\hat{L}_z &= -i\hbar\frac{\partial}{\partial\varphi} \\
\hat{L}_y &= -i\hbar\left(+\cos\left(\varphi\right)\frac{\partial}{\partial\theta} - \sin\left(\varphi\right)\cot\left(\theta\right)\frac{\partial}{\partial\varphi}\right) \\
\hat{L}_x &= -i\hbar\left(-\sin\left(\varphi\right)\frac{\partial}{\partial\theta} - \cos\left(\varphi\right)\cot\left(\theta\right)\frac{\partial}{\partial\varphi}\right).
\end{aligned}$$

6.8 Spin

In short, The algebraic theory of spin is a *carbon copy of the theory of orbital/normal angular momentum*, beginning with the fundamental commutation relations:

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

Therefore, since this is **the same setup as before**, we can just borrow the solutions:

$$\hat{S}^2 |s_m\rangle = \hbar^2 s(s+1) |s_m\rangle$$
$$\hat{S}_z |s_m\rangle = \hbar m |s_m\rangle .$$

where we have basically changed $f_l^m \to |s_m\rangle$, and $l \to s$ representing (fixed) spin quantum number. Additionally:

$$\hat{S}_+ |s_m\rangle = \hbar\sqrt{s(s+1) - m(m+1)}\, |s_{m+1}\rangle$$
$$\hat{S}_- |s_m\rangle = \hbar\sqrt{s(s+1) - m(m-1)}\, |s_{m-1}\rangle .$$

Theorem 6.7: Fixed Spin Quantum Number

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

- π mesons have spin $s = 0$;
- electrons have spin $s = \frac{1}{2}$;
- photons have spin $s = 1$;
- etc.

However, since the equation/solution is the same, $l \equiv s$ can be *any one number of the following for a particle*:

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, ...$$

Therefore, since the spin s **is fixed for a particle**, we just need to consider the m:

$$m = -s, -s+1, ...s-1, s$$

so that the eigenvector (**here is no longer the Spherical Harmonics** Y_l^m **since spin is not a function of** θ, φ) now can be represented simply as:

$$|s_m\rangle$$

6.8.1 Spin 1/2

By far the most important case is $s = \frac{1}{2}$, for this is the spin of the particles that *make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons*.

Since we only have a fixed $l \equiv s = \frac{1}{2}$, I only have **two possible states**:

$$\begin{cases} s = \frac{1}{2}, m = -\frac{1}{2}; & \text{spin down} \\ s = \frac{1}{2}, m = \frac{1}{2}; & \text{spin up} \end{cases}$$

Representing the eigenstates as **eigenvectors**:

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \iff |\frac{1}{2}, \frac{1}{2}\rangle$$

$$\chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \iff |\frac{1}{2}, -\frac{1}{2}\rangle$$

representing spin up and spin down state, respectively. The **rest of the section uses the above two as basis vectors**.

Note:

Later you shall see that, because

$$\hat{S}_z |s_m\rangle = \hbar m |s_m\rangle$$

this means that the **eigenstates we used for basis** can also be interpreted as the **eigenstates for spin in z-direction**

- spin up χ_+ => eigenstate in z-direction
- spin down χ_- => eigenstate in z-direction

Theorem 6.8: Spin Matrices

Using the basis, we have the **general state** of a spin-1/2 particle being:

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

for $|a|^2 + |b|^2 = 1$ if normalized. We can have **all the operators we**

had before become matrices:

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$
$$\hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$
$$\hat{S}_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$
$$\hat{S}_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$
$$\hat{S}_y = -\frac{i}{2}\left(\hat{S}_+ - \hat{S}_-\right) = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$
$$\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}.$$

notice that $\hat{S}^2$ is actually just an **identity matrix**.

Note:

Notice that $\hat{S}^2, \hat{S}_x, \hat{S}_y, \hat{S}_z$ are **Hermitian**, which makes sense as they represent observables.

Proof. In summary, you would just need to utilize the eigenequations we have established.

- first, we can *prove the $\hat{S}^2$ matrix*. We now that:

  $$\hat{S}^2 |s_m\rangle = \hbar^2 s(s+1) |s_m\rangle$$

  since the eigenvectors are χ_+, χ_-, we know that:

  $$\hat{S}^2 \chi_\pm = \frac{1}{2} \cdot \frac{3}{2}\hbar^2 \chi_\pm = \frac{3}{4}\chi_\pm.$$

  Therefore, we know that:

  $$\hat{S}^2 \chi_+ = \frac{3}{4}\hbar^2 \chi_+$$
  $$\hat{S}^2 \chi_- = \frac{3}{4}\hbar^2 \chi_-.$$

  Since the vector $\chi_\pm$ is 2 dimension, then let:

  $$\hat{S}^2 = \begin{bmatrix} c & d \\ e & f \end{bmatrix}$$

  Substituting this *back into our eigenequation*, and we get:

  $$\begin{bmatrix} c & d \\ e & f \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$
  $$\begin{bmatrix} c \\ e \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 \\ 0 \end{bmatrix}.$$

which solved c, e. Doing the same for the other eigenequation:

$$\begin{bmatrix} c & d \\ e & f \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$
$$\begin{bmatrix} d \\ f \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

which solved d, f. Therefore, putting them back:

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

- Next, *for* $\hat{S}_z$, we do the same. Since we know:

$$\hat{S}_z\chi_+ = \frac{\hbar}{2}\chi_+$$
$$\hat{S}_z\chi_- = -\frac{\hbar}{2}\chi_-.$$

Using the same trick of letting:

$$\hat{S}_z = \begin{bmatrix} c & d \\ e & f \end{bmatrix}$$

we get:

$$\begin{bmatrix} c \\ e \end{bmatrix} = \frac{\hbar}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

which solved c, e, and:

$$\begin{bmatrix} d \\ f \end{bmatrix} = -\frac{\hbar}{2} \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

which solved d, f. Putting them back:

$$\hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

- then, *find* $\hat{S}_+, \hat{S}_-$ first. We use the equation:

$$\hat{S}_+ |s_m\rangle = \hbar\sqrt{s(s+1) - m(m+1)}\,|s_{m+1}\rangle$$
$$\hat{S}_- |s_m\rangle = \hbar\sqrt{s(s+1) - m(m-1)}\,|s_{m-1}\rangle.$$

if $s = \frac{1}{2}, m = \frac{1}{2}$, we have χ_+, then:

$$\hat{S}_+\chi_+ = 0$$
$$\hat{S}_-\chi_+ = \hbar\chi_-.$$

where we see that the first one **must be zero because** $|s_{m=\frac{3}{2}}\rangle$ **DEN!** similarly:

$$\hat{S}_+\chi_- = \hbar \cdot \chi_+$$
$$\hat{S}_-\chi_- = 0.$$

Again, first solving $\hat{S}_+$:

$$\hat{S}_+ = \begin{bmatrix} c & d \\ e & f \end{bmatrix}$$

skipping some steps, you will get:

$$\hat{S}_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

doing the same trick for $\hat{S}_-$, you will get:

$$\hat{S}_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

- Lastly, *using the aid from above*, I can *compute $\hat{S}_x, \hat{S}_y$ as well*, because I know:

