CHAPTER TEN

The Time Dependent Schrödinger Equation

Up to this point we considered problems in which the essential characteristics of the particle, such as its energy and probability function $\psi(x)$, were not functions of time. The eigenfunction of a particle with energy E_n was obtained by solving the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right)u_n(\mathbf{r})=E_n u_n(\mathbf{r}) \tag{10.1}$$

In the case of a free particle [$V(\mathbf{r})=0$], we found in Section 2.2 that the solution of (10.1) is [see (2.6)] in the form of a plane wave

$$u(\mathbf{r},\mathbf{p})\propto e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{10.2}$$

We have, however, learned that certain experimental situations such as electron diffraction in crystals, for example, can only be explained by postulating a wavelike wavefunction that, by its nature, must be time-dependent [see (1.20)]:

$$\psi(\mathbf{r},t)\propto e^{i(\mathbf{p}\cdot\mathbf{r}/\hbar-Et/\hbar)} \tag{10.3}$$

We conclude that the time-independent Schrödinger equation does not tell the whole story. What is needed is thus an extension of the Schrödinger equation that accounts explicitly for the effects of time. A clue to the form of the sought equation is obtained by realizing that (10.3) satisfies

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r},t)\right)\psi(\mathbf{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) \tag{10.4}$$

or, in general,

$$\mathcal{H}(\mathbf{r},-i\hbar\nabla,t)\psi(\mathbf{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) \tag{10.5}$$

Equation (10.5) is the time-dependent Schrödinger equation. The justification for its use is: (a) When the Hamiltonian does not depend on time the predictions of the theory are identical with that of the time-independent Schrödinger equation; (b) the prediction of the theory agrees with experiment; and (c) in the limit $\hbar\to 0$ with classical physics.

We find by substitution that in the special case when $\mathcal{H}$ does not depend explicitly on time, the general solution of (10.5) can be taken as

$$\psi(\mathbf{r},t)=\sum_n a_n u_n(\mathbf{r})e^{-iE_nt/\hbar} \tag{10.6}$$

where u_n is the eigenfunction of $\mathcal{H}$ with energy E_n:

$$\mathcal{H}u_n(\mathbf{r})=E_n u_n(\mathbf{r}) \tag{10.7}$$

and a_n does not depend on time.

The probability of finding the system in the state u_n with energy E_n is then

$$\begin{aligned}P_n&=|\langle\psi(t)|u_n\rangle|^2\\&=|a_n|^2\end{aligned}$$

10.1 THE STATISTICAL INTERPRETATION OF $\psi(\mathbf{r},t)$

The interpretation of $\psi(\mathbf{r},t)$ is similar to that postulated in Section 3.1 for $\psi(\mathbf{r})$. The probability $P(\mathbf{r},t)$ of finding a particle inside a differential volume $d^3\mathbf{r}$ at time t is

$$P(\mathbf{r},t)=|\psi(\mathbf{r},t)|^2d^3\mathbf{r} \tag{10.8}$$

Since the probability of finding the particle somewhere in space is unity, we must have

$$\int|\psi(\mathbf{r},t)|^2d^3\mathbf{r}=1$$

so that

$$\frac{d}{dt}\int|\psi(\mathbf{r},t)|^2d^3\mathbf{r}=0 \tag{10.9}$$

This last statement of the conservation of probability is proved as follows:

$$\frac{d}{dt}\int\psi^*\psi\,d^3\mathbf{r}=\int\frac{\partial}{\partial t}(\psi^*\psi)\,d^3\mathbf{r}$$

$$=\int\left(\psi\frac{\partial\psi^*}{\partial t}+\frac{\partial\psi}{\partial t}\psi^*\right)d^3\mathbf{r}$$

Substituting for $\partial\psi/\partial t$ and $\partial\psi^*/\partial t$ from (10.4) leads to

$$\frac{d}{dt}\int_V|\psi|^2\,d^3\mathbf{r}=\frac{i\hbar}{2m}\int_V(\psi^*\nabla^2\psi-\psi\nabla^2\psi^*)\,d^3\mathbf{r} \qquad (10.10)$$

We use Green's theorem[1] to rewrite the last integral as

$$\frac{d}{dt}\int_V|\psi|^2\,d^3\mathbf{r}=\frac{i\hbar}{2m}\int_V(\psi^*\nabla^2\psi-\psi\nabla^2\psi^*)\,d^3\mathbf{r}$$

$$=\frac{i\hbar}{2m}\int_A(\psi^*\nabla\psi-\psi\nabla\psi^*)\cdot\hat{n}\,da \qquad (10.11)$$

Since ψ vanishes at infinity, the last integral is zero when V extends over all space. This completes the proof.

10.2 EXPECTATION VALUES OF OPERATORS

The expectation value of some physical quantity whose quantum mechanical operator is $\hat{A}$ is obtained according to (3.12) by

$$\langle A\rangle=\int\psi^*(\mathbf{r},t)\hat{A}\psi(\mathbf{r},t)\,d^3\mathbf{r} \qquad (10.12)$$

and is, in general, time dependent. The time evolution of $\langle A\rangle$ can also be expressed in a convenient differential form. To do so we start with the Schrödinger equation (10.5) using the Dirac notation:

$$\frac{1}{i\hbar}\mathcal{H}|\psi\rangle=|\dot{\psi}\rangle \quad \left(|\dot{\psi}\rangle\equiv\frac{\partial}{\partial t}|\psi\rangle\right) \qquad (10.13)$$

so that

$$-\frac{1}{i\hbar}\langle\psi|\mathcal{H}=\langle\dot{\psi}| \qquad (10.14)$$

and (10.12) is written as

$$\langle A\rangle=\langle\psi|\hat{A}|\psi\rangle \qquad (10.15)$$

Taking the time derivative of (10.15),

$$\frac{d}{dt}\langle A\rangle=\langle\dot{\psi}|\hat{A}|\psi\rangle+\langle\psi|\hat{A}|\dot{\psi}\rangle+\langle\psi|\dot{\hat{A}}|\psi\rangle$$

$$=-\frac{1}{i\hbar}\langle\psi|\mathcal{H}\hat{A}|\psi\rangle+\frac{1}{i\hbar}\langle\psi|\hat{A}\mathcal{H}|\psi\rangle+\langle\psi|\dot{\hat{A}}|\psi\rangle \qquad (10.16)$$

