Quantum Mechanics Subject Notes

Basic Formalism

Postulates of Quantum Mechanics

1. At each moment of time t, the state of a physical system is represented by a ket $|\psi(t)\rangle$ in the vector space of states.
2. Every observable characteristic of a physical system is described by a Hermitian operator A that acts on the ket.
3. The only possible result of the measurement of an observable is one of the eigenvalues of the operator A, such that $A|\psi(t)\rangle = E_A|\psi(t)\rangle$.
4. When a measurement of an observable A is made on a generic state $|\psi\rangle$, the probability of obtaining an eigenvalue a_i is given by $|\langle\phi_i|\psi\rangle|^2$, where $|\phi_i\rangle$ is the eigenstate of the operator A which has the eigenvalue a_i.
5. Immediately after the measurement of state $|\psi\rangle$ has yielded the value a_i, the state of the system is said to have 'collapsed' into the normalised eigenstate $|\phi_i\rangle$.
6. The time evolution of a state $|\psi\rangle$ is given by $|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle$ for the unitary operator $\widehat{U}$, where $\widehat{U}$ satisfies the Schrodinger equation $i\hbar\frac{\partial U(t,t_0)}{\partial t} = H(t)U(t,t_0)$.
7. The state space of a composite quantum system is the tensor product of the state spaces of its constituent system, such that $|\Psi\rangle = \sum_i C_{12\ldots N}|\psi_1\rangle|\psi_2\rangle \ldots |\psi_N\rangle$.

Useful identities

Identities relating to state kets:

$$\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*$$
$$|\alpha\rangle = \sum_{a'}|a'\rangle\langle a'|\alpha\rangle$$
$$\sum_{a'}|a'\rangle\langle a'| = 1$$
$$A|\alpha\rangle\langle\alpha| = |\alpha\rangle\langle\alpha|A^\dagger$$
$$A|a,b\rangle = a|a,b\rangle \text{ and } B|a,b\rangle = b|a,b\rangle \text{ iff } AB = BA$$

Commutation of a function of an operator is given by:

$$[A, f(B)] = i\hbar\frac{\partial f}{\partial B}$$

Generator of translation

The space translation operator is given by:

$$T_{\Delta x} = 1 - iG\Delta x$$

We identify the momentum operator as the generator of motion, yielding:

$$T_{\Delta x} = 1 - \frac{ip_x}{\hbar}\Delta x$$

A finite translation is made up of repeated infinitesimal translations:

$$T(\Delta x) = \lim_{N\to\infty}\left[1 - i\frac{p_x}{\hbar}\frac{\Delta x}{N}\right]^N$$
$$T(\Delta x) = \exp\left(-\frac{ip_x\Delta x}{\hbar}\right)$$

Projection probabilities

Suppose we have an eigenvalue relation:

$$A|\alpha\rangle = a|\alpha\rangle$$

Suppose we are in state $|\alpha\rangle$, but we now measure some other variable B. The probability of getting the value $B = b$ is found by considering the eigenket corresponding to b:

$$B|\beta\rangle = b|\beta\rangle$$

The probability we want is then simply the projection of $|\alpha\rangle$ onto the state $|\beta\rangle$:

$$P_{\text{get } b \text{ in } \alpha} = |\langle\beta|\alpha\rangle|^2$$

Expectation values

The expectation value of an operator A measuring state $|\alpha\rangle$ is found by computing:

$$\langle A\rangle = \langle\alpha|A|\alpha\rangle = \sum_k \langle\alpha|A|k\rangle\langle k|\alpha\rangle = \sum_k k'\langle\alpha|k\rangle\langle k|\alpha\rangle$$

If no state $|\alpha\rangle$ is specified, we can write a general state in some given basis just by using undetermined coefficients. Likewise we find:

$$\langle A^2\rangle = \langle AA\rangle = \langle\alpha|AA|\alpha\rangle$$

These can be combined to get the uncertainty:

$$(\Delta A)^2 = \langle A^2\rangle - \langle A\rangle^2$$

Matrix elements

An operator can be written as the outer product of two sets of basis kets $\{|a'\rangle\}$ and $\{|a''\rangle\}$:

$$X = \sum_{a''}\sum_{a'} |a''\rangle\langle a''|X|a'\rangle\langle a'|$$

Written in matrix form this becomes:

$$X = \begin{bmatrix} \langle a_1''|X|a_1'\rangle & \langle a_1''|X|a_2'\rangle & \dots \\ \langle a_2''|X|a_1'\rangle & \langle a_2''|X|a_2'\rangle & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

For example if $X = |\alpha\rangle\langle\beta|$ then we have for basis kets $|a\rangle, |b\rangle$:

$$X = \begin{bmatrix} \langle a_1|\alpha\rangle\langle\beta|b_1\rangle & \langle a_2|\alpha\rangle\langle\beta|b_1\rangle & \dots \\ \langle a_2|\alpha\rangle\langle\beta|b_1\rangle & \langle a_2|\alpha\rangle\langle\beta|b_2\rangle & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

Suppose we have $|\alpha\rangle = |s_z = \frac{\hbar}{2}\rangle$ and $|\beta\rangle = |s_x = \frac{\hbar}{2}\rangle$, then we have:

$$X = \begin{bmatrix} \langle a_1|s_z = \hbar/2\rangle\langle s_x = \hbar/2|b_1\rangle & \langle a_1|s_z = \hbar/2\rangle\langle s_x = \hbar/2|b_2\rangle \\ \langle a_2|s_z = \hbar/2\rangle\langle s_x = \hbar/2|b_1\rangle & \langle a_2|s_z = \hbar/2\rangle\langle s_x = \hbar/2|b_2\rangle \end{bmatrix}$$

Now we need to choose a basis to expand this matrix in. Let's choose the usual $|s_z^{\pm}\rangle$ basis, in which we write the various spin component kets as:

$$\begin{aligned} |s_z^+\rangle &= |+\rangle \\ |s_z^-\rangle &= |-\rangle \\ |s_x^+\rangle &= \frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}|-\rangle \\ |s_x^-\rangle &= \frac{1}{\sqrt{2}}|+\rangle - \frac{1}{\sqrt{2}}|-\rangle \\ |s_y^+\rangle &= \frac{1}{\sqrt{2}}|+\rangle + \frac{i}{\sqrt{2}}|-\rangle \\ |s_y^-\rangle &= \frac{1}{\sqrt{2}}|+\rangle - \frac{i}{\sqrt{2}}|-\rangle \end{aligned}$$

Our matrix then becomes:

$$X = \begin{bmatrix} \langle +|s_z = \hbar/2\rangle\langle s_x = \hbar/2|+\rangle & \langle +|s_z = \hbar/2\rangle\langle s_x = \hbar/2|-\rangle \\ \langle -|s_z = \hbar/2\rangle\langle s_x = \hbar/2|+\rangle & \langle -|s_z = \hbar/2\rangle\langle s_x = \hbar/2|-\rangle \end{bmatrix}$$

$$X = \begin{bmatrix} \langle +|+\rangle\left(\frac{1}{\sqrt{2}}\langle +|+\rangle + \frac{1}{\sqrt{2}}\langle -|+\rangle\right) & \langle +|+\rangle\left(\frac{1}{\sqrt{2}}\langle +|-\rangle + \frac{1}{\sqrt{2}}\langle -|-\rangle\right) \\ \langle -|+\rangle\left(\frac{1}{\sqrt{2}}\langle +|+\rangle + \frac{1}{\sqrt{2}}\langle -|+\rangle\right) & \langle -|+\rangle\left(\frac{1}{\sqrt{2}}\langle +|-\rangle + \frac{1}{\sqrt{2}}\langle -|-\rangle\right) \end{bmatrix}$$

$$X = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 0 & 0 \end{bmatrix}$$

Change of basis

To convert a given state $|\alpha\rangle$ from being represented in the basis $\{|a\rangle\}$ to the basis $\{|b\rangle\}$, we use the operator:

$$\begin{aligned} |\alpha\rangle_b &= U|\alpha\rangle_a \\ |\alpha\rangle_b &= \sum_k |b^k\rangle\langle a^k\,|\alpha\rangle_a \end{aligned}$$

For example, let's consider two sets of states: $\{|s_x^{\pm}\rangle\}$ and $\{|s_z^{\pm}\rangle\} = \{|+\rangle, |-\rangle\}$. The operator to convert from the z-basis (a) to the x-basis (b) will therefore be:

$$\begin{aligned} U &= \sum_k |b^k\rangle\langle a^k| \\ &= (|s_x^+\rangle\langle +|) + (|s_x^-\rangle\langle -|) \\ &= \frac{1}{\sqrt{2}}(|+\rangle\langle +| + |-\rangle\langle +|) + \frac{1}{\sqrt{2}}(|+\rangle\langle -| - |-\rangle\langle -|) \\ &= \frac{1}{\sqrt{2}}(|+\rangle\langle +| + |-\rangle\langle +| + |+\rangle\langle -| - |-\rangle\langle -|) \\ U &= \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \end{aligned}$$

Time Evolution

Time evolution of the Schrodinger Equation

The state of a system evolves over time according to:

$$|\alpha, t\rangle = U(t, t_0)|\alpha, t_0\rangle$$

Where the evolution operator is given by:

$$U(t_0 + dt, t_0) = \tilde{I} - \frac{i}{\hbar}\hat{H}dt$$

To get an expression for $U(t, t_0)$, we need to have an equation to solve for it. We can find one by considering:

$$\begin{aligned} U(t + dt, t_0) &= U(t + dt, t)U(t, t_0) \\ U(t + dt, t_0) &= \left(\tilde{I} - \frac{i}{\hbar}\hat{H}dt\right)U(t, t_0) \\ U(t + dt, t_0) - U(t, t_0) &= \frac{i}{\hbar}HdtU(t, t_0) \\ i\hbar\frac{\partial}{\partial t}U(t, t_0) &= HU(t, t_0) \end{aligned}$$

So now we can solve for U by substituting our expression into the Schrodinger equation and solving. This yields an integral equation:

$$U(t, t_0) = \tilde{I} - \frac{i}{\hbar}\int_{t_0}^{t} H(t_1)\, U(t_1, t_0)dt_1$$

