Lecture 14

Fermi's "Golden Rule"

Now that we have worked out the general idea of time-dep perturbations, let us summarise and look at cases of physical interest. We found that

$$P_{km} = \frac{|\lambda \tilde{W}_{mk}|^2}{4\hbar^2} \left| \frac{1-e^{i\omega_+ t}}{\omega_+} \mp \frac{1-e^{i\omega_- t}}{\omega_-} \right|^2$$

where P_{km} is the probability of a transition from E_k to E_m in time t, the perturbation is $\lambda W(x,t) = \lambda \tilde{W}(x) \sin \omega t$ or $\lambda W(x) \cos \omega t$ (corresponding to the two signs on the RHS) and $\tilde{W}_{mk} = \langle \psi_m | \tilde{W} | \psi_k \rangle$. Also

$$\omega_\pm = \omega_{mk} \pm \omega$$

where $\omega_{mk} = \dfrac{E_m - E_k}{\hbar}$ is the Bohr frequency of the two levels, and ω is the externally supplied frequency.

The three special cases of interest are:

$\omega \ll \omega_{mk}$: nearly constant perturbation,

$\omega \simeq \pm\omega_{mk}$: resonant perturbation,

$\omega \gg \omega_{mk}$: rapidly oscillating perturbation.

We have already investigated the first two cases. The first case ~~makes~~ $\omega \sim 0$ makes sense for the cos perturbation and gives:

$$P_{km} \simeq \frac{|\lambda \tilde{W}_{mk}|^2}{\hbar^2} \left[\frac{\sin \omega_{mk} t/2}{\omega_{mk}/2} \right]^2$$

The second case, say $\omega \sim -\omega_{mk}$, so $\omega_+ \simeq 0$, gives:

$$P_{km} \simeq \frac{|\lambda \tilde{W}_{mk}|^2}{4\hbar^2} \left[\frac{\sin \omega_+ t/2}{\omega_+/2} \right]^2$$

as long as $t \gg \frac{1}{\omega} \sim \frac{1}{\omega_{mk}}$. Note that $[\;]^2 \sim t^2$, for small t.

For the third case, which we have not yet considered, take the sin perturbation and $\omega \gg \omega_{mk}$. Then $\omega_\pm \simeq \pm\omega$, and

$$P_{km} \simeq \frac{|\lambda \tilde{W}_{mk}|^2}{4\hbar^2} \left| \frac{1-e^{i\omega_+ t}}{\omega_+} - \frac{1-e^{i\omega_- t}}{\omega_-} \right|^2$$

$$\simeq \frac{|\lambda \tilde{W}_{mk}|^2}{4\hbar^2} \left| \frac{1-e^{i\omega t}}{\omega} - \frac{1-e^{-i\omega t}}{-\omega} \right|^2$$

$$= \frac{|\lambda \tilde{W}_{mk}|^2}{(\hbar\omega)^2} |1-\cos\omega t|^2$$

Now let us consider the case where we have a $\sin\omega t$ perturbation and the near-resonance condition is satisfied, i.e.

$$P_{km} = \frac{|\lambda \tilde{W}_{mk}|^2}{4\hbar^2} \left[\frac{\sin \omega_+ t/2}{\omega_+/2} \right]^2$$

For large times this tends to a δ-function.

We now show that:

$$\lim_{t\to\infty} \frac{\sin^2 \alpha t}{\pi t \alpha^2} = \delta(\alpha)$$

where α is a constant. Proof:

i) for $\alpha \neq 0$, $\lim\limits_{t\to\infty} \dfrac{\sin^2 \alpha t}{\pi t \alpha^2} = 0$

ii) for $\alpha \to 0$, $\dfrac{\sin^2 \alpha t}{\pi t \alpha^2} \to \dfrac{\alpha^2 t^2}{\pi t \alpha^2} = \dfrac{t}{\pi}$

Hence $\lim\limits_{t\to\infty} \dfrac{t}{\pi} = \infty$ as desired.

iii) $$\int_{-\infty}^{+\infty} d\alpha \left(\frac{\sin^2 \alpha t}{\pi t \alpha^2} \right) =$$

$$\frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{dy}{y} \frac{\sin^2 y}{y}$$ using $(y = \alpha t)$

$= 1$. Hence $\displaystyle\int_{-\infty}^{+\infty} d\alpha \lim_{t\to\infty} \frac{\sin^2 \alpha t}{\pi t \alpha^2} = 1$

which proves the result.