The last result can be rewritten as

$$\frac{d}{dt}\langle\hat{A}\rangle=\frac{i}{\hbar}\langle[\mathcal{H},\hat{A}]\rangle+\left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle \qquad (10.17)$$

which is the sought result. We next make use of (10.17) to prove some important results.

Ehrenfest's Theorem

According to Ehrenfest's theorem the classical equations

$$m\frac{d\mathbf{r}}{dt}=\mathbf{p} \quad \text{and} \quad \frac{d\mathbf{p}}{dt}=-\nabla V \qquad (10.18)$$

[$V(\mathbf{r})$ is the potential energy function] are also valid in quantum mechanics, provided we replace all the classical quantities by the expectation values of their corresponding quantum mechanical operators.

Proof: We apply (10.17) to the operator x.

$$\frac{d\langle x\rangle}{dt}=\frac{i}{\hbar}\langle[\mathcal{H},x]\rangle$$

$$=\frac{i}{\hbar}\left\langle\left[\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right),x\right]\right\rangle$$

$$=\frac{i}{\hbar}\left\langle\left[-\frac{\hbar^2}{2m}\nabla^2,x\right]\right\rangle$$

$$=-\frac{i\hbar}{2m}\int\psi^*(\nabla^2x-x\nabla^2)\psi\,d^3\mathbf{r}$$

but $\nabla^2x=x\nabla^2-2(\partial/\partial x)$; therefore,

$$\frac{d\langle x\rangle}{dt}=-\frac{i\hbar}{m}\int\psi^*\frac{\partial}{\partial x}\psi\,d^3\mathbf{r}$$

$$=\frac{1}{m}\langle p_x\rangle$$

where we used $\hat{p}_x=-i\hbar(\partial/\partial x)$ and $[V(\mathbf{r}),x]=0$. This completes the proof of the first of relations (10.18).

---

[1] Green's theorem states that for any two scalar functions $f(r)$ and $g(r)$,

$$\int_V(f\nabla^2g-g\nabla^2f)\,d^3\mathbf{r}=\int_A(f\nabla g-g\nabla f)\cdot\mathbf{n}\,da$$

A is the surface bounding the arbitrary volume V. $\mathbf{n}$ is the unit outward normal vector, $d^3\mathbf{r}$ and da are, respectively, differential volume and area elements.

The second proof starts, again, with (10.17) applied to $\hat{p}_x$:

$$
\begin{aligned}
\frac{d\langle \hat{p}_x\rangle}{dt} &= \frac{i}{\hbar}\langle[\mathcal{H},\hat{p}_x]\rangle\\
&= \frac{i}{\hbar}\left\langle\left[\left(-\frac{\hbar^2}{2m}\nabla^2+V\right),-i\hbar\frac{\partial}{\partial x}\right]\right\rangle\\
&= \left\langle\left[V,\frac{\partial}{\partial x}\right]\right\rangle\\
&= \int\left[\psi^*\left(V\frac{\partial}{\partial x}\right)\psi-\psi^*\frac{\partial}{\partial x}(V\psi)\right]d^3\mathbf{r}\\
&= -\int\psi^*\frac{\partial V}{\partial x}\psi\, d^3\mathbf{r}\\
&= -\left\langle\frac{\partial V}{\partial x}\right\rangle
\end{aligned}
$$

where we used $[\nabla^2,\partial/\partial x]=0$.

This completes the proof.

PROBLEMS

1. If the dominant term in $\psi(\mathbf{r},t)$ $(r\to\infty)$ varies as r^{-n}, what values can n possess in order that the integral in (10.11) taken over the surface at infinity is to vanish?
2. Show that if $\psi(\mathbf{r},t)$ defined by

$$\psi(\mathbf{r},t)=\left(\frac{1}{2\pi\hbar}\right)^{3/2}\int_{-\infty}^{+\infty}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\Phi(\mathbf{p},t)\,d^3\mathbf{p}.$$

is to satisfy Schrödinger's equation, $\Phi(\mathbf{p},t)$ satisfies the equation

$$\left(\frac{p^2}{2m}+V(\mathbf{r}\to i\hbar\nabla_p,\mathbf{p},t)\right)\Phi(\mathbf{p},t)=i\hbar\frac{\partial\Phi(\mathbf{p},t)}{\partial t}$$

where $\mathbf{r}\to i\hbar\nabla_p$ means that x_i is to be replaced by $i\hbar(\partial/\partial p_i)$.

Hint: Show that

$$\int_{-\infty}^{+\infty}\frac{\partial\Phi}{\partial p}e^{ipx/\hbar}\,dp=-\frac{ix}{\hbar}\int_{-\infty}^{+\infty}\Phi e^{ipx/\hbar}\,dp$$

for $\Phi(-\infty)=\Phi(+\infty)=0$.

