

Time-Dependent Perturbation Theory

The Time-Evolution Operator

The time-evolution of a wavefunction can be expressed by the effect of a time evolution operator on an initial wavefunction through the relation

$$\Psi(\vec{r}, t) = U(t)\Psi(\vec{r}, 0), \text{ with } U(0) = 1. \quad (1)$$

Stationary States

Given a Hamiltonian \mathcal{H}_o for which eigenfunctions $\{\phi_i\}$ and eigenvalues $\{\epsilon_i\}$ can be found, the time-dependence of any state ϕ_k is the simple time-dependent phase factor

$$U_o(t) = e^{-i\epsilon_k t/\hbar}. \quad (2)$$

This is readily seen by using the definition $\phi(t) = U_o(t)\phi_k$ in the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \phi(t) = \mathcal{H}_o \phi(t). \quad (3)$$

Since \mathcal{H}_o and ϕ_k are independent of time,

$$i\hbar \frac{\partial}{\partial t} U_o \phi_k = \mathcal{H}_o U_o \phi_k \implies \frac{dU_o}{U_o} = -\frac{i}{\hbar} \mathcal{H}_o dt \implies U_o(t) = e^{-\frac{i}{\hbar} \mathcal{H}_o t}, \quad (4)$$

and

$$U_o(t)\phi_k = e^{-\frac{i}{\hbar} \mathcal{H}_o t} \phi_k = e^{-\frac{i}{\hbar} \epsilon_k t} \phi_k. \quad (5)$$

Thus, the states are stationary, that is, the wavefunctions are independent of time to within a phase factor and the probabilities are independent of time.

General Time Evolution Operator

Using the definition of equation (1) in the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \mathcal{H}\psi(\vec{r}, t) \implies i\hbar \left(\frac{\partial}{\partial t} U(t) \right) \psi(\vec{r}, 0) = \mathcal{H}U(t)\psi(\vec{r}, 0), \quad (6)$$

yields the differential equation for $U(t)$

$$i\hbar \frac{\partial}{\partial t} U(t) = \mathcal{H}U(t) \text{ or } dU(t) = -\frac{i}{\hbar} \mathcal{H}U(t) dt. \quad (7)$$

When the Hamiltonian is a general function of time, this equation can be integrated to yield

$$U(t) = U(0) - \frac{i}{\hbar} \int_0^t \mathcal{H}(t_1)U(t_1) dt_1. \quad (8)$$

The solution to this integral equation can be obtained by iteration. The first order approximation can be obtained by substituting the zero order approximation $U(0) = 1$ into the integral

$$U(t) = 1 - \frac{i}{\hbar} \int_0^t \mathcal{H}(t_1) dt_1. \quad (9)$$

The second order approximation is obtained by replacing $U(t)$ in the integral with the first order expression

$$U(t_1) = 1 - \frac{i}{\hbar} \int_0^{t_1} \mathcal{H}(t_2) dt_2, \quad (10)$$

which results in

$$U(t) = 1 - \frac{i}{\hbar} \int_0^t \mathcal{H}(t_1) dt_1 + \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t_1} \mathcal{H}(t_1) \mathcal{H}(t_2) dt_2 dt_1. \quad (11)$$

Iterating indefinitely,

$$U(t) = 1 - \frac{i}{\hbar} \int_0^t \mathcal{H}(t_1) dt_1 + \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t_1} \mathcal{H}(t_1) \mathcal{H}(t_2) dt_1 dt_2 + \left(-\frac{i}{\hbar}\right)^3 \int_0^t \int_0^{t_1} \int_0^{t_2} \mathcal{H}(t_1) \mathcal{H}(t_2) \mathcal{H}(t_3) dt_1 dt_2 dt_3 + \dots \quad (12)$$

Thus, $U(t)$ can be evaluated to any order in the Hamiltonian. Notice that the integrals are ordered in time, that is $t > t_1 > t_2 \dots$, and that the ordering of the Hamiltonian operators must be preserved in the general case.

Effect of a Time-Dependent Perturbation

Consider the case $\mathcal{H} = \mathcal{H}_o + V(t)$, where $V(t)$ is an operator representing a much smaller energy than the eigenvalues of \mathcal{H}_o . V is said to be a small perturbation to the initial physical system. Notice that $V \ll \mathcal{H}_o$ in an operator sense, that is, the expectation value of V is much less than that of \mathcal{H}_o . In the time-independent case, the perturbation created corrections to the initial wavefunctions, corrections of various orders in the perturbation. With a time-dependent perturbation, these corrections will now be dependent upon time as well. The initial wavefunctions are solutions to the time-independent Schrödinger equation determined using analytical or variational methods, and they can include the effects of a static perturbation included in \mathcal{H}_o .

