12.1: Preliminary Analysis

Suppose that at $t = 0$ the state of the system is represented by

$$\psi(0) = \sum_m c_m \, \psi_m, \tag{12.1.1}$$

where the c_m are complex numbers. Thus, the initial state is some linear superposition of the unperturbed energy eigenstates. In the absence of the time-dependent perturbation, the time evolution of the system is simply (see Section [sstat])

$$\psi(t) = \sum_m c_m \, \exp(-\mathrm{i}\, E_m \, t/\hbar) \psi_m. \tag{12.1.2}$$

Now, the probability of finding the system in state n at time t is

$$P_n(t) = |\langle \psi_n | \psi \rangle|^{\,2} = |c_n \, \exp(-\mathrm{i}\, E_n \, t/\hbar)|^{\,2} = |c_n|^{\,2} = P_n(0), \tag{12.1.3}$$

because the unperturbed eigenstates are assumed to be orthonormal: that is,

$$\langle n | m \rangle = \delta_{nm}. \tag{12.1.4}$$

Clearly, with $H_1 = 0$, the probability of finding the system in state ψ_n at time t is exactly the same as the probability of finding the system in this state at the initial time, $t = 0$. However, with $H_1 \neq 0$, we expect the P_n—and, hence, the c_n—to vary with time. Thus, we can write

$$\psi(t) = \sum_m c_m(t) \, \exp(-\mathrm{i}\, E_m \, t/\hbar) \psi_m, \tag{12.1.5}$$

where $P_n(t) = |c_n(t)|^{\,2}$. Here, we have carefully separated the fast phase oscillation of the eigenstates, which depends on the unperturbed Hamiltonian, from the slow variation of the amplitudes $c_n(t)$, which depends entirely on the perturbation (i.e., c_n is constant in time if $H_1 = 0$). Note that in Equation ([e13.7]) the eigenstates ψ_m are time-independent (they are actually the eigenstates of H_0 evaluated at the initial time, $t = 0$).

The time-dependent Schrödinger equation [see Equation ([etimed])] yields

$$\mathrm{i}\,\hbar \frac{\partial \psi(t)}{\partial t} = H(t)\,\psi(t) = [H_0 + H_1(t)]\,\psi(t). \tag{12.1.6}$$

Now, it follows from Equation ([e13.7]) that

$$(H_0 + H_1)\,\psi = \sum_m c_m \, \exp(-\mathrm{i}\, E_m \, t/\hbar)(E_m + H_1)\,\psi_m. \tag{12.1.7}$$

We also have

$$\mathrm{i}\,\hbar \frac{\partial \psi}{\partial t} = \sum_m \left(\mathrm{i}\,\hbar \frac{dc_m}{dt} + c_m \, E_m \right) \exp(-\mathrm{i}\, E_m \, t/\hbar) \psi_m, \tag{12.1.8}$$

because the ψ_m are time-independent. According to Equation ([e13.8]), we can equate the right-hand sides of the previous two equations to obtain

$$\sum_m \mathrm{i}\,\hbar \frac{dc_m}{dt} \exp(-\mathrm{i}\, E_m \, t/\hbar) \psi_m = \sum_m c_m \, \exp(-\mathrm{i}\, E_m \, t/\hbar) H_1 \, \psi_m. \tag{12.1.9}$$

Projecting out the component of the previous equation which is proportional to ψ_n, using Equation ([e13.6]), we obtain

$$\mathrm{i}\,\hbar \frac{dc_n(t)}{dt} = \sum_m H_{nm}(t) \, \exp(\,\mathrm{i}\,\omega_{nm}\, t) c_m(t), \tag{12.1.10}$$

where

$$H_{nm}(t) = \langle n | H_1(t) | m \rangle, \tag{12.1.11}$$

and

$$\omega_{nm} = \frac{E_n - E_m}{\hbar}. \tag{12.1.12}$$

Suppose that there are N linearly independent eigenstates of the unperturbed Hamiltonian. According to Equations ([e13.12]), the time dependence of the set of N coefficients c_n, which specify the probabilities of finding the system in these eigenstates at time t, is determined by N coupled first-order differential equations. Note that Equations ([e13.12]) are exact—we have made no approximations at this stage. Unfortunately, we cannot generally find exact solutions to these equations. Instead, we have to obtain approximate solutions via suitable expansions in small quantities. However, for the particuilarly simple case of a two-state system (i.e., $N = 2$), it is actually possible to solve Equations ([e13.12]) without approximation. This solution is of great practical importance.