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y$$
$$\hat{S}_- = \hat{S}_x - i\hat{S}_y.$$

which comes from the *definition of ladder operators* ***for*** $\hat{L}^2, \hat{L}_z$. Then, we see that:

$$\begin{cases} \hat{S}_+ + \hat{S}_- = 2\hat{S}_x \\ \hat{S}_+ - \hat{S}_- = 2i\hat{S}_y \end{cases}$$

Therefore, using the *matrices for $\hat{S}_\pm$ from previous part*:

$$\hat{S}_y = -\frac{i}{2}\left(\hat{S}_+ - \hat{S}_-\right) = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$
$$\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}.$$

This finished the proof. □

Corollary 6.8: Pauli Spin Matrices

We know that:

$$\hat{S}_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$
$$\hat{S}_y = -\frac{i}{2}\left(\hat{S}_+ - \hat{S}_-\right) = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$
$$\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}.$$

They **all had a factor of** $\frac{\hbar}{2}$, so we can have:

$$\hat{S}_z = \frac{\hbar}{2}\sigma_z; \quad \hat{S}_y = \frac{\hbar}{2}\sigma_y; \quad \hat{S}_x = \frac{\hbar}{2}\sigma_x.$$

for:

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}; \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \quad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

being the **Pauli Spin Matrices**.

Corollary 6.9: Eigenfunctions and Eigenvalues for Spin Matrices

We knew the eigen-equations are:

$$\hat{S}^2 |s_m\rangle = \hbar^2 s(s+1) |s_m\rangle$$
$$\hat{S}_z |s_m\rangle = \hbar m |s_m\rangle .$$

so for $\hat{S}_z$, with $s = \frac{1}{2}$, this is simply:

$$\begin{cases} |s_{m=1/2}\rangle = \chi_+^{(z)} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, & \text{eigenvalue} = \frac{\hbar}{2} \\ |s_{m=-1/2}\rangle = \chi_-^{(z)} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, & \text{eigenvalue} = -\frac{\hbar}{2} \end{cases}$$

which means that if you **measure $\hat{S}_z$ on a particle in the general state** $\chi = \begin{bmatrix} a \\ b \end{bmatrix}$, you could get $\frac{\hbar}{2}$ with probability $|a|^2$, or $-\frac{\hbar}{2}$ with probability $|b|^2$. Continuing, you will see that: for x-direction:

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \chi_+^{(z)} + \frac{1}{\sqrt{2}} \chi_-^{(z)}$$
$$\chi_-^{(x)} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} = \frac{1}{\sqrt{2}} \chi_+^{(z)} - \frac{1}{\sqrt{2}} \chi_-^{(z)}.$$

which is **different from those of $\hat{S}_z$**.

$$\lambda_+ = \frac{\hbar}{2}; \quad \lambda_- = -\frac{\hbar}{2}$$

which happens to be the *same as that of $\hat{S}_z$*.

Lastly, we can put them together:

$$\begin{aligned} \chi &= a\chi_+^{(z)} + b\chi_-^{(z)} \\ &= \frac{a+b}{\sqrt{2}} \chi_+^{(x)} + \frac{a-b}{\sqrt{2}} \chi_-^{(x)}. \end{aligned}$$

Note:

Because:

$$\hat{S}_z |s_m\rangle = \hbar m |s_m\rangle$$

this means that the **eigenstates we used for basis** can also be interpreted as the **eigenstates for spin in z-direction**

- spin up => z-direction

- spin down => z-direction

Proof. To find the eigenvalue/eigenvector for $\hat{S}_x$, we consider our equation:

$$\hat{S}_x \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \lambda \begin{bmatrix} \alpha \\ \beta \end{bmatrix}.$$

since we know what $\hat{S}_x$ is from the previous theorem, we can compute:

$$\begin{aligned} \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} &= \lambda \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \\ \begin{bmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} &= 0. \end{aligned}$$

for non-trivial solutions, we get:

$$\det \begin{bmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{bmatrix} = 0.$$

so we get two solutions:

$$\lambda_+ = \frac{\hbar}{2}; \quad \lambda_- = -\frac{\hbar}{2}$$

which happens to be the *same as that of* $\hat{S}_z$. However, solving for eigenvectors/states, you will see that:

$$\begin{aligned} \chi_+^{(x)} &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \chi_+^{(z)} + \frac{1}{\sqrt{2}} \chi_-^{(z)} \\ \chi_-^{(x)} &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} = \frac{1}{\sqrt{2}} \chi_+^{(z)} - \frac{1}{\sqrt{2}} \chi_-^{(z)}. \end{aligned}$$

which is **different from those of** $\hat{S}_z$. □

Corollary 6.10: Expectation Values of Spin

We know (y-direction omitted):

$$\begin{aligned} \chi &= a\chi_+^{(z)} + b\chi_-^{(z)} \\ &= \frac{a+b}{\sqrt{2}} \chi_+^{(x)} + \frac{a-b}{\sqrt{2}} \chi_-^{(x)}. \end{aligned}$$

this is perhaps already obvious:

$$\begin{aligned} \left\langle \hat{S}_z \right\rangle &= |a|^2 \frac{\hbar}{2} + |b|^2 \left(-\frac{\hbar}{2} \right) \\ &= \frac{\hbar}{2} (|a|^2 - |b|^2). \end{aligned}$$

where $\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$ are the **eigenvalues for** $\hat{S}_z$.

Another way to solve it would be:

$$\begin{aligned}\left\langle \hat{S}_z \right\rangle &= \langle \chi | \hat{S}_z \chi \rangle \\ &= \begin{bmatrix} a^* & b^* \end{bmatrix} \left(\frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \begin{bmatrix} a \\ b \end{bmatrix} \\ &= \frac{\hbar}{2} \left(|a|^2 - |b|^2 \right).\end{aligned}$$

Similarly, for $\hat{S}_x$, we will have:

$$\begin{aligned}\left\langle \hat{S}_x \right\rangle &= \frac{\hbar}{2} \left(\frac{a+b}{\sqrt{2}} \right)^2 + \left(-\frac{\hbar}{2} \right) \left(\frac{a-b}{\sqrt{2}} \right)^2 \\ &= \frac{\hbar}{2} \frac{|a+b|^2}{2} - \frac{\hbar}{2} \frac{|a-b|^2}{2} \\ &= \frac{\hbar}{2} \left(a^* b + a b^* \right).\end{aligned}$$

the other method is skipped.

