Quantum Dynamics

February 14, 2015

As in classical mechanics, time is a parameter in quantum mechanics. It is distinct from space in the sense that, while we have Hermitian operators, $\hat{\mathbf{X}}$, for position and therefore expect a measurement of postion to yield any eigenvalue of $\hat{\mathbf{X}}$, the same is not true of time. We cannot expect measurement to yield arbitrary eigenvalues of time, perhaps because we are stuck in one particular time ourselves. In any case, while there are differences between time and space, the infinitesimal generator, energy, is an important observable.

We take states of a system to have time dependence, but there are two ways to do this. We can describe the system by an explicitly time-dependent ket,

$$|\psi\rangle = |\psi, t\rangle$$

taking the basis kets, $|a\rangle$, (whatever they are) as fixed. The state is then a time varying vector in the space spanned by the fixed basis kets. It is also sometimes useful to let the system be a fixed ket, while the basis kets evolve in time, $|a, t\rangle$. In perturbation theory, as we shall see later, it is even useful to mix these two simple pictures. For the moment, we consider time-dependent states in a fixed basis.

1 The time translation operator

We define the time translation operator to be the mapping that takes the state from some initial time, t_0, to a later time, t,

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

In the limit as $t \to t_0$, this must be the identity,

$$\begin{aligned}\hat{\mathcal{U}}(t_0, t_0)|\psi, t_0\rangle &= |\psi, t_0; t_0\rangle \\ &= |\psi, t_0\rangle\end{aligned}$$

We require time evolution to preserve total probability, so it cannot change the norm of any state. Therefore,

$$\begin{aligned}\langle\psi, t_0 \,|\psi, t_0\rangle &= \langle\psi, t_0; t \,|\psi, t_0; t\rangle \\ &= \langle\psi, t_0|\hat{\mathcal{U}}^\dagger(t, t_0)\hat{\mathcal{U}}(t, t_0)|\psi, t_0\rangle\end{aligned}$$

so up to a phase which does not affect probabilities, we may take $\hat{\mathcal{U}}(t, t_0)$ to be unitary,

$$\hat{\mathcal{U}}^\dagger(t, t_0)\hat{\mathcal{U}}(t, t_0) = \hat{1}$$

In a fixed basis $|a\rangle$, we may expand any state as

$$|\psi, t\rangle = \sum_a c_a(t)|a\rangle$$

Notice that the time dependence allows the state to move from one eigenstate to another. The normalization, and preseververation of the norm, require

$$\begin{aligned}
1 &= \langle\psi, t_0; t \,|\psi, t_0; t\rangle \\
&= \left(\sum_{a'} c_a^* (t) \langle a'|\right)\left(\sum_a c_a (t) |a\rangle\right) \\
&= \sum_a \sum_{a'} c_a^* (t)\, c_a (t) \langle a' \,|a\rangle \\
&= \sum_a \sum_{a'} c_a^* (t)\, c_a (t)\, \delta_{aa'} \\
&= \sum_a |c_a (t)|^2
\end{aligned}$$

This must hold at any time t.

We may write $\hat{\mathcal{U}} (t, t_0)$ as an exponential,

$$\hat{\mathcal{U}} (t, t_0) = e^{-i\hat{\Omega}(t)}$$

Then, for an infinitesimal time change, $t = t_0 + dt$,

$$\hat{\mathcal{U}} (t_0 + dt, t_0) = \hat{1} - \frac{i}{\hbar}\hat{\Omega} (t)\, dt$$

where unitarity of $\hat{\mathcal{U}} (t, t_0)$ requires $\hat{\Omega}^\dagger = \hat{\Omega}$. With this choice of constants, the observable $\hat{\Omega} (t)$ has units of energy, and recalling the suggestive form of a plane wave,

$$Ae^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)} = Ae^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{x}-Et)}$$

we identify it with the Hamiltonian operator,

$$\hat{\Omega} (t) = \hat{H}$$

Consider the effect of $\hat{\mathcal{U}} (t_0 + dt, t_0) = \hat{1} - \frac{i}{\hbar}\hat{\Omega} (t)\, dt$ on a plane wave, $\langle\mathbf{x} \,|\psi, t\rangle = Ae^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{x}-Et)}$. The time-translated state will be

