QUANTUM DYNAMICS[1]

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

$$\left|\psi(\bar{r},t_0)\right\rangle \overset{?}{\rightarrow} \left|\psi(\bar{r},t)\right\rangle \quad t > t_0$$

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

We start by assuming causality: $\left|\psi(t_0)\right\rangle$ precedes and determines $\left|\psi(t)\right\rangle$.

Also assume time is a continuous parameter:

$$\lim_{t \to t_0} \left|\psi(t)\right\rangle = \left|\psi(t_0)\right\rangle$$

Define an operator that gives time-evolution of system.

$$\left|\psi(t)\right\rangle = U(t,t_0)\left|\psi(t_0)\right\rangle$$

This "time-displacement operator" is similar to the "space-diplacement operator"

$$\left|\psi(r)\right\rangle = e^{ik(r-r_0)}\left|\psi(r_0)\right\rangle$$

which moves a wavefunction in space.

U does not depend on $\left|\psi\right\rangle$. It is a linear operator.

$$\text{if } \left|\psi(t_0)\right\rangle = a_1\left|\varphi_1(t_0)\right\rangle + a_2\left|\varphi(t_0)\right\rangle$$

$$\left|\psi(t)\right\rangle = U(t,t_0)\left|\psi(t_0)\right\rangle$$

$$= a_1 U(t,t_0)\left|\varphi_1(t_0)\right\rangle + a_2 U(t,t_0)\left|\varphi_2(t_0)\right\rangle$$

$$= a_1(t)\left|\varphi_1\right\rangle + a_2(t)\left|\varphi_2\right\rangle$$

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[1] From Merzbacher, Sakurai, Mukamel

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

$$\sum_n |a_n(t)| = \sum_n |a_n(t_0)|$$

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!

$$\begin{aligned} |\psi(t_2)\rangle &= U(t_2,t_1)U(t_1,t_0)|\psi(t_0)\rangle \\ &= U(t_2,t_1)|\psi(t_1)\rangle \end{aligned}$$

$$\therefore U(t,t_0)U(t_0,t) = 1$$

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

Let's write the time-evolution for an infinitesimal time-step, δt.

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

We expect that for small δt, the difference between $U(t_0,t_0)$ and $U(t_0 + \delta t, t_0)$ will be linear in δt. (Think of this as an expansion for small t):

$$U(t_0 + \delta t, t_0) = U(t_0, t_0) - i\Omega\delta t$$

Ω is a time-dependent Hermetian 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

$$U^\dagger(t_0 + \delta t, t_0)U(t_0 + \delta t, t_0) = (\mathbf{1} + i\Omega^\dagger\delta t)(\mathbf{1} - i\Omega\delta t) \approx \mathbf{1}$$

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 δt allows us to write a differential equation for the time-development of $U(t,t_0)$. Equation of motion for U:

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

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 Ω has units of frequency. Noting (1) quantum mechanics says $E = \hbar\omega$ and (2) in classical mechanics Hamiltonian generates time-evolution, we write

$$\Omega = \frac{H}{\hbar} \qquad \Omega \text{ can be a function of time!}$$

$$i\hbar \frac{\partial}{\partial t} U(t,t_0) = HU(t,t_0) \qquad \text{eqn. of motion for } U$$

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 $U^\dagger$. 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 $i\hbar\,\partial U/\partial t = HU$ 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:

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

(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:

$$H|n\rangle = E_n|n\rangle \qquad \sum_n |n\rangle\langle n| = 1$$

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,

$$\begin{aligned}\left|\psi(t)\right\rangle &= U(t,t_0)\left|\psi(t_0)\right\rangle \\ &= \sum_n |n\rangle \underbrace{\langle n|\psi(t_0)\rangle}_{c_n(t_0)} \exp\left[\frac{-i}{\hbar}E_n(t-t_0)\right] \\ &= \sum_n |n\rangle\, c_n(t) \qquad\qquad c_n(t) = c_n(t_0)\exp\left[-i\omega_n(t-t_0)\right]\end{aligned}$$

Expectation values of operators are given by

$$\begin{aligned}\langle A(t)\rangle &= \langle \psi(t)|A|\psi(t)\rangle \\ &= \left\langle \psi(0)\left|U^\dagger(t,0)\,A\,U(t,0)\right|\psi(0)\right\rangle\end{aligned}$$

