Phys 506 lecture 25: Time-dependent Schrödinger equation

1 Time-dependent problems

Recall the time-dependent Schrödinger equation:

$$i\hbar\, \partial_t \left|\psi(t)\right\rangle = \hat{H}(t) \left|\psi(t)\right\rangle$$

Question: Suppose we are in the state $|\psi(t_0)\rangle$ at time t_0. What state are we in at some later time t? Note that this question is complicated by the fact that the Hamiltonian now changes with respect to time.

2 Time-independent Hamiltonians

As a start, we suppose $\hat{H}$ is independent of time. Introduce energy eigenstates $\{|n\rangle\}$ such that $\hat{H}|n\rangle = E_n |n\rangle$ and $\langle m|n\rangle = \delta_{mn}$. Then, expand

$$|\psi(t_0)\rangle = \sum_n c_n(t_0) |n\rangle$$

Inserting into the Schrödinger equation,

$$\sum_n i\hbar\, \partial_t c_n(t) |n\rangle = \sum_n E_n c_n(t) |n\rangle$$

Multiply by $\langle m|$,

$$i\hbar\, \partial_t c_m(t) = E_m c_m(t)$$

which is solved by

$$c_m(t) = c_m(t_0) e^{-iE_m(t-t_0)/\hbar}$$

Hence,

$$\boxed{|\psi(t)\rangle = \sum_n c_n(t_0) e^{-iE_n(t-t_0)/\hbar} |n\rangle}$$

An alternate way to do this is as follows.

$$|\psi(t)\rangle = e^{-i\hat{H}(t-t_0)/\hbar} |\psi(t_0)\rangle$$

Since,

$$e^{-i\hat{H}(t-t_0)/\hbar} |n\rangle = e^{-iE_n(t-t_0)/\hbar} |n\rangle$$

because $|n\rangle$ is an eigenstate of $\hat{H}$, we then find that

$$|\psi(t)\rangle = \sum_n c_n(t_0) e^{-iE_n(t-t_0)/\hbar} |n\rangle$$

as before.

3 Time-dependent Hamiltonians

Now assume that $\hat{H}(t)$ is time-dependent ($\partial_t \hat{H} \neq 0$).

Method A: Introduce *any* complete orthonormal basis $\{|n\rangle\}$.

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle$$

Then,

$$i\hbar\, \partial_t |\psi(t)\rangle = \sum_n i\hbar\, \partial_t c_n(t) |n\rangle = \hat{H}(t) |\psi(t)\rangle = \sum_n c_n(t) \hat{H}(t) |n\rangle$$

Multiplying by $\langle m|$,

$$i\hbar\, \partial_t c_m(t) = \sum_n c_n(t) \left\langle m \middle| \hat{H}(t) \middle| n \right\rangle$$

so

$$i\hbar\, \partial_t c_m(t) = \sum_n H_{mn}(t) c_n(t)$$

This is a matrix differential equation that is hard to solve except for small-finite sized problems. This is because there is nothing we know about the matrix $H_{mn}(t)$ and it can be a complicated object to work with, especially if it is infinite dimensional.

Method B: Introduce instantaneous eigenstates.

$$\hat{H}(t) |n(t)\rangle = E_n(t) |n(t)\rangle$$

So now, everything depends on time. But, we still have orthonormality and completeness:

$$\langle m(t)|n(t)\rangle = \delta_{mn} \quad \text{and} \quad \sum_m |m(t)\rangle \langle m(t)| = \mathbb{I}.$$

Then, let

$$|\psi(t)\rangle = \sum_n c_n(t) |n(t)\rangle .$$

Inserting into the Schrödinger equation,

$$\sum_n i\hbar\, \partial_t c_n(t) |n(t)\rangle + \sum_n i\hbar c_n(t) \partial_t |n(t)\rangle = \sum_n c_n(t) E_n(t) |n(t)\rangle$$

Multiply by $\langle m|$,

$$i\hbar\, \partial_t c_m(t) + i\hbar \sum_n c_n(t) \langle m(t)|\partial_t|n(t)\rangle = c_m(t) E_m(t).$$

In general, it is hard to calculate the middle term. But note,

$$\langle m(t)|n(t)\rangle = \delta_{mn} \implies \partial_t \langle m(t)|n(t)\rangle + \langle m(t)|\partial_t|n(t)\rangle = 0$$

and

$$\hat{H}(t) |n(t)\rangle = E_n(t) |n(t)\rangle \implies \partial_t \hat{H}(t) |n(t)\rangle + \hat{H}(t) \partial_t |n(t)\rangle = \partial_t E_n(t) |n(t)\rangle + E_n(t) \partial_t |n(t)\rangle$$

Multiply by $\langle m|$,

$$\left\langle m(t) \middle| \partial_t \hat{H}(t) \middle| n(t) \right\rangle + E_m(t) \langle m(t)|\partial_t|n(t)\rangle = \partial_t E_n(t) \delta_{mn} + E_n(t) \langle m(t)|\partial_t|n(t)\rangle$$

Then, break out into cases:

- If $m = n$, then we find $\left\langle n(t) \middle| \partial_t \hat{H}(t) \middle| n(t) \right\rangle = \partial_t E_n(t)$.
- If $m \neq n$, then we find $\frac{\langle m(t)|\partial_t \hat{H}(t)|n(t)\rangle}{E_n(t)-E_m(t)} = \langle m(t)|\partial_t|n(t)\rangle$

So,

$$i\hbar\, \partial_t c_m(t) + i\hbar c_m(t) \langle m(t)|\partial_t|m(t)\rangle + i\hbar \sum_{m\neq n} c_n(t) \frac{\left\langle m(t) \middle| \partial_t \hat{H}(t) \middle| n(t) \right\rangle}{E_n(t) - E_m(t)} = c_m(t) E_m(t)$$

The derivative matrix element is still hard to deal with, but at least now there is only one such term.

