Time dependence in quantum mechanics

The Schrödinger picture: time-dependent wave functions

The time-dependent Schrödinger equation is

$$H\psi = i\hbar\frac{\partial\psi}{\partial t}$$

The formal solution is

$$\psi_S(t) = e^{-iHt/\hbar}\psi_S(0) = e^{-iEt/\hbar}\psi_S(0)$$

provided ψ_S is an eigenfunction of H. The subscript S refers to the Schrödinger equation. The time-independent Schrödinger equation is a special case

$$H\psi = E\psi$$

We can treat ψ as an eigenfunction of the time-independent equation and then the factor $e^{-iEt/h}$ is an arbitrary phase factor.

The Schrödinger Representation

To proceed we introduce bra-ket notation.
We can express the time-dependent wave function as:

$$|\psi_S(t)\rangle = e^{-iHt/\hbar}|\psi_S(0)\rangle$$

$$\langle\psi_S(t)| = \langle\psi_S(0)|e^{iHt/\hbar}$$

The expectation value at time t is

$$\begin{aligned} \langle A(t)\rangle &= \langle\psi_S(t)|A_S|\psi_S(t)\rangle \\ &= \langle\psi_S(0)|e^{iHt/\hbar}A_S e^{-iHt/\hbar}|\psi_S(0)\rangle \end{aligned}$$

where A_S represents the operator in the Schrödinger representation.

The Heisenberg Representation

The above expectation value suggests that we may define the operator to be time-dependent (instead of the wave function). This is known as the Heisenberg representation. The connection is given by

$$A_H(t) = e^{iHt/\hbar} A_S e^{-iHt/\hbar}$$

We may obtain an equation of motion by taking the time-derivative of both sides of the above expectation value.

$$\begin{aligned}
\frac{d}{dt} < A(t) > &= \frac{d}{dt} < \psi_S(0) | e^{iHt/\hbar} A_S e^{-iHt/\hbar} | \psi_S(0) > \\
&= \; < \psi_S(0) | \left(\frac{d}{dt} e^{iHt/\hbar} \right) A_S e^{-iHt/\hbar} | \psi_S(0) > \\
&+ < \psi_S(0) | e^{iHt/\hbar} \frac{dA_S}{dt} e^{-iHt/\hbar} | \psi_S(0) > \\
&+ \; < \psi_S(0) | e^{iHt/\hbar} A_S \left(\frac{de^{-iHt/\hbar}}{dt} \right) | \psi_S(0) >
\end{aligned}$$

The Heisenberg Representation

We have applied the product rule to the three quantities that depend on the time. Since

$$\frac{de^{iHt/\hbar}}{dt} = \frac{iH}{\hbar}e^{iHt/\hbar}$$

we can write the above expression as

$$\begin{aligned}
\frac{d}{dt}A(t) &= \frac{i}{\hbar} < \psi_S(0)|e^{iHt/\hbar}HA_S e^{-iHt/\hbar}|\psi_S(0) > \\
&\quad + < \psi_S(0)|e^{iHt/\hbar}\frac{dA_S}{dt}e^{-iHt/\hbar}|\psi_S(0) > \\
&\quad + \frac{i}{\hbar} < \psi_S(0)|e^{iHt/\hbar}\left(-A_S H\right)e^{-iHt/\hbar}|\psi_S(0) > \\
&= < \psi_S(0)|e^{iHt/\hbar}\frac{dA_S}{dt}e^{-iHt/\hbar}|\psi_S(0) > \\
&\quad + \frac{i}{\hbar} < \psi_S(0)|e^{iHt/\hbar}[H,A_S]e^{-iHt/\hbar}|\psi_S(0) >
\end{aligned}$$

The Heisenberg Representation

If the expression is evaluated at t = 0 then it can be written as

$$\frac{d}{dt} < A(t) >_{t=0} = < \frac{dA_S}{dt} > + \frac{i}{\hbar} < [H, A_S] >$$

where the angle brackets represent averages with respect to $\psi_S(0)$.

