13.4: Fermi's Golden Rule

In the first section, we saw how to formulate the Hamiltonian of a material system coupled to an external electromagnetic field. Moreover, we obtained solutions for the electromagnetic field in the absence of sources or physical boundaries, namely, solutions of the free-field wave equations. In this chapter, we will focus primarily on weak fields. We will also focus on a class of experiments in which the wavelength of electromagnetic radiation is taken to be long compared to the size of the sample under investigation. In this case, the spatial dependence of the electromagnetic field can also be neglected, since

$$\cos(\mathbf{k}\cdot\mathbf{r}-\omega t+\varphi_0)=\mathrm{Re}\{\exp(i\mathbf{k}\cdot\mathbf{r}-i\omega t+\varphi_0)\}$$

and

$$\exp(i\mathbf{k}\cdot\mathbf{r})\approx 1$$

in the long-wavelength limit. In this case, it is sufficient to consider $H_1(t)$ to be of the general form

$$\mathrm{H}_1(t)=-\mathcal{V}F(\omega)e^{-i\omega t} \tag{13.4.1}$$

where $\mathcal{V}$ is a Hermitian operator.

> Although we could use $\sin$ and $\cos$ to express the perturbation, the form in Equation 13.4.1 is a particularly convenient one, and since we will be seeking probabilities of transitions, the results we obtain will be real in the end.

Again, the question we seek to answer is given this form for the perturbation, what is the probability that the material system will be excited from an initial eigenstate $|E_i\rangle$ with energy E_i to a final state $|E_f\rangle$ with energy E_f? However, since the perturbation is periodic in time, what we really seek to know is if the perturbation is applied over a long time interval, what is the probability per unit time or rate at which transitions will occur. Thus, in order to make the calculation somewhat easier, let us consider a time interval T and choose $t_0=-T/2$ and $t=T/2$. At first order, the transition rate $R_{fi}^{(1)}(T)$ is just the total probability $P_{fi}^{(1)}(T)$ divided by the interval length T:

$$R_{fi}^{(1)}(T)=\frac{P_{fi}^{(1)}(T)}{T} \tag{13.4.2}$$

$$=\frac{1}{T\hbar^2}|F(\omega)|^2\left|\int_{-T/2}^{T/2}e^{i(\omega_{fi}-\omega)t}dt\right|^2|\langle E_f|\mathcal{V}|E_i\rangle|^2 \tag{13.4.3}$$

For finite T, the integral can be carried out explicitly yielding

$$\int_{-T/2}^{T/2}e^{i(\omega_{fi}-\omega)t}dt=\frac{\sin(\omega_{fi}-\omega)T/2}{(\omega_{fi}-\omega)/2} \tag{13.4.4}$$

Thus, the transition rate can be expressed as

$$R_{fi}^{(1)}(T)=\frac{1}{\hbar^2}T|F(\omega)|^2|\langle E_f|\mathcal{V}|E_i\rangle|^2\frac{\sin^2(\omega_{fi}-\omega)T/2}{[(\omega_{fi}-\omega)T/2]^2} \tag{13.4.5}$$

In the limit of T very large, this expression becomes highly peaked only if $\omega_{fi}=\omega$. Otherwise, as $T\to\infty$, the expression vanishes. The condition $\omega_{fi}=\omega$ is equivalent to the condition $E_f=E_i+\hbar\omega$, which is a statement of energy conservation. Since $\hbar\omega$ is the energy quantum of the electromagnetic field, the transition can only occur if the energy of the field is exactly "tuned" for the the transition, and this "tuning" depends on the frequency of the field. In this way, the frequency of the field can be used as a probe of the allowed transitions, which then serves to probe the eigenvalue structure of H_0.

Now, let us consider the $T\to\infty$ more carefully. We shall denote the rate in this limit simply as R_{fi}. In this limit, the integral becomes

$$\lim_{T\to\infty}\int_{-T/2}^{T/2} e^{-i(\omega_{fi}-\omega)t}dt = \int_{-\infty}^{\infty} e^{i(\omega_{fi}-\omega)t}dt \tag{13.4.6}$$

$$= 2\pi\delta(\omega_{fi}-\omega) \tag{13.4.7}$$

$$= (2\pi\hbar\delta(E_f - E_i - \hbar\omega) \tag{13.4.8}$$

Therefore, the expression for the rate in this limit can be written as

$$R_{fi}(\omega) = \lim_{T\to\infty}\frac{P_{fi}^{(1)}(T)}{T} = \lim_{T\to\infty}\frac{1}{T\hbar^2}\left|\int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t}dt\right|^2 |F(\omega)|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \tag{13.4.9}$$

$$= \lim_{T\to\infty}\frac{1}{T\hbar^2}\left[\int_{-T/2}^{T/2} e^{-i(\omega_{fi}-\omega)t}dt\right]\left[\int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t}dt\right] |F(\omega)|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \tag{13.4.10}$$

where we have dropped the "(1)" superscript (it is understood that the result is derived from first-order perturbation theory), and indicate explicitly the dependence on the frequency ω. When one the first integral is replaced by the δ-function, the remaining integral becomes simply T, which cancels the T in the denominator. Thus, the expression for the rate is finally

$$R_{fi}(\omega) = \frac{2\pi}{\hbar}|F(\omega)|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \delta(E_f - E_i - \hbar\omega) \tag{13.4.11}$$

which is known as **Fermi's Golden Rule**. It states that, to first-order in perturbation theory, the transition rate depends only the square of the matrix element of the operator $\mathcal{V}$ between initial and final states and includes, via the δ-function, an energy-conservation condition. We will make use of the Fermi Golden Rule expression to analyze the application of an external monochromatic field to an ensemble of systems in order to derive expressions for the observed frequency spectra.