Hence

$$P_{km} \overset{t\to\infty}{\simeq} \frac{|\lambda \tilde{W}_{mk}|^2}{4\hbar^2} \lim_{t\to\infty} \left(\frac{\sin \omega_+ t/2}{\omega_+/2}\right)^2$$

$$\Downarrow$$

$$\pi t \, \delta\left(\frac{\omega_+}{2}\right)$$

$$= 2\pi t \, \delta(\omega_+)$$

Now $\omega_+ = \frac{1}{\hbar}(E_m - E_k + \hbar\omega)$

So $\delta(\omega_+) = \hbar \, \delta(E_m - E_k + \hbar\omega)$

Hence

$$P_{km} \simeq \frac{|\lambda \tilde{W}_{mk}|^2}{4\hbar^2} \cdot 2\pi\hbar t \cdot \delta(E_m - E_k + \hbar\omega)$$

$$= |\lambda \tilde{W}_{mk}|^2 \frac{\pi}{2\hbar} \delta(E_m - E_k + \hbar\omega) \, t$$

Since P_{km} grows like t in this limit, we may define

$$\frac{dP_{km}}{dt} = |\lambda \tilde{W}_{mk}|^2 \frac{\pi}{2\hbar} \delta(E_m - E_k + \hbar\omega)$$

Finally, the physical transition ~~probability~~ rate (given that E_m is in the continuous spectrum) is

$$\frac{d\,\Delta P_{km}}{dt} = \int_\Delta dE \, \rho(E) \, \delta(E - E_k + \hbar\omega) \cdot |\lambda \tilde{W}_{mk}|^2 \frac{\pi}{2\hbar}$$

→ Fermi's Golden Rule.

Transitions from one state to another one that is different (hence orthogonal) but degenerate in energy, satisfy a similar formula but now $\omega \to 0$ so we have:

$$\frac{d}{dt}\Delta P_{km} = \oint |\lambda \tilde{W}_{mk}|^2 \frac{2\pi}{\hbar} \int_{\Delta} dE\, \rho(E)\, \delta(E_* - E_k)$$

Note that there is a factor 4 difference compared with the resonant case, because this time both terms in the $\cos \omega t$ function contribute.

This is explained in more detail on the next page.

Comment on normalisations:

i) We have used $\sin\omega t$ (or $\cos\omega t$) as the perturbation. Some books use $e^{\pm i\omega t}$ instead. With Sin/Cos, when we have resonance then only one term is used:

$$e^{i\omega_{mk}t}\sin\omega t = \frac{1}{2}\left(e^{i\omega t} - e^{-i\omega t}\right)e^{i\omega_{mk}t}$$

$$= \frac{1}{2}e^{i\omega_+ t} \quad \text{(neglecting the 2nd term near } \omega_+ \sim 0\text{)}$$

Thus the answer has a factor $\frac{1}{4}$ for Sin/Cos relative to $e^{\pm i\omega t}$ perturbations.

ii) However when we consider <u>constant</u> rather than <u>resonant</u> frequencies, ie $\omega \sim 0$, then $\cos\omega t \to 1$ and $e^{\pm i\omega t} \to 1$ as well. So this time there is no relative factor.

Atomic transitions

One of the most important applications of time-dependent perturbation theory is to atomic transitions induced by an electromagnetic field.

Here we will work in an approximation where the electromagnetic field is treated as classical. It provides a perturbation of the atomic Hamiltonian, but is not itself quantised. Most (but not all) of the relevant phenomena can be understood in this approximation.

We assume an electromagnetic wave incident on an atom. The wave is specified by $\vec{A}(\vec{x}, t)$ and $\varphi(\vec{x}, t)$ the vector and scalar potentials. We have seen (Lecture 0) that the combined system is invariant under:

$$\left.\begin{aligned} \varphi &\to \varphi + \dot{\chi} \\ \vec{A} &\to \vec{A} - \vec{\nabla}\chi \end{aligned}\right\} \text{gauge transformations}$$

where $\chi = \chi(\vec{x}, t)$ and we work in units where $c = 1$.

We use this freedom to set $\varphi = 0$:

Given some $\varphi(\vec{x}, t)$ we have

$$\varphi'(\vec{x}, t) = \varphi(\vec{x}, t) + \frac{\partial}{\partial t} \chi(\vec{x}, t)$$

Choosing $\chi(\vec{x}, t) = -\int^{t} dt' \, \varphi(\vec{x}, t')$

we ensure that $\varphi'(\vec{x}, t) = 0$.