CHAPTER ELEVEN

Perturbation Theory

In the first part of this book we dealt with a variety of problems in which the eigenfunctions and eigenvalues of some operators were obtained. Special emphasis was placed on solutions of the energy eigenvalue problem (the time-independent Schrödinger equation):

$$\mathcal{H}_0u_m=E_mu_m$$

In this chapter we consider the effect on the energies E_m and on the eigenfunction u_m of small perturbations of the Hamiltonian $\mathcal{H}_0$. Such perturbations arise in practice from the presence of electric and magnetic fields or from the interactions with other particles when these effects are not included in the unperturbed Hamiltonian $\mathcal{H}_0$. Since exact solutions of the full Schrödinger equation are seldom possible, the perturbation methods discussed below are some of the main practical tools in quantum mechanics.

11.1 TIME-INDEPENDENT PERTURBATION THEORY

The problem we pose is the following: Given a Hamiltonian $\mathcal{H}_0$, its eigenfunctions u_m, and the eigenvalues E_m so that

$$\mathcal{H}_0u_m=E_mu_m \tag{11.1}$$

What are the new eigenfunctions and eigenvalues when the Hamiltonian is perturbed from $\mathcal{H}_0$ to $\mathcal{H}_0+\mathcal{H}'$? One method of solution would be to diagonalize the matrix of $\mathcal{H}_0+\mathcal{H}'$ in some arbitrary representation as discussed in Section 9.3. This method is often used in practice. If $\mathcal{H}_0\gg\mathcal{H}'$, we can employ perturbation techniques and obtain expressions for the perturbation of u_m and E_m to any desired order. This is the concern of this section.

First-Order Perturbation

The Hamiltonian operator is taken as $\hat{\mathcal{H}}_0 + \lambda\hat{\mathcal{H}}'$, where $0<\lambda<1$ is a parameter that "turns the perturbation on" ($\lambda=1$) or "off" ($\lambda=0$). We are looking for the energies W and functions ψ that satisfy

$$(\hat{\mathcal{H}}_0+\lambda\hat{\mathcal{H}}')\psi = W\psi \tag{11.2}$$

Expanding ψ and W in a power series in λ,

$$\begin{aligned}\psi &= \psi_0+\lambda\psi_1+\lambda^2\psi_2+\cdots\\ W &= W_0+\lambda W_1+\lambda^2 W_2+\cdots\end{aligned} \tag{11.3}$$

and substituting in (11.2), gives

$$(\hat{\mathcal{H}}_0+\lambda\hat{\mathcal{H}}')(\psi_0+\lambda\psi_1+\lambda^2\psi_2+\cdots) = (W_0+\lambda W_1+\lambda^2 W_2+\cdots)\times(\psi_0+\lambda\psi_1+\lambda^2\psi_2+\cdots)$$

Equating the coefficients for λ^0, λ^1, and λ^2 on both sides of the last equation gives

$$\begin{aligned}\hat{\mathcal{H}}_0\psi_0 &= W_0\psi_0\\ \hat{\mathcal{H}}_0\psi_1+\hat{\mathcal{H}}'\psi_0 &= W_0\psi_1+W_1\psi_0\\ \hat{\mathcal{H}}_0\psi_2+\hat{\mathcal{H}}'\psi_1 &= W_0\psi_2+W_1\psi_1+W_2\psi_0\end{aligned} \tag{11.4a}$$

respectively. Comparing the first of Eqs. (11.4a) with (11.1) identifies the zero-order solutions as

$$\begin{aligned}\psi_0 &= u_m\\ W_0 &= E_m\end{aligned} \tag{11.4b}$$

where u_m and E_m are the eigenfunctions and eigenvalues at the absence of perturbation. Next we expand ψ_1 in terms of u_n as

$$\psi_1 = \sum a_n^{(1)} u_n \tag{11.5}$$

and substitute it in the second of Eqs. (11.4a). The result is

$$\sum_n a_n^{(1)} E_n u_n + \hat{\mathcal{H}}' u_m = E_m \sum_n a_n^{(1)} u_n + W_1 u_m$$

premultiplying by u_k^*, and integrating and recalling that $\langle u_n|u_k\rangle=\delta_{kn}$, gives

$$E_k a_k^{(1)} + \mathcal{H}'_{km} = E_m a_k^{(1)} + W_1\delta_{km} \tag{11.6}$$

which for $k\neq m$ yields

$$a_k^{(1)} = \frac{\mathcal{H}'_{km}}{E_m-E_k} \quad (k\neq m) \tag{11.7}$$

Putting $k=m$ in (11.6) gives

$$W_1 = \mathcal{H}'_{mm} \tag{11.8}$$

According to (11.3) and (11.4b), W_1 is the first-order correction to energy E_m. We still need to evaluate $a_m^{(1)}$. This is done by requiring that the first-order corrected wavefunction $\psi = u_m+\psi_1$ be normalized to unity:

$$\int\Big(u_m+\lambda\sum_n a_n^{(1)}u_n\Big)^*\Big(u_m+\lambda\sum_s a_s^{(1)}u_s\Big)\,dv = 1+\lambda a_m^{(1)}+\lambda a_m^{*(1)}+\lambda^2\sum_n a_n^{(1)}a_n^{*(1)} = 1 \tag{11.9}$$

which, neglecting the second-order term, gives $a_m^{(1)}=0$ as a possible solution. The eigenfunction and eigenvalue to first-order perturbation are thus given as

$$\psi = u_m + \sum_{k\neq m}\frac{\mathcal{H}'_{km}}{E_m-E_k}u_k \tag{11.10a}$$

$$W = E_m + \mathcal{H}'_{mm} \tag{11.10b}$$

Second-Order Perturbation

Our aim here is to obtain expressions for W_2 and ψ_2. The second order correction to the eigenfunction, ψ_2, may be expanded as

$$\psi_2 = \sum_n a_n^{(2)} u_n$$

This expansion is next used in the third of Eqs. (11.4a)

$$\sum_n a_n^{(2)} E_n u_n + \hat{\mathcal{H}}'\sum_n a_n^{(1)} u_n = \sum_n a_n^{(2)} E_m u_n + W_1\psi_1 + W_2 u_m$$

