# CHM 502 - Module 2 - An Aside on Time Evolution

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Let's take a moment to talk about time-dependent quantum mechanics in a more general way, and introduce some machinery that will be useful to us soon. A hat tip to

## 1 The Time Evolution Operator

We've talked about how the wavefunction of a system evolves according to the time-dependent Schrödinger equation (TDSE):

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \tag{1}$$

and how we can expand a general time-dependent wavefunction in the basis of energy eigenstates:

$$|\psi(t)\rangle = \sum_n c_n(0) \cdot e^{-iE_n t/\hbar} |\psi_n\rangle \tag{2}$$

Assuming for the moment that we have a time-independent Hamiltonian, we can manipulate (or "integrate") the TDSE to find:

$$\frac{d}{dt} |\psi(t)\rangle = -\frac{i\hat{H}}{\hbar} |\psi(t)\rangle \tag{3}$$

$$\rightarrow |\psi(t)\rangle = e^{-\frac{i\hat{H}}{\hbar}t} |\psi(0)\rangle \equiv \hat{U}(t,0)\ |\psi(0)\rangle \tag{4}$$

We are arguing here that if the temporal derivative of $\frac{d}{dt} |\psi(t)\rangle$ returns a quantity proportional to itself, then we can quickly write down a solution that looks like a complex exponential.

In the meantime, we have defined $\hat{U}(t,0)$ as the *time evolution* operator or *propagator*, whose application evolves our wavefunction forward in time from $|\psi(0)\rangle$ to $|\psi(t)\rangle$.

What does it mean to have an operator living inside a complex exponential? We can write this down explicitly as a Taylor expansion of powers of that operator. Let's check that our expression for $|\psi(t)\rangle$ in Eqn. 4 behaves as we expect:

$$\begin{aligned}
\hat{U}(t,0)\,|\psi(t_0)\rangle &= e^{-i\hat{H}t/\hbar}\,|\psi(0)\rangle && (5)\\
&= \left[1 - \frac{i\hat{H}t}{\hbar} + \frac{1}{2}\left(\frac{-i\hat{H}t}{\hbar}\right)^2 + \cdots\right]\sum_n c_n(0)\,|\psi_n\rangle && (6)\\
&= \sum_n c_n(0)\left[1 - \frac{i\hat{H}t}{\hbar} + \frac{1}{2}\left(\frac{-i\hat{H}t}{\hbar}\right)^2 + \cdots\right]|\psi_n\rangle && (7)\\
&= \sum_n c_n(0)\left[1 - \frac{iE_nt}{\hbar} + \frac{1}{2}\left(\frac{-iE_nt}{\hbar}\right)^2 + \cdots\right]|\psi_n\rangle && (8)\\
&= \sum_n c_n(0)e^{-iE_nt/\hbar}\,|\psi_n\rangle = |\psi(t)\rangle \qquad \checkmark && (9)
\end{aligned}$$

A few more notes on how this $\hat{U}(t,0)$ beast behaves:

- $\hat{U}(t,0)$ acts to the right on *kets* to evolve forward in time
- $\hat{U}^\dagger(t,0)$ acts to the left on *bras* to evolve forward in time. However, one can show that

$$\hat{U}^\dagger(t,0) = \exp\left[\frac{i\hat{H}t}{\hbar}\right] = \hat{U}^{-1}(t,0) \tag{10}$$

  so the $\hat{U}^\dagger(t,0)$ operator will also act to the right on on *kets* to evolve them backwards in time. $\hat{U}^\dagger(t,0)$ is therefore also referred to as the time reversal operator.

- $\hat{U}(t,0)$ is unitary, meaning that $\hat{U}^\dagger(t,0)\,\hat{U}(t,0) = \hat{I}$. This is important, because the normalization of wavefunctions must be preserved as you propagate them in time.
- Finally, the time evolution operator has the nice property that:

$$\hat{U}(t_2,t_0) = \hat{U}(t_2,t_1)\hat{U}(t_1,t_0) \tag{11}$$

  Though note that order is important here. In general, $\hat{U}$ does not commute with itself at different times and $\hat{U}(t_2,t_1)\hat{U}(t_1,t_0) \neq \hat{U}(t_1,t_0)\hat{U}(t_2,t_1)$.

## 2 The Time Evolution Operator in Time-Dependent Systems

In going from Eqn. 3 to Eqn. 4 above, we assumed that we had a time-independent Hamiltonian. What does the time evolution operator look like for a time-dependent Hamiltonian? Let's go back to the TDSE to investigate.