Iterating this results in the Dyson series solution:

$$U(t, t_0) = \tilde{I} + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t}\int_{t_0}^{t_1}\dots\int_{t_0}^{t_{n-1}} H(t_1)H(t_2)\dots H(t_n)\, dt_1 dt_2 \dots dt_n$$

If we introduce a time-ordering all the upper integrands become the same:

$$U(t, t_0) = \tilde{I} + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t}\int_{t_0}^{t}\dots\int_{t_0}^{t} T[H(t_1)H(t_2)\dots H(t_n)]\, dt_1 dt_2 \dots dt_n$$

If all the different $H(t_i)$ commute with each other, then this greatly simplifies to:

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} H(t')\, dt'\right]$$

And most straight-forward of all if H is independent of time we get:

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}Ht\right]$$

Energy eigenkets

Energy eigenstates are those states that do not change over time under operation of the Schrodinger equation. To see this, we start with the definition of energy eigenkets of A:

$$H|a'\rangle = E_{a'}|a'\rangle$$

Now expand the time-evolution operator (with time-constant Hamiltonian) to get:

$$\begin{aligned} U(t,t_0) &= \exp\left[-\frac{i}{\hbar}Ht\right] \\ &= \sum_{a'}\sum_{a''}|a''\rangle\langle a''|\exp\left[-\frac{i}{\hbar}Ht\right]|a'\rangle\langle a'| \\ &= \sum_{a'}\sum_{a''}|a''\rangle\langle a''|\exp\left[-\frac{i}{\hbar}E_a t\right]|a'\rangle\langle a'| \\ U(t,t_0) &= \sum_{a'}|a'\rangle\exp\left[-\frac{i}{\hbar}E_a t\right]\langle a'| \end{aligned}$$

Thus we can time-evolve any arbitrary ket $|\alpha\rangle$ by expanding in energy eigenkets:

$$|\alpha,t_0\rangle = \sum_{a'}|a'\rangle\langle a'|\alpha,t_0\rangle = \sum_{a'}c_{a'}|a'\rangle$$

Hence we have:

$$\begin{aligned} |\alpha,t\rangle &= \exp\left[-\frac{i}{\hbar}Ht\right]|\alpha,t_0\rangle \\ &= \sum_{a'}|a'\rangle\exp\left[-\frac{i}{\hbar}E_{a'}t\right]\langle a'|\alpha,t_0\rangle \\ &= \exp\left[-\frac{i}{\hbar}E_{a'}t\right]|\alpha,t_0\rangle \\ |\alpha,t\rangle &= \sum_{a'}c_{a'}\exp\left(-\frac{iE_{a'}t}{\hbar}\right)|a'\rangle \end{aligned}$$

In the special case where the system begins in an energy eigenstate we have:

$$|\alpha,t\rangle = \exp\left(-\frac{iE_{a'}t}{\hbar}\right)|a'\rangle$$

The only thing changing is the phase, hence why we say that energy eigenkets are constant with time.

Time dependence of expectation values

If B is an observable that does not commute with H or operator A, then the expectation of state $|\alpha,t\rangle$ with respect to B is given by:

$$\begin{aligned} \langle B\rangle &= \langle a'\exp\left(\frac{iE_{a'}t}{\hbar}\right)|B|\exp\left(-\frac{iE_{a'}t}{\hbar}\right)a'\rangle \\ \langle a',t|B|a',t\rangle &= \langle a'|B|a\rangle \end{aligned}$$

Thus the expectation values of energy eigenstates $|a'\rangle$ are independent of time – they are called stationary states.

To see what happens when the system is in a superposition of states, consider the example of a spin ½ system in a uniform magnetic field along the z-axis. In this situation we have:

$$H = -\left(\frac{eB}{mc}\right)S_z$$

Thus H eigenstates will also be S_z eigenstates, and we have:

$$E_{\pm} = \mp\left(\frac{e\hbar B}{2mc}\right)$$

Now consider the superposition state:

$$|\alpha, 0\rangle = c_+|+\rangle + c_-|-\rangle$$

Time evolving this system we have:

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} H(t')\,dt'\right]$$
$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}\left(\frac{eB}{mc}\right)S_z t\right]$$

$$|\alpha, t\rangle = c_+ U(t,0)|+\rangle + c_- U(t,0)|-\rangle$$
$$|\alpha, t\rangle = c_+ \exp\left[-\frac{i}{\hbar}\left(\frac{eB}{mc}\right)S_z t\right]|+\rangle + c_- \exp\left[-\frac{i}{\hbar}\left(\frac{eB}{mc}\right)S_z t\right]|-\rangle$$

Using $S_z|\pm\rangle = \pm\frac{\hbar}{2}|\pm\rangle$ we get:

$$|\alpha, t\rangle = c_+ \exp\left[-\frac{i}{\hbar}\left(\frac{eB}{mc}\right)\left(+\frac{\hbar}{2}\right)t\right]|+\rangle + c_- \exp\left[-\frac{i}{\hbar}\left(\frac{eB}{mc}\right)\left(-\frac{\hbar}{2}\right)t\right]|-\rangle$$
$$|\alpha, t\rangle = c_+ \exp\left[-i\left(\frac{eB}{2mc}\right)t\right]|+\rangle + c_- \exp\left[i\left(\frac{eB}{2mc}\right)t\right]|-\rangle$$

What is the probability that it will be found in the state $|\beta\rangle = \frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}|-\rangle$ at time t?

$$|\langle\beta|\alpha, t\rangle|^2 = \left|\frac{1}{\sqrt{2}}[\langle+| + \langle-|]\left[c_+ \exp\left[-i\left(\frac{eB}{2mc}\right)t\right]|+\rangle + c_- \exp\left[i\left(\frac{eB}{2mc}\right)t\right]|-\rangle\right]\right|^2$$
$$= \frac{1}{2}\left|c_+ \exp\left[-i\left(\frac{eB}{2mc}\right)t\right] + c_- \exp\left[i\left(\frac{eB}{2mc}\right)t\right]\right|^2$$
$$= \frac{1}{2}\left\{c_+ \exp\left[-i\left(\frac{eB}{2mc}\right)t\right] + c_- \exp\left[i\left(\frac{eB}{2mc}\right)t\right]\right\}\left\{c_+ \exp\left[i\left(\frac{eB}{2mc}\right)t\right] + c_- \exp\left[-i\left(\frac{eB}{2mc}\right)t\right]\right\}$$
$$= \frac{1}{2}\left\{c_- c_+ \exp\left[-i\left(\frac{eB}{mc}\right)t\right] + c_- c_+ \exp\left[i\left(\frac{eB}{mc}\right)t\right] + 2\right\}$$
$$= \frac{1}{2}c_- c_+\left\{\left(\cos\left(\frac{eB}{mc}\right)t - i\sin\left(\frac{eB}{mc}\right)t\right) + \left(\cos\left(\frac{eB}{mc}\right)t + i\sin\left(\frac{eB}{mc}\right)t\right) + 2\right\}$$
$$= \frac{1}{2}c_- c_+\left\{2\left(\cos\left(\frac{eB}{mc}\right)t\right) + 2\right\}$$
$$|\langle\beta|\alpha, t\rangle|^2 = 2c_- c_+\left[\cos^2\left(\frac{eB}{2mc}t\right)\right]$$

Heisenberg and Interaction pictures

In the Schrodinger picture, state vectors evolve in time while operators remain fixed. Let's consider now the Heisenberg picture, related to the Schrodinger picture by:

$$A_H(t) = U^\dagger(t, t_0)A_S U(t, t_0)$$

Expected values are related by:

$$\langle\alpha, 0|A_H(t)|\alpha, 0\rangle = \langle\alpha, 0|U^\dagger(t, t_0)A_S U(t, t_0)|\alpha, 0\rangle$$

$$\langle \alpha, 0|A_H(t)|\alpha, 0\rangle = \langle \alpha, t|A_S|\alpha, t\rangle$$

The Heisenberg equation of motion is given by (the latter when H is independent of time):

$$\frac{dA_H}{dt} = \frac{1}{i\hbar}\left[A_H, U^\dagger(t,t_0)HU(t,t_0)\right] = \frac{1}{i\hbar}[A_H, H]$$

We have the following summary comparison of the three pictures:

Evolution of:	Picture		
	Heisenberg	Interaction	Schrödinger
Ket state	constant	$\|\psi_{\mathrm{I}}(t)\rangle = e^{iH_{0,\mathrm{S}}t/\hbar}\|\psi_{\mathrm{S}}(t)\rangle$	$\|\psi_{\mathrm{S}}(t)\rangle = e^{-iH_{\mathrm{S}}t/\hbar}\|\psi_{\mathrm{S}}(0)\rangle$
Observable	$A_{\mathrm{H}}(t) = e^{iH_{\mathrm{S}}t/\hbar}A_{\mathrm{S}}e^{-iH_{\mathrm{S}}t/\hbar}$	$A_{\mathrm{I}}(t) = e^{iH_{0,\mathrm{S}}t/\hbar}A_S e^{-iH_{0,\mathrm{S}}t/\hbar}$	constant
Density matrix	constant	$\rho_{\mathrm{I}}(t) = e^{iH_{0,\mathrm{S}}t/\hbar}\rho_{\mathrm{S}}(t)e^{-iH_{0,\mathrm{S}}t/\hbar}$	$\rho_{\mathrm{S}}(t) = e^{-iH_{\mathrm{S}}t/\hbar}\rho_{\mathrm{S}}(0)e^{iH_{\mathrm{S}}t/\hbar}$

Note that the Schrodinger equation also takes a somewhat different form in each picture.