Substituting for ψ_1 its expansion according to (11.5), then multiplying by u_k^* and integrating, results in

$$a_k^{(2)}E_k + \sum_n a_n^{(1)}\mathcal{H}'_{kn} = a_k^{(2)}E_m + W_1 a_k^{(1)} + W_2\delta_{mk} \tag{11.11}$$

Setting $k=m$ gives

$$\begin{aligned}W_2 &= \sum_n a_n^{(1)}\mathcal{H}'_{mn} - W_1 a_m^{(1)}\\ &= \sum_{n\neq m} a_n^{(1)}\mathcal{H}'_{mn} + a_m^{(1)}\mathcal{H}'_{mm} - W_1 a_m^{(1)}\end{aligned}$$

Using (11.7) for $a_n^{(1)}$ and (11.8) for W_1, the last two terms cancel each other with the result

$$W_2 = \sum_{n\neq m}\frac{|\mathcal{H}'_{mn}|^2}{E_m-E_n} \tag{11.12}$$

Going back to (11.11) for the case $k\neq m$, using (11.7), (11.8), and the result $a_m^{(1)}=0$, gives

$$\underset{k\neq m}{a_k^{(2)}} = \sum_{n\neq m}\frac{\mathcal{H}'_{kn}\mathcal{H}'_{nm}}{(E_m-E_n)(E_m-E_k)} - \frac{\mathcal{H}'_{mm}\mathcal{H}'_{km}}{(E_m-E_k)^2}$$

To find $a_m^{(2)}$ we go back to the normalization integral (11.9). Adding the second-order correction to ψ gives

$$\int \left(u_m + \lambda \sum_n a_n^{(1)} u_n + \lambda^2 \sum_n a_n^{(2)} u_n \right)^* \left(u_m + \lambda \sum_s a_s^{(1)} u_s + \lambda^2 \sum_s a_s^{(2)} u_s \right) dv = 1$$

Using the result $a_m^{(1)} = 0$, the last equation yields

$$a_m^{(2)} = -\tfrac{1}{2} \sum_n |a_n^{(1)}|^2$$

$$= -\tfrac{1}{2} \sum_{n \neq m} \frac{|\mathcal{H}'_{mn}|^2}{(E_m - E_n)^2} \tag{11.13}$$

Finally, we let $\lambda \to 1$ and write the eigenfunction and the energy, to second order, as

$$\psi = u_m + \sum_{k \neq m} \frac{\mathcal{H}'_{km}}{E_m - E_k} u_k$$

$$+ \sum_{k \neq m} \left[\left(\sum_{n \neq m} \frac{\mathcal{H}'_{kn} \mathcal{H}'_{nm}}{(E_m - E_n)(E_m - E_k)} - \frac{\mathcal{H}'_{mm} \mathcal{H}'_{km}}{(E_m - E_k)^2} \right) u_k - \frac{|\mathcal{H}'_{km}|^2}{2(E_m - E_k)^2} u_m \right] \tag{11.14}$$

$$W = E_m + \mathcal{H}'_{mm} + \sum_{n \neq m} \frac{|\mathcal{H}'_{mn}|^2}{E_m - E_n} \tag{11.15}$$

Notice that the second-order correction tends, according to (11.12), to increase the energy separation $|E_m - E_n|$. This fact is often expressed in the physics jargon as "energy levels repel each other."

11.2 TIME-DEPENDENT PERTURBATION THEORY

Time-dependent perturbation theory is the main analytical tool for treating the transitions of quantum mechanical systems from one energy state to another.

We have shown [see (10.6)] that if the Hamiltonian of a system does not depend on time, the general solution of the Schrödinger equation

$$\mathcal{H}_0 \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \tag{11.16}$$

is in the form of

$$\psi(\mathbf{r}, t) = \sum_n a_n u_n(\mathbf{r}) e^{-iE_n t/\hbar} \tag{11.17}$$

where the coefficients a_n are constant and $\mathcal{H}_0 u_n = E_n u_n$. If the system is found to possess at some time, say $t = 0$, an energy E_m, then we have

$$\left. \begin{aligned} a_m &= 1 \\ a_n &= 0 \end{aligned} \right\} \quad (n \neq m) \tag{11.18}$$

for all subsequent times.

Let us assume next that the system is perturbed in such a way that the Hamiltonian is modified from $\mathcal{H}_0$ to

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}'(t) \tag{11.19}$$

The wavefunction $\psi(t)$ is now a solution of the Schrödinger equation

$$[\mathcal{H}_0 + \mathcal{H}'(t)]\psi = i\hbar \frac{\partial \psi}{\partial t} \tag{11.20}$$

At some particular time t, we may, using the completeness property, expand $\psi(\mathbf{r}, t)$ in terms of u_n:

$$\psi(\mathbf{r}, t) = \sum_n a_n(t) u_n(\mathbf{r}) e^{-iE_n t/\hbar} \tag{11.21}$$

Since the Hamiltonian is time dependent, the coefficients a_n, unlike (11.17), are now functions of time. The significance of this time dependence is of fundamental importance. Let us assume that a measurement of the unperturbed energy at some time, say $t = 0$, yields E_m. We thus have

$$\left. \begin{aligned} a_m(0) &= 1 \\ a_n(0) &= 0 \end{aligned} \right\} \quad (n \neq m) \tag{11.22}$$

Since the coefficients a_n evolve with time, a subsequent measurement of the energy, say at time t, may yield the value E_k. The probability of such an event is $|a_k(t)|^2$, which is thus the probability of finding the system in the state k at time t given that at $t = 0$ it occupied the state m. The solution of the time-dependent Schrödinger equation thus provides a description of the manner in which the probability of finding the system in the various eigenstates u_n of $\mathcal{H}_0$ evolves with time under the influence of the perturbation $\mathcal{H}'(t)$.