We can still perform gauge transformations by $\chi(\vec{x})$ indep of t, since φ remains zero under those. Consider

$$\vec{\nabla} \cdot \vec{A}' = \vec{\nabla} \cdot \vec{A} - \vec{\nabla}^2 \chi$$

we can use χ to set the RHS to zero:

$$\vec{\nabla}^2 \chi = \vec{\nabla} \cdot \vec{A} = \text{some given function.}$$

With suitable boundary conditions at ∞, this can be uniquely inverted to determine χ.

Under these conditions we choose $\vec{A}$ to satisfy the Maxwell eqn:

$$\partial^\mu (\partial_\mu A_\nu - \partial_\nu A_\mu) = 0$$

ie $$\eta^{\mu\alpha} \frac{\partial}{\partial x^\alpha} \left(\frac{\partial}{\partial x^\mu} A_\nu - \frac{\partial}{\partial x^\nu} A_\mu \right) = 0$$

where $\mu = 0, 1, 2, 3$ and $\eta_{\mu\nu} = \begin{pmatrix} -1 & & & \\ & +1 & & \\ & & +1 & \\ & & & +1 \end{pmatrix} = \eta^{\mu\nu}$

From $A_0 = 0 = \varphi$ and $\vec{\nabla}\cdot\vec{A} = 0$, the Maxwell eqns in free space are:

$$\partial^\mu \partial_\mu \vec{A} = 0 \qquad (i = 1, 2, 3)$$

or $$\left(-\partial_t^2 + \vec{\nabla}^2\right)\vec{A} = 0.$$

This is solved in general by

$$\vec{A} = \vec{a}\, e^{i(\vec{k}\cdot\vec{x} - \omega t)} + \vec{a}^* e^{-i(\vec{k}\cdot\vec{x} - \omega t)}$$

where $\omega = |\vec{k}|$ and $\vec{a}$ is a (possibly complex) constant.

Now $\vec{\nabla}\cdot\vec{A} = 0 \Rightarrow \vec{k}\cdot\vec{a} = 0$

Let us choose $\vec{a} = a(0,0,1) = a\hat{z}$

Then $\vec{k}$ can point anywhere along x or y.

By an x-y rotation we choose $\vec{k} = (0, \underset{\omega}{\overset{\shortparallel}{k}}, 0)$.

Hence

$$\vec{A} = a\vec{e}_z e^{i(ky - \omega t)} + a^* \vec{e}_z e^{-i(ky - \omega t)}$$

from which

$$\vec{E} = -\frac{\partial}{\partial t}\vec{A} = i\omega\left[a\vec{e}_z e^{i(ky-\omega t)} - a^*\vec{e}_z e^{-i(ky-\omega t)}\right]$$

$$\vec{B} = \vec{\nabla}\times\vec{A} = ik\left[a\vec{e}_x e^{i(ky-\omega t)} - a^*\vec{e}_x e^{-i(ky-\omega t)}\right]$$

where $\vec{e}_x, \vec{e}_y, \vec{e}_z$ are the three unit vectors.

Choosing a = pure imaginary (this just corresponds to choosing the origin of time), ~~~~ $a = -\frac{i}{2}\alpha$, we have:

$$\vec{A} = \alpha \vec{e}_z \sin(kx - \omega t)$$

$$\vec{E} = \omega\alpha \vec{e}_z \cos(kx - \omega t)$$

$$\vec{B} = k\alpha \vec{e}_x \cos(kx - \omega t)$$

How does this couple to the electron in an atom? We already wrote, for a spinless charged particle,

$$H = \frac{1}{2m}(\vec{p} - e\vec{A})^2 + e\varphi + V(\vec{x})$$

where now the last term is the Coulomb potential of the nucleus. For a spinning electron we have an additional term

$$-\frac{e}{m}\vec{S}\cdot\vec{B}(\vec{x},t)$$

where $\vec{S}$ represents the spin ~~state~~ operator.

Since we have put $\varphi = 0$ we get for our case:

$$H = \frac{\vec{p}^2}{2m} + V(\vec{x}) - \frac{e}{2m}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{e^2}{2m}\vec{A}\cdot\vec{A} - \frac{e}{m}\vec{S}\cdot\vec{B}$$

Clearly we should choose

$$H_0 = \frac{\vec{p}^2}{2m} + V(\vec{x})$$

(which for example can describe the Hydrogen atom). The last three terms all depend on the electromagnetic field and are time-dependent.