Propagators

Time evolution for a constant $\hat{H}$ is given by:

$$|a,t\rangle = \hat{U}(t,t_0)|a,t_0\rangle$$
$$|a,t\rangle = e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}|a,t_0\rangle$$
$$\langle r''|a,t\rangle = \langle r''|e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}|a,t_0\rangle$$

Inserting two complete sets of states:

$$\langle r''|a,t\rangle = \langle r''|e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}\sum_E |E\rangle\langle E|\int |r'\rangle\langle r'|d^3r'a,t_0\rangle$$
$$\langle r''|a,t\rangle = \int\sum_E \langle r''|E\rangle\langle E|r'\rangle\, e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}\langle r'|a,t_0\rangle d^3r'$$
$$\psi_a(r'',t) = \int\sum_E \langle r''|E\rangle\langle E|r'\rangle\, e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}\psi_a(r',t)\, d^3r'$$

The wave-mechanical propagator for time-independent $\hat{H}$ is then defined to be:

$$K(r'',t;r',t_0) = \sum_E \langle r''|E\rangle\langle E|r'\rangle e^{-\frac{i}{\hbar}(t-t_0)E}$$
$$K(r'',t;r',t_0) = \sum_E \Phi_E(r'')\Phi_E(r')e^{-\frac{i}{\hbar}(t-t_0)E}$$

It is the wave function of a particle that was localised precisely at $r'' = r'$ at $t = t_0$, as we see in:

$$\lim_{t\to t_0} K(r'',t;r',t_0) = \sum_E \langle r''|E\rangle\langle E|r'\rangle$$
$$= \langle r''|r'\rangle$$
$$= \delta(r''-r')$$

We define the retarded Green's function to ensure propagation is only in the forward direction of time:

$$K_{ret}(r'',t;r',t_0) = \theta(t-t_0)\sum_E \Phi_E(r'')\Phi_E(r')e^{-\frac{i}{\hbar}(t-t_0)E}$$

We can see that this is a Green's function by using the result:

$$\left[-\frac{\hbar^2}{2m}\nabla''^2 + \mathrm{V}(r'') - i\hbar\frac{\partial}{\partial t}\right]K(r'',t;r',t_0) = 0$$

And thus we can show that:

$$\begin{aligned}\frac{\partial}{\partial t}K_{ret}(r'',t;r',t_0) &= \frac{\partial}{\partial t}\big(\theta(t-t_0)\big)K(r'',t;r',t_0) + \frac{\partial}{\partial t}K(r'',t;r',t_0)\\ &= \delta(t-t_0)\delta(r''-r')\end{aligned}$$

So K is the space propagator, representing a Green's function for the equation:

$$\psi_a(r'',t) = \int K_{ret}(r'',t;r',t_0)\,\psi_a(r',t)\,d^3r'$$

It is the transition amplitude for a particle localised at r' at t_0 to be found at r'' at time t.

Path integral methods

Consider a time $t_N - t_1$ and divide it up into $N-1$ equal intervals, such that $t_n - t_{n-1} = \Delta t = \frac{t_N - t_1}{N-1}$.
Now we consider the transition amplitude:

$$\langle x_N,t_N|x_1,t_1\rangle = \int\int \dots \int \langle x_N,t_N|x_{N-1},t_{N-1}\rangle\langle x_{N-1},t_{N-1}|x_{N-2},t_{N-2}\rangle \dots \langle x_2,t_2|x_1,t_1\rangle\, dx_{N-1}dx_{N-2}\dots dx_2$$

Here we have inserted $N-2$ full sets of complete states so as to represent a single transition as the sum of many smaller transitions over all possible paths. If we now consider:

$$\begin{aligned}\lim_{\Delta t\to 0}\langle x_n t_{n-1}+\Delta t|x_{n-1},t_{n-1}\rangle &= \langle x_n t_{n-1}|e^{-\frac{i}{\hbar}\Delta t\hat{H}}|x_{n-1},t_{n-1}\rangle\\ &= \int\langle x_n t_{n-1}|p\rangle\langle p|e^{-\frac{i}{\hbar}\Delta t\hat{H}}|x_{n-1},t_{n-1}\rangle\,dp\end{aligned}$$

If Δt is small we can expand the exponential as a series and neglect $O(\Delta t)^2$ terms:

$$= \int\langle x_n t_{n-1}|p\rangle\langle p|\left[1-\frac{i}{\hbar}\Delta t\hat{H}\right]|x_{n-1},t_{n-1}\rangle\,dp$$

Consider the special case when $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$, then we have:

$$\begin{aligned}&= \int\langle x_n t_{n-1}|p\rangle\langle p|\left[1-\frac{i}{\hbar}\Delta t\frac{\hat{p}^2}{2m} - \frac{i}{\hbar}\Delta t V(\hat{x})\right]|x_{n-1},t_{n-1}\rangle\,dp\\ &= \int\langle x_n t_{n-1}|p\rangle\left[1-\frac{i}{\hbar}\Delta t\frac{p^2}{2m} - \frac{i}{\hbar}\Delta t V(x_{n-1})\right]\langle p|x_{n-1},t_{n-1}\rangle\,dp\\ &= \int\langle x_n t_{n-1}|p\rangle\exp\left[-\frac{i}{\hbar}\Delta t\left(\frac{p^2}{2m}+V(x_{n-1})\right)\right]\langle p|x_{n-1},t_{n-1}\rangle\,dp\end{aligned}$$

Using the fact that $\langle x_n t_{n-1}|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}px_n}$ and similarly $\langle p|x_{n-1},t_{n-1}\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{i}{\hbar}px_{n-1}}$ we get:

$$= \int \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px_n} \exp\left[-\frac{i}{\hbar}\Delta t\left(\frac{p^2}{2m} + V(x_{n-1})\right)\right] \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{i}{\hbar}px_{n-1}}\, dp$$

$$= \int \frac{1}{2\pi\hbar} \exp\left[-\frac{i}{\hbar}\left(\frac{p^2}{2m}\Delta t + V(x_{n-1})\Delta t + px_n - px_{n-1}\right)\right] dp$$

$$= \int \frac{1}{2\pi\hbar} \exp\left[\frac{i}{\hbar}\left(p\left(\frac{x_n - x_{n-1}}{\Delta t}\right) - \frac{p^2}{2m} - V(x_{n-1})\right)\Delta t\right] dp$$

Completing the square in the exponent we have:

$$= \sqrt{\frac{m}{2\pi i\hbar\,\Delta t}} \exp\left[\frac{i}{\hbar}\left(\frac{1}{2}m\left(\frac{x_n - x_{n-1}}{\Delta t}\right)^2 - V(x_{n-1})\right)\Delta t\right]$$

$$= \sqrt{\frac{m}{2\pi i\hbar\,\Delta t}} \exp\left[\frac{i}{\hbar}\left(\frac{1}{2}m(\dot{x}_{n-1})^2 - V(x_{n-1})\right)\Delta t\right]$$

$$\lim_{\Delta t\to 0}\langle x_n t_{n-1} + \Delta t | x_{n-1}, t_{n-1}\rangle = \sqrt{\frac{m}{2\pi i\hbar\,\Delta t}} \exp\left[\frac{i}{\hbar}L(x_{n-1}, \dot{x}_{n-1})\Delta t\right]$$

Now if we substitute this expression into the transition amplitude we had before we get:

$$\langle x_N, t_N | x_1, t_1\rangle = \int\int \dots \int \langle x_N, t_N | x_{N-1}, t_{N-1}\rangle\langle x_{N-1}, t_{N-1} | x_{N-2}, t_{N-2}\rangle \dots \langle x_2, t_2 | x_1, t_1\rangle\, dx_{N-1}dx_{N-2}\dots dx_2$$

$$= \lim_{N\to\infty}\left(\frac{m}{2\pi i\hbar\,\Delta t}\right)^{\frac{N-1}{2}} \int\int \dots \int \exp\left[\frac{i}{\hbar}L(x_{n-1}, \dot{x}_{n-1})\Delta t\right] \dots \exp\left[\frac{i}{\hbar}L(x_1, \dot{x}_1)\Delta t\right] dx_{N-1}dx_{N-2}\dots dx_2$$

$$= \lim_{N\to\infty}\left(\frac{m}{2\pi i\hbar\,\Delta t}\right)^{\frac{N-1}{2}} \int\int \dots \int \prod_{n=2}^{\infty} \exp\left[\frac{i}{\hbar}L(x_{n-1}, \dot{x}_{n-1})\Delta t\right] dx_{N-1}dx_{N-2}\dots dx_2$$

$$\langle x_N, t_N | x_1, t_1\rangle = \lim_{N\to\infty}\left(\frac{m}{2\pi i\hbar\,\Delta t}\right)^{\frac{N-1}{2}} \int\int \dots \int \exp\left[\frac{i}{\hbar}\sum_{n=2}^{\infty} S(x_{n-1}, \dot{x}_{n-1})\right] dx_{N-1}dx_{N-2}\dots dx_2$$

Which is often written in the shorthand as the Feynman path integral:

$$\langle x_N, t_N | x_1, t_1\rangle = \int_{x_1}^{x_N} \mathbb{D}[x(t)] \exp\left[\frac{i}{\hbar}\int_{t_1}^{t_N} L(x_{n-1}, \dot{x}_{n-1})\, dt\right]$$

Density Matrices

Density matrix operator

This is defined as:

$$\hat{\rho} = \sum_i w_i |\alpha^i\rangle\langle\alpha^i|$$

Matrix elements of the density matrix are:

$$\rho_{jk} = \langle j|\hat{\rho}|k\rangle = \sum_i w_i \langle k|\alpha^i\rangle\langle\alpha^i|j\rangle$$

It evolves over time as:

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\}$$

The ensemble average is given by $[A] = \mathrm{Tr}(\rho A)$.

Density matrix examples

1. A completely polarized beam with all spins in the state $|\uparrow_z\rangle$ has density matrix

$$\hat{\rho} = |\uparrow_z\rangle\langle\uparrow_z| = \begin{pmatrix} 1 \\ 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} \langle\uparrow|\hat{\rho}|\uparrow\rangle & \langle\uparrow|\hat{\rho}|\downarrow\rangle \\ \langle\downarrow|\hat{\rho}|\uparrow\rangle & \langle\downarrow|\hat{\rho}|\downarrow\rangle \end{pmatrix}.$$

2. A completely polarized beam with all spins in the state $|\uparrow_x\rangle$ has

$$|\uparrow_x\rangle = \tfrac{1}{\sqrt{2}}\big(|\uparrow_z\rangle + |\downarrow_z\rangle\big)$$

and therefore the density matrix

$$\hat{\rho} = \tfrac{1}{2}\big(|\uparrow_z\rangle + |\downarrow_z\rangle\big)\big(|\uparrow_z\rangle + |\downarrow_z\rangle\big) = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$$

noting that $\hat{\rho}^2 = \hat{\rho}$, $\mathrm{Tr}(\hat{\rho}S_x) = \hbar/2$ and $(\hat{\rho}S_z) = 0$.