To describe the evolution of the system we thus need to solve for the coefficients $a_n(t)$. We substitute (11.21) in (11.20), obtaining

$$\sum_n u_n \left[a_n \left(-\frac{iE_n}{\hbar} \right) e^{-iE_n t/\hbar} + \dot{a}_n e^{-iE_n t/\hbar} \right] = -\frac{i}{\hbar} \sum_n a_n (\mathcal{H}_0 + \mathcal{H}') u_n e^{-iE_n t/\hbar}$$

which after multiplying by u_k^* and integrating becomes

$$\dot{a}_k = -\frac{i}{\hbar} \sum_n a_n \mathcal{H}'_{kn}(t) e^{i\omega_{kn} t} \quad = \frac{1}{i\hbar} \sum a_n \mathcal{H}'_{kn}(t) e^{i\omega_{kn} t} \tag{11.23}$$

where ω_{kn} is defined by

$$\omega_{kn} \equiv \frac{E_k - E_n}{\hbar}$$

Up to this point the analysis is exact, and solving Eqs. (11.23) is fully equivalent to a solution of the Schrödinger equation. In a manner similar to that used in Section 11.1, we introduce the "turning on" parameter λ by taking the perturbation as $\lambda\hat{\mathcal{H}}'$ so that the Hamiltonian becomes

$$\hat{\mathcal{H}}_0 + \lambda\hat{\mathcal{H}}'(t)$$

The power-series expansion for a_n is written as

$$a_n = a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \cdots$$

which, when substituted in (11.23), becomes

$$\dot{a}_k^{(0)} + \lambda\dot{a}_k^{(1)} + \lambda^2\dot{a}_k^{(2)} + \cdots = -\frac{i}{\hbar}\sum_n \left(a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \cdots\right)\lambda\mathcal{H}'_{kn}e^{i\omega_{kn}t}$$

Equating the same powers of λ results in the set of relations

$$\begin{aligned} \dot{a}_k^{(0)} &= 0 \\ \dot{a}_k^{(1)} &= -\frac{i}{\hbar}\sum_n a_n^{(0)}\mathcal{H}'_{kn}(t)e^{i\omega_{kn}t} \\ \dot{a}_k^{(2)} &= -\frac{i}{\hbar}\sum_n a_n^{(1)}\mathcal{H}'_{kn}(t)e^{i\omega_{kn}t} \qquad (11.24) \\ &\ \vdots \\ \dot{a}_k^{(s)} &= -\frac{i}{\hbar}\sum_n a_n^{(s-1)}\mathcal{H}'_{kn}(t)e^{i\omega_{kn}t} \end{aligned}$$

The solution of the zero-order equation is $a_k^{(0)} = \text{constant}$. The $a_k^{(0)}$ are thus the initial values for the problem. These are chosen as

$$a_m^{(0)} = 1$$

$$a_n^{(0)} = 0 \quad (n \neq m)$$

so that at $t = 0$ the system is known with certainty to occupy a state with energy E_m. The second of Eqs. (11.24) now reduces to

$$\dot{a}_k^{(1)} = -\frac{i}{\hbar}\mathcal{H}'_{km}e^{i\omega_{km}t} \quad \approx \frac{1}{i\hbar} H'_{km} e^{i\omega_{km}t} \qquad (11.25)$$

$|a_k^{(1)}(t)|^2$ is the probability to first order of finding the system at time t in the state k given that at $t = 0$ it is in the state m.

Harmonic Perturbation

As a special case we consider a perturbation that varies sinusoidally with time:

$$\hat{\mathcal{H}}'(t) = \hat{H}'e^{-i\omega t} + (\hat{H}')^\dagger e^{i\omega t} \qquad (11.26a)$$

The breakdown of $\hat{\mathcal{H}}'(t)$ into the two parts is done so as to ensure its Hermiticity. The result of substituting $\hat{\mathcal{H}}'(t)$ into (11.25) and performing the integration is

$$\begin{aligned} a_k^{(1)}(t) &= \int_0^t \left(-\frac{i}{\hbar}\right) H'_{km}(t')e^{i\omega_{km}t'}\,dt' \\ &= -\hbar^{-1}\left(H'_{km}\frac{e^{i(\omega_{km}-\omega)t}-1}{\omega_{km}-\omega} + H'^{*}_{mk}\frac{e^{i(\omega_{km}+\omega)t}-1}{\omega_{km}+\omega}\right) \qquad (11.26b) \end{aligned}$$

where the lower limit of the integration is zero, since $a_{k\neq m}^{(1)}(0) = 0$. We limit ourselves next to a case in which ω is nearly equal to $|\omega_{km}|$—that is, $\hbar\omega \simeq |E_k - E_m|$. The transition probability from the state m to k is then

$$P_k \approx |a_k^{(1)}|^2 \cong \frac{4|H'_{km}|^2}{\hbar^2}\,\frac{\sin^2\left[\frac{1}{2}(\omega_{km}\pm\omega)t\right]}{(\omega_{km}\pm\omega)^2} \qquad (11.27)$$

