Lecture 26 (Dec. 11, 2017)

26.1 Harmonic Perturbations

We now study perturbations of the form

$$H_1(t) = Ve^{-i\omega t} + V^\dagger e^{i\omega t}\,. \tag{26.1}$$

Here, V is some operator acting on the Hilbert space that depends on the degrees of freedom in the system. We assume that V is "weak," so that we can hope to treat it perturbatively.

If this perturbation acts for a long time, we expect that it will induce a transition from the initially prepared state $|i\rangle$ to some final state $|f\rangle$ where the system has absorbed energy $\hbar\omega$ from the perturbation, i.e.,

$$E_f - E_i = \hbar\omega\,. \tag{26.2}$$

In the last class, we computed the transition amplitude for an arbitrary time-dependent perturbation at first order:

$$c_{fi}(t) = -\frac{i}{\hbar}\int_0^t \mathrm{d}t'\ \langle f|H_1|i\rangle e^{i\omega_{fi}t'}\,. \tag{26.3}$$

For the case of harmonic perturbations, we find

$$\begin{aligned} c_{fi}(t) &= -\frac{i}{\hbar}\int_0^t \mathrm{d}t'\ \left[\langle f|V|i\rangle e^{i(\omega_{fi}-\omega)t'} + \langle f|V^\dagger|i\rangle e^{i(\omega_{fi}+\omega)t'}\right] \\ &= \frac{1}{\hbar}\left[\langle f|V|i\rangle\left(\frac{1-e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega}\right) + \langle f|V^\dagger|i\rangle\left(\frac{1-e^{i(\omega_{fi}+\omega)t}}{\omega_{fi}+\omega}\right)\right]. \end{aligned} \tag{26.4}$$

As $t\to\infty$, $|c_{fi}|^2$ is appreciable if either $\omega_{fi}-\omega\approx 0$, i.e., $E_f\approx E_i+\hbar\omega$ (absorption), or if $\omega_{fi}+\omega\approx 0$, i.e., $E_f = E_i - \hbar\omega$ (emission).

We now specialize to the case where ω is tuned so that

$$E_f - E_i \approx \hbar\omega\,. \tag{26.5}$$

In this case, the second term in Eq. (26.4) is small compared to the first, so we can write

$$c_{fi}(t) \approx \frac{1}{\hbar}\langle f|V|i\rangle\left(\frac{1-e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega}\right). \tag{26.6}$$

The transition probability is then

$$\begin{aligned} P_{fi}(t) &= |c_{fi}(t)|^2 \\ &= \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2\frac{\left|1-e^{i(\omega_{fi}-\omega)t}\right|^2}{(\omega_{fi}-\omega)^2} \\ &= \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2\frac{\sin^2\left(\frac{(\omega_{fi}-\omega)t}{2}\right)}{\left(\frac{(\omega_{fi}-\omega)t}{2}\right)^2}t^2\,. \end{aligned} \tag{26.7}$$

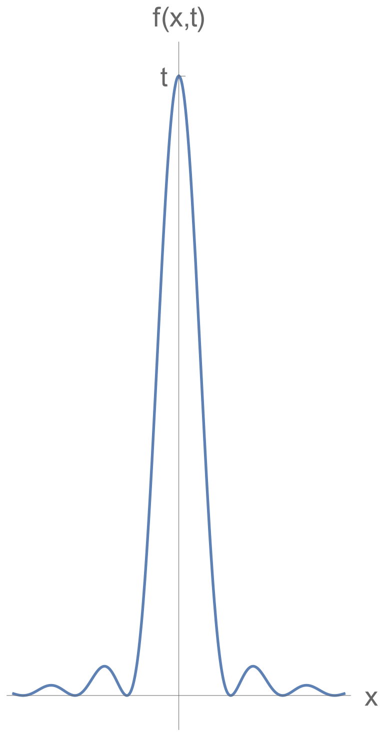
In this last line, we have simply used

$$\begin{aligned} \left|1-e^{i\theta}\right|^2 &= \left|e^{i\theta/2}\left(e^{-i\theta/2}-e^{i\theta/2}\right)\right|^2 \\ &= \left|-2i\sin\frac{\theta}{2}\right|^2 \\ &= 4\sin^2\frac{\theta}{2}\,. \end{aligned} \tag{26.8}$$

Now, consider the function

$$f(x,t) = \frac{\sin^2 tx}{tx^2}\,, \tag{26.9}$$

which is shown below:



At $x = 0$, we have $f(0,t) = t$. As $x \to \infty$, $f(x,t) \to 0$. The function oscillates with a period proportional to $1/t$. As $t \to \infty$, the function decays to zero very quickly, but $f(0,t) = t \to \infty$. Thus, this appears to be approaching something like a delta function. We can check this by noting that

$$\begin{aligned}\int_{-\infty}^{\infty} \mathrm{d}x\, \frac{\sin^2 tx}{tx^2} &= \int_{-\infty}^{\infty} \frac{\mathrm{d}(tx)}{t}\, \frac{\sin^2 tx}{tx^2} \\ &= \int_{-\infty}^{\infty} \mathrm{d}u\, \frac{\sin^2 u}{u^2} \\ &= \pi\,,\end{aligned} \tag{26.10}$$

which we see is independent of t. We conclude that

$$\lim_{t\to\infty} \frac{\sin^2 tx}{tx^2} = \pi\delta(x)\,. \tag{26.11}$$

Thus,

$$\lim_{t\to\infty} P_{fi}(t) = \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2 \pi\delta\left(\frac{\omega_{fi}-\omega}{2}\right)t = \frac{2\pi}{\hbar^2}|\langle f|V|i\rangle|^2\delta(\omega_{fi}-\omega)t\,. \tag{26.12}$$

This may seem odd, because the result we found is that as $t \to \infty$, the probability of transition diverges to infinity, because it is proportional to t. The interpretation here is that there is a constant transition rate,

$$R_{fi} = \frac{P_{fi}}{t} = \frac{2\pi}{\hbar^2}|\langle f|V|i\rangle|^2\delta(\omega_{fi}-\omega)\,. \tag{26.13}$$

In general, there will be several possible final states $|f\rangle$ to which H_1 can induce a transition. The total transition rate is then given by the sum over all final states $|f\rangle$ of this rate. We define the density of states $\rho(E)$ such that $\rho(E)\,\mathrm{d}E$ is the number of states between E and $E+\mathrm{d}E$. Then the net transition rate out of the initial state is given by

$$\begin{aligned} W_{i,\text{out}} &= \sum_f R_{fi} \\ &= \int \mathrm{d}E_f\ \rho(E_f)\frac{2\pi}{\hbar^2}|\langle f|V|i\rangle|^2\delta(\omega_f-\omega_i-\omega)\,. \end{aligned} \tag{26.14}$$

Changing variables in the delta function, we reach

$$W_{i,\text{out}} = \int \mathrm{d}E_f\ \rho(E_f)\frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2\delta(E_f-E_i-\hbar\omega)\,. \tag{26.15}$$

This famous result is known as *Fermi's Golden Rule.*

26.1.1 The Photoelectric Effect

Consider an electron in a hydrogen atom interacting with an external EM field. This system has Hamiltonian

$$H = \frac{\left(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\right)^2}{2m} - \frac{e^2}{r}\,, \tag{26.16}$$

where $\boldsymbol{A}$ is the external vector potential. Take the vector potential to be of the form

$$\boldsymbol{A} = \boldsymbol{A}_0\cos(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})\,, \tag{26.17}$$

and assume that $\boldsymbol{A}_0$ is weak. We can then write

$$H = \underbrace{\frac{\boldsymbol{p}^2}{2m} - \frac{e^2}{r}}_{H_0} - \frac{e}{2mc}(\boldsymbol{p}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\boldsymbol{p}) + \frac{e^2}{2mc^2}\boldsymbol{A}^2\,. \tag{26.18}$$

where H_0 is the hydrogen atom Hamiltonian. The final term, proportional to $\boldsymbol{A}^2$, does not contribute to the problem we are considering at first order in perturbation theory, so we will simply drop it here.

It is convenient to work in Coulomb gauge, $\nabla\cdot\boldsymbol{A}=0$. In this gauge,

$$(\boldsymbol{p}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\boldsymbol{p})\psi = (-i\hbar\nabla\cdot\boldsymbol{A}+2\boldsymbol{A}\cdot\boldsymbol{p}) = 2\boldsymbol{A}\cdot\boldsymbol{p}\psi\,. \tag{26.19}$$

Thus, we can use

$$H = H_0 + H_1 \tag{26.20}$$

with

$$\begin{aligned} H_1 &= -\frac{e}{mc}\cos(\omega t-\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{A}_0\cdot\boldsymbol{p} \\ &= -\frac{e}{2mc}\left(e^{i(\omega t-\boldsymbol{k}\cdot\boldsymbol{r})}+e^{-i(\omega t-\boldsymbol{k}\cdot\boldsymbol{r})}\right)\boldsymbol{A}_0\cdot\boldsymbol{p}\,. \end{aligned} \tag{26.21}$$

The first term gives the transition rate proportional to $\delta(E_f-E_i+\hbar\omega)$, while the second term gives the transition rate proportional to $\delta(E_f-E_i-\hbar\omega)$.