Note:

Since the eigenstate basis could also be interpreted as *eigenstates for* $\hat{S}_z$, this also means that from knowing its spin in z-direction, we can **compute the x/y-component from it**

Example

Now *suppose a spin-1/2 particle is in the state*:

$$\chi = \frac{1}{\sqrt{6}} \begin{bmatrix} 1+i \\ 2 \end{bmatrix}$$

Then, if we want to **calculate the expectation values for** $\hat{S}_x, \hat{S}_z$, we can think about:
First, this means:

$$a = \frac{1}{\sqrt{6}}(1+i), \quad b = \frac{2}{\sqrt{6}}$$

so that:

$$\chi = a\chi_+^{(z)} + b\chi_-^{(z)}$$

then everything is straightforward:

$$\left\langle \hat{S}_z \right\rangle = |a|^2 \frac{\hbar}{2} + |b|^2 \left(-\frac{\hbar}{2} \right) = -\frac{\hbar}{6}$$

and:

$$\left\langle \hat{S}_x \right\rangle = \frac{\hbar}{2} \left(a^* b + a b^* \right) = \frac{\hbar}{3}$$

though not covered before, you will also see that:

$$\left\langle \hat{S}_y \right\rangle = -\frac{\hbar}{3}$$

6.8.2 Electron in a Magnetic Field

Theorem 6.9: Magnetic Dipole Moment

A **spinning, charged particle** constitutes a **dipole moment** $\vec{\mu}$, which is:

$$\vec{\mu} = \gamma \hat{S}$$

where:

- γ is the *proportionality constant*, called the *gyromagnetic ratio*
- $\hat{S}$ is the *spin matrix of the particle*, $\hat{S} = \hat{S}_x + \hat{S}_y + \hat{S}_z$

In particular, you will also later see that:

$$\gamma = -\frac{2\mu_B}{\hbar}, \qquad \mu_B = \left| \frac{\hbar e}{2m_e} \right|$$

for electron, and the value is roughly $\mu_B \approx 0.927 \times 10^{-28}$erg/gauss

When a magnetic dipole is placed in a magnetic field B, it experiences a torque.

Theorem 6.10: Torque from Magnetic Field

If we have a **magnetic field** $\vec{B}$, then the **torque** is:

$$\vec{\mu} \times \vec{B}$$

and the **energy associated** with the torque is (*classically*):

$$E = -\vec{\mu} \cdot \vec{B}$$

quantum mechanically:

$$\hat{H} = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{B} \cdot \hat{S}$$

where we have interchanged the dot product since $\vec{B}$ is a *classical quantity*, and realize that:

- S is the spin **matrix**, and so is $\hat{H}$ being a matrix
- $\hat{S} = \hat{S}_x \hat{i} + \hat{S}_y \hat{j} + \hat{S}_z \hat{z}$, so it also has components

***Example*: Larmor precession**

Consider a magnetic field of:

$$\vec{B} = B_0 \hat{k}$$

Then, first we can think about its *energy splitting*:

$$\begin{aligned}\hat{H} &= -\gamma \vec{B} \cdot \vec{S} \\ &= -\gamma B_0 \hat{S}_z \\ &= -\gamma B_0 \left(\frac{\hbar}{2}\right) \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.\end{aligned}$$

Then, we need to *solve for eigenvalues and eigenfunctions*. However, notice that we basically just have $\hat{S}_z$, so the **eigenstates/vector for $\hat{H}$ is the same as $\hat{S}_z$**:

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \qquad \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

Putting them back in, we can *solve for eigenvalues*:

$$E_+ = -\frac{\gamma B_0 \hbar}{2}, \qquad E_- = \frac{\gamma B_0 \hbar}{2}$$

this gives the **energy splitting**. (note that γ was negative)

Now, we want to find out **how spin changes in time**. To do this, we need to compute $\chi(t)$. Suppose:

$$\chi(t=0) = \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) \\ \sin\left(\frac{\alpha}{2}\right) \end{bmatrix}$$

Without a loss of generality, since $|a|^2 + |b|^2 = 1$, then I can just represent is by one *unknown α.* then, the general solution is:

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

again, you should think about χ being some *generalized wave function projected to the spin space*. The solution to the above is:

$$\begin{aligned}\chi(t) &= a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} \\ &= \begin{bmatrix} a e^{i\gamma B_0 t/2} \\ b e^{-i\gamma B_0 t/2} \end{bmatrix} \\ &= \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \\ \sin\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \end{bmatrix}.\end{aligned}$$

Once we know the spin χ state, we can compute the spins:

- consider the $\left\langle \hat{S}_x \right\rangle$ and its *time dependence*

$$\begin{aligned}
\left\langle \hat{S}_x \right\rangle &= \langle \chi(t) | \hat{S}_x \chi(t) \rangle \\
&= \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} & \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \end{bmatrix} \left(\frac{\hbar}{2}\right) \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \\ \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \end{bmatrix} \\
&= \frac{\hbar}{2} \left[\cos\left(\frac{\alpha}{2}\right) \sin\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t} + \sin\left(\frac{\alpha}{2}\right) \cos\left(\frac{\alpha}{2}\right) e^{+i\gamma B_0 t} \right] \\
&= \frac{\hbar}{2} \sin(\alpha) \cos(\gamma B_0 t).
\end{aligned}$$

  which shows the *observable movement of spin in x-direction*

- next, consider $\langle S_y \rangle$ using the same idea:

$$\begin{aligned}
\left\langle \hat{S}_y \right\rangle &= \langle \chi(t) | \hat{S}_y \chi(t) \rangle \\
&= \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} & \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \end{bmatrix} \left(\frac{\hbar}{2}\right) \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \\ \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \end{bmatrix} \\
&= -\frac{\hbar}{2} \sin(\alpha) \sin(\gamma B_0 t).
\end{aligned}$$

  which *also moves but differently than x-direction*

- Lastly, consider $\left\langle \hat{S}_z \right\rangle$:

$$\begin{aligned}
\left\langle \hat{S}_y \right\rangle &= \langle \chi(t) | \hat{S}_y \chi(t) \rangle \\
&= \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} & \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \end{bmatrix} \left(\frac{\hbar}{2}\right) \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \\ \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \end{bmatrix} \\
&= \frac{\hbar}{2} \cos(\alpha).
\end{aligned}$$

  which is *constant*

Therefore, now I have:

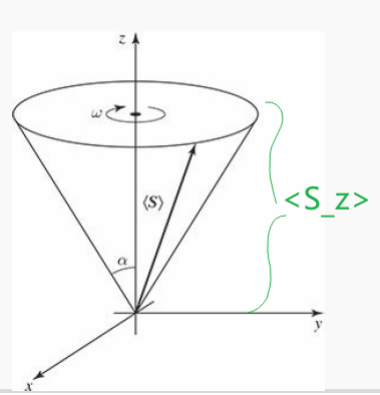
$$\begin{aligned}
\left\langle \hat{S}_x \right\rangle &= \frac{\hbar}{2} \sin(\alpha) \cos(\gamma B_0 t) \\
\left\langle \hat{S}_y \right\rangle &= -\frac{\hbar}{2} \sin(\alpha) \sin(\gamma B_0 t) \\
\left\langle \hat{S}_z \right\rangle &= \frac{\hbar}{2} \cos(\alpha).
\end{aligned}$$

and notice that this means:

- the magnitude of the spin $\left\langle \hat{S} \right\rangle^2 = \left(\frac{\hbar}{2}\right)^2$ is a *constant*

- the z-component stays the same but x-and-y-component moves
- the movement is at frequency $\omega = \gamma B_0$, which is known as the **Larmor Frequency**

Graphically, the above basically *precesses* like:

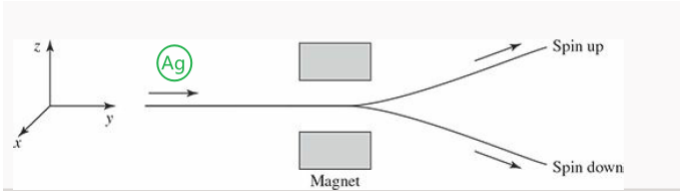


which happens in a *uniform magnetic field* $\vec{B} = B_0\hat{z}$.

Another important example is SternGerlach experiment, which:

- proved the existence of spin of electron
- proved the spin is $\pm\frac{1}{2}$

The setup is as follows:



***Example*: SternGerlach experiment**

Firs of all, silver atoms are used. This is because:

1. since they are neutral, the force:
$$\vec{F} = q\vec{v} \times \vec{B} = 0$$
2. the electron configuration of silver is $(Kr)\,4d^{10}5s^1$, which means that the *net spin* is simply that of the outermostunpairedelectron, so that:
$$s = \frac{1}{2}$$

Now, the setup has the following *in homogeneous magnetic field*:

$$\vec{B} = -\alpha x\hat{i} + (B_0 + \alpha z)\,\hat{k}$$

which is an allowable field since $\vec{\nabla} \cdot \vec{B} = 0$.
Then, in an inhomogeneous magnetic field, there is not only a torque, but also a force, on a magnetic dipole:

$$\vec{F} = \vec{\nabla}\left(\vec{u} \cdot \vec{B}\right)$$

Using $\vec{\mu} = \gamma\vec{S}$, I have:

$$\begin{aligned}\vec{F} &= \vec{\nabla}\left(\mu_x B_x + \mu_z B_z\right) \\ &= \vec{\nabla}\left[\gamma S_x\left(-\alpha x\right) + \gamma S_z\left(B_0 \alpha z\right)\right] \\ &= \gamma\alpha\left(-\hat{S}_x\right)\hat{i} + \gamma\alpha\left(\hat{S}_z\right)\hat{k}.\end{aligned}$$

Note:

> Now, we are treating the operators:
>
> $$\hat{S}_x, \hat{S}_z$$
>
> as **operators in the "differential form"**, **not in the matrix form**.

But because of the Larmor precession about $B_0\hat{k}$, $\left\langle \hat{S}_x \right\rangle$ oscillates rapidly (in previous problem), and averages to zero; the net force is in the z direction:

$$\vec{F} = F_z\hat{k} = \gamma\alpha\hat{S}_z\hat{k}$$

Now, this means that if at $t = 0$, we have $\chi_(0)$, then *consider its time dependence*:

$$\hat{H} = \begin{cases} 0, & t \leq 0 \\ -\gamma\left(B_0 + \alpha z\right)\hat{S}_z, & 0 < t < T \\ 0, & t \geq T \end{cases}$$

where we omitted $\hat{S}_x$ because constant α describes a small deviation from homogeneity. Also, T means the time it exists the magnets.
Then, we could have:

$$\chi(0) = a\chi_+ + b\chi_-$$

to start with. Then, we have:

$$\chi(t) = \alpha\chi_+ e^{-iE_+/\hbar t} + b\chi_- e^{+iE_-/\hbar t}.$$

with the energies:

$$E_\pm = \mp\gamma\left(B_0 + \alpha z\right)\frac{\hbar}{2}$$

lastly, for $t > T$, we have:

$$\chi(T) = \alpha e^{i\frac{\gamma T B_0}{2}} \chi_+ e^{i\left(\frac{\alpha\gamma T}{2}\right)z} + be^{-i\frac{\gamma T B_0}{2}} \chi_- e^{-i\left(\frac{\alpha\gamma T}{2}\right)z}$$

where the terms:

- $e^{i\left(\frac{\alpha\gamma T}{2}\right)z}$ signifies the *spin up in z-direction*
- $e^{-i\left(\frac{\alpha\gamma T}{2}\right)z}$ signifies the *spin down in z-direction*

6.8.3 Generalized Magnetic Moment

In general, we will have:

$$\vec{\mu}_J = \gamma_J \vec{J}$$

for any kind of **angular momentum** $\vec{J} = \vec{L}, \vec{S}, ...$

Theorem 6.11: General Magnetic Moment

In Quantum Mechanics, we have

$$\vec{\mu} = g\frac{\mu_L}{\hbar}\vec{L}$$

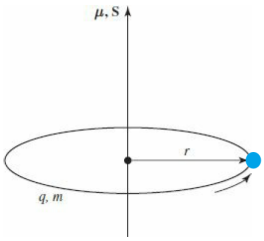
for:

- some charge q orbiting around a center producing angular momentum $\vec{L}$
- μ_L is related to the charge of that particle:

$$\mu_L \equiv \frac{q\hbar}{2m}$$

- g is the **gyromagnetic ratio** which is specified for each type of particle

Proof. Starting with the **classical view point**, we have some charge q orbiting:



where for a **diatomic molecule case**, you can think of boosting into the **frame of one of the nucleus**.
Then, we have the angular momentum being:

$$\begin{aligned}\left|\vec{L}\right| &= \vec{r} \times (m\vec{v}) \\ &= mr\frac{2\pi r}{T}\hat{k} \\ &= \frac{2\pi m r^2}{T}\hat{k}.\end{aligned}$$

Additionally, the **magnetic moment** is defined to be:

$$\begin{aligned}\mu &= IA \\ &= \frac{q}{T}\pi r^2 \\ &= q\frac{\pi r^2}{T}.\end{aligned}$$

Therefore, we then get:

$$\vec{\mu} = \frac{q}{2m}\vec{L}.$$

for an particle in the system with **angular momentum $\vec{L}$ and charge q**. Putting it into another form:

$$\begin{aligned}\vec{\mu} &= \frac{q\hbar}{2m}\frac{1}{\hbar}\vec{L} \\ &= \mu_L\frac{\vec{L}}{\hbar} \\ &= \frac{\mu_L}{\hbar}\vec{L}.\end{aligned}$$

where we have:

- $\mu_L \equiv \frac{q\hbar}{2m}$
- for electron, then we have:

$$\mu_L = -\mu_B = -\left|\frac{e\hbar}{2m_e}\right|$$

  where μ_B is called the **Bohr Magneton**.

