QUANTUM DYNAMICS

The motion of a particle is described by a complex wavefunction \( \psi(\vec{r}, t) \) that gives the probability amplitude of finding a particle at point \( \vec{r} \) at time \( t \). If we know \( \psi(\vec{r}, t_0) \), how does it change with time?

\[
\psi(\vec{r}, t) \rightarrow \psi(\vec{r}, t) \quad t > t_0
\]

We will use our intuition here (largely based on correspondence to classical mechanics)

We start by assuming causality: \( \psi(t_0) \) precedes and determines \( \psi(t) \). So will be deriving a deterministic equation of motion for \( \psi(\vec{r}, t) \). Also, we assume time is a continuous parameter:

\[
\lim_{t \to t_0} \psi(t) = \psi(t_0)
\]

Define an operator that gives time-evolution of system.

\[
\psi(t) = U(t, t_0) \psi(t_0)
\]

This “time-displacement operator” is similar to the “space-displacement operator”

\[
\psi(\vec{r}) = e^{ik(\vec{r} - \vec{r}_0)} \psi(\vec{r}_0)
\]

which moves a wavefunction in space.

We also say that \( U \) does not depend on \( \psi \). It is a linear operator. This is necessary for conservation of probability, i.e. to retain normalization for the system.

\[
\text{if } \psi(t_0) = a_1 \psi_1(t_0) + a_2 \psi_2(t_0)
\]
\[ |\psi(t)\rangle = U(t,t_0) |\psi(t_0)\rangle \]

\[ = a_1 U(t,t_0) |\varphi_1(t_0)\rangle + a_2 U(t,t_0) |\varphi_2(t_0)\rangle \]

\[ = a_1(t)|\varphi_1\rangle + a_2(t)|\varphi_2\rangle \]

while \(|a_i(t)\rangle\) typically not equal to \(|a_i(0)\rangle\),

\[ \sum_n |a_n(t)|^2 = \sum_n |a_n(t_0)|^2 \]

**Properties of U(t,t_0)**

Time continuity: \( U(t,t) = 1 \)

Composition property: \( U(t_2,t_0) = U(t_2,t_1) U(t_1,t_0) \) (This should suggest an exponential form).

Note: Order matters!

\[ |\psi(t_2)\rangle = U(t_2,t_1) U(t_1,t_0) |\psi(t_0)\rangle = U(t_2,t_0) U(t_0,t) |\psi(t_0)\rangle \]

\[ \therefore U(t,t_0) U(t_0,t) = 1 \]

\[ \therefore U^{-1}(t,t_0) = U(t_0,t) \text{ inverse is time-reversal} \]

**Finding an equation of motion for U:**

Let’s write the time-evolution for an infinitesimal time-step, \( \delta t \).

\[ \lim_{\delta t \to 0} U(t_0 + \delta t, t_0) = 1 \]

We expect that for small \( \delta t \), the difference between \( U(t_0,t_0) \) and \( U(t_0 + \delta t, t_0) \) will be linear in \( \delta t \). (Think of this as an expansion for small \( t \):)
\[ U(t_0 + \delta t, t_0) = U(t_0, t_0) - i\Omega \delta t \]

\(\Omega\) is a time-dependent Hermitian operator. We’ll see later why the expansion must be complex.

Also, \(U(t_0 + \delta t, t_0)\) is unitary. We know that \(U^{-1}U = 1\) and also

\[ U^\dagger(t_0 + \delta t, t_0)U(t_0 + \delta t, t_0) = (1 + i\Omega^\dagger \delta t)(1 - i\Omega \delta t) \approx 1 \]

So, now we can write a differential equation for \(U\). We know that

\[ U(t + \delta t, t_0) = U(t + \delta t, t)U(t, t_0). \]

Knowing the change of \(U\) during the period \(\delta t\) allows us to write a differential equation for the time-development of \(U(t, t_0)\). Equation of motion for \(U\):

\[ \frac{d}{dt}U(t, t_0) = \lim_{\delta t \to 0} \frac{U(t + \delta t, t_0) - U(t, t_0)}{\delta t} = \lim_{\delta t \to 0} \frac{1}{\delta t} \left[ U(t + \delta t, t) - I \right] U(t, t_0) \]

The definition of our infinitesimal time step operator says that

\[ U(t + \delta t, t) = U(t, t) - i\Omega \delta t = 1 - i\Omega \delta t. \]

So we have:

\[ \frac{\partial U(t, t_0)}{\partial t} = -i\Omega U(t, t_0) \]

You can now see that the operator needed a complex argument, because otherwise probability amplitude would not be conserved (it would rise or decay). Rather it oscillates through different states of the system.