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

$$\begin{aligned}\langle A\rangle &= \sum_{n,m} c_m^* \langle m|m\rangle e^{+i\omega_m t}\langle m|A|n\rangle e^{-i\omega_n t}\langle n|n\rangle c_n \\ &= \sum_{n,m} c_m^* c_n A_{mn} e^{-\omega_{nm} t} \\ &= \sum_{n,m} c_m^*(t)\, c_n(t)\, A_{mn}\end{aligned}$$

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

$$\begin{aligned}c_k(t) = \langle k|\psi(t)\rangle &= \langle k|U(t,t_0)|\psi(t_0)\rangle \\ &= \sum_n \langle k|n\rangle\langle n|\psi(t_0)\rangle\, e^{-i\omega_n(t-t_0)}\end{aligned}$$

Evaluating the time-evolution operator: Time-Dependent Hamiltonian

If H is a function of time, then the formal integration of $i\hbar\,\partial U/\partial t = HU$ 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.

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

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

<u>This is generally not the case in optical + mag. res. spectroscopy.</u> 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 ½ system) with a time-dependent coupling.

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

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

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

$$U(t, {}_0) = \sum_j |j\rangle \exp\left[\frac{-i}{\hbar}\int_{t_0}^{t} \varepsilon_j(t')dt'\right]\langle j|$$

More generally: We assume <u>the Hamiltonian at different times do not commute</u>. Let's proceed a bit more carefuly:

Integrate $$\frac{\partial}{\partial t}U(t, {}_0) = \frac{-i}{\hbar}H(t)U(t, {}_0)$$

To give: $$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)U(\tau, {}_0)$$

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:

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} d\tau H(\tau)\left[1 - \frac{i}{\hbar}\int_{t_0}^{\tau} d\tau' H(\tau')U(\tau', {}_0)\right]$$

$$= 1 + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} d\tau H(\tau) \quad \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' H(\tau)H(\tau')U(\tau', {}_0)$$

Next Step:

$$U(t,t_0)=1+\left(\frac{-i}{\hbar}\right)\int_{t_0}^{t}d\tau H(\tau)$$
$$+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}d\tau\int_{t_0}^{\tau}d\tau' H(\tau)H(\tau')$$
$$+\left(\frac{-i}{\hbar}\right)^3\int_{t_0}^{t}d\tau\int_{t_0}^{\tau}d\tau'\int_{t_0}^{\tau'}d\tau'' H(\tau)H(\tau')H(\tau'')U(\tau'',t_0)$$

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

Notice also that the operators act to the right.

This is known as the (positive) time-ordered exponential.

$$U(t,t_0)\equiv \exp_+\left[\frac{-i}{\hbar}\int_{t_0}^{t}d\tau\, H(\tau)\right]=\hat{T}\exp\left[\frac{-i}{\hbar}\int_{t_0}^{t}d\tau\, H(\tau)\right]$$
$$=1+\sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n\int_{t_0}^{t}d\tau_n\int_{t_0}^{\tau}d\tau_n\ldots\int_{t_0}^{t}d\tau_1\quad H(\tau_n)H(\tau_{n-1})\ldots H(\tau_1)$$

Here the time-ordering is:

$$t_0\to\tau_1\to\tau_2\to\tau_3 \ldots .\ \tau_n\to t$$
$$t_0\to\qquad \ldots\qquad \tau''\to\tau'\to\tau$$

Compare this with the expansion of an exponential:

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

Here the time-variables assume all values, and therefore all orderings for $H(\tau_i)$ are calculated. The areas are normalized by the $n!$ factor. (There are $n!$ time-orderings of the τ_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:

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

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:

$$\begin{aligned} U^\dagger(t, t_0) &= \exp_{-}\left[\frac{i}{\hbar} \int_{t_0}^{t} d\tau\, H(\tau)\right] \\ &= 1 + \sum_{n=1}^{\infty} \left(\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1 H(\tau_1) H(\tau_2) \ldots H(\tau_n) \end{aligned}$$

Here the $H(\tau_i)$ act to the left.