$$\begin{aligned}
\langle\mathbf{x}| \hat{\mathcal{U}} (t_0 + dt, t_0) |\psi, t_0\rangle &= \langle\mathbf{x} \,|\psi, t_0 + dt\rangle \\
\langle\mathbf{x}| \left(\hat{1} - \frac{i}{\hbar}\hat{\Omega} (t)\, dt\right) |\psi, t_0\rangle &= \langle\mathbf{x} \,|\psi, t_0 + dt\rangle \\
\langle\mathbf{x} \,|\psi, t_0\rangle - \frac{i}{\hbar} dt \,\langle\mathbf{x}| \hat{\Omega} (t) |\psi, t_0\rangle &= \langle\mathbf{x} \,|\psi, t_0 + dt\rangle
\end{aligned}$$

For the plane wave, we have

$$\begin{aligned}
\langle\mathbf{x} \,|\psi, t_0 + dt\rangle &= Ae^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{x}-Et_0-Edt)} \\
&= Ae^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{x}-Et_0)}\left(1 - \frac{i}{\hbar}Edt\right) \\
&= \langle\mathbf{x} \,|\psi, t_0\rangle - \langle\mathbf{x}| \frac{i}{\hbar}Edt \,|\psi, t_0\rangle
\end{aligned}$$

Therefore,

$$\begin{aligned}
\langle\mathbf{x} \,|\psi, t_0\rangle - \frac{i}{\hbar} dt \,\langle\mathbf{x}| \hat{\Omega} (t) |\psi, t_0\rangle &= \langle\mathbf{x} \,|\psi, t_0\rangle - \langle\mathbf{x}| \frac{i}{\hbar}Edt \,|\psi, t_0\rangle \\
\langle\mathbf{x}| \hat{\Omega} (t) |\psi, t_0\rangle &= \langle\mathbf{x}| E \,|\psi, t_0\rangle
\end{aligned}$$

or without the basis,

$$\hat{\Omega} (t) |\psi, t_0\rangle = E \,|\psi, t_0\rangle$$

We identify $\hat{\Omega} (t)$ with the Hamiltonian, $\hat{\Omega} (t) = \hat{H} (t)$.

2 The Schrödinger equation

Consider the time evolution of the time translation operator, $\hat{\mathcal{U}}(t, t_0)$, at some time t. Translating the time by an additional small amount Δt,

$$\begin{aligned}
\hat{\mathcal{U}}(t+\Delta t, t_0) &= \left(\hat{1} - \frac{i}{\hbar}\hat{H}(t)\,\Delta t\right)\hat{\mathcal{U}}(t, t_0) \\
\hat{\mathcal{U}}(t+\Delta t, t_0) &= \hat{\mathcal{U}}(t, t) - \frac{i\Delta t}{\hbar}\hat{H}(t)\hat{\mathcal{U}}(t, t_0)
\end{aligned}$$

Rearranging,

$$\hat{H}(t)\hat{\mathcal{U}}(t, t_0) = i\hbar\;\frac{\hat{\mathcal{U}}(t+\Delta t, t_0) - \hat{\mathcal{U}}(t, t_0)}{\Delta t}$$

so taking the limit as $\Delta t \to 0$,

$$\hat{H}(t)\hat{\mathcal{U}}(t, t_0) = i\hbar\frac{\partial}{\partial t}\hat{\mathcal{U}}(t, t_0)$$

This is the Schrödinger equation for the time evolution operator. If we let this operator relation act on an initial state, $|\psi, t_0\rangle$, we get the time evolution equation for that state,

$$\begin{aligned}
\hat{H}(t)\hat{\mathcal{U}}(t, t_0)|\psi, t_0\rangle &= i\hbar\frac{\partial}{\partial t}\hat{\mathcal{U}}(t, t_0)|\psi, t_0\rangle \\
\hat{H}(t)|\psi, t\rangle &= i\hbar\frac{\partial}{\partial t}|\psi, t\rangle
\end{aligned}$$

This is basis independent form of the familiar Schrödinger equation.