In general, this is almost true in quantum , expect that we have:

$$\vec{\mu} = g\frac{\mu_L}{\hbar}\vec{L}$$

where g, μ_L is **specific to the type of the particle**. □

***Example*: Proton Spin Magnetic Moment**

Consider for proton orbiting a nucleus, then we have:

$$\begin{aligned}\gamma_p &= 5.58 \\ \mu_L = \mu_p &= \frac{e\hbar}{2m_p}.\end{aligned}$$

Therefore, we get:

$$\vec{\mu} = g_p\frac{\mu_n}{\hbar}\vec{S}$$

since we are **considering Spinning**.
Now, for protons, we know that $s = \frac{1}{2}$ just like electrons, we can consider:

$$\vec{B} = B_0\hat{k}$$

then we can compute:

$$\begin{aligned}\hat{H} &= -\vec{\mu}\cdot\vec{B} \\ &= -\left(5.58\frac{\mu_n}{\hbar}\right)\hat{S}_z B_0 \\ &= -\left(5.58 B_0\frac{\mu_n}{\hbar}\right)\hat{S}_z.\end{aligned}$$

so we immediately see that the eigenvector and eigenvalue is the **same as** $\hat{S}_z$, so we get:

$$\begin{aligned}\lambda_\uparrow &= \frac{\hbar}{2} \\ \lambda_\downarrow &= -\frac{\hbar}{2}.\end{aligned}$$

Therefore, the **energy splitting due to spin is**:

$$\begin{aligned}E_\uparrow &= -2.79 B_0\mu_n \\ E_\downarrow &= 2.79 B_0\mu_n\end{aligned}$$

.

6.9 Superposition of Angular Momentum

This section discusses the case when you have situations such as:

- a particle with **both spin S and orbital angular momentum L**
- two particles each with angular momentum L_1, L_2
- two particles each with spin S_1, S_2
- ... can be **generalized to multi-particle/angular momentum**

In the end, it turns out for most of the case, it is **all about additions**.

Theorem 6.12: Two Electron Spin

For two particles, the **new spin-z operator becomes**

$$\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}$$

The eigenstate and eigenvalue for the $\hat{S}_z$ of this new system becomes:

$$|s_1 m_1; s_2 m_2\rangle, \qquad \hbar(m_1 + m_2)$$

where:

- $|s_i m_i\rangle$ was the S_z **eigenstate of i-th particle**
- $\hbar m_i$ was the $\hat{S}_z$ **eigenvalue of i-th particle**
- this representation, as you shall see later, is called the **uncoupled representation**

Proof. Consider the case when we have **two electrons in the system**, and each has spin $s = \frac{1}{2}$. **What is the spin eigenstate now**, and **what are the eigenvalues for spin**?

Reminder:

For a multi-particle system without spin, we dealt with it by having:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + ...$$

*and the **eigenfunctions become**:*

$$\psi = \psi_1 \psi_2 ...$$

we employ a **similar idea**, such that we have the **spin matrix** being:

$$\hat{S} = \hat{S}^{(1)} + \hat{S}^{(2)}$$

where $\hat{S}^{(i)}$ correspond to the **spin matrix of particle/electron** i. Similarly:

$$\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}$$

then, again defining:

$$|\uparrow\rangle \equiv \chi_+ \equiv \begin{bmatrix}1\\0\end{bmatrix} = |s=\frac{1}{2}, m=\frac{1}{2}\rangle = |\frac{1}{2}\frac{1}{2}\rangle$$
$$|\downarrow\rangle \equiv \chi_- \equiv \begin{bmatrix}0\\1\end{bmatrix} = |s=\frac{1}{2}, m=-\frac{1}{2}\rangle = |\frac{1}{2}-\frac{1}{2}\rangle\,.$$

all of which are **equivalent representations**.
Then, we have the following **combinations of possible spins**:

$$\begin{cases}\chi_+^{(1)}\chi_+^{(2)} = |\uparrow\uparrow\rangle\,, & = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{1}{2}\rangle\\ \chi_+^{(1)}\chi_-^{(2)} = |\uparrow\downarrow\rangle\,, & = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{-1}{2}\rangle\\ \chi_-^{(1)}\chi_+^{(2)} = |\downarrow\uparrow\rangle\,, & = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{1}{2}\rangle\\ \chi_-^{(1)}\chi_-^{(2)} = |\downarrow\downarrow\rangle\,, & = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{-1}{2}\rangle\end{cases}$$

Now, for any (**uncoupled**) spin eigenstate:

$$|s_1 m_1; s_2, m_2\rangle = |s_1 m_1\rangle\,|s_2 m_2\rangle$$

notice the **analogy with multi-particle analysis without spin**, where we had $\Psi = \Psi_1\Psi_2....$

Note:

> The analogy becomes even more obvious if you consider not spin S, but L, so that the **eigenstate are**
>
> $$\chi \to f_l^m = Y_l^m$$
>
> then we are just having all the **individual spherical harmonics multiplied**

The upshot of this is, as expected:

$$\begin{aligned}\hat{S}_z\,|s_1 m_1; s_2 m_2\rangle &= \left(\hat{S}_z^{(1)} + \hat{S}_z^{(2)}\right)|s_1 m_1; s_2 m_2\rangle\\ &= \hat{S}_z^{(1)}\,|s_1 m_1; s_2 m_2\rangle + \hat{S}_z^{(2)}\,|s_1 m_1; s_2 m_2\rangle\\ &= \hbar m_1\,|s_1 m_1; s_2 m_2\rangle + \hbar m_2\,|s_1 m_1; s_2 m_2\rangle\\ &= \hbar(m_1+m_2)\,|s_1 m_1; s_2 m_2\rangle\,.\end{aligned}$$

Therefore, we have seen that the eigenstate for $\hat{S}_z^{(total)}$ is the same as **combining individual eigenstates → uncoupled states**, and the eigenvalue is simply the **sum**:

$$|s_1 m_1; s_2 m_2\rangle\,, \qquad \hbar(m_1+m_2)$$

□

6.9.1 Coupled and Uncoupled State

In this case, we continue with the **two electron example**, so that we have the possibilities of:

$$\begin{cases} \chi_+^{(1)}\chi_+^{(2)} = |\uparrow\uparrow\rangle\,, & = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{1}{2}\rangle \\ \chi_+^{(1)}\chi_-^{(2)} = |\uparrow\downarrow\rangle\,, & = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{-1}{2}\rangle \\ \chi_-^{(1)}\chi_+^{(2)} = |\downarrow\uparrow\rangle\,, & = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{1}{2}\rangle \\ \chi_-^{(1)}\chi_-^{(2)} = |\downarrow\downarrow\rangle\,, & = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{-1}{2}\rangle \end{cases}$$

But notice that for the above combinations:

$$\begin{cases} |\uparrow\uparrow\rangle = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{1}{2}\rangle\,, & m = m_1 + m_2 = 1 \\ |\uparrow\downarrow\rangle = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{-1}{2}\rangle\,, & m = m_1 + m_2 = 0 \\ |\uparrow\uparrow\rangle = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{1}{2}\rangle\,, & m = m_1 + m_2 = 0 \\ |\uparrow\uparrow\rangle = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{-1}{2}\rangle\,, & m = m_1 + m_2 = -1 \end{cases}$$

which an also be emitted if we have $s = 1$, so that $m = -1, 0, 1$ as shown above.