3. An unpolarized beam consisting of a 50-50 mixture has density matrix

$$\hat{\rho} = \tfrac{1}{2}\big(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\big) = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

noting that $\mathrm{Tr}(\hat{\rho}S_x) = \mathrm{Tr}(\hat{\rho}S_y) = \mathrm{Tr}(\hat{\rho}S_z) = 0$, so there is no preferred spin direction, and that this system cannot be represented by a state vector.

4. A partially polarized beam – say, 75% $|\uparrow_z\rangle$ and 25% $|\uparrow_x\rangle$ – has density matrix

$$\hat{\rho} = \tfrac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \tfrac{1}{4}\begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} = \begin{pmatrix} 7/8 & 1/8 \\ 1/8 & 1/8 \end{pmatrix}.$$

To find the density matrix of a state of 75% $|s_z+\rangle$ and 25% $|s_x+\rangle$ in the usual basis we have:

$$\begin{aligned}
\rho &= \frac{3}{4}|S_z^+\rangle\langle S_z^+| + \frac{1}{4}|S_x^+\rangle\langle S_x^+| \\
&= \frac{3}{4}|+\rangle\langle+| + \frac{1}{4}\left(\frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}|-\rangle\right)\left(\frac{1}{\sqrt{2}}\langle+| + \frac{1}{\sqrt{2}}\langle-|\right) \\
&= \frac{3}{4}|+\rangle\langle+| + \frac{1}{8}(|+\rangle\langle+| + |-\rangle\langle+| + |+\rangle\langle-| + |-\rangle\langle-|) \\
&= \frac{3}{4}|+\rangle\langle+| + \frac{1}{8}(|+\rangle\langle+| + |-\rangle\langle+| + |+\rangle\langle-| + |-\rangle\langle-|) \\
\rho &= \frac{7}{8}|+\rangle\langle+| + \frac{1}{8}|-\rangle\langle+| + \frac{1}{8}|+\rangle\langle-| + \frac{1}{8}|—|
\end{aligned}$$

Bloch sphere

The Bloch sphere is the most general density matrix for representing a two-state system. Written in terms of Pauli matrices it takes the form:

$$\hat{\rho} = \frac{1}{2}\big(\hat{I} + \hat{P}\cdot\hat{\sigma}\big) = \frac{1}{2}\big(\hat{I} + P_x\sigma_x + P_y\sigma_y + P_z\sigma_z\big) = \frac{1}{2}\begin{pmatrix} 1+P_z & P_z - iP_y \\ P_x + iP_y & 1-P_z \end{pmatrix}$$

Where $\hat{P}$ is the polarisation vector and points in the direction of the particle's spin. There is a one-to-one correspondence between possible density matrices of a two-state system and points on the unit 3-ball. Points on the boundary of the ball have $P^2 = 1$ and are pure states.

The polarisation vector evolves as evolves as:

$$\frac{d\tilde{P}}{dt} = \frac{1}{\hbar}\tilde{Q} \times \tilde{P}$$

Where the Hamiltonian is paramaterised as:

$$\tilde{H} = \frac{\hbar}{2}\tilde{\Omega} \cdot \tilde{\sigma} = \frac{\hbar}{2}\left(\Omega_x\sigma_x + \Omega_y\sigma_y + \Omega_z\sigma_z\right)$$

Therefore under time evolution, the polarization vector P maintains a constant length. P precesses about Q with a constant angular velocity $\omega = \tilde{Q}/\hbar$.

Angular Momentum

Generator of rotation

By the necessary properties of Unitarity, combination of rotations, etc, we know that the infinitesimal rotation operator $D_\epsilon(r)$ must take the form:

$$U_\epsilon = 1 - iG\epsilon$$

We identify the angular momentum $J/\hbar$ as the generator of rotation:

$$D(\hat{n}, d\phi) = 1 - \frac{i(\tilde{J} \cdot \hat{n})}{\hbar}d\phi$$

A finite rotation is obtained by performing successive infinitesimal rotations about the same axis. If we take the z-axis for example we have:

$$D_z(\phi) = \lim_{N\to\infty}\left[1 - \frac{iJ_z}{\hbar}\frac{\phi}{N}\right]^N$$
$$D_z(\phi) = \exp\left(-\frac{iJ_z\phi}{\hbar}\right)$$

Operators and commutators

Some of the most important results for angular momentum are summarised below:

$$[J_x, J_y] = i\hbar J_z$$
$$[J_x, J_z] = i\hbar J_y$$
$$[J_y, J_z] = i\hbar J_x$$
$$[J^2, J_k] = 0$$
$$[S_x, S_y] = i\hbar S_z$$

Note that the J operator is total angular momentum, S is spin angular momentum:

$$J^2|j,m\rangle = j(j+1)\hbar^2|j,m\rangle$$
$$J_z|j,m\rangle = m\hbar|j,m\rangle$$

$$J_+|j,m\rangle = \sqrt{(j-m)(j+m+1)}\hbar|j,m+1\rangle$$
$$J_-|j,m\rangle = \sqrt{(j+m)(j-m+1)}\hbar|j,m-1\rangle$$
$$S^2|s,m\rangle = s(s+1)\hbar^2$$
$$S_z|s,m\rangle = m\hbar$$
$$m = -j, -j+1, .., j-1, j = 2j+1 \text{ states}$$

Note that $J^2|j\rangle = j(j+1)|j\rangle$ is the eigenvalue equation for j only, so $|1,0\rangle + |1,1\rangle$ would be an eigenstate of J^2.

Euler angles

An arbitrary euler rotation can be represented as:

$$D(\alpha,\beta,\gamma) = D_z(\alpha)D_y(\beta)D_z(\gamma)$$

With the rotation operator defined as:

$$D(R) = D_{\hat{n}}(\phi) = \exp\left(-i\frac{\tilde{J}\cdot\hat{n}}{\hbar}\phi\right)$$

The arbitrary euler rotation then becomes:

$$D_z(\alpha)D_y(\beta)D_z(\gamma) = \exp\left(-i\frac{J_z}{\hbar}\alpha\right)\exp\left(-i\frac{J_y}{\hbar}\beta\right)\exp\left(-i\frac{J_z}{\hbar}\gamma\right)$$

If we have $j = \frac{1}{2}$ this becomes:

$$D_z(\alpha)D_y(\beta)D_z(\gamma) = \exp\left(-i\frac{\sigma_3}{\hbar}\alpha\right)\exp\left(-i\frac{\sigma_2}{\hbar}\beta\right)\exp\left(-i\frac{\sigma_3}{\hbar}\gamma\right)$$
$$= \begin{pmatrix} e^{-i\alpha/2} & 0 \\ 0 & e^{i\alpha/2} \end{pmatrix}\begin{pmatrix} \cos\left(\frac{\beta}{2}\right) & -\sin\left(\frac{\beta}{2}\right) \\ \sin\left(\frac{\beta}{2}\right) & \cos\left(\frac{\beta}{2}\right) \end{pmatrix}\begin{pmatrix} e^{-i\gamma/2} & 0 \\ 0 & e^{i\gamma/2} \end{pmatrix}$$

Using the relation:

$$\exp\left(-\frac{i\sigma_i\phi}{2}\right) = \tilde{I}\cos\left(\frac{\phi}{2}\right) - i\tilde{\sigma_i}\sin\left(\frac{\phi}{2}\right)$$

Matrix elements of angular momentum

For a given rotation operator $d(R)$, the matrix elements are called Wigner functions are written as:

$$D^j_{m,m'}(R) = \langle j,m'|D(R)|j,m\rangle$$

Rotations change m but do not change total angular momentum j.

Wigner rotation matrices form a group, and so are related as:

$$\sum_{m'} D^j_{m'',m'}(R_1)D^j_{m',m}(R_2) = D^j_{m'',m}(R_1R_2)$$

Wigner matrices are an irreducible representation of the rotational group, and take block-diagonal form.

$$\langle j',m'|J^2|j,m\rangle = j(j+1)\hbar^2\delta_{j'j}\delta_{m'm}$$

$$\langle j', m'|J_z|j, m\rangle = m\hbar^2\delta_{j'j}\delta_{m'm}$$
$$\langle j', m'|J_\pm|j, m\rangle = \sqrt{(j \mp m)(j \pm m + 1)}\hbar\delta_{j'j}\delta_{m'm\pm1}$$

Upon rotation by angles $R = (\alpha, \beta, \gamma)$ the new matrix elements are given by:

$$D^j_{m'm}(R) = \langle j, m'|\exp\left(-i\frac{\tilde{J}\cdot\hat{n}}{\hbar}\phi\right)|j, m\rangle$$
$$D^j_{m'm}(\alpha, \beta, \gamma) = \langle j, m'|\exp\left(-i\frac{J_z}{\hbar}\alpha\right)\exp\left(-i\frac{J_y}{\hbar}\beta\right)\exp\left(-i\frac{J_z}{\hbar}\gamma\right)|j, m\rangle$$
$$= e^{-i(m'\alpha+m\gamma)}\langle j, m'|\exp\left(-i\frac{J_y}{\hbar}\beta\right)|j, m\rangle$$
$$= e^{-i(m'\alpha+m\gamma)}\langle j, m'|\exp\left(-\frac{(J_+ - J_-)}{2\hbar}\beta\right)|j, m\rangle$$
$$D^j_{m'm}(\alpha, \beta, \gamma) = e^{-i(m'\alpha+m\gamma)}d^j_{m',m}(\beta)$$

We thus need to compute the matrix of dimensionality determined by j:

$$J^{(j=1)}_{m',m;y} = \langle j, m'|\frac{(J_+ - J_-)}{2\hbar}|j, m\rangle$$

We then take the Taylor expansion to find the matrix exponential:

$$\exp\left(-J^{(j=1)}_{m',m;y}\beta\right) = -J^{(j=1)}_{m',m;y}\beta + \frac{1}{2!}\left(J^{(j=1)}_{m',m;y}\beta\right)^2 - \frac{1}{3!}\left(J^{(j=1)}_{m',m;y}\beta\right)^3 + \cdots$$

So to first order we have:

$$D^j_{m'm}(\alpha, \beta, \gamma) = -e^{-i(m'\alpha+m\gamma)}\langle j, m'|\frac{(J_+ - J_-)}{2\hbar}|j, m\rangle\beta$$

The internal matrix elements can be calculated by using the known $J_\pm$ matrix elements.