3 The full time evolution operator

From the infinitesimal solution we may recover the full transformation. There are three cases:

1. $\hat{H}$ independent of time
2. $\hat{H}$ depends on time, but $\left[\hat{H}(t), \hat{H}(t')\right] = 0$ for any two times, t, t'.
3. $\left[\hat{H}(t), \hat{H}(t')\right] \neq 0$

We solve by iterating the infinitesimal transformation. This is not difficult in the first case. Setting $t = \lim_{n\to\infty}(ndt)$,

$$\begin{aligned}
\hat{\mathcal{U}}(t, t_0) &= \lim_{n\to\infty}\left(\hat{1} - \frac{i}{\hbar}\hat{H}dt\right)^n \\
&= \lim_{n\to\infty}\sum_{k=0}^{n}\frac{n!}{k!\,(n-k)!}\left(-\frac{i}{\hbar}\hat{H}dt\right)^k\hat{1}^{n-k} \\
&= \lim_{n\to\infty}\sum_{k=0}^{n}\frac{n\,(n-1)\,(n-2)\cdots(n-k+1)}{k!}\frac{n^k}{n^k}\left(-\frac{i}{\hbar}\hat{H}dt\right)^k \\
&= \lim_{n\to\infty}\sum_{k=0}^{n}\frac{n\,(n-1)\,(n-2)\cdots(n-k+1)}{k!n^k}\left(-\frac{i}{\hbar}\hat{H}ndt\right)^k \\
&= \lim_{n\to\infty}\sum_{k=0}^{n}\frac{1\left(1-\frac{1}{n}\right)\left(1-\frac{2}{n}\right)\cdots\left(1-\frac{k-1}{n}\right)}{k!}\left(-\frac{i}{\hbar}\hat{H}\,(ndt)\right)^k
\end{aligned}$$

$$
\begin{aligned}
&= \sum_{k=0}^{\infty} \frac{1}{k!} \left(-\frac{i}{\hbar} \hat{H} t \right)^{k} \\
&= \exp \left(-\frac{i}{\hbar} \hat{H} t \right)
\end{aligned}
$$

The second case, we have to pay attention to the changing Hamiltonian operators, but do not have to worry about their *ordering*. In this case, we have

$$
\begin{aligned}
\hat{\mathcal{U}} (t, t_0) &= \lim_{n \to \infty} \left(\hat{1} - \frac{i}{\hbar} \hat{H} (t_0) \Delta t \right) \left(\hat{1} - \frac{i}{\hbar} \hat{H} (t_0 + \Delta t) \Delta t \right) \left(\hat{1} - \frac{i}{\hbar} \hat{H} (t_0 + 2\Delta t) \Delta t \right) \ldots \\
&= \lim_{n \to \infty} \left(\hat{1} - \frac{i}{\hbar} \left(\hat{H} (t_0) \Delta t + \hat{H} (t_0 + \Delta t) \Delta t + \hat{H} (t_0 + 2\Delta t) \Delta t \right) + \ldots \right) \\
&= \exp \left(-\frac{i}{\hbar} \int_{t_0}^{t} \hat{H} (t') \, dt' \right)
\end{aligned}
$$

Here it is clear that the terms linear in Δt will approach the integral in the limit,

$$
\lim_{n \to \infty} \left(\hat{H} (t_0) \Delta t + \hat{H} (t_0 + \Delta t) \Delta t + \hat{H} (t_0 + 2\Delta t) \Delta t \right) = \int_{t_0}^{t} \hat{H} (t') \, dt'
$$

but it is nontrivial to demonstrate that the terms quadratic and higher in Δt approach powers of this integral. However, now that we see the pattern, we can postulate this form for $\hat{\mathcal{U}} (t, t_0)$ and simply show that it satisfied the Schrödinger equation

$$
\hat{H} (t) \hat{\mathcal{U}} (t, t_0) = i\hbar \frac{\partial}{\partial t} \hat{\mathcal{U}} (t, t_0)
$$