Theorem 6.13: Coupled and Uncoupled States

The uncoupled states are just the pure combinations:

$$\begin{cases} |\uparrow\uparrow\rangle = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{1}{2}\rangle\,, & m = m_1 + m_2 = 1 \\ |\uparrow\downarrow\rangle = |\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{-1}{2}\rangle\,, & m = m_1 + m_2 = 0 \\ |\uparrow\uparrow\rangle = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{1}{2}\rangle\,, & m = m_1 + m_2 = 0 \\ |\uparrow\uparrow\rangle = |\frac{1}{2}\frac{-1}{2};\frac{1}{2}\frac{-1}{2}\rangle\,, & m = m_1 + m_2 = -1 \end{cases}$$

the **coupled states** are **linear combinations of the uncoupled states**, so that it is generated by a s, m pair:

$$\begin{cases} |11\rangle\,, & s = 1, m = 1 \\ |10\rangle\,, & s = 1, m = 0 \\ |1-1\rangle\,, & s = 1, m = -1 \\ |00\rangle\,, & s = 0, m = 0 \end{cases}$$

where:

- the first three shared the same $s = 1$, which is also called a **triplet**
- the latter one is on its own $s = 0$, which is also called the **singlet**
- the **number of uncoupled state = number of coupled state**, and we see that **all the m values are covered here**

Triplet Proof. We can **convert from coupled state to uncoupled state**, by considering **raising and lowering** $\hat{S}_\pm$:

$$\hat{S}_-^{\text{total}}\,|\uparrow\uparrow\rangle = \hat{S}_-^{(1)}\,|\uparrow\uparrow\rangle + \hat{S}_-^{(2)}\,|\uparrow\uparrow\rangle\,.$$

However, recall that:

$$\hat{S}_-\,|\uparrow\rangle = \hbar\hat{|}\downarrow, \qquad \hat{S}_-\,|\downarrow\rangle = 0$$

Therefore, we have:

$$\begin{aligned}\hat{S}_-^{\text{total}} |\uparrow\uparrow\rangle &= \hat{S}_-^{(1)} |\uparrow\uparrow\rangle + \hat{S}_-^{(2)} |\uparrow\uparrow\rangle \\ &= \hbar \left(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle \right).\end{aligned}$$

which **generated the $|10\rangle$ state**

$$|10\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right)$$

continuing, we do:

$$\begin{aligned}\hat{S}_- \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) &= \left(\hat{S}_-^{(1)} + \hat{S}_-^{(2)} \right) \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) \\ &= \hat{S}_-^{(1)} |\uparrow\downarrow\rangle + \hat{S}_-^{(2)} |\downarrow\uparrow\rangle \\ &= 2\hbar |\downarrow\downarrow\rangle .\end{aligned}$$

which spits out the $|1, -1\rangle$ **state**:

$$|1, -1\rangle = |\downarrow\downarrow\rangle$$

and if you continue doing $\hat{S}_-$, you will get 0. Alternatively, you can start from here and do $\hat{S}_+$ to go back up as well. □

Singlet Proof. The only other case left that we can get $m = 0$ would be considering:

$$\frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)$$

Consider raising operator:

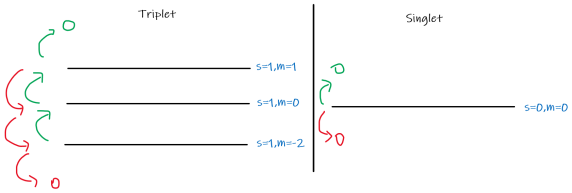
$$\begin{aligned}\hat{S}_+ \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) &= -\hbar |\uparrow\uparrow\rangle + \hbar |\uparrow\uparrow\rangle \\ &= 0.\end{aligned}$$

Similarly, doing the lowering operator:

$$\hat{S}_- \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) = 0$$

Therefore, this state is living on its own, being a **singlet**. □

Graphically, we have the following situation:



6.9.2 Other Operators with Coupled/Uncoupled States

Note:

> Before continuing the example, note that this procedure works with **any angular momentum quantity**, including combining $\vec{L}, \vec{S}$.

Continuing the example of **two electrons**:

Reminder:

> *We have shown the operators $\hat{S}_z^{(total)}$ had eigenvectors being the **uncoupled state***
>
> $$|s_1 m_1; s_2 m_2\rangle, \qquad \hbar(m_1 + m_2)$$

We will soon show that $\hat{S}^{2(\text{total})}$ has eigenstate of the **coupled states**.

Theorem 6.14: Eigenstates of $\hat{S}^2$

In short, the total spin squared $\hat{S}^2$ will have the **coupled states** being eigenstates, and the **eigenvalue** is still $s(s+1)\hbar^2$:

$$\begin{aligned}
\hat{S}^2 |10\rangle &= \left(\hat{S}^{(1)^2} + \hat{S}^{(2)^2} + 2S^{(1)} \cdot S^{(2)}\right) |10\rangle \\
&= \frac{3}{4}\hbar^2 |10\rangle + \frac{3}{4}\hbar^2 10 + 2\frac{\hbar^2}{4} |10\rangle \\
&= 2\hbar^2 |10\rangle \\
&= (1)(1+1)\hbar^2 |10\rangle .
\end{aligned}$$

And for the state $s = 0, m = 0$

$$\begin{aligned}
\hat{S}^2 |00\rangle &= \left(\hat{S}^{(1)^2} + \hat{S}^{(2)^2} + 2S^{(1)} \cdot S^{(2)}\right) |00\rangle \\
&= 0 \\
&= (0)(0+1)\hbar^2 |00\rangle .
\end{aligned}$$

Proof. First, we know that:

$$\hat{S} = \hat{S}^{(1)} + \hat{S}^{(2)}$$

and that:

$$\hat{S}^{(1)} = \hat{S}_x^{(1)} + \hat{S}_y^{(1)} + \hat{S}_z^{(1)}$$

now, consider the total:

$$\hat{S}^2 = \hat{S}^{(1)^2} + \hat{S}^{(2)^2} + 2S^{(1)} \cdot S^{(2)}.$$

where notice that $\hat{S}^{(1)}, \hat{S}^{(2)}$ are independent.