Notice that $\vec{p}$ and $\vec{A}$ commute because

$$[\vec{p}, \vec{A}] = -i\hbar \vec{\nabla}\cdot\vec{A} = 0$$

due to the choice of gauge. Thus we have:

$$W(\vec{x},t) = -\frac{e}{m}\vec{p}\cdot\vec{A} - \frac{e}{m}\vec{S}\cdot\vec{B} + \frac{e^2}{2m}\vec{A}^2$$

The last term is important only for very strong fields and we neglect it here. Likewise, the $\vec{S}\cdot\vec{B}$ coupling is small compared to the first term (both these facts will be seen in future exercises).

Hence finally we will consider

$$H = H_0 - \frac{e}{m}\vec{p}\cdot\vec{A}(\vec{x})$$

Since $\vec{A} = \alpha \vec{e}_z \sin(kx - \omega t)$, we have

$$-\frac{e}{m}\vec{p}\cdot\vec{A} = -\frac{e}{m}\alpha \hat{p}_z \sin(k\hat{x} - \omega t)$$

Finally we note that $k = \frac{2\pi}{\lambda}$ where λ is the wavelength of the incident wave, while $\langle \hat{y} \rangle \sim a_0$, the Bohr radius.
We know that $a_0 \sim 0.5$ Å while $\lambda \sim 1000$ Å (visible) so $\frac{a_0}{\lambda} \ll 1$. Hence we can replace $e^{ik\hat{y}}$ by 1, ie $\sin(ky - \omega t)$ by $-\sin \omega t$.

It follows that the perturbation is

$$W_{E.D.} = \frac{e\alpha}{m} \hat{p}_z \sin \omega t = \frac{eE_0}{m\omega} \hat{p}_z \sin \omega t$$

(where $E_0 = \omega\alpha$ is the amplitude of the electric field).

This perturbation is called "electric dipole".
It is actually gauge-equivalent to the more familiar

$$\tilde{W}_{E.D.} = -\vec{D}.\vec{E}$$

where $\vec{D} = e\vec{\hat{x}}$ is the electric dipole moment operator and $\vec{E} = E_0 \cos \omega t \, \vec{e}_z$.

Hence $-\vec{D}.\vec{E} = -eE_0 \hat{z} \cos \omega t$

To see the gauge equivalence of these two, consider the ~~[illegible]~~ vector & scalar potentials in the E.D. approximation $ky \simeq 0$:

$$\vec{A} = -\frac{E_0}{\omega}\vec{e}_z \sin\omega t$$

$$\varphi = 0$$

Now we can make $\vec{A}$ vanish by a gauge transformation:

$$\vec{A} \to \vec{A}' = \vec{A} - \vec{\nabla}\chi$$

if we choose $\chi = -\frac{E_0}{\omega} z \sin\omega t$

(because then $\vec{\nabla}\chi = -\frac{E_0}{\omega}\vec{e}_z \sin\omega t$). In the process, the scalar potential becomes nonzero:

$$\varphi' = \varphi + \dot{\chi} = -E_0 z \cos\omega t$$

which gives rise to the term

$$e\varphi' = -eE_0\hat{z}\cos\omega t$$

in the Hamiltonian.

We continue to use $\vec{A} = -\frac{E_0}{\omega}\vec{e}_z \sin\omega t$ because higher multipole corrections are obtained by going back from $\sin\omega t$ to $-\sin(k\hat{y} - \omega t)$ and keeping powers of $\hat{y}$.

We are now in a position to evaluate the matrix element of the E.D. perturbation

$$(W_{ED})_{mk} = \langle \psi_m | W_{ED} \psi_k \rangle$$

$$= \frac{eE_0}{m\omega} \sin\omega t \, \langle \psi_m | \hat{p}_z | \psi_k \rangle$$

One can replace $\hat{p}_z$ in terms of $\hat{z}$ as follows:

$$\hat{p}_z = m \frac{\partial}{\partial \hat{p}_z} H_0 \qquad \left(\text{because } H_0 = \frac{\hat{p}_z^2}{2m} \right)$$

$$= \frac{1}{i\hbar} [\hat{z}, H_0]$$

So

$$\langle \psi_m | \hat{p}_z | \psi_k \rangle = \frac{m}{i\hbar} \langle \psi_m | [\hat{z}, H_0] | \psi_k \rangle$$

$$= \frac{m}{i\hbar} (E_k - E_m) \langle \psi_m | \hat{z} | \psi_k \rangle$$

$$= \frac{-m\omega_{mk}}{i} \langle \psi_m | \hat{z} | \psi_k \rangle$$

$$= i m \omega_{mk} \langle \psi_m | \hat{z} | \psi_k \rangle$$

Then

$$\langle \psi_m | W_{ED} | \psi_k \rangle = \frac{eE_0}{m\omega} \cdot i m \omega_{mk} \langle \psi_m | \hat{z} | \psi_k \rangle \sin\omega t$$

$$= i e E_0 \frac{\omega_{mk}}{\omega} \sin\omega t \, \langle \psi_m | \hat{z} | \psi_k \rangle$$

We now see that $\langle \Psi_m | \hat{z} | \Psi_k \rangle$ can be zero or nonzero depending on the angular properties of the wave fns.