If we take the atom to initially be in its ground state, then only the second term can contribute, so Fermi's Golden Rule gives

$$R_{0\to f} = \frac{2\pi}{\hbar}\sum_{\boldsymbol{k}_f}\left|\langle \boldsymbol{k}_f|\frac{e}{2mc}\boldsymbol{A}_0\cdot\boldsymbol{p}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}|0\rangle\right|^2\delta(E_f - E_0 - \hbar\omega)\,. \tag{26.22}$$

Here, $|0\rangle$ denotes the ground state of the hydrogen atom, with wavefunction

$$\psi_0(\boldsymbol{x}) = \langle \boldsymbol{x}|0\rangle = \frac{1}{\left(\pi a_0^3\right)^{1/2}}e^{-r/a_0}\,, \tag{26.23}$$

where a_0 is the Bohr radius. The ket $|\boldsymbol{k}_f\rangle$ is a plane wave state with wave vector $\boldsymbol{k}_f$, which describes the electron that is kicked out of the atom by the perturbation.

We can compute the matrix element in the transition rate by putting the system in a box of side length L, which gives

$$\begin{aligned}\frac{e}{2mc}\boldsymbol{A}_0\cdot\int \mathrm{d}^3x\,\frac{e^{-i\boldsymbol{k}_f\cdot\boldsymbol{r}}}{L^{3/2}}(-i\hbar\nabla)\frac{e^{-r/a_0}}{\left(\pi a_0^3\right)^{1/2}} &= \frac{e}{2mc}\boldsymbol{A}_0\cdot\int\frac{\mathrm{d}^3x}{L^{3/2}}\left(i\hbar\nabla\left(e^{-i\boldsymbol{k}_f\cdot\boldsymbol{r}}\right)\right)\frac{e^{-r/a_0}}{\left(\pi a_0^3\right)^{1/2}}\\ &= \frac{e\hbar}{2mc}\frac{\boldsymbol{A}_0\cdot\boldsymbol{k}_f}{L^{3/2}\left(\pi a_0^3\right)^{1/2}}\int\mathrm{d}^3x\,e^{-i\boldsymbol{k}_f\cdot\boldsymbol{r}}e^{-r/a_0}\\ &= \frac{e\hbar}{2mc}\frac{\boldsymbol{A}_0\cdot\boldsymbol{k}_f}{L^{3/2}\left(\pi a_0^3\right)^{1/2}}\frac{8\pi}{a_0\left(k_f^2+1/a_0^2\right)^2}\,.\end{aligned} \tag{26.24}$$

Note that we have ignored the factor of $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ in this matrix element; this was not an accident. For typical wavelengths involved in photo-ionization, $|\boldsymbol{k}| \ll |\boldsymbol{k}_f|$.

For the sum over final states, we make the replacement

$$\sum_{\boldsymbol{k}_f} \to L^3\int\frac{\mathrm{d}^3k_f}{(2\pi)^3}\,. \tag{26.25}$$

The logic is that, in a box of size L, the set of allowed momenta has spacing $2\pi/L$, and so each differential element in the integral is of the form

$$\frac{\mathrm{d}k_x}{(2\pi/L)}\,, \tag{26.26}$$

which gives the form of the replacement above.

Putting everything together, we then have

$$\begin{aligned}R_{0\to f} &= \frac{2\pi}{\hbar}\frac{L^3}{L^3}\int\frac{\mathrm{d}^3k_f}{(2\pi)^3}\left(\frac{e\hbar}{2mc}\right)^2\frac{(\boldsymbol{A}_0\cdot\boldsymbol{k}_f)^2}{\pi a_0^3}\frac{(8\pi)^2}{a_0^2\left(k_f^2+1/a_0^2\right)^4}\delta(E_f - E_0 - \hbar\omega)\\ &= \frac{e^2\hbar}{2m^2c^2a_0^5}\int\frac{\mathrm{d}k_f\,k_f^2\,\mathrm{d}\Omega}{(2\pi)^3}\frac{(\boldsymbol{A}_0\cdot\boldsymbol{k}_f)^2(8\pi)^2}{\left(k_f^2+1/a_0^2\right)^4}\delta\left(\frac{\hbar^2k_f^2}{2m} - E_0 - \hbar\omega\right)\\ &= \frac{e^2k_f}{2mc^2a_0^5\hbar}\int\frac{\mathrm{d}\Omega}{(2\pi)^3}\frac{(\boldsymbol{A}_0\cdot\boldsymbol{k}_f)^2(8\pi)^2}{\left(k_f^2+1/a_0^2\right)^4}\,,\end{aligned} \tag{26.27}$$

with k_f determined by energy conservation. The only angular dependence is in $\boldsymbol{A}_0 \cdot \boldsymbol{k}_f$, so using

$$\int \mathrm{d}\Omega \cos^2\theta = \frac{4\pi}{3} \tag{26.28}$$

we reach the final result,

$$R_{0\to f} = \frac{16 e^2 k_f^3 A_0^2}{3mc^2 \hbar a_0^5} \frac{1}{\left(k_f^2 + 1/a_0^2\right)^4} \,. \tag{26.29}$$