The general case is considerably more involved because we have to keep track of the order of the terms in the power series. The result, called the Dyson series, has the form

$$
\begin{aligned}
\hat{\mathcal{U}} (t, t_0) &= \lim_{n \to \infty} \left(\hat{1} - \frac{i}{\hbar} \hat{H} (t_0) \Delta t \right) \left(\hat{1} - \frac{i}{\hbar} \hat{H} (t_0 + \Delta t) \Delta t \right) \left(\hat{1} - \frac{i}{\hbar} \hat{H} (t_0 + 2\Delta t) \Delta t \right) \ldots \\
&= \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar} \right)^{n} \int_{t_0}^{t} \hat{H} (t_1) \, dt_1 \int_{t_0}^{t_1} \hat{H} (t_2) \, dt_2 \ldots \int_{t_0}^{t_{n-1}} \hat{H} (t_n) \, dt_n \\
&\equiv \mathbb{T} \exp \left(-\frac{i}{\hbar} \int_{t_0}^{t} \hat{H} (t') \, dt' \right)
\end{aligned}
$$

where the final exponential is simply shorthand for the whole series, and $\mathbb{T}$ is the time-ordering operator, indicating that the limits on the integrals in the second line are chosen so that the factors of the Hamiltonian are ordered with later times to the right, i.e., $\hat{H} (t_1) \hat{H} (t_2) \ldots \hat{H} (t_n)$ where $t_1 < t_2 < \ldots < t_n$.

Almost all of the applications we consider will involve time-independent Hamiltonians.

4 Energy eigenkets

Suppose we choose as a basis the eigenkets of an operator $\hat{A}$ which commutes with the (time-independent) Hamiltonian,

$$
\left[\hat{A}, \hat{H} \right] = 0
$$

This operator could be the Hamiltonian itself, or another observable, but in either case, the eigenkets, $|a\rangle$, may be chosen to simultaneously be eigenkets of $\hat{H}$,

$$\hat{H}\,|a\rangle = E_a\,|a\rangle$$

Consider the time evolution of an arbitrary initial state, $|\psi, t_0\rangle$. In terms of the $\hat{A}$ basis,

$$\begin{aligned} |\psi, t_0\rangle &= \sum_a |a\rangle\,\langle a\,|\psi, t_0\rangle \\ &= \sum_a c_a\,|a\rangle \end{aligned}$$

Then the time evolution is given by

$$\begin{aligned} |\psi, t_0; t\rangle &= \exp\left(-\frac{i}{\hbar}\hat{H}t\right)|\psi, t_0\rangle \\ &= \sum_a c_a \exp\left(-\frac{i}{\hbar}\hat{H}t\right)|a\rangle \\ &= \sum_a c_a \exp\left(-\frac{i}{\hbar}E_n t\right)|a\rangle \end{aligned}$$

Defining time dependent expansion coefficients, $c_a(t) \equiv c_a e^{-\frac{i}{\hbar}E_a t}$, the state becomes

$$|\psi, t_0; t\rangle = \sum_a c_a(t)\,|a\rangle$$

In general, this means that the probabilities for measuring the system to be in different eigenstates varies with time. However, if the system starts in an eigenstate, it stays there with only a time-dependent phase,

$$\begin{aligned} |\psi, t_0\rangle &= |a_k\rangle \\ |\psi, t_0; t\rangle &= e^{-\frac{i}{\hbar}E_k t}\,|a_k\rangle \end{aligned}$$

The problem of quantum dynamics is now reduced to finding a maximal set of operators which commute with the Hamiltonian. We may then label states using these and study the time evolution of arbitrary initial states.