Here \(\Omega\) has units of frequency. Noting (1) quantum mechanics says \(E = \hbar \omega\) and (2) in classical mechanics Hamiltonian generates time-evolution, we write
\[ \Omega = \frac{H}{\hbar} \quad \Omega \text{ can be a function of time!} \]

\[ \text{eqn. of motion for } U(t, t_0) = HU(t, t_0) \]

Multiplying from right by \( |\psi(t_0)\rangle \) gives

\[ i\hbar \frac{\partial}{\partial t} |\psi\rangle = H|\psi\rangle \]

We are also interested in the equation of motion for \( U^\dagger \) which describes the time-evolution of the conjugate wavefunctions. Following the same approach and recognizing that \( U^\dagger(t, t_0) \) acts to the left:

\[ \langle \psi(t) | = \langle \psi(t_0) | U^\dagger(t, t_0) \]

we get

\[ -i\hbar \frac{\partial}{\partial t} U^\dagger(t, t_0) = U^\dagger(t, t_0)H \]

**Evaluating \( U(t, t_0) \): Time-Independent Hamiltonian**

Direct integration of \( i\hbar \frac{\partial U}{\partial t} = HU \) suggests that \( U \) can be expressed as:

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

Since \( H \) is an operator, we will define this operator through the expansion:

\[ \exp \left[ -\frac{iH}{\hbar} (t-t_0) \right] = 1 - \frac{iH}{\hbar} (t-t_0) + \left( \frac{-i}{\hbar} \right)^2 \left[ \frac{H(t-t_0)}{2} \right]^2 + \ldots \]

(NOTE: \( H \) commutes at all \( t \).)

You can confirm the expansion satisfies the equation of motion for \( U \).
For the time-independent Hamiltonian, we have a set of eigenkets:

\[ H |n\rangle = E_n |n\rangle \quad \sum_n |n\rangle \langle n| = 1 \]

So we have

\[
U(t, t_0) = \sum_n \exp\left[-iH(t-t_0)/\hbar\right] |n\rangle \langle n|
= \sum_n |n\rangle \exp\left[-iE_n (t-t_0)/\hbar\right] \langle n|
\]

So,

\[
|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle \\
= \sum_n |n\rangle \langle n| \psi(t_0) \rangle \exp\left[-iE_n (t-t_0)/\hbar\right] \\
= \sum_n |n\rangle c_n(t) \\
c_n(t) = c_n(t_0) \exp[-i\omega_n(t-t_0)]
\]

Expectation values of operators are given by

\[
\langle A(t) \rangle = \langle \psi(t) | A | \psi(t) \rangle \\
= \langle \psi(0) | U^\dagger(t, t_0) A U(t, t_0) | \psi(0) \rangle
\]

For an initial state \( |\psi(0)\rangle = \sum_n c_n(0) |n\rangle \)

\[
\langle A \rangle = \sum_{n,m} c_{m}^* |m\rangle \langle m| A |n\rangle e^{-i\omega_{m} t} \langle n| \rangle c_{n} \\
= \sum_{n,m} c_{m}^* c_{n} A_{mn} e^{-i\omega_{m} t} \\
= \sum_{n,m} c_{m}^* (t) c_{n} (t) A_{mn}
\]

What is the correlation amplitude for observing the state \( k \) at the time \( t \)?

\[
c_k(t) = \langle k | \psi(t) \rangle = \langle k | U(t, t_0) | \psi(t_0) \rangle \\
= \sum_n \langle k | n \rangle \langle n | \psi(t_0) \rangle e^{-i\omega_{n}(t-t_0)}
\]
Evaluating the time-evolution operator: Time-Dependent Hamiltonian

If \( H \) is a function of time, then the formal integration of \( i\hbar \frac{\partial U}{\partial t} = HU \) gives

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

Again, we can expand the exponential in a series, and substitute into the eqn. of motion to confirm it; however, we are treating \( H \) as a number.

\[
U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} H(t') \, dt' + \frac{1}{2!} \left( \frac{-i}{\hbar} \right)^2 \int_{t_0}^{t} \int_{t_0}^{t} dt' dt'' H(t') H(t'') + \ldots
\]

NOTE: This assumes that the Hamiltonians at different times commute! \( [H(t'), H(t'')] = 0 \)

This is generally not the case in optical + mag. res. spectroscopy. It is only the case for special Hamiltonians with a high degree of symmetry, in which the eigenstates have the same symmetry at all times. For instance the case of a degenerate system (for instance spin \( \frac{1}{2} \) system) with a time-dependent coupling.