Let $\Psi_k \sim R_{n_1 \ell_1}(r)\, Y_{\ell_1 m_1}(\theta, \varphi)$

$\Psi_m \sim R_{n_2 \ell_2}(r)\, Y_{\ell_2 m_2}(\theta, \varphi)$

Now $z = r \cos\theta = \sqrt{\frac{4\pi}{3}}\, r\, Y_{10}(\theta)$

So

$$\langle \Psi_m | \hat{z} | \Psi_k \rangle \approx \int d\Omega\, Y^*_{\ell_2 m_2}\, Y_{10}\, Y_{\ell_1 m_1}$$

$\times$ other factors.

Now we know from properties of the $Y_{\ell m}$ that the above integral vanishes unless $m_2 = m_1$ and $\ell_2 = \ell_1 \pm 1$.

Now we note that the restriction of the wave along the $\vec{e}_z$ axis was artificial: we could have chosen $\vec{A}$ and therefore $\vec{E}$ along $\vec{e}_x$ or $\vec{e}_y$. In these cases the ~~integral~~ matrix element would be ~~along~~

$$\langle Y_{\ell_2 m_2} | \hat{x} | Y_{\ell_1 m_1} \rangle \quad \text{or} \quad \langle Y_{\ell_2 m_2} | \hat{y} | Y_{\ell_1 m_1} \rangle$$

Using $x = r \sin\theta \cos\varphi$, $y = r \sin\theta \sin\varphi$ we get an extra factor of $e^{\pm i\varphi}$ in the integral.

It follows that $m_2 = m_1, m_1 \pm 1$ which along with $l_2 = l_1 \pm 1$ gives the electric dipole selection rules.

If the ED transition is zero because it violates this selection rule, then we must go to higher order, ie use

$$e^{\pm ik\hat{y}} = 1 \pm ik\hat{y}$$

and keep the second term. We must also bring back the neglected term $-\frac{e}{m}\vec{S}\cdot\vec{B}$ which as we will see is comparable. We expand:

$$-\frac{e}{m}\hat{\vec{p}}\cdot\vec{A} = -\frac{e\alpha}{m} p_z \sin(k\hat{y} - \omega t)$$

$$= \frac{e\alpha}{m}\hat{p}_z \sin\omega t - \frac{e\alpha}{m}\cdot k\hat{y}\hat{p}_z \cos\omega t + \cdots$$

The second term is suggestively written

$$-\frac{e}{m} B_0 \hat{y}\hat{p}_z \cos\omega t \qquad (\text{where } B_0 = k\alpha = \omega\alpha = E_0)$$

We can rewrite $\hat{y}\hat{p}_z$ in terms of angular momentum:

$$\hat{y}\hat{p}_z = \cancel{\tfrac{1}{2}(\hat{p}_z\hat{y} - \hat{y}\hat{p}_z)}\ \frac{1}{2}(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) + \frac{1}{2}(\hat{y}\hat{p}_z + \hat{z}\hat{p}_y) = \frac{1}{2}\hat{L}_x + \frac{1}{2}(\hat{y}\hat{p}_z + \hat{z}\hat{p}_y)$$

In comparison, the leading term in $-\frac{e}{m}\vec{S}\cdot\vec{B}$ (putting $k\hat{y} \simeq 0$) is

$$-\frac{e}{m} S_x B_x = -\frac{e}{m}\hat{S}_x B_0 \cos\omega t$$

Hence to this order the two terms are:

$$-\frac{eB_0}{2m}\left(\hat{L}_x + \hat{y}\hat{p}_z + \hat{z}\hat{p}_y\right)\cos\omega t$$

and $-\frac{eB_0}{m}\hat{S}_x \cos\omega t$.

We combine them as:

$$W_{MD} = -\frac{e}{2m}\left(\hat{L}_x + 2\hat{S}_x\right) B_0 \cos\omega t$$

$$W_{EQ} = -\frac{e}{2m}\left(\hat{y}\hat{p}_z + \hat{z}\hat{p}_y\right) E_0 \cos\omega t$$

where we used $B_0 = E_0$. The reason to call the first term "magnetic dipole" is