Exercise: Find the time evolution of a particle in an infinite square well,

$$V(x) = \begin{cases} \infty & x < -\frac{L}{2} \\ 0 & -\frac{L}{2} < x < \frac{L}{2} \\ \infty & x > \frac{L}{2} \end{cases}$$

when its state at time t_0 is:

1. $\langle x\,|\psi\rangle = \sqrt{\frac{2}{L}}\cos\frac{\pi x}{L}$
2. $\langle x\,|\psi\rangle = \sqrt{\frac{1}{L}}\cos\frac{\pi x}{L} + \sqrt{\frac{1}{L}}\cos\frac{3\pi x}{L}$

5 Expectation values of observables

Once we have the state of a system expanded in energy eigenkets, we can find the time dependence of the expectation values for any observable, $\hat{\mathcal{O}}$,

$$\begin{aligned}\langle\psi,t_0;t|\,\hat{\mathcal{O}}\,|\psi,t_0;t\rangle &= \sum_{a,a'}\langle\psi,t_0;t\,|a'\rangle\,\langle a'|\,\hat{\mathcal{O}}\,|a\rangle\,\langle a\,|\psi,t_0;t\rangle \\ &= \sum_{a,a'}c^*_{a'}(t)\,\langle a'|\,\hat{\mathcal{O}}\,|a\rangle\,c_a(t) \\ &= \sum_{a,a'}c^*_{a'}c_a e^{-\frac{i}{\hbar}(E_a-E_{a'})t}\,\langle a'|\,\hat{\mathcal{O}}\,|a\rangle\end{aligned}$$

As an example, consider a 2-state system. The Hamiltonian for a spin-$\frac{1}{2}$ particle with magnetic moment $\boldsymbol{\mu}=\frac{e}{mc}\mathbf{S}$, in a magnetic field, $\mathbf{B}$, is

$$\begin{aligned}\hat{H} &= -\hat{\boldsymbol{\mu}}\cdot\mathbf{B} \\ &= -\frac{e}{mc}\hat{\mathbf{S}}\cdot\mathbf{B}\end{aligned}$$

Let $\mathbf{B}=B\hat{\mathbf{k}}$ be constant, so the time-independent Hamiltonian is

$$\hat{H} = -\frac{eB}{mc}\hat{S}_z$$

The energy eigenkets are then just the $|\pm\rangle$ eigenkets of $\hat{S}_z$ with energies

$$\begin{aligned}\hat{H}\,|\pm\rangle &= E_\pm\,|\pm\rangle \\ &= \mp\frac{e\hbar B}{2mc}\,|\pm\rangle \\ &= \mp\frac{\hbar\omega}{2}\,|\pm\rangle\end{aligned}$$

where $\omega\equiv\frac{eB}{mc}$. Setting $t_0=0$, the time evolution of a general normalized state,

$$|\chi\rangle = \cos\theta\,|+\rangle+e^{i\varphi}\sin\theta\,|-\rangle$$

is

$$\begin{aligned}|\chi,t\rangle &= \hat{\mathcal{U}}(t,0)\,|\chi\rangle \\ &= e^{-\frac{i}{\hbar}\hat{H}t}\,|\chi\rangle \\ &= e^{-\frac{i}{\hbar}\hat{H}t}\left(\cos\theta\,|+\rangle+e^{i\varphi}\sin\theta\,|-\rangle\right) \\ &= e^{-\frac{i}{\hbar}E_+t}\cos\theta\,|+\rangle+e^{-\frac{i}{\hbar}E_-t}e^{i\varphi}\sin\theta\,|-\rangle \\ &= e^{\frac{i\omega t}{2}}\cos\theta\,|+\rangle+e^{-\frac{i\omega t}{2}}e^{i\varphi}\sin\theta\,|-\rangle \\ &= e^{\frac{i\omega t}{2}}\left[\cos\theta\,|+\rangle+e^{-i(\omega t-\varphi)}\sin\theta\,|-\rangle\right]\end{aligned}$$

The probability for measuring the system to be in the spin-up state is then

$$\begin{aligned}|\langle+\,|\chi,t\rangle|^2 &= \left|e^{\frac{i\omega t}{2}}\left[\cos\theta\,\langle+\,|+\rangle+e^{-i(\omega t-\varphi)}\sin\theta\,\langle+\,|-\rangle\right]\right|^2 \\ &= \cos^2\theta\end{aligned}$$

which is the same as the initial probability. However, if we look at the probability that the x-component of spin is up, we find