In terms of d functions a rotation then takes the form:

$$D(\alpha, \beta, \gamma)|j, m\rangle = \sum_{m'}|j, m'\rangle\langle j, m'|D(R)|j, m\rangle$$
$$D(\alpha, \beta, \gamma)|j, m\rangle = \sum_{m'}|j, m'\rangle e^{-i(m'\alpha+m\gamma)}d^j_{m',m}(\beta)$$

Matrix elements with spherical harmonics

An easier way to calculate the same thing is to use spherical harmonics. The general formula here is:

$$D^j_{m,0}(R) = \langle j, 0|D(\alpha, \beta, \gamma = 0)|j, m\rangle = \sqrt{\frac{4\pi}{(2l+1)}}Y_l^{m^*}(\theta = \beta, \phi = \alpha)$$

For example, consider rotating the state $|l = 2, m = 0\rangle = |2,0\rangle$ by an angle β. We can compute this as:

$$D(0, \beta, 0)|2,0\rangle = \sum_{m'}|2, m'\rangle\langle 2, m'|\, D(0, \beta, 0)|2,0\rangle$$
$$= \sum_{m'}|2, m'\rangle D^2_{m,0}(R)$$

$$= \sum_{m'} |2,m'\rangle \sqrt{\frac{4\pi}{5}} Y_2^{m^*}(\beta,0)$$

$$D(0,\beta,0)|2,0\rangle = \sqrt{\frac{4\pi}{5}} \sum_{m'} |2,m'\rangle Y_2^{m^*}(\beta,0)$$

So for a given final state $|2,m'\rangle$ the probability of finding the system in the new state after rotation is:

$$|\langle 2,0|D(R)|2,m'\rangle|^2 = \frac{4\pi}{5} \left| \sum_{m'} \langle 2,0|2,m'\rangle Y_2^{m^*}(\beta,0) \right|^2$$
$$= \frac{4\pi}{5} \left| Y_2^{m^*}(\beta,0) \right|^2$$

Matrix elements of linear momentum

These can be found using the commutator relation for dx/dt:

$$\langle n'l'm'|p_x|nlm\rangle = \langle n'l'm'|m_0 \frac{dx}{dt}|nlm\rangle$$
$$= \langle n'l'm'|\frac{m_0}{i\hbar}[x,H]|nlm\rangle$$
$$= \frac{m_0}{i\hbar}\langle n'l'm'|(xH - Hx)|nlm\rangle$$
$$= \frac{m_0}{i\hbar}(\langle n'l'm'|xH|nlm\rangle - \langle n'l'm'|Hx|nlm\rangle)$$
$$= \frac{m_0}{i\hbar}(E_n\langle n'l'm'|x|nlm\rangle - E_{n'}\langle n'l'm'|x|nlm\rangle)$$
$$\langle n'l'm'|p_x|nlm\rangle = \frac{m_0}{i\hbar}(E_n - E_{n'})$$

Intrinsic Spin

Considering intrinsic spin, we have $J \to S$, with S obeying the same commutation relations as J. In the case of spin ½ particles, we have the specific form:

$$\tilde{S} = \hbar\frac{\tilde{\sigma}}{2}$$

Where the Pauli matrices are:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Giving the components of angular momentum:

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

This can also be written in terms of outer products. When acting on arbitrary kets written in the usual $\{|+\rangle, |-\rangle\}$ basis, they deliver the x,y, or z components of spin angular momentum in the $\{|+\rangle, |-\rangle\}$ basis:

$$S_x = \frac{\hbar}{2}(|+\rangle\langle -| + |-\rangle\langle +|)$$
$$S_y = \frac{\hbar}{2}(-|+\rangle\langle -| + |-\rangle\langle +|)$$

$$S_z = \frac{\hbar}{2}(|+\rangle\langle+| - |-\rangle\langle-|)$$

With basis vectors typically written as:

$$|+\rangle = |1/2, 1/2\rangle = \begin{pmatrix}1\\0\end{pmatrix}$$
$$\langle+| = \langle 1/2, 1/2| = (1 \quad 0)$$
$$|-\rangle = |1/2, -1/2\rangle = \begin{pmatrix}0\\1\end{pmatrix}$$
$$\langle-| = \langle 1/2, -1/2| = (0 \quad 1)$$

An arbitrary spin ½ state can be written as:

$$|\alpha\rangle = a|+\rangle + b|-\rangle$$

This rotates by angle ϕ about the z axis as:

$$D_z(\phi)|\alpha\rangle = \exp\left(-\frac{i}{\hbar}S_z\phi\right)$$

Addition of angular momenta

When considering both orbital and spin angular momentum, the total angular momentum becomes:

$$J = L + S$$

A combined rotation on two angular momentum is written as:

$$D_1(R)\otimes D_2(R) = \exp\left(-i\frac{\tilde{J}_1\cdot\hat{n}}{\hbar}\phi\right)\exp\left(-i\frac{\tilde{J}_2\cdot\hat{n}}{\hbar}\phi\right)$$

We have two possible choices for base kets of the total angular momentum system:

$$|j_1 j_2; m_1 m_2\rangle$$
$$|j_1 j_2; jm\rangle$$

The relevant eigenvalue relations are:

$$J_1^2|j_1 j_2; m_1 m_2\rangle = j_1(j_1+1)\hbar^2|j_1 j_2; m_1 m_2\rangle$$
$$J_{1z}|j_1 j_2; m_1 m_2\rangle = m_1\hbar|j_1 j_2; m_1 m_2\rangle$$
$$J_2^2|j_1 j_2; m_1 m_2\rangle = j_2(j_2+1)\hbar^2|j_1 j_2; m_1 m_2\rangle$$
$$J_{2z}|j_1 j_2; m_1 m_2\rangle = m_2\hbar|j_1 j_2; m_1 m_2\rangle$$

$$J_1^2|j_1 j_2; jm\rangle = j_1(j_1+1)\hbar^2|j_1 j_2; jm\rangle$$
$$J_2^2|j_1 j_2; jm\rangle = j_2(j_2+1)\hbar^2|j_1 j_2; jm\rangle$$
$$J^2|j_1 j_2; jm\rangle = j(j+1)\hbar^2|j_1 j_2; jm\rangle$$
$$J_z|j_1 j_2; jm\rangle = m\hbar|j_1 j_2; jm\rangle$$

These are connected by the relation:

$$|j_1 j_2; jm\rangle = \sum_{m_1}\sum_{m_2}|j_1 j_2; m_1 m_2\rangle\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle$$

Where the matrix elements to the right are called the Clebsch-Gordan coefficients. They are always zero unless both of the following conditions are satisfied:

- $m = m_1 + m_2$
- $|j_1 - j_2| \leq j \leq j_1 + j_2$

These two rules allow us to determine the only allowed value of m, and all possible allowed values of j, given an initial j_1 and j_2.

Useful formula for intrinsic spin:

$$S^2 = S_x^2 + S_y^2 + S_z^2 = \left(\frac{3}{4}\right)\hbar^2 I$$
$$= S_1^2 + S_2^2 + 2S_1 \cdot S_2$$

Tensor operators

In quantum mechanics a vector operator is defined to be one with the following commutation relation relative to total angular momentum:

$$\left[V_i, J_j\right] = i\epsilon_{ijk}\hbar V_k$$

Tensor operators are generalisations of vector operators. One problem with working with tensor operators is that Cartesian coordinate matrix representations of them are reducible, but we want an irreducible representation. That is why we often use spherical tensors instead.

It is often useful to express angular momentum eigenstates in a spherical harmonic basis:

$$\langle \hat{n} | l, m \rangle = Y_l^m(\theta, \phi) = Y_l^m(\hat{n})$$

A spherical tensor is computed similarly, by taking a tensor of rank k and magnetic quantum number q, written T_q^k, and writing this as a spherical harmonic function with V replacing $\hat{n}$:

$$T_q^k = Y_{l=k}^{m=q}(\tilde{V})$$

The basic idea is simply to take a Cartesian tensor of rank k and write it as a spherical harmonic function with $l = k$. This is easiest to do by consulting a table of spherical harmonics, and the transformation laws:

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

For example, if we wanted to write $\tilde{V} = \left(V_x, V_y, V_z\right)$ with $k = 1$ as a spherical tensor, we would have:

$$T_q^1(\tilde{V}) = Y_1^q\left(\frac{\tilde{x}}{r} \to \tilde{V}\right)$$
$$= \left\{Y_1^{-1}\left(\frac{\tilde{x}}{r} \to \tilde{V}\right), Y_1^0\left(\frac{\tilde{x}}{r} \to \tilde{V}\right), Y_1^{+1}\left(\frac{\tilde{x}}{r} \to \tilde{V}\right)\right\}$$
$$= \left\{\sqrt{\frac{3}{4\pi}}\frac{V_x - iV_y}{\sqrt{2}}, \sqrt{\frac{3}{4\pi}}V_z, -\sqrt{\frac{3}{4\pi}}\frac{V_x + iV_y}{\sqrt{2}}\right\}$$
$$T_q^1(\tilde{V}) = \sqrt{\frac{3}{4\pi}}\left\{\frac{V_x - iV_y}{\sqrt{2}}, V_z, -\frac{V_x + iV_y}{\sqrt{2}}\right\}$$