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = \hat{H}(t)\left|\psi(t)\right\rangle \tag{12}$$

$$i\hbar\frac{d}{dt}\left[\hat{U}(t,0)\left|\psi(0)\right\rangle\right] = \hat{H}(t)\left[\hat{U}(t,0)\left|\psi(0)\right\rangle\right] \tag{13}$$

$$\left[i\hbar\frac{d}{dt}\hat{U}(t,0)\right]\left|\psi(0)\right\rangle = \left[\hat{H}(t)\hat{U}(t,0)\right]\left|\psi(0)\right\rangle \tag{14}$$

The two operators acting on $|\psi(0)\rangle$ on either side of the equals sign above must be equivalent, so:

$$i\hbar\frac{d}{dt}\hat{U}(t,0) = \hat{H}(t)\hat{U}(t,0) \tag{15}$$

**Aside:** Why not try to just directly integrate Eqn. 15? Let's see what happens and why it turns out to be problematic:

$$i\hbar\frac{d}{dt}\hat{U}(t,0) = \hat{H}(t)\hat{U}(t,0) \tag{16}$$

$$\frac{d\hat{U}(t,0)}{U(t,0)} = -\frac{i}{\hbar}\hat{H}(t)dt \tag{17}$$

$$\int_{U(t_0,0)}^{U(t,0)}\frac{d\hat{U}(t',0)}{U(t',0)} = \ln\left[U(t,0)\right] - \ln\left[U(t_0,0)\right] = -\frac{i}{\hbar}\int_{t_0}^{t}dt'\hat{H}(t') \tag{18}$$

$$\frac{U(t,0)}{U(t_0,0)} = \frac{U(t,t_0)\cancel{U(t_0,0)}}{\cancel{U(t_0,0)}} = U(t,t_0) = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t}dt'\hat{H}(t')\right] \tag{19}$$

We can now attempt to evaluate this complex exponential with its Taylor expansion:

$$U(t,t_0) \stackrel{?}{=} 1 - \frac{i}{\hbar}\int_{t_0}^{t}dt'\,\hat{H}(t') + \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2\left[\int_{t_0}^{t}dt'\,\hat{H}(t')\right]^2 + \cdots \tag{20}$$

Let's inspect just the second term of this expansion a little more closely:

$$\left[\int_{t_0}^{t}dt'\,\hat{H}(t')\right]^2 = \left[\int_{t_0}^{t}dt'\,\hat{H}(t')\right]\cdot\left[\int_{t_0}^{t}dt''\,\hat{H}(t'')\right] = \int_{t_0}^{t}\int_{t_0}^{t}dt'dt''\,\hat{H}(t')\hat{H}(t'') \tag{21}$$

And now we see the problem: this expression integrates factors of $\hat{H}(t')$ and $\hat{H}(t'')$ over a range of times that scrambles their relative time orderings. Unfortunately, we are not guaranteed that $[\hat{H}(t'),\hat{H}(t'')] = 0$. We have therefore not treated $\hat{H}$ properly as an operator here, and none of this math is really valid.

Let's proceed a bit more carefully instead and see what happens if we integrate both sides of Eqn. 15 with respect to time using $\tau$ as a dummy variable for integration:

$$i\hbar\int_0^t \frac{d}{d\tau}\hat{U}(\tau,0)d\tau = \int_0^t \hat{H}(\tau)\hat{U}(\tau,0)d\tau \tag{22}$$

$$=i\hbar\left[\hat{U}(\tau,0)\right]_0^t = i\hbar\left[\hat{U}(t,0)-\hat{U}(0,0)\right] = i\hbar\left[\hat{U}(t,0)-1\right] \tag{23}$$

$$\rightarrow \quad \boxed{\hat{U}(t,0) = 1 - \frac{i}{\hbar}\int_0^t d\tau \hat{H}(\tau)\hat{U}(\tau,0)} \tag{24}$$

This is a bit of a weird expression, since it casts $\hat{U}(t,0)$ in terms of an integral involving itself. But we can work with it by iteratively substituting $\hat{U}(t,0)$ into the above, e.g.

$$\hat{U}(t,0) = 1 - \frac{i}{\hbar}\int_0^t d\tau\,\hat{H}(\tau)\left[1 - \frac{i}{\hbar}\int_0^\tau d\tau'\,\hat{H}(\tau')\hat{U}(\tau',0)\right] \tag{25}$$

$$= 1 + \left(\frac{-i}{\hbar}\right)\int_0^t d\tau\,\hat{H}(\tau) \tag{26}$$

$$+ \left(\frac{-i}{\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau'\,\hat{H}(\tau)\,\hat{H}(\tau')$$

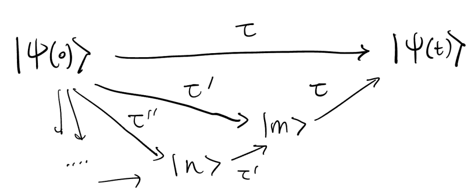
$$+ \left(\frac{-i}{\hbar}\right)^3 \int_0^t d\tau \int_0^\tau d\tau' \int_0^{\tau'} d\tau''\,\hat{H}(\tau)\,\hat{H}(\tau')\,\hat{H}(\tau'')\,\hat{U}(\tau'',0)$$

$$= ... = 1 + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \ldots \int_0^{\tau_2} d\tau_1\,\hat{H}(\tau_n)\hat{H}(\tau_{n-1})\,\ldots\,\hat{H}(\tau_2)\,\hat{H}(\tau_1) \tag{27}$$

Note that there is a time-ordering to each of these terms such that $t \geq \tau \geq \tau' \geq \tau''\ldots$ and $t \geq \tau_n \geq \cdots \geq \tau_2 \geq \tau_1$. By keeping careful track of this time ordering, we avoid the pitfalls discussed in the aside above.