If the operator A_S does not depend on time (this is usually the case for a Schrödinger operator) then the equation becomes:

$$\frac{d}{dt} < A(t) >_{t=0} = \frac{i}{\hbar} < [H, A_S] >$$

Time-dependent perturbation theory

We treat the hamiltonian as a zero-order part that does not depend on time, H_0 and a perturbation H' that does. The Schrödinger equation then takes the form

$$\left(H_0 + H'\right)\psi = i\hbar\frac{\partial\psi}{\partial t}$$

We assume that the zero-order eigenfunctions and eigenvalues are known. Defining $\psi_n(0) \equiv |n\rangle$ as eigenfunctions of H, $H|n\rangle = E|n\rangle$, we can use these zero-order solutions as a basis for expanding the perturbed wave function.

$$|\psi\left(t\right)> = \sum_n c_n\left(t\right)e^{-iE_n t/\hbar}|n>$$

The coefficients $c_n(t)$ and phase factor $e^{-iEt/h}$ carry the time dependence. The coefficients give the time-dependent probability amplitudes for the zero order states n.

Time-dependent perturbation theory

We substitute this first-order expression into the Schrödinger equation to obtain

$$\sum_n c_n(t)e^{-iE_nt/\hbar}\left(H_0 + H'\right)|n> = i\hbar\sum_n \frac{\partial}{\partial t}\left\{c_n(t)e^{-iE_nt/\hbar}|n>\right\}$$

The sum over n runs over an infinite number of eigenstates. If we pick one of these states (call it m) and multiply both sides by the complex conjugate of the wave function of state m and then integrate over all space we find

$$\sum_n c_n(t)e^{-iE_nt/\hbar}\left(<m|H_0|n> + <m|H'|n>\right)$$

$$= i\hbar\sum_n \frac{\partial}{\partial t}\left\{c_n(t)e^{-iE_nt/\hbar}<m|n>\right\}$$

The eigenfunctions are orthonormal $\langle n|m\rangle = \delta_{nm}$ so out of the infinite sum on the right-hand side only the term in n = m survives.

Time-dependent perturbation theory

Since $$<m|H_0|n> = E_m\delta_{nm}$$

we have
$$c_m(t)e^{-iE_m t/\hbar}E_m + \sum_n c_n(t)e^{-iE_n t/\hbar} <m|H'|n>$$
$$= i\hbar\frac{\partial c_m(t)}{\partial t}e^{-iE_m t/\hbar} + i\hbar\left(\frac{-iE_m}{\hbar}\right)c_m(t)e^{-iE_m t/\hbar}$$

Note that there are terms on each side that cancel and thus we can write a set of coupled linear equations for the coefficients
$$\frac{dc_m(t)}{dt} = \frac{-i}{\hbar}\sum_n c_n(t)e^{-i\omega_{nm}t}V_{mn}(t)$$

where some standard definitions have been used:

$$V_{mn}(t) \equiv <m|H'|n>$$
$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar}$$

Time-dependent perturbation theory

The solution thus far is exact. However, because the coefficients comprise a set of linear coupled equations the solution is still not practical. We can obtain a perturbation theory solution by assuming that all of the coefficients on the right hand side are equal to their values at t = 0, $c_n(t) \approx c_n(0) = \delta_{ni}$. This eliminates all of the terms in the summation on the right hand side except one. We assume that the wave function starts out in an initial state i and thus at time zero all of the population is in I ($c_i(0) = 1$). We wish to know the time dependence of the coefficient for a final state f. We can integrate directly to find this.

$$\frac{dc_f(t)}{dt} = \frac{-i}{\hbar} e^{i\omega_{fi}t} V_{fi}(t)$$

$$c_f(t) = \frac{-i}{\hbar}\int_0^t dt' e^{i\omega_{fi}t'} V_{fi}(t')$$

Time-dependent perturbation theory

The coefficient gives a probability amplitude. The probability is the square of the wave function ($\Psi^*\Psi = \Psi^2$ if Ψ is real). Thus, the probability for observing population in state f at time t is

$$P_f(t) = \frac{1}{\hbar^2}\left(\int_0^t dt' e^{i\omega_{fi}t'} V_{fi}(t')\right)^2$$