If $V_x = x, V_y = y, V_z = z$ then we can write this as a sum of spherical harmonics directly:

$$\{x,y,z\} = \sqrt{\frac{3}{4\pi}}\left\{\frac{r\sin\theta\cos\phi - ir\sin\theta\sin\phi}{\sqrt{2}}, r\cos\theta, -\frac{r\sin\theta\cos\phi + ir\sin\theta\sin\phi}{\sqrt{2}}\right\}$$

$$= \left\{\frac{r}{\sqrt{2}}\sqrt{\frac{3}{4\pi}}e^{-i\phi}\sin\theta, r\sqrt{\frac{3}{4\pi}}\cos\theta, -\frac{r}{\sqrt{2}}\sqrt{\frac{3}{4\pi}}e^{i\phi}\sin\theta\right\}$$

$$\{x,y,z\} = \left\{\frac{r}{\sqrt{2}}Y_1^{-1}(\theta,\phi), rY_0^0(\theta,\phi), \frac{r}{\sqrt{2}}Y_1^1(\theta,\phi)\right\}$$

One can also work backwards, beginning with the xy term (for example), and finding how to represent this in terms of spherical harmonics.

l = 0[1] [edit]

$$Y_0^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$$

l = 1[1] [edit]

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x-iy)}{r}$$

$$Y_1^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\frac{z}{r}$$

$$Y_1^1(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x+iy)}{r}$$

l = 2[1] [edit]

$$Y_2^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)^2}{r^2}$$

$$Y_2^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot\cos\theta = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)z}{r^2}$$

$$Y_2^0(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta - 1) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot\frac{(2z^2 - x^2 - y^2)}{r^2}$$

$$Y_2^1(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot\cos\theta = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)z}{r^2}$$

$$Y_2^2(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)^2}{r^2}$$

Wigner-Eckart theorem

This theorem states that matrix elements of spherical tensor operators on the basis of angular momentum eigenstates can be expressed as the product of two factors, one of which is independent of angular momentum orientation, and the other a Clebsch–Gordan coefficient which depends purely on geometric factors and is independent of the particular tensor in question.

$$\langle\alpha', j', m'|T_q^k|\alpha, j, m\rangle = \langle jk; mq|jk; j'm'\rangle\frac{\langle\alpha' j'|T^k|\alpha j\rangle}{\sqrt{2j+1}}$$

Where α is some (optional) additional quantum number, and once again:

- $m' = m + q$
- $|j - k| \leq j' \leq j + k$

Many-body Quantum Physics

The spin-statistics theorem

Half integer spin particles are fermions. When two identical particles are interchanged in a fermion wavefunction, the result is anti-symmetric.

$$P_{ij}|N \text{ identical bosons}\rangle = +|N \text{ identical bosons}\rangle$$
$$P_{ij}|N \text{ identical fermions}\rangle = -|N \text{ identical fermions}\rangle$$

The Pauli exclusion principle is an immediate corollary. Consider all possible linear combinations of a two-state system. Note that there are three possibilities for a boson:

$$|k'\rangle|k'\rangle, \qquad |k''\rangle|k''\rangle, \qquad \frac{1}{\sqrt{2}}(|k'\rangle|k''\rangle + |k''\rangle|k'\rangle)$$

But for a fermion there is only one possibility:

$$\frac{1}{\sqrt{2}}(|k'\rangle|k''\rangle - |k''\rangle|k'\rangle)$$

The only fermion possibility involves each individual fermion in a different state – both states involving two fermions in the same state are bosons. Thus it follows that no two fermions can occupy the same state. This special state is called the singlet state (since it is by itself), and is anti-symmetrical.

Slater determinants

A fermionic wavefunction can be written as:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\big(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\big)$$

This can be written as a determinant:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(x_1) & \phi_2(x_1)\\ \phi_1(x_2) & \phi_2(x_2)\end{vmatrix}$$

This can be generalised to an arbitrary number of fermions, resulting in what is called a slater determinant:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(x_1) & \phi_2(x_1) & \dots & \phi_N(x_1)\\ \phi_1(x_2) & \phi_2(x_2) & \dots & \phi_N(x_2)\\ \vdots & \vdots & \ddots & \vdots\\ \phi_1(x_N) & \phi_2(x_N) & \dots & \phi_N(x_N)\end{vmatrix}$$

Fock space

Since quantum particles are identical, it is often useful to simply specify the total number in each state:

$$|\alpha\rangle = |n_1, n_2, \dots, n_N\rangle$$
$$N = \sum_{\lambda} n_\lambda$$

This is called the occupation-number representation. We can also construct this formalism to work using creation and annihilation operators.

For bosons:

$$a_\lambda^\dagger|n_1, n_2, \dots, n_\lambda, \dots\rangle = \sqrt{n_\lambda + 1}|n_1, n_2, \dots, n_\lambda + 1, \dots\rangle$$
$$a_\lambda|n_1, n_2, \dots, n_\lambda, \dots\rangle = \sqrt{n_\lambda}|n_1, n_2, \dots, n_\lambda - 1, \dots\rangle$$
$$n_\lambda = a_\lambda^\dagger a_\lambda$$

For fermions:

$$a_\lambda^\dagger|n_1, n_2, \dots, n_\lambda, \dots\rangle = \epsilon_\lambda\sqrt{n_\lambda - 1}|n_1, n_2, \dots, n_\lambda + 1, \dots\rangle$$
$$a_\lambda|n_1, n_2, \dots, n_\lambda, \dots\rangle = \epsilon_\lambda\sqrt{n_\lambda}|n_1, n_2, \dots, n_\lambda - 1, \dots\rangle$$
$$n_\lambda = a_\lambda^\dagger a_\lambda$$
$$\epsilon_\lambda = \begin{cases} -1, & \text{if } \sum_{\beta<\lambda} n_\beta \text{ is even} \\ +1, & \text{if } \sum_{\beta<\lambda} n_\beta \text{ is odd} \end{cases}$$

An arbitrary state in fock space can be generated by applying creation operators to the vacuum state:

$$|n_1, n_2, \dots\rangle_B = \prod_\lambda \frac{\left(a_\lambda^\dagger\right)^{n_\lambda}}{\sqrt{n_\lambda!}}|0\rangle$$
$$|n_1, n_2, \dots\rangle_F = \prod_\lambda \left(a_\lambda^\dagger\right)^{n_\lambda}|0\rangle$$

The field operator $\hat{\psi}^\dagger(r)$ creates a particle at r, and is written in terms of its corresponding ket $|\alpha\rangle$ as:

$$\hat{\psi}^\dagger(r) = \sum_\lambda \langle\alpha^\lambda|r\rangle a_\lambda^\dagger$$

Single particle operators (such as position and momentum) in Fock space operate on only one energy state at a time:

$$\begin{aligned} \mathcal{F}(r_1, r_2, \dots, r_N) &= \sum_{k=1}^{N} f(r_k) \\ &= \int \hat{\psi}^\dagger(r) f(r) \hat{\psi}(r)\, dr \\ &= \sum_{\lambda\mu} \langle\alpha^\lambda|f|\alpha^\mu\rangle\, a_\lambda^\dagger a_\lambda \end{aligned}$$

Hartree-Fock approximation

The Hartree-Fock Hamiltonian is given by:

$$\widehat{H} = \sum_{\lambda\mu} \langle\alpha^\lambda|h|\alpha^\mu\rangle\, a_\lambda^\dagger a_\mu + \frac{1}{2}\sum_{\lambda\mu}\sum_{\lambda\mu} \langle\alpha^\lambda\alpha^\mu|g|\alpha^{\lambda'}\alpha^{\mu'}\rangle a_\lambda^\dagger a_\mu^\dagger a_{\mu'} a_{\lambda'}$$

Where h is the single-particle interaction and g the two-particle interaction. The ground state of this system is given by:

$$|\Phi_0\rangle = |n_1, n_2, \dots, n_N, 0, 0, \dots\rangle = a_1^\dagger a_2^\dagger \dots a_N^\dagger|0\rangle$$

A more general state can be written as a particle-hole expansion, with particles places in states $r, s, u \dots$ and eliminated from states $a, b, c \dots$

$$|\Psi\rangle = \left|\Phi_{abc\ldots}^{rst\ldots}\right\rangle = a_r^\dagger a_s^\dagger a_u^\dagger \ldots a_a a_b a_c \ldots |\Phi_0\rangle$$

We can expand this arbitrary state as a series in terms of the number of excitations by which it differs from the ground state:

$$|\Psi\rangle = c_0|\Phi_0\rangle + \left(\frac{1}{1!}\right)^2 \sum_a \sum_r c_a^r |\Phi_a^r\rangle + \left(\frac{1}{2!}\right)^2 \sum_{ab} \sum_{rs} c_{ab}^{rs} |\Phi_{ab}^{rs}\rangle + \left(\frac{1}{3!}\right)^2 \sum_{abc} \sum_{rst} c_{abc}^{rst} |\Phi_{abc}^{rst}\rangle + \cdots$$

The Hartree-Fock approximation truncates this series to a single particle-hole excitation, so that we get:

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_a \sum_r c_a^r |\Phi_a^r\rangle$$

If a state is to be the ground state, it must be orthogonal to all the excited states (otherwise it would be an excited state and not the ground state). Thus we must have what is called the Brillouin condition:

$$\begin{aligned} &E_0\langle\Phi_a^r|\Phi_0\rangle = 0 \\ &\langle\Phi_a^r|\hat{H}|\Phi_0\rangle = 0 \\ &\langle\Phi_a^r|a_a^\dagger a_r \hat{H}|\Phi_0\rangle = 0 \\ &\langle r|h|a\rangle + \sum_b [\langle rb|g|ab\rangle - \langle rb|g|ba\rangle] = 0 \end{aligned}$$

Energy levels are then given by:

$$\begin{aligned} &\langle\Psi|\hat{H}|\Psi\rangle = \langle\phi_0|\hat{H}|\phi_0\rangle + 2c_a^r\langle\Phi_a^r|\hat{H}|\Phi_0\rangle + O((c_a^r)^2) \\ &\langle\Psi|\hat{H}|\Psi\rangle = E_0 + O(E_0^2) \end{aligned}$$

Single Hartree-Fock energies are given by:

$$\epsilon_a = \langle a|h|a\rangle + \sum_b [\langle ab|g|ab\rangle - \langle ab|g|ba\rangle]$$

Excited state energies are likewise given by:

$$E_0^a = E_0 - \langle a|h|a\rangle - \sum_b [\langle ab|g|ab\rangle - \langle ab|g|ba\rangle]$$

We thus have Koopman's Theorem, which is useful for estimating ionisation energies:

$$E_0 - E_0^a \approx \epsilon_a$$

Approximation Methods

Perturbation theory

We consider a time-dependent Hamiltonian decomposed into a part with known solutions H_0 and a small perturbation V.

$$H = H_0 + V$$

We can consider a series of energy corrections of the form:

$$E = E_0 + E_1 + E_2 + \cdots$$

Where:

$$E_0 = \langle\psi_0|H_0|\psi_0\rangle$$
$$E_1 = \langle\psi_0|V|\psi_0\rangle$$
$$E_2 = \sum_{k\neq 0} \frac{\langle\psi_0|V|\psi_k\rangle\langle\psi_k|V|\psi_0\rangle}{\epsilon_0 - \epsilon_k}$$

Note that all energy corrections above E_0 are negative, since more accurate approximations will always deliver a lower minimum energy than poorer ones.