where the $(-)$ sign is to be used when $\omega_{km} \simeq \omega$ while the $(+)$ sign applies when $\omega_{mk} \simeq \omega$. The cross terms with a denominator involving the product $(\omega_{km}+\omega)(\omega_{km}-\omega)$ have been left out since, for the conditions of interest, $|\omega_{km}| \simeq \omega$, their contribution can be neglected. The first expression on the right side of (11.26*b*) dominates when $E_k > E_m$ and $E_k - E_m \sim \hbar\omega$, while the second expression dominates when $E_k < E_m$ and $E_m - E_k \sim \hbar\omega$. The harmonic perturbation can thus cause both upward and downward transitions from state m to states k, separated in energy by $\sim\hbar\omega$.

To be specific, let us calculate the transition probability from m to a *group* of states clustered about state k, where $E_k > E_m$. Let the density of these final states per unit of ω_{km} be $\rho(\omega_{km})$. Since $\omega_{km} \simeq \omega$, we use the $(-)$ sign in (11.27) and obtain

$$|a_k^{(1)}|^2 = \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} |H'_{km}|^2 \frac{\sin^2\left[\frac{1}{2}(\omega_{km}-\omega)t\right]}{\left[\frac{1}{2}(\omega_{km}-\omega)\right]^2}\rho(\omega_{km})\,d\omega_{km} \qquad (11.28)$$

If $|H'_{km}|^2$ is not a strong function of the final state k, we can take it outside the integral sign. The remaining integrand is then a product of two functions:

$$(1)\quad g(\omega_{km}, t) = \frac{\sin^2\left[\frac{1}{2}(\omega_{km}-\omega)t\right]}{\left[\frac{1}{2}(\omega_{km}-\omega)\right]^2} \quad \text{and} \quad (2)\quad \rho(\omega_{km})$$

These functions are plotted in Fig. 11.1, the independent variable being ω_{km}. The interval in ω_{km}, where the function

$$g(\omega_{km}, t) = \frac{\sin^2\left[\frac{1}{2}(\omega_{km}-\omega)t\right]}{\left[\frac{1}{2}(\omega_{km}-\omega)\right]^2} \qquad (11.29)$$

is appreciable, is $\sim 2\pi/t$ and can be made arbitrarily small by increasing the time of observation t. The area under this function is

$$\int_{-\infty}^{\infty} \frac{\sin^2\left[\frac{1}{2}(\omega_{km}-\omega)t\right]}{\left[\frac{1}{2}(\omega_{km}-\omega)\right]^2}\,d\omega_{km} = 2\pi t \qquad (11.30)$$

Φ (Intuition t

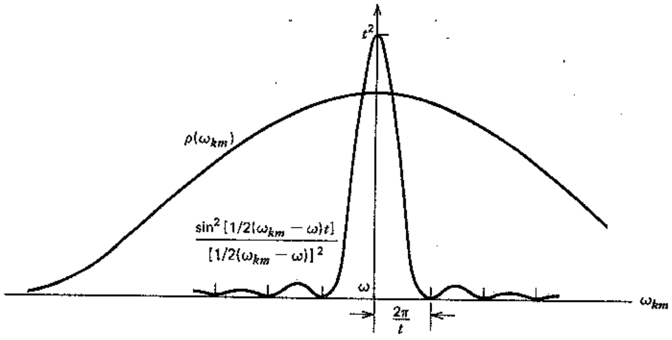

Figure 11.1 The two components: the density of final states function $\rho(\omega_{km})$ and the transition probability function $g(\omega_{km}, t) \equiv \sin^2[\frac{1}{2}(\omega_{km}-\omega)t]/[\frac{1}{2}(\omega_{km}-\omega)]^2$ involved in the integral of Eq. (11.28).

Let us consider the case when t is big enough so that $2\pi/t$, the width of $g(\omega_{km}, t)$, is very much smaller than $\Delta\omega$, the width of $\rho(\omega_{km})$. The integral (11.28) becomes

$$|a_k^{(1)}(t)|^2 = \frac{1}{\hbar^2}|H'_{km}|^2\rho(\omega_{km}=\omega)\int_{-\infty}^{\infty}\frac{\sin^2\left[\frac{1}{2}(\omega_{km}-\omega)t\right]}{\left[\frac{1}{2}(\omega_{km}-\omega)\right]^2}d\omega_{km}$$
$$= \frac{2\pi}{\hbar^2}|H'_{km}|^2\rho(\omega_{km}=\omega)t \qquad (11.31)$$

and the transition rate per unit time is

$$W_{m\to k} = \frac{d}{dt}|a_k^{(1)}(t)|^2$$
$$= \frac{2\pi}{\hbar}|H'_{km}|^2\rho(E=E_m\pm\hbar\omega) \qquad (11.32)$$

where $\rho(E)$ is the density of final states expressed as a function of energy $[\rho(\omega)=\hbar\rho(E)]$. The minus sign is to be used when $E_k < E_m$ and is due to the second term on the right side of (11.26).

The result (11.32) is consistent with writing the transition rate from $|m\rangle$ to $|k\rangle$, where $|k\rangle$ is a single state *within* a *continuum*

$$V_{fk} = W_{m\to k} = \frac{d}{dt}|a_k^{(1)}(t)|^2$$
$$= \frac{2\pi}{\hbar}|H'_{km}|^2\delta(E_k-E_m-\hbar\omega) \qquad (11.33)$$

If $E_k - E_m \simeq -\hbar\omega$ we replace the argument of the δ function by $(E_k - E_m + \hbar\omega)$. In writing (11.33), we used the fact that for sufficiently long t, $\sin^2(xt/2)/(x/2)^2 \to 2\pi t\delta(x)$.

how long?