$$\begin{aligned}
\left|\left\langle \hat{S}_x, + \left|\chi, t\right.\right\rangle\right|^2 &= \left|\left(\frac{1}{\sqrt{2}}\left\langle +\right| + \frac{1}{\sqrt{2}}\left\langle -\right|\right) e^{\frac{i\omega t}{2}}\left[\cos\theta\left|+\right\rangle + e^{-i(\omega t-\varphi)}\sin\theta\left|-\right\rangle\right]\right|^2 \\
&= \frac{1}{2}\left|\left(\cos\theta + e^{-i(\omega t-\varphi)}\sin\theta\right)\right|^2 \\
&= \frac{1}{2}\left(\cos\theta + e^{-i(\omega t-\varphi)}\sin\theta\right)\left(\cos\theta + e^{i(\omega t-\varphi)}\sin\theta\right) \\
&= \frac{1}{2}\left(1+\sin 2\theta\cos\left(\varphi+\omega t\right)\right)
\end{aligned}$$

6 Time-energy uncertainty

Consider a system with a continuous energy spectrum and many particles. Let the state be expanded in energy eigenkets,

$$\begin{aligned}
\left|\psi, t_0; t\right\rangle &= \exp\left(-\frac{i}{\hbar}\hat{H}t\right)\left|\psi, t_0\right\rangle \\
&= \int \rho\left(E\right) dE\, c\left(E\right)\exp\left(-\frac{i}{\hbar}\hat{H}t\right)\left|E\right\rangle \\
&= \int \rho\left(E\right) dE\, c\left(E\right) e^{-\frac{i}{\hbar}Et}\left|E\right\rangle
\end{aligned}$$

where $\rho\left(E\right)$ characterizes the distritubion of energy eigenstates and the orthonormality relation is

$$\rho\left(E'\right)\left\langle E'\left|E\right.\right\rangle = \delta\left(E-E'\right)$$

Consider the correlation between the initial state, $\left|\psi, t_0\right\rangle$, and the state at time t,

$$\begin{aligned}
C\left(t\right) \equiv \left\langle \psi, t_0\left|\psi, t_0; t\right.\right\rangle &= \left\langle \psi, t_0 \exp\left(-\frac{i}{\hbar}\hat{H}t\right)\right|\psi, t_0\rangle \\
&= \int \rho\left(E'\right) dE'\, c^*\left(E'\right)\left\langle E'\right|\int \rho\left(E\right) dE\, c\left(E\right) e^{-\frac{i}{\hbar}Et}\left|E\right\rangle \\
&= \int \rho\left(E'\right) dE' \int \rho\left(E\right) dE\, c^*\left(E'\right) c\left(E\right) e^{-\frac{i}{\hbar}Et}\left\langle E'\left|E\right.\right\rangle \\
&= \int dE' \int \rho\left(E\right) dE\, c^*\left(E'\right) c\left(E\right) e^{-\frac{i}{\hbar}Et}\delta\left(E-E'\right) \\
&= \int \rho\left(E\right) dE\, \left|c\left(E\right)\right|^2 e^{-\frac{i}{\hbar}Et}
\end{aligned}$$

Suppose the initial distribution is peaked around some energy E_0. Write $C\left(t\right)$ as

$$\begin{aligned}
C\left(t\right) &= \int \rho\left(E\right) dE\, \left|c\left(E\right)\right|^2 e^{-\frac{i}{\hbar}Et} \\
&= e^{-\frac{i}{\hbar}E_0 t}\int \rho\left(E\right) dE\, \left|c\left(E\right)\right|^2 e^{-\frac{i}{\hbar}\left(E-E_0\right)t}
\end{aligned}$$

For energies far from E_0, the exponential $e^{-\frac{i}{\hbar}\left(E-E_0\right)t}$ oscillates rapidly and the value of the integral is small as long as $\rho\left(E\right)$ and $c\left(E\right)$ vary slowly. Therefore, for times such that

$$\frac{\left(E-E_0\right)t}{\hbar} > 1$$

there is little contribution and the energy stays peaked around E_0. At times Δt, only energies $E = E_0 + \Delta E$ will contribute significantly, where

$$\Delta E \Delta t \lesssim \hbar$$

This is a very different statement than the necessary relationship between the uncertainties in conjugate observables. In particular, recall that there is no Hermitian operator corresponding to a measurement of time.