It can be difficult to conceptualize what is going on here. One way to think about it is that these nested integrals are counting up all the possible ways the time evaluation operator can take us from initial state $|\psi(0)\rangle$ to the final state $|\psi(t)\rangle$. The different trajectories, represented by different terms in the sum, are mediated by visits to all possible intermediate states of the system at all possible intermediate times. All of these different paths interfere with each other as they acquire their own phases.

That's all we will say about this machinery for the time being. It crops up when you are considering the dynamics of systems that are perturbed with a time-dependent Hamiltonian at various points in time, as you might have in a nonlinear spectroscopy experiment, where time-ordered pulses interact with the system. More on this later, time permitting.



# 3 The "Pictures" of Time-Dependent Quantum Mechanics

Now that we have introduced the time evolution operator, it's a good time to make one final aside about the various ways to think about our formulation of time-dependent quantum mechanics.

## 3.1 The Schrödinger Picture

So far, we have worked within the "Schrödinger picture," where wavefunctions are time-dependent, and are propagated in time as:

$$|\psi(t)\rangle = \hat{U}(t,0)\,|\psi(0)\rangle \tag{28}$$

Meanwhile, we think of most operators as time-independent quantities. We don't write down operators like position and momentum as functions of time:

$$\hat{x} = x \neq \hat{x}(t) \tag{29}$$

$$\hat{p} = -i\hbar\frac{d}{dx} \neq \hat{p}(t) \tag{30}$$

And while the expectation values of these operators may evolve with time, we ascribe this to the time-dependent behavior of the wavefunction:

$$\begin{aligned}\langle\hat{A}(t)\rangle &= \langle\psi(t)|\hat{A}|\psi(t)\rangle & (31)\\ &\equiv \langle\psi_S(t)|\hat{A}_S|\psi_S(t)\rangle & (32)\end{aligned}$$

where I've added the subscript "$S$" to denote wavefunctions and operators within the Schrödinger picture.

## 3.2 The Heisenberg Picture

Let's now introduce the "Heisenberg picture," in which operators are time-propagated while wavefunctions are time-independent. This turns out to be entirely equivalent to the Schrödinger picture.

Consider:

$$\begin{aligned}\langle\hat{A}(t)\rangle &= \langle\psi_S(t)|\hat{A}_S|\psi_S(t)\rangle & (33)\\ &= \langle\psi_S(0)|\hat{U}^\dagger(t,0)\hat{A}_S\hat{U}(t,0)|\psi_S(0)\rangle & (34)\\ &\equiv \langle\psi_H|\hat{A}_H(t)|\psi_H\rangle & (35)\end{aligned}$$

where we've now defined wavefunctions and operators with "$H$" subscripts within the Heisenberg picture:

$$\hat{A}_H(t) \equiv \hat{U}^\dagger(t,0)\,\hat{A}_S\,\hat{U}(t,0); \qquad \hat{A}_S = \hat{A}_H(0) \tag{36}$$

$$|\psi_H\rangle \equiv |\psi_S(0)\rangle\,; \qquad |\psi_S(t)\rangle = \hat{U}(t,0)\,|\psi_H\rangle \tag{37}$$

Here, Heisenberg wavefunction is at all times the initial, stationary wavefunction given by the Schrödinger wavefunction at time zero. Meanwhile, the operators that describe physical observables like the position and momentum of the particle evolve in time (which admittedly makes some physical sense). The Heisenberg picture is sometimes more convenient to work with mathematically; we'll see it crop up a bit later on.

### 3.3 The Interaction Picture

A final note that there is also a useful representation called the "interaction picture" which is invoked for problems with time-dependent Hamiltonians that can be written as a time-independent reference system plus a small time-dependent perturbation:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) \tag{38}$$

where $\hat{H}_0$ is a relatively simple reference system that we can solve exactly, and $\hat{V}(t)$ is small, time-dependent, and possibly quite complicated.

Within the interaction picture, we define a time-evolution operator that involves just the reference Hamiltonian:

$$\hat{U}_0(t,0) = e^{-i\hat{H}_0 t/\hbar} \tag{39}$$

We relate the interaction picture to the Schrödinger as follows:

$$|\psi_S(t)\rangle = \hat{U}_0(t,0)\,|\psi_I(t)\rangle \quad \rightarrow \quad \boxed{|\psi_I(t)\rangle = \hat{U}_0^{-1}(t,0)\,|\psi_S(t)\rangle} \tag{40}$$

The interaction representation defines wavefunctions in such a way that we strip away the (uninteresting) $e^{-i\hat{H}_0 t/\hbar}$ modulation that arises from the time-independent part of the wavefunction, $\hat{H}_0$. This leaves behind a representation of the wavefunction $|\psi_I(t)\rangle$ whose only-time dependence arises from the (much more interesting) time-dependence of the perturbation $V(t)$. More on this later!