Equation (11.32) is known as Fermi's Golden Rule. We must remember when applying (11.32) that it applies to transitions from a *single* state m to a *continuum* of states k. If the final state k is single and not part of a continuum, we need to go back to (11.27).

Step Function Perturbation

A second case of interest is one in which the perturbation has the form of a step function applied at $t=0$, that is,

$$\mathcal{H}'(t) = 0 \quad (t \le 0)$$
$$\mathcal{H}'(t) = H' \quad (t \ge 0) \qquad (11.34)$$

This situation may be regarded as a limiting case of the harmonic perturbation discussed above with $\omega \to 0$.

Using the second of Eqs. (11.24) with $a_n^{(1)}(0) = \delta_{nm}$ (i.e., the system is initially in the state m) and repeating the steps leading to (11.32), yields

$$W_{m\to k} = \frac{2\pi}{\hbar}|H'_{km}|^2\delta(E_m - E_k)$$
$$= \frac{1}{\hbar^2}|H'_{km}|^2\delta(\nu_m - \nu_k) \qquad (11.35)$$

The form of $W_{m\to k}$ is similar to that of (11.33). The important difference is in the argument of the delta function, which involves an initial state (m) and a final state of the same energy. It must be emphasized that (11.35) applies, as does (11.33), to a case where the single state k is part of a continuum. The total transition rate out of $|m\rangle$ is obtained by summing $W_{m\to k}$ over all final states.

2D satisfy this
∴ ρ = constant!

Limits of Validity of the Golden Rule

Two conditions were used in deriving Eqs. (11.31) and (11.33). The first was that $2\pi/t$ be small compared with the width $2\pi\Delta\nu$ of $\rho(\omega_{km})$. The second condition results from our use of first-order perturbation theory and requires that $|a_k^{(1)}(t)|^2 \ll 1$; otherwise higher-order terms must be considered. This second condition can be stated using (11.27) as

$$\frac{H'_{km}}{\hbar} \ll \frac{1}{t} \qquad (11.36)$$

Its physical significance is that the results of first-order perturbation theory are only valid for times short enough so that the probability for transitions out of the initial state m is very small compared with unity. Combining these two conditions leads to

for all t?

$$\frac{|H'_{km}|}{\hbar} \ll \frac{1}{t} \ll \Delta\nu$$

as the validity limits for Eqs. (11.33) and (11.35). Cases in which the last condition is not fulfilled have to be treated separately. This is done in Section 13.1. i.e. exact solution

11.3 THE DENSITY MATRIX FORMALISM

The density matrix formalism to be introduced in this section is one of the most powerful and widely used methods for describing the time evolution of large systems ~~of~~ indistinguishable atomic particles, because it is constructed in such a way that it is especially convenient for ensemble averaging. We will put it to work in Chapter 13 in describing absorption and dispersion of electromagnetic radiation in atomic media.

Consider the wavefunction $\psi(\mathbf{r},t)$ of a single isolated atomic system. This function satisfies the time-dependent Schrödinger equation

$$\hat{\mathcal{H}}(t)\psi(\mathbf{r},t)=i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} \tag{11.37}$$

$\psi(\mathbf{r},t)$ can be expanded in some *arbitrary* but complete orthonormal set $u_n(\mathbf{r})$ according to

but have same degree of freedom

$$\begin{aligned}\psi(\mathbf{r},t)&=\sum_n C_n(t)u_n(\mathbf{r})\\&=\sum_n C_n|n\rangle\end{aligned} \tag{11.38}$$

Using

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

we obtain from (11.38)

$$C_n=\int u_n^*\psi(\mathbf{r},t)\,d^3\mathbf{r}\equiv\langle n|\psi\rangle \tag{11.39}$$

The expectation value of some observable A is given by (10.13) as

$$\langle A\rangle=\int\psi^*\hat{A}\psi\,d^3\mathbf{r}=\langle\psi|\hat{A}|\psi\rangle \tag{11.40}$$

which, using (2.32*b*), can be written as

$$\begin{aligned}\langle A\rangle&=\sum_n\sum_m\langle\psi|m\rangle\langle m|\hat{A}|n\rangle\langle n|\psi\rangle\\&=\sum_n\sum_m C_m^*C_nA_{mn}\end{aligned} \tag{11.41}$$

Equation (11.41) applies to a single isolated atomic entity (to be called, in what follows, the atom). In most real systems the observations involve a very large number of identical atoms. In such cases the measured quantity is not $\langle A\rangle$ but involves an averaging of $\langle A\rangle$ over the ensemble of similar particles. We denote this average by a bar on top of the affected variables:

$$\overline{\langle A\rangle}=\sum_n\sum_m\overline{C_m^*C_n}\,A_{mn} \tag{11.42}$$

We find it convenient to define

$$\rho_{nm}\equiv\overline{C_nC_m^*} \tag{11.43}$$

$$=\overline{\langle n|\psi\rangle\langle\psi|m\rangle} \tag{11.44}$$

– elements of representation of $\{u_n(\mathbf{r})\}$

so that

$$\begin{aligned}\overline{\langle A\rangle}&=\sum_n\sum_m\rho_{nm}A_{mn}=\sum_n(\rho A)_{mn}\\&=\operatorname{tr}(\rho A)\end{aligned} \tag{11.45}$$

It follows directly from (11.44) and the definition of matrix products that ρ_{nm} may be viewed formally as the nm matrix element of the operator

$$\hat{\rho}=\overline{|\psi\rangle\langle\psi|}\quad=\sum_\psi P_\psi|\psi\rangle\langle\psi| \tag{11.46}$$

or $\int f(q,r)|\psi\rangle\langle\psi|\,d^3r$

which is referred to as the *density* operator.

attained by general statistic theory

We note that according to (11.43) $\rho_{mn}=\rho_{nm}^*$ so that the operator $\hat{\rho}$ is Hermitian.