This approach can be used to develop what is called adiabatic perturbation theory, where we assume the changes of the Hamiltonian in time are slow. Griffiths textbook has an excellent treatment of this problem.

4 Time evolution operator

Define $\hat{U}(t, t_0)$ by

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle .$$

U takes us from time t_0 to t. If $\hat{H}(t)$ is time-independent then

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

as we saw earlier. Here are some general properties of $\hat{U}$.

1.) $\hat{U}(t_0, t_0) = \mathbb{I}$

2.) $\hat{U}(t, t')\hat{U}(t', t_0) = \hat{U}(t, t_0)$

3.) Due to the Hermiticity of $\hat{H}$, $\hat{H}^\dagger = \hat{H}$.

$$\begin{aligned} i\hbar\, \partial_t |\psi(t)\rangle &= \hat{H}(t) |\psi(t)\rangle \\ \langle\psi(t)| (-i\hbar\partial_t) &= \langle\psi(t)| \hat{H}(t), \end{aligned}$$

where the operator acts to the left. Therefore,

$$\begin{aligned} \partial_t \langle\psi(t)|\psi(t)\rangle &= \langle\psi(t)|\partial_t|\psi(t)\rangle + \langle\psi(t)|\partial_t|\psi(t)\rangle \\ &= \frac{i}{\hbar}\left\langle\psi(t)\middle|\hat{H}(t)\middle|\psi(t)\right\rangle - \frac{i}{\hbar}\left\langle\psi(t)\middle|\hat{H}(t)\middle|\psi(t)\right\rangle \\ &= 0. \end{aligned}$$

Hence, normalized states remain normalized for all t. This tells us that

$$\langle\psi(t)|\psi(t)\rangle = \left\langle\psi(t_0)\middle|\hat{U}^\dagger(t, t_0)\hat{U}(t, t_0)\middle|\psi(t_0)\right\rangle = \langle\psi(t_0)|\psi(t_0)\rangle .$$

Hence $\hat{U}^\dagger(t, t_0)\hat{U}(t, t_0) = \mathbb{I}$ meaning $\hat{U}$ is unitary.

4.) Plugging $|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle$ into the Schrödinger equation,

$$i\hbar\, \partial_t\hat{U}(t, t_0) |\psi(t_0)\rangle = \hat{H}(t)\hat{U}(t, t_0) |\psi(t_0)\rangle$$

Since this is true for all t_0,

$$\boxed{i\hbar\,\partial_t\hat{U}(t,t_0) = \hat{H}(t)\hat{U}(t,t_0)}$$

which is called the equation of motion.

5 Time ordered products

Now, we wish to integrate the equation of motion to obtain an expression for $\hat{U}(t,t_0)$.

$$i\hbar(\hat{U}(t,t_0) - \hat{U}(t_0,t_0)) = \int_{t_0}^{t}\hat{H}(t')U(t',t_0)\,dt'$$

$$\implies \hat{U}(t,t_0) = \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t}\hat{H}(t')\hat{U}(t',t_0)\,dt'.$$

If we iterate,

$$\begin{aligned}\hat{U}(t,t_0) &= \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t}\hat{H}(t')\,dt' + \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}dt'\int_{t_0}^{t_1}dt_2\hat{H}(t_1)\hat{H}(t_2) + \cdots \\ &= \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t}dt_1 T(\hat{H}(t_1)) + \left(\frac{-i}{\hbar}\right)^2\frac{1}{2!}\int_{t_0}^{t}dt_1\int_{t_0}^{t}T(\hat{H}(t_1)\hat{H}(t_2)) + \cdots\end{aligned}$$

where the time-ordered product T is defined by

$$\begin{aligned}&T(\hat{A}_1(t_1)) = \hat{A}_1(t_1)\\ &T(\hat{A}_1(t_1)\hat{A}_2(t_2)) = \Theta(t_1-t_2)\hat{A}_1(t_1)\hat{A}_2(t_2) + \Theta(t_2-t_1)\hat{A}_2(t_2)\hat{A}_1(t_1).\end{aligned}$$

The rule is to "put Later times to the Left". The proof of this formula is simple. Each time-ordered piece gives the same result as the original series. There are $n!$ different orderings of n operators so this cancels out the $\frac{1}{n!}$. We write

$$\hat{U}(t,t_0) = T\exp(-\frac{i}{\hbar}\int_{t_0}^{t}dt'\hat{H}(t')) = \sum_{n=0}^{\infty}\left(\frac{-i}{\hbar}\right)^n\frac{1}{n!}\int_{t_0}^{t}\cdots\int_{t_0}^{t}dt_n T(\hat{H}(t_1)\hat{H}(t_2)\cdots\hat{H}(t_n))$$

This is a power series in $\hat{H}$ not in some time-dependent perturbation $\hat{V}(t)$, hence it often is not useful for applications. Note that property 4 says

$$i\hbar\,\partial_t T\exp(-\frac{i}{\hbar}\int_{t_0}^{t}dt'\hat{H}(t')) = \hat{H}(t)T\exp(-\frac{i}{\hbar}\int_{t_0}^{t}dt'\hat{H}(t'))$$

So time-ordered products generalize to operators the fundamental property of an exponential function - namely that the derivative of an exponential is the derivative of the argument times the exponential. This is nontrivial because the operators may not commute at different times.