Variational principle

The variational principle begins by specifying a trial wavefunction $\psi_t(\alpha_k)$ which is a function of some parameters α_k. The parameters are then incrementally adjusted so that they yield the minimum energy:

$$\frac{\partial}{\partial\alpha_k}\left[\frac{\langle\psi(\alpha_k)|H|\psi(\alpha_k)\rangle}{\langle\psi(\alpha_k)|\psi(\alpha_k)\rangle}\right] = 0$$

The linear variational method makes use of the expansion:

$$|\psi(c_k)\rangle = \sum_k c_k|\phi_k\rangle$$

Numerically solving this equation is facilitated by calculation of the secular determinant:

$$\det\left[\langle\phi_j|H|\phi_i\rangle - E\langle\phi_i|\phi_j\rangle\right] = 0$$

Once we have solved this for the eigenvalues E, we substitute these into the following equation to solve for the expansion coefficients:

$$\sum_i \left(\langle\phi_j|H|\phi_i\rangle - E\langle\phi_i|\phi_j\rangle\right)c_i = 0$$

Dirac's interaction picture

Consider a time-dependent Hamiltonian:

$$H = H_0 + V(t)$$

In the Schrodinger picture, we determine the time-dependent coefficients such that:

$$|\alpha, t\rangle_S = \sum_n c_n(t)\exp[-iE_nt/\hbar]\,|n\rangle$$

The time-dependent coefficients accommodate the time-dependent potential $V(t)$, while the time-variation of the constant part H_0 is incorporated into the exponential term.

By contrast, in the Interaction picture we define:

$$|\alpha, t\rangle_I = \exp[-iH_0t/\hbar]\,|\alpha, t\rangle_S$$

Interaction picture operators are defined as:

$$A_I = \exp[iH_0 t/\hbar] A_S \exp[-iH_0 t/\hbar]$$

Or in the case of the time-dependent potential:

$$V_I = \exp[iH_0 t/\hbar] V \exp[-iH_0 t/\hbar]$$

If we differentiate the equation for $|\alpha, t\rangle_S$ we find that for state kets:

$$i\hbar \frac{\partial}{\partial t} |\alpha, t\rangle_I = V_I |\alpha, t\rangle_I$$

The time evolution of operators is given by:

$$\frac{\partial A_I}{\partial t} = -\frac{i}{\hbar}[A_I, H_0]$$

Thus in the interaction picture both kets and operators evolve with time, but operators only evolve with the time-independent part of the Hamiltonian, with kets evolve with the interaction representation of the time-dependent part of the Hamiltonian only.

We can solve for the interaction picture ket by finding the time-dependent expansion coefficients:

$$|\alpha, t\rangle_I = \sum_n c_n(t) |n\rangle$$

These coefficients solve the set of coupled differential equations:

$$i\hbar \frac{\partial c_n(t)}{\partial t} = \langle n|V(t)|m\rangle \exp\left[i\left(\frac{E_n - E_m}{\hbar}\right)t\right] c_m(t)$$

This is called Dirac's variation of constants.

Time-dependent perturbation theory

We want to find an approximation for a series expansion of the constants that appear in Dirac's variation of constants method. If we assume that the state $|\alpha, t\rangle_I$ begins at $t = 0$ in state $|i\rangle$, then at any future time it will be given by:

$$|\alpha, t\rangle_I = U_I(t, t_0)|i\rangle$$

Expanding in terms of eigenkets $\{|m\rangle\}$ we have:

$$|\alpha, t\rangle_I = \sum_m |m\rangle\langle m|\, U_I(t, 0)|i\rangle$$
$$|\alpha, t\rangle_I = \sum_m c_m(t)|m\rangle$$

Thus we want to solve for:

$$c_m(t) = c_m^0 + c_m^1 + c_m^2 + \cdots$$

With $c_m(t) = \langle m|U_I(t, 0)|i\rangle$. In the most general case we have a Dyson series expansion for U_I:

$$U_I(t, t_0) = \tilde{I} + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} \int_{t_0}^{t_1} \dots \int_{t_0}^{t_{n-1}} V_I(t_1) V_I(t_2) \dots V_I(t_n)\, dt_1 dt_2 \dots dt_n$$

$$U_I(t,t_0) = \tilde{I} - \left(\frac{i}{\hbar}\right)\int_{t_0}^{t} V_I(t_1)\,dt_1 + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t}\int_{t_0}^{t_1} V_I(t_1)V_I(t_2)\,dt_1 dt_2 + \cdots$$

Pre and post multiplying by the appropriate kets we get:

$$c_m(t) = \langle m|i\rangle - \left(\frac{i}{\hbar}\right)\int_{t_0}^{t}\langle m|V_I(t_1)|i\rangle\,dt_1 + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t}\int_{t_0}^{t_1}\langle m|V_I(t_1)\sum_n |n\rangle\langle n|\,V_I(t_2)|i\rangle\,dt_1 dt_2 + \cdots$$

$$c_m(t) = \delta_{mi} - \left(\frac{i}{\hbar}\right)\int_{t_0}^{t}\langle m|V_I(t_1)|i\rangle\,dt_1 + \left(\frac{i}{\hbar}\right)^2 \sum_n \int_{t_0}^{t}\int_{t_0}^{t_1}\langle m|V_I(t_1)|n\rangle\langle n|V_I(t_2)|i\rangle\,dt_1 dt_2 + \cdots$$

This leads us to the coefficients for the series expansion:

$$c_m^0 = \delta_{mi}$$

$$c_m^1 = -\left(\frac{i}{\hbar}\right)\int_{t_0}^{t}\langle m|V(t_1)|i\rangle \exp\left(i\left(\frac{E_m - E_i}{\hbar}\right)t\right)dt_1$$

$$c_m^2 = \left(\frac{i}{\hbar}\right)^2 \sum_n \int_{t_0}^{t}\int_{t_0}^{t_1}\langle m|V(t_1)|n\rangle \exp\left(i\left(\frac{E_m - E_n}{\hbar}\right)t\right)\langle n|V(t_2)|i\rangle \exp\left(i\left(\frac{E_n - E_i}{\hbar}\right)t\right)dt_1 dt_2$$

Matrix elements will usually be provided in the question, or may need to be computed using spherical harmonics:

$$\begin{aligned}\langle nlm|\hat{x}|nlm\rangle &= \int \langle nlm|\hat{x}|x\rangle\langle x|nlm\rangle\ dx \\ &= \int x\langle nlm|x\rangle\langle x|nlm\rangle\ dx \\ &= \int x\left|Y_m^l\right|^2\ dx\end{aligned}$$

Scattering Theory

Scattering as a time-dependent perturbation

We model a scattering event as a time-dependent perturbation, in which the particle undergoing scattering experiences a scattering potential V which is non-zero over most of space, and only operates over a finite domain.

Let us here consider a system that evolves in the interaction picture according to:

$$|\alpha,t\rangle_I = U_I(t,t_0)|\alpha,t_0\rangle$$

With equation of motion:

$$i\hbar\frac{\partial}{\partial t}|\alpha,t\rangle = H|\alpha,t\rangle$$

Writing this in the interaction form this becomes:

$$i\hbar\frac{d}{dt}U_I(t,t_0) = V_I(t)U_I(t,t_0)$$
$$V_I(t) = \exp(iH_0 t\hbar)\,V(t)$$

We solve for the time evolution operator using the initial condition $U_I(t_0,t_0) = I$:

$$U_I(t,t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')U_I(t',t_0)\,dt'$$

We thus arrive at a formula for the transition amplitude from $|i\rangle$ to $|\alpha,t\rangle_I$

$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}\int_{t_0}^{t} \langle n|\exp(iH_0t\hbar)\,V(t)U_I(t',t_0)|i\rangle\,dt'$$
$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}\sum_m \langle n|V|m\rangle \int_{t_0}^{t} \exp(i(E_n-E_m)t\hbar)\,\langle m|U_I(t',t_0)|i\rangle\,dt'$$

Realising that the largest contribution to this integral will occur when $\langle m|U_I(t',t_0)|i\rangle = \delta_{mi}$ we can make approximation:

$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}\langle n|V|i\rangle \int_{t_0}^{t} \exp(i(E_n-E_i)t\hbar)\,dt'$$

Finally, we introduce a positive cut-off parameter $\epsilon \ll 1/t$ which ensures that the potential does not act in the limit $t_0 \to -\infty$. Hence we have:

$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}T_{ni} \int_{t_0}^{t} \exp(i(E_n-E_i)t\hbar)\exp(\epsilon t')\,dt'$$

Transition rate – Fermi's Golden Rule

The rate at which state $|n\rangle$ is populated from the initial state $|i\rangle$ is the time-derivative of the scattering probability:

$$\begin{aligned}
w_{in} &= \frac{d}{dt}|\langle n|U_I(t,-\infty)|i\rangle|^2 \\
&= \frac{1}{\hbar^2}\frac{d}{dt}\left|T_{ni}\int_{-\infty}^{t}\exp(i(E_n-E_i)t\hbar)\exp(\epsilon t')\,dt'\right|^2 \\
&= \frac{1}{\hbar^2}\frac{d}{dt}\left|T_{ni}\frac{\exp(i(E_n-E_i)t\hbar)\exp(\epsilon t)}{i(E_n-E_i)/\hbar+\epsilon}\right|^2 \\
&= \frac{1}{\hbar^2}\frac{d}{dt}\left[|T_{ni}|^2\frac{\hbar^2\exp(2\epsilon t)}{(E_n-E_i)^2+\epsilon^2}\right] \\
w_{in} &= \frac{2}{\hbar^2}|T_{ni}|^2\lim_{\epsilon\to 0}\left[\frac{\epsilon\hbar^2\exp(2\epsilon t)}{(E_n-E_i)^2+\epsilon^2}\right]
\end{aligned}$$

This limit is equal to $\pi\hbar\delta(E_n-E_i)$ so we get:

$$w_{in} = \frac{2}{\hbar^2}|T_{ni}|^2\pi\hbar\delta(E_n-E_i)$$
$$w_{i\to n} = \frac{2\pi}{\hbar}|T_{ni}|^2\delta(E_n-E_i)$$

This is known as Fermi's golden rule.