**Special Case:** If the Hamiltonian does commute at all times, then we can evaluate the time-evolution operator in the exponential form or the expansion.

\[
U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} H(t') \, dt' + \frac{1}{2!} \left( \frac{-i}{\hbar} \right)^2 \int_{t_0}^{t} \int_{t_0}^{t} dt' dt'' H(t') H(t'') + \ldots
\]

If we also know the time-dependent eigenvalues from diagonalizing the time-dependent Hamiltonian (i.e., a degenerate two-level system problem), then:

\[
U(t, t_0) = \sum_j |j\rangle \exp\left[ -\frac{i}{\hbar} \int_{t_0}^{t} \varepsilon_j(t') \, dt' \right] \langle j|
\]
More generally: We assume the Hamiltonian at different times do not commute. Let’s proceed a bit more carefully:

Integrate

\[
\frac{\partial}{\partial t} U(t, t_0) = -\frac{i}{\hbar} H(t) U(t, t_0)
\]

To give:

\[
U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau \, H(\tau) U(\tau, t_0)
\]

This is the solution; however, \(U(t, t_0)\) is a function of itself. We can solve by iteratively substituting \(U\) into itself:

First Step:

\[
U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau \, [1 - \frac{i}{\hbar} \int_{t_0}^\tau d\tau' H(\tau') U(\tau', t_0)]
\]

Note that \(\tau'\) precedes \(\tau\).

Next Step:

\[
U(t, t_0) = 1 + \left(\frac{i}{\hbar}\right) \int_{t_0}^t d\tau H(\tau) + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^\tau d\tau' \int_{t_0}^{\tau'} d\tau'' H(\tau) H(\tau') U(\tau', t_0)
\]

From this expansion, you should be aware that there is a time-ordering to the interactions. For the third term, \(\tau''\) acts before \(\tau'\), which acts before \(\tau\): \(t_0 \leq \tau'' \leq \tau' \leq \tau \leq t\).

Notice also that the operators act to the right.
Imagine you are starting in state $|\psi_0\rangle = |l\rangle$ and you are working toward a target state $|\psi\rangle = |k\rangle$.

The possible paths and associated time variables are:

![Diagram](https://via.placeholder.com/150)

The solution for $U$ obtained from this iterative substitution is known as the (positive) time-ordered exponential

$$U(t, t_0) = \exp\left[ -\frac{i}{\hbar} \int_{t_0}^{t} d\tau H(\tau) \right] = \hat{T} \exp\left[ -\frac{i}{\hbar} \int_{t_0}^{t} d\tau H(\tau) \right]$$

$$= 1 + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} d\tau \int_{t_0}^{\tau_1} d\tau \cdots \int_{t_0}^{\tau_{n-1}} d\tau \ H(\tau_n) H(\tau_{n-1}) \cdots H(\tau)$$

Here the time-ordering is:

$$t_0 \to \tau_1 \to \tau_2 \to \tau_3 \to \cdots \to \tau_n \to t$$

$$t_0 \to \cdots \tau'' \to \tau' \to \tau$$

So, this expression tells you about how a quantum system evolves over a given time interval, and it allows for any possible trajectory from an initial state to a final state through any number of intermediate states. Each term in the expansion accounts for more possible transitions between different intermediate quantum states during this trajectory.
Compare the time-ordered exponential with the traditional expansion of an exponential:

\[
1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{-i}{\hbar} \right)^n \int_{t_0}^{t} dt_{n} \cdots \int_{t_0}^{t} dt_{1} H(\tau_{n})H(\tau_{n-1})\cdots H(\tau_{1})
\]

Here the time-variables assume all values, and therefore all orderings for \(H(\tau)\) are calculated. The areas are normalized by the \(n!\) factor. (There are \(n!\) time-orderings of the \(\tau_{n}\) times.)

We are also interested in the Hermetian conjugate of \(U(t,t_{0})\), which has the equation of motion

\[
\frac{\partial}{\partial t} U^\dagger(t,t_{0}) = \frac{+i}{\hbar} U^\dagger(t,t_{0}) H(t)
\]

If we repeat the method above, remembering that \(U^\dagger(t,t_{0})\) acts to the left:

\[
\langle \psi(t) \rangle = \langle \psi(t_{0}) | U^\dagger(t,t_{0})
\]

then from \(U^\dagger(t,t_{0}) = U^\dagger(t_{0},t_{0}) + \frac{i}{\hbar} \int_{t_{0}}^{t} d\tau U^\dagger(t,\tau) H(\tau)\) we obtain a negative-time-ordered exponential:

\[
U^\dagger(t,t_{0}) = \exp \left[ \frac{i}{\hbar} \int_{t_{0}}^{t} d\tau H(\tau) \right]
\]

\[
= 1 + \sum_{n=1}^{\infty} \left( \frac{i}{\hbar} \right)^n \int_{t_{0}}^{t} dt_{n} \cdots \int_{t_{0}}^{t} dt_{1} H(\tau_{n})H(\tau_{n-1})\cdots H(\tau_{1})
\]

Here the \(H(\tau)\) act to the left.