Reminder:

> *The operator $\hat{S}^2$ for a single electron was the **identity operator**, so that whatever you give becomes the eigenvector, such that:*
>
> $$\hat{S}^2 |s, m\rangle = s(s+1)\hbar^2 |s, m\rangle$$

*for **any** s, m*

Therefore, in this case if we consider:

$$\hat{S}^2\left[\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)\right] = \left(\hat{S^{(1)}}^2 + \hat{S^{(2)}}^2 + 2S^{(1)}\cdot S^{(2)}\right)\left[\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)\right].$$

we already know that:

$$\begin{aligned}\hat{S^{(1)}}^2\left[\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)\right] &= \frac{1}{\sqrt{2}}\left[\frac{3}{4}\hbar^2|\uparrow\downarrow\rangle + \frac{3}{4}\hbar^2|\downarrow\uparrow\rangle\right]\\ &= \frac{3}{4}\hbar^2|10\rangle.\end{aligned}$$

for basically doing nothing with it. Then, the same applies for $\hat{S^{(2)}}^2$. Therefore, all we need to calculate would be the cross term:
First consider:

$$\hat{S}^{(1)}\hat{S}^{(2)}|\uparrow\downarrow\rangle = \hat{S}_x^{(1)}\hat{S}_x^{(2)}|\uparrow\downarrow\rangle + \hat{S}_y^{(1)}\hat{S}_y^{(2)}|\uparrow\downarrow\rangle + \hat{S}_z^{(1)}\hat{S}_z^{(2)}|\uparrow\downarrow\rangle.$$

Now, recall that:

$$\begin{aligned}S_x|\downarrow\rangle &= \frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix} = \frac{\hbar}{2}|\uparrow\rangle\\ S_x|\uparrow\rangle &= \frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{\hbar}{2}|\downarrow\rangle\\ S_y|\uparrow\rangle &= \frac{\hbar}{2}i|\downarrow\rangle\\ S_y|\uparrow\rangle &= \frac{\hbar}{2}(-i)|\uparrow\rangle\\ S_z|\uparrow\rangle &= \frac{\hbar}{2}|\uparrow\rangle\\ S_y|\uparrow\rangle &= \frac{\hbar}{2}|\downarrow\rangle.\end{aligned}$$

Therefore, we get:

$$\begin{aligned}\hat{S}^{(1)}\hat{S}^{(2)}|\uparrow\downarrow\rangle &= \hat{S}_x^{(1)}\hat{S}_x^{(2)}|\uparrow\downarrow\rangle + \hat{S}_y^{(1)}\hat{S}_y^{(2)}|\uparrow\downarrow\rangle + \hat{S}_z^{(1)}\hat{S}_z^{(2)}|\uparrow\downarrow\rangle\\ &= \left(\frac{\hbar}{2}\right)^2|\downarrow\uparrow\rangle + \left(\frac{\hbar}{2}\right)^2(i)(-i)|\downarrow\uparrow\rangle - \left(\frac{\hbar}{2}\right)^2|\uparrow\downarrow\rangle\\ &= \frac{\hbar^2}{4}\left(2|\downarrow\uparrow\rangle - |\downarrow\uparrow\rangle\right).\end{aligned}$$

Similarly, just **flipping the arrows**:

$$\begin{aligned}\hat{S}^{(1)}\hat{S}^{(2)}|\downarrow\uparrow\rangle &= \hat{S}_x^{(1)}\hat{S}_x^{(2)}|\downarrow\uparrow\rangle + \hat{S}_y^{(1)}\hat{S}_y^{(2)}|\downarrow\uparrow\rangle + \hat{S}_z^{(1)}\hat{S}_z^{(2)}|\downarrow\uparrow\rangle\\ &= \frac{\hbar^2}{4}\left(2|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right).\end{aligned}$$

Therefore, combining the two result back, we get want we wanted:

$$\begin{aligned}\hat{S}^{(1)}\hat{S}^{(2)}|10\rangle &= \hat{S}^{(1)}\hat{S}^{(2)}\left[\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)\right]\\ &= \frac{\hbar^2}{4}|10\rangle.\end{aligned}$$

finally:

$$\begin{aligned}\hat{S}^2\left[\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle\right]\right. &= \left(\hat{S}^{(1)^2}+\hat{S}^{(2)^2}+2S^{(1)}\cdot S^{(2)}\right)|10\rangle \\ &= \frac{3}{4}\hbar^2|10\rangle+\frac{3}{4}\hbar^2 10+2\frac{\hbar^2}{4}|10\rangle \\ &= 2\hbar^2|10\rangle \\ &= (1)(1+1)\hbar^2|10\rangle\,.\end{aligned}$$

which basically saying that the **coupled states are the eigenstates**, and the eigenvalue is **still in the form of** $s(s+1)\hbar^2$

Now, consider the other relevant **singlet eigenstate**:

$$\hat{S}^2\left[\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle\right]\right. = \left(\hat{S}^{(1)^2}+\hat{S}^{(2)^2}+2S^{(1)}\cdot S^{(2)}\right)|00\rangle\,.$$

Again, the problem is with $\hat{S}^{(1)}\hat{S}^{(2)}$. Essentially doing the same steps above, expect that we now **have a minus sign**. Therefore, flipping the sign for the result on $|10\rangle$, we have:

$$\begin{aligned}\hat{S}^{(1)}\hat{S}^{(2)}|00\rangle &= \frac{1}{\sqrt{2}}\left[\frac{\hbar^2}{4}\left(2|\downarrow\uparrow\rangle-|\uparrow\downarrow\rangle\right)-\frac{\hbar^2}{4}\left(2|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle\right)\right] \\ &= \frac{3}{4}\hbar^2\left[\frac{1}{\sqrt{2}}\left(|\downarrow\uparrow\rangle\right)-|\uparrow\downarrow\rangle\right] \\ &= -\frac{3}{4}\hbar^2|00\rangle\,.\end{aligned}$$

Therefore, we can compute:

$$\begin{aligned}\hat{S}^2|00\rangle &= \left(\hat{S}^{(1)^2}+\hat{S}^{(2)^2}+2S^{(1)}\cdot S^{(2)}\right)|00\rangle \\ &= \frac{3}{4}\hbar^2|00\rangle+\frac{3}{4}\hbar^2 00-2\frac{3\hbar^2}{4}|00\rangle \\ &= 0 \\ &= (0)(0+1)\hbar^2|00\rangle\,.\end{aligned}$$

which again shows that the **coupled state being the eigenstate**, and the eigenvalue is still $s(s+1)\hbar^2$ □