Scattering cross section

The scattering cross section is given by:

$$\frac{d\sigma}{d\Omega} = \left(\frac{mL^3}{2\pi h^2}\right)|T_{ni}|^2$$

Substituting in for the T-matrix which is derived in the next section, to second order this is:

$$\frac{d\sigma}{d\Omega} = \left(\frac{mL^3}{2\pi h^2}\right)\left|\langle n|V|i\rangle + \sum_m \langle n|V|m\rangle \frac{1}{E_i - E_m + i\epsilon}\langle m|V|i\rangle\right|^2$$

The T-matrix

To actually calculate anything we still need to determine what this T-matrix is. We can derive an expression for this matrix by equating the two different representations derived before for $\langle n|U_I(t,-\infty)|i\rangle$. We thus have:

$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}\sum_m \langle n|V|m\rangle \int_{-\infty}^{t} \exp(i(E_n - E_m)t'\hbar)\,\langle m|U_I(t',t_0)|i\rangle\,dt'$$

$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}T_{ni}\exp(i(E_n - E_i)t\hbar)\exp(\epsilon t)$$

Substituting the second into the first we get:

$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}\sum_m \langle n|V|m\rangle \int_{-\infty}^{t} \exp(i(E_n - E_m)t'\hbar)\left(\delta_{ni} - \frac{i}{\hbar}T_{ni}\exp(i(E_n - E_i)t'\hbar)\exp(\epsilon t')\right)dt'$$

$$\langle n|U_I(t,t_0)|i\rangle = \delta_{ni} - \frac{i}{\hbar}\left[\langle n|V|i\rangle + \sum_m \frac{\langle n|V|m\rangle T_{mi}}{(E_i - E_m) + i\epsilon}\right]\int_{-\infty}^{t} \exp(i(E_n - E_m)t'\hbar)\,dt'$$

$$T_{ni}\exp(i(E_n - E_i)t\hbar)\exp(\epsilon t) = \left[\langle n|V|i\rangle + \sum_m \frac{\langle n|V|m\rangle T_{mi}}{(E_i - E_m) + i\epsilon}\right]\int_{-\infty}^{t} \exp(i(E_n - E_m)t'\hbar)\,dt'$$

$$T_{ni} = \langle n|V|i\rangle + \sum_m \frac{\langle n|V|m\rangle T_{mi}}{(E_i - E_m) + i\epsilon}$$

Now we define a new set of kets $|\psi^+\rangle$, which are related to the T matrix by:

$$\begin{aligned} T_{ni} &= \langle n|T|i\rangle \\ &= \langle n|V|\psi^+\rangle \\ T_{ni} &= \sum_j \langle n|V|j\rangle\langle j|\psi^+\rangle \end{aligned}$$

So now we can write:

$$\langle n|V|\psi^+\rangle = \langle n|V|i\rangle + \sum_m \frac{\langle n|V|m\rangle\langle m|V|\psi^+\rangle}{(E_i - E_m) + i\epsilon}$$

$$|\psi^+\rangle = |i\rangle + \sum_m \frac{|m\rangle\langle m|V|\psi^+\rangle}{E_i - E_m + i\epsilon}$$

$$|\psi^+\rangle = |i\rangle + \frac{1}{E_i - E_m + i\epsilon}V|\psi^+\rangle$$

This is the Lippmann-Schwinger equation, which we will consider in more detail in the next section. Here we continue solving for the T-matrix by multiplying this equation by V:

$$V|\psi^+\rangle = V|i\rangle + V\frac{1}{E_i - E_m + i\epsilon}V|\psi^+\rangle$$

$$T|i\rangle = V|i\rangle + V\frac{1}{E_i - E_m + i\epsilon}T|i\rangle$$
$$T = V + V\frac{1}{E_i - E_m + i\epsilon}T$$

We have at last a recursive definition for T:

$$T = V + V\frac{1}{E_i - E_m + i\epsilon}V + V\frac{1}{E_i - E_m + i\epsilon}V\frac{1}{E_i - E_m + i\epsilon}V + \cdots$$

To second order, Fermi's golden rule therefore becomes:

$$w_{i\to n} = \frac{2\pi}{\hbar}\left|V + V\frac{1}{E_i - E_m + i\epsilon}V\right|^2 \delta(E_n - E_i)$$

Lippmann-Schwinger equation

This gives an expression for the scattered wave $|\psi^+\rangle$ in terms of the initial wave $|i\rangle$, the interaction potential V, and the green's function:

$$|\psi^+\rangle = |i\rangle = \frac{1}{E_i - H_0 + i\hbar\epsilon}V|\psi^+\rangle$$

This can also be written as an integral equation in position space:

$$\langle x|\psi^+\rangle = \langle x|i\rangle + \int \langle x|\frac{1}{E_i - H_0 + i\hbar\epsilon}|x'\rangle\langle x'|V|\psi^+\rangle\, d^3x'$$
$$\langle x|\psi^+\rangle = \langle x|i\rangle - \frac{2m}{\hbar^2}\int \frac{e^{\pm ik|x-x'|}}{4\pi|x-x'|}\langle x'|V|\psi^+\rangle\, d^3x'$$

For a local potential $\langle x'|V|x''\rangle = V(x')\delta(x' - x'')$ this simplifies to:

$$\langle x|\psi^+\rangle = \langle x|i\rangle - \frac{2m}{\hbar^2}\int \frac{e^{\pm ik|x-x'|}}{4\pi|x-x'|}V(x')\langle x'|\psi^+\rangle\, d^3x'$$

Since the Green's function:

$$G(x - x') = \frac{e^{\pm ik|x-x'|}}{4\pi|x-x'|}$$

Is the solution to the inhomogenous Helmholtz equation:

$$(\nabla^2 + k^2)G(x - x') = \delta^3(x - x')$$

The optical theorem

The optical theorem states that the total cross-section is directly related to the imaginary part of the scattering amplitude:

$$\sigma = \frac{4\pi}{k}\mathrm{Im}[f(k', k)]$$

Where the scattering amplitude is:

$$f(k', k) = -\frac{mL^3}{2\pi\hbar^2}\langle k'|T|k\rangle$$

The Born approximation

As long as the perturbation is relatively weak, we have the approximation scheme:

$$T = V + V\frac{1}{E_i - E_m + i\epsilon}V + V\frac{1}{E_i - E_m + i\epsilon}V\frac{1}{E_i - E_m + i\epsilon}V + \cdots$$

We are interested in solving for:

$$\langle k'|V|\psi^+\rangle = \langle k'|T|k\rangle$$

The first order Born approximation is thus to take:

$$T = V$$
$$|\psi^+\rangle = |k\rangle$$

The first order Born approximation is similarly:

$$T = V + V\frac{1}{E_i - E_m + i\epsilon}$$

Additional Notes

- To find the eigenvalues and eigenkets of an operator, write the operator in matrix form using the given basis, then just find the eigenvalues using the usual algebraic method. Eigenkets will be linear combinations of the basis you started with, so you just need to solve for the coefficients.
- If all else fails, try inserting a complete set of states
- Don't forget to normalise any eigenkets that you find
- $V(t) = -\int F(t)dx$
- $V|x\rangle = V(x)|x\rangle$
- Energy levels for the Harmonic oscillator: $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$
- When we measure spin in the x direction we are working in the x-basis, so we don't use the S_x operator in terms of Pauli matrices (that is expressed in the z-basis $+, -$). Instead we use the state ket for x or y written in the z-basis, and take the projection $\langle s_{xy}^{\pm}|\psi\rangle$.
- $Y_l^m(\theta, \phi) = \langle\hat{n}|lm\rangle$
- $L = x \times p \rightarrow L_i = \epsilon_{ijk}x_j p_k$
- $\langle n|V|i\rangle = \int\langle n|x\rangle V\langle x|i\rangle\, dx = \int \phi_i(x)V(x)\phi_i(x)dx$
- $$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} f(r,\theta,\varphi)r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi$$
- $\langle x|k\rangle = e^{ikx}$ and $\langle k|x\rangle = e^{-ikx}$
- $\hat{p} = -i\hbar\frac{\partial}{\partial x}$
- $\sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \sigma_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$
- $\tilde{S}\cdot\hat{n} = S_x\cos\alpha\sin\beta + S_y\sin\alpha\sin\beta + S_z\cos\beta$
- $H = p_x^2/2m$ for a free particle
- $\exp\left(-\frac{i\sigma_i\phi}{2}\right) = \tilde{I}\cos\left(\frac{\phi}{2}\right) - i\tilde{\sigma_i}\sin\left(\frac{\phi}{2}\right)$
- $|\alpha\rangle = \cos\left(\frac{\beta}{2}\right)|+\rangle + e^{i\alpha}\sin\left(\frac{\beta}{2}\right)|-\rangle$
- $[A] = \mathrm{Tr}(\rho A)$

- Sakurai problems:
    - Scattering - 6.1, 6.2, 6.3, 6.6, 6.7, 6.8, 6.10, 6.12
    - Approximation - 5.25, 5.26, 5.27, 5.28, 5.29, 5.30, 5.38
    - Angular momentum - 3.2, 3.8, 3.9, 3.14, 3.15, 3.21, 3.29, 3.30, 3.31, 3.32