It is often advantageous to use a differential equation for obtaining $\hat{\rho}(t)$. We start with (11.46):

$$\frac{d\hat{\rho}}{dt}=\overline{|\dot{\psi}\rangle\langle\psi|}+\overline{|\psi\rangle\langle\dot{\psi}|} \tag{11.47a}$$

We can rewrite (11.37) as

$$|\dot{\psi}\rangle=\frac{1}{i\hbar}\hat{\mathcal{H}}|\psi\rangle \tag{11.47b}$$

Using the Hermiticity of $\hat{\mathcal{H}}$, we write[1]

$$\langle\dot{\psi}|=-\frac{1}{i\hbar}\langle\psi|\hat{\mathcal{H}} \tag{11.47c}$$

which substituted in (11.47) gives

$$\begin{aligned}\frac{d\hat{\rho}}{dt}&=\frac{1}{i\hbar}\hat{\mathcal{H}}\overline{|\psi\rangle\langle\psi|}-\frac{1}{i\hbar}\overline{|\psi\rangle\langle\psi|}\hat{\mathcal{H}}\\&=\frac{1}{i\hbar}\left[\hat{\mathcal{H}},\overline{|\psi\rangle\langle\psi|}\right]\end{aligned}$$

Using (11.46),

$$\frac{d\hat{\rho}}{dt}=\frac{1}{i\hbar}\left[\hat{\mathcal{H}},\hat{\rho}\right] \tag{11.48}$$

---

[1] Equation (11.47*c*) is a formal and concise way of stating that since $\hat{\mathcal{H}}$ is Hermitian,

$$\langle\dot{\psi}|f\rangle=\left\langle\frac{1}{i\hbar}\hat{\mathcal{H}}\psi\,|\,f\right\rangle=-\frac{1}{i\hbar}\langle\psi|\hat{\mathcal{H}}|f\rangle$$

where f and ψ are arbitrary state functions.

In practice one solves the series of equations

$$\frac{d\rho_{nm}}{dt} = \frac{1}{i\hbar}[\mathcal{H}, \rho]_{nm} + \text{relaxation terms} \qquad (11.49)$$

The relaxation terms are added phenomenologically to account for the ensemble aspects of the problem. A representative example of such an application will be found in Chapter 13, where (11.49) will be used to describe the absorption and dispersion of electromagnetic waves in atomic media.

PROBLEMS

1. According to Eq. (11.27) or Fig. 11.1, a transition can take place due to an electrical field oscillating at a radian frequency ω between two states k and m where $E_k - E_m = \omega + \delta$. The energy discrepancy δ can be as large as $\sim 2\pi/t$ where t is the observation time.

   Is this result a violation of the law of conservation of energy? Is it consistent with the uncertainty principle relating the measurement of time and energy?

2. Consider a circularly polarized electric field

$$E_x = E_0 \cos \omega t$$
$$E_y = E_0 \sin \omega t$$

   interacting with hydrogenic atoms initially in the state $|n, l, m=0\rangle$ and causing an induced transition to the state $|n', l', m'\rangle$.

   What are the necessary relations between n', l', m' and n, l, m for a transition to take place when:
   (a) $E_{n'} > E_n$
   (b) $E_{n'} < E_n$

3. Same as Problem 2 except that the sense of circular polarization of the applied is reversed; that is,

$$E_x = E_0 \cos \omega t$$
$$E_y = -E_0 \sin \omega t$$

4. Same as Problem 2 except that now the field is linearly polarized, in the z direction; that is,

$$\mathbf{E} = \hat{z} E_0 \cos \omega t$$

5. (a) Show that one can resolve a linearly polarized electric field, say

$$\mathbf{E} = \hat{x} E_0 \cos \omega t$$

   into two oppositely circularly polarized fields in the $x - y$ plane.
   (b) What are the selection rules, that is, the necessary relations between n, l, m and n', l', m' for transitions to take place between states $|n, l, m$ and $|n', l', m'\rangle$ due to this field?

CHAPTER TWELVE

The Interaction of Electromagnetic Radiation with Atomic Systems

In this chapter we consider the interaction of atomic systems with electromagnetic fields. We will apply these concepts to describe the processes of spontaneous and induced transitions and the phenomena of absorption and amplification of radiation. The material of this chapter will serve as background for the treatment of laser oscillators.

12.1 SOME BASIC ELECTROMAGNETIC BACKGROUND

The Maxwell equations describing the propagation of electromagnetic fields are

MKS

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \qquad \nabla \cdot \mathbf{D} = \rho$$
$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}, \qquad \nabla \cdot \mathbf{B} = 0 \qquad (12.1)$$

where $\mathbf{J}$ is the current density; the other symbols have their conventional definitions. In a homogeneous isotropic medium $\mathbf{B}$ and $\mathbf{D}$ are related to $\mathbf{H}$ and $\mathbf{E}$ by

$$\mathbf{B} = \mu \mathbf{H}$$
$$\mathbf{D} = \varepsilon \mathbf{E} \qquad (12.2)$$

where μ and ε are, respectively, the magnetic permeability and the dielectric constant of the medium.