If the perturbation $V(t)$ is suddenly switched on at $t = 0$, then the wavefunction will gradually evolve from an initial stationary state of \mathcal{H}_o as a time-dependent coherent superposition of the eigenstates of \mathcal{H}_o . This is expressed mathematically as

$$\phi(t) = U(t)\phi_i = \sum_k c_{ik}(t)\phi_k = \sum_k c_{ik}|k\rangle. \quad (13)$$

Using the concept of a vector space, the set $\{|k\rangle\}$ is presumed to be a complete basis for the description of any state vector $|\phi(t)\rangle$. An important general expression for the coefficients is

$$c_k(t) = \langle k|\phi(t)\rangle, \quad (14)$$

which is simply the projection of $\phi(t)$ on to the $|k\rangle$ axis. Thus, the set of coefficients $\{c_{ik}\}$ can be determined using

$$c_{ik} = \langle k|\phi(t)\rangle = \langle k|U(t)\phi_i\rangle = \langle k|U(t)|i\rangle = U_{ki}. \quad (15)$$

Time Evolution Operator for a Time-Dependent Perturbation

To determine $U(t)$ for this additive Hamiltonian, it is reasonable to assume that the operator is can be written in the form

$$U(t) = U_{\circ}(t)U_v(t), \text{ where } U_{\circ}(t) = e^{-\frac{i}{\hbar}\mathcal{H}_{\circ}t}. \quad (16)$$

Using this definition in the Schrodinger equation yields

$$i\hbar \left[\left(\frac{\partial}{\partial t} U_{\circ} \right) U_v + U_{\circ} \left(\frac{\partial}{\partial t} U_v \right) \right] = \mathcal{H}U_{\circ}U_v = \mathcal{H}_{\circ}U_{\circ}U_v + V(t)U_{\circ}U_v. \quad (17)$$

Then, (4) leads to

$$\mathcal{H}_{\circ}U_{\circ}U_v + i\hbar U_{\circ} \frac{\partial}{\partial t} U_v = \mathcal{H}_{\circ}U_{\circ}U_v + V(t)U_{\circ}U_v, \quad (18)$$

or simply

$$i\hbar U_{\circ} \frac{\partial}{\partial t} U_v = V(t)U_{\circ}U_v. \quad (19)$$

Operating on the left with U_{\circ}^{\dagger} yields the relation

$$i\hbar \frac{\partial}{\partial t} U_v = U_{\circ}^{\dagger} V(t) U_{\circ} U_v = V_H(t) U_v, \quad (20)$$

where $V_H(t)$ is the Heisenberg representation of the operator $V(t)$. Solving the resulting integral equation by iteration yields

$$\begin{aligned} U_v(t) = 1 - \frac{i}{\hbar} \int_0^t V_H(t_1) dt_1 + \left(-\frac{i}{\hbar} \right)^2 \int_0^t \int_0^{t_1} V_H(t_1) V_H(t_2) dt_1 dt_2 \\ + \left(-\frac{i}{\hbar} \right)^3 \int_0^t \int_0^{t_1} \int_0^{t_2} V_H(t_1) V_H(t_2) V_H(t_3) dt_1 dt_2 dt_3 + \dots \end{aligned} \quad (21)$$

First-Order Evolution of the Wavefunction

The first-order approximation to $U_v(t)$, the second term in Eq. (21), describes the most simple interaction between the quantum system and the agent creating the perturbation. When the perturbation arises from an applied electromagnetic field, this terms describes the interaction of the system with the field once, that is, the absorption or emission of a single photon. The zero-order expression for $c_k(t)$ arises from the zero-order approximation for U , that is $U(t) = U_{\circ}U_v = U_{\circ}$. Then

$$c_k(t) = \langle k | U_{\circ} | i \rangle = \langle k | e^{-\frac{i}{\hbar}\mathcal{H}_{\circ}t} | i \rangle = e^{-\frac{i}{\hbar}\epsilon_i t} \langle k | i \rangle = e^{-\frac{i}{\hbar}\epsilon_i t} \delta_{ki}. \quad (22)$$

So, the state of the system does not change. The first order term in U_v contributes

$$c_k(t) = \langle k | U_{\circ} \left(-\frac{i}{\hbar} \int_0^t e^{\frac{i}{\hbar}\mathcal{H}_{\circ}t_1} V(t_1) e^{-\frac{i}{\hbar}\mathcal{H}_{\circ}t_1} dt_1 \right) | i \rangle, \quad (23)$$