6.9.3 Aggregate Properties of Superposed Angular Momenta

Before, we have consider the case of combing two spins. In general, we could have any setup of:

$$\vec{J} = \vec{J}_1 + \vec{J}_2$$

where:

- $\vec{J}_i$ could be either $\vec{L}, \vec{S}$

Theorem 6.15: Aggregate Spin l and m

Notice that for any angular momenta we have, we **only needed two indices**:

- $\vec{L}$ needs l, m (recall the spherical harmonics $f_l^m = Y_l^m$)
- $\vec{S}$ needs s, m

Therefore, any angular momenta can be generalized to:

$$|j, m\rangle$$

and if we have **two angular momentum to combine**:

$$\begin{cases} j_1, & m_1 = -j_1, ...j_1 \\ j_2, & m_2 = -j_2, ...j_2 \end{cases}$$

Then the **total is**:

$$\begin{cases} j = |j_1 - j_2|, |j_1 - j_2| + 1, ...j_1 + j_2 & \\ m = -j, ..., j; & \text{for each possible } j \end{cases}$$

Therefore, we have in total:

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1)$$

being the **total number of possible uncoupled/coupled states**.

Example

Consider if I have a spin and an orbital angular momentum:

$$\begin{cases} l = 1 \\ s = 3 \end{cases}$$

Then this means:

$$\begin{cases} j_1 = 1 \\ j_2 = 3 \end{cases}$$

Therefore, I have the following possibilities:

$$\begin{cases} j = 2, 3, 4 \\ m = -j, ..., j; \quad \text{for each } j \end{cases}$$

In total, there are:

$$(2(1) + 1)\,(2(3) + 1) = 21$$

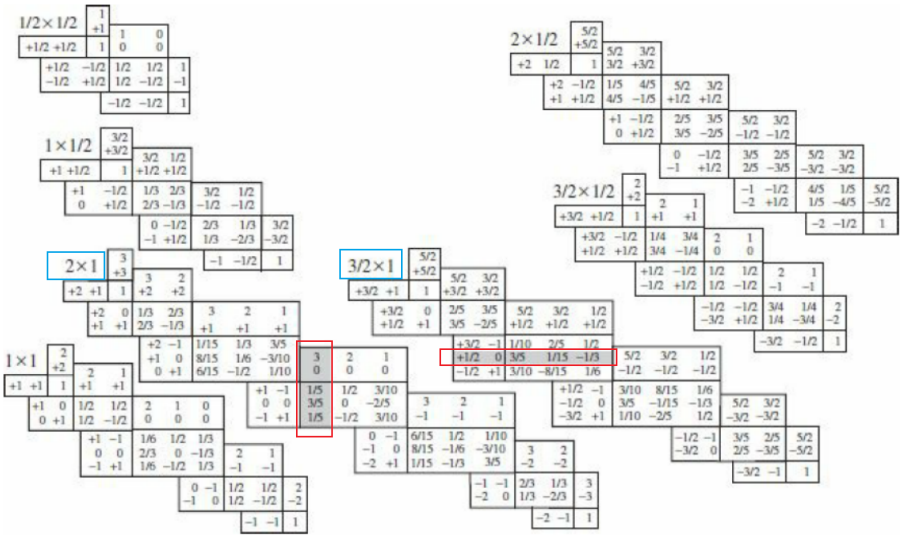
possible coupled/uncoupled states.

6.9.4 ClebschGordan Coefficients

This is useful for **computing coupled state from uncoupled state AND vice versa**.
In general, when we have two momenta with j_1, j_2 to combine, we might want to convert back and forth for:

$$|j,m\rangle_{\text{coupled}} = \sum C^{j_1,j_2,j}_{m_1,m_2,m} \, |j_1,m_1;j_2,m_2\rangle_{\text{uncoupled}}$$
$$|j_1,m_1;j_2,m_2\rangle_{\text{uncoupled}} = \sum C^{j_1,j_2,j}_{m_1,m_2,m} \, |j,m\rangle_{\text{coupled}} \, .$$

Then the **coefficients can be found by using the following Clebsch-Gordan table**



where:

- the blue part indicates the j_1, j_2 combination we are looking at
- each **horizontal red box** means transforming from **coupled state to uncoupled states**
- each **vertical red box** means transforming from **uncoupled state to coupled states**
- the coefficients are to be taken **square root of**, and if there is a negative sign, it is **outside of the square root**

***Example*: Uncoupled to Coupled**

Consider the case of:

$$\begin{cases} j_1 = 2 \\ j_2 = 1 \end{cases}$$

We want to know that is the expression for the **coupled state**:

$$|30\rangle =?$$

we can use the table easily by:

1. finding the 2×1 part
2. need $|30\rangle$, so look for a **vertical column** with $3, 0$
3. copy down the **coefficients** in the same column and the **corresponding uncoupled state** on the left:

$$\begin{cases} j_1 = 2, m_1 = 1; j_2 = 1, m_2 = -1, & \sqrt{1/5} \\ j_1 = 2, m_1 = 0; j_2 = 1, m_2 = 0, & \sqrt{3/5} \\ j_1 = 2, m_1 = -1; j_2 = 1, m_2 = 1, & \sqrt{1/5} \end{cases}$$

Therefore, we get:

$$|30\rangle = \sqrt{\frac{1}{5}}\,|2, 1; 1, -1\rangle + \sqrt{\frac{3}{5}}\,|2, 0; 1, 0\rangle + \sqrt{\frac{1}{5}}\,|2, -1; 1, 1\rangle$$

***Example*: Coupled to Uncoupled**

Consider the case of:

$$\begin{cases} j_1 = \frac{3}{2} \\ j_2 = 1 \end{cases}$$

We want to know that is the expression for the **uncoupled state**:

$$|\frac{3}{2}, \frac{1}{2}; 1, 0\rangle =?$$

we can use the table easily by:

1. finding the $\frac{3}{2} \times 1$ part
2. need $|30\rangle$, so look for a **horizontal row** with $\frac{1}{2}, 0$
3. copy down the **coefficients** in the same row and the **corresponding coupled state** on the top:

$$\begin{cases} j = \frac{5}{2}, m = \frac{1}{2}; & \sqrt{3/5} \\ j = \frac{3}{2}, m = \frac{1}{2}; & \sqrt{1/15} \\ j = \frac{1}{2}, m = \frac{1}{2}; & -\sqrt{1/3} \end{cases}$$

Therefore, we get:

$$|\frac{3}{2}, \frac{1}{2}; 1, 0\rangle = \sqrt{\frac{3}{5}}\,|\frac{5}{2}, \frac{1}{2}\rangle + \sqrt{\frac{1}{15}}\,|\frac{3}{2}, \frac{1}{2}\rangle - \sqrt{\frac{1}{3}}\,|\frac{1}{2}, \frac{1}{2}\rangle$$