Chapter 15
Time-Dependent Perturbations

It was noted in Section 3.3 that, although the emphasis in introductory courses in quantum physics is, necessarily, on stationary states and the solution of the TISE for various potential energy functions, physical systems do not typically “live” in stationary states. Generally, they are in a time-dependent superposition of states that, as long as the potential energy is independent of time, can be determined by applying the time evolution operator to the wave function at some specific time (see the discussion of Postulate VI in Section 6.3.2).

Now, suppose at some time, say $t = 0$, a perturbation is applied to the system. We wish to describe the reaction of the system to the perturbation. An example of such a perturbation might be one such that at $t = 0$ a constant field, electric or magnetic, is applied. Because the field is turned on at a particular time the perturbation is time-dependent, so we expect the time dependence of the state vector to be altered. To determine how the system evolves in time, we must solve the TDSE. Indeed, in a limited number of cases, this is possible. When it is not possible to solve the problem exactly we must find approximate solutions. One such approximation method is time-dependent perturbation theory. We begin the discussion with the exact solution to the TDSE and then elaborate on the approximations that can be made in given physical situations.

15.1 Time Dependence of the State Vector

To this point we have dealt only with Hamiltonians that do not contain time. Before studying time-dependent perturbation theory we examine the time evolution of a system when the Hamiltonian contains the time. To do this we assume that the Hamiltonian $\hat{H}(r,t)$ can be separated into the sum of two terms, $\hat{H}_0$ a time-independent Hamiltonian and $\hat{W}(t)$ which depends upon time, although it may depend upon other observables as well. It is also assumed that $\hat{W}(t)$ is turned on at $t = 0$. Thus,

$$\hat{H}(r,t) = \hat{H}_0(r) + \lambda \hat{W}(t) \quad (15.1)$$
where $\lambda$ is a parameter that is used to keep track of the order of the approximation. It may be set equal to unity at any time. As in time-independent perturbation theory, we assume that the eigenkets and energy eigenvalues of $\hat{H}_0$ are known and that to each eigenket there is one energy eigenvalue. These eigenkets and eigenvalues are designated $|\psi_n\rangle$ and $E_n$, respectively. We do not require superscripts as in the case of time-independent perturbation theory because we will use the $|\psi_n\rangle$ as a basis set throughout. That is, the only possible final states will be one of the $|\psi_n\rangle$. It is the probability of finding the system in one of these eigenstates that is affected by the time-dependent perturbation. The TISE is

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle \tag{15.2}$$

and we seek the ket $|\Psi(r, t)\rangle$ that is the superposition of the $|\psi_n\rangle$ states that result from the perturbation $\hat{W}(t)$. This superposition may be written as a linear combination of the time-independent eigenkets with time-dependent expansion coefficients. Thus,

$$|\Psi(r, t)\rangle = \sum_n c_n(t) |\psi_n\rangle \exp \left(-i \frac{E_n}{\hbar} t \right) \tag{15.3}$$

where the time dependence of the Hamiltonian has been accounted for by making the expansion coefficients functions of time. Note that we cannot use the time evolution operator because the Hamiltonian is not independent of time. Clearly the probability of measuring the system to be in a given stationary state, say $|\psi_m\rangle$, is $|c_m(t)|^2$, which is time-dependent.

The state vector, $|\Psi(r, t)\rangle$, is determined by the TDSE

$$\hat{H}(r, t) |\Psi(r, t)\rangle = i \hbar \frac{\partial}{\partial t} |\Psi(r, t)\rangle \tag{15.4}$$

Substituting Equations 15.1 and 15.3 into the TDSE we have

$$\left[ \hat{H}_0(r) + \lambda \hat{W}(t) \right] \sum_n c_n(t) |\psi_n\rangle \exp \left(-i \frac{E_n}{\hbar} t \right)$$

$$= i \hbar \frac{\partial}{\partial t} \sum_n c_n(t) |\psi_n\rangle \exp \left(-i \frac{E_n}{\hbar} t \right) \tag{15.5}$$

Using Equation 15.2 and regrouping we have

$$\lambda \sum_n c_n(t) \hat{W}(t) |\psi_n\rangle \exp \left(-i \frac{E_n}{\hbar} t \right) = i \hbar \sum_n \dot{c}_n(t) |\psi_n\rangle \exp \left(-i \frac{E_n}{\hbar} t \right) \tag{15.6}$$

where $\dot{c}_n(t)$ is the time derivative of $c_n$. Taking the inner product with $\langle \psi_k |$, multiplying by $\exp(i E_k t / \hbar)$ and solving for $\dot{c}_k(t)$ we have