Lecture 15

In the previous lecture we formulated the time-dependent Hamiltonian

$$H = H_0 - \frac{e}{m}\alpha\, \hat{p}_z \sin(k\hat{y} - \omega t)$$

where α gives the strength of the electromagnetic ~~potential~~ field in the problem. This was obtained after neglecting the $\vec{A}\cdot\vec{A}$ and $\vec{S}\cdot\vec{B}$ interactions.

There is a further approximation that can now be made. 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. Now $a_0 \sim 0.5$ Å while $\lambda \sim 10^3$ Å so $\frac{a_0}{\lambda} \ll 1$ (assuming the incident radiation is in the visible spectrum).

Hence it is reasonable to replace $k\hat{y}$ by 1 in $\sin(k\hat{y} - \omega t)$. Then the perturbation becomes:

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

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

This perturbation is called "electric dipole". Though this is **not** immediately apparent, $\tilde{W} = \frac{eE_0}{m\omega} \hat{p}_z \sin\omega t$ is equivalent under a gauge transformation to

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

where $\vec{D} = e\,\hat{\vec{x}}$ and $\vec{E} = E_0 \cos\omega t\, \vec{e}_z$.

The "standard" form of the electric dipole perturbation is therefore:

$$\tilde{W}_{ED} = -eE_0 \hat{z} \cos\omega t .$$

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

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

$$\varphi = 0$$

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 ~~to~~ 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

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

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

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

$$\hat{p}_z = \frac{m}{\cancel{i\hbar}} \frac{\partial}{\partial \hat{p}_z} H_0 \qquad \left(\text{because } H_0 = \frac{\hat{p}_z^2}{2m} + V(\hat{x}) \right)$$

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

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 $\Psi_k \sim R_{n_1 l_1}(r)\, Y_{l_1 m_1}(\theta, \varphi)$

$\Psi_m \sim R_{n_2 l_2}(r)\, Y_{l_2 m_2}(\theta, \varphi)$

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

So

$$\langle \Psi_m | \hat{z} | \Psi_k \rangle \approx \int d\Omega\, Y^*_{l_2 m_2}\, Y_{10}\, Y_{l_1 m_1}$$

$\times$ other factors.

Now we know from properties of the Y_{lm} that the above integral vanishes unless $m_2 = m_1$ and $l_2 = l_1 \pm 1$.

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

$$\langle Y_{l_2 m_2} | \hat{x} | Y_{l_1 m_1} \rangle \quad \text{or} \quad \langle Y_{l_2 m_2} | \hat{y} | Y_{l_1 m_1} \rangle$$

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.

Higher order

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:

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

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

The second term is suggestively written

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

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:

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

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

We combine them as:

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

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

where we used $B_0 = E_0$. The reason to call the first term "magnetic dipole" is that it has a term proportional to the spin and orbital angular momentum, both of which contribute magnetic dipole interactions.

~~The other term has~~

The two terms W_{MD} and W_{EQ} are comparable in magnitude, as one can see by inspection of their form.

While detailed calculation of matrix elements of magnetic dipole and electric quadrupole perturbations is outside the scope of this course, we may again derive selection rules.

For the magnetic dipole, we recall that $\hat{L}_x$ and $\hat{S}_x$ both commute with $\hat{L}^2$ whose eigenvalue determines l. Therefore l does not change. But $\hat{L}_x \sim \hat{L}^+ + \hat{L}^-$ changes m by ± 1, similarly $\hat{S}_x$ changes m_s by ± 1.

If the magnetic field was polarized along $\vec{e}_z$ instead of $\vec{e}_x$ then the MD term would contain $(\hat{L}_z + 2\hat{S}_z)$. This does not change l, ~~$\not{}$~~ m, m_s. Thus finally we have:

$$\Delta l = 0$$
$$\Delta m = \pm 1, 0$$
$$\Delta m_s = \pm 1, 0$$

(Here we neglect spin-orbit coupling: in presence of that the rules look different — see e.g. Cohen-Tannoudji's book)

For the electric quadrupole, we have:

$$\hat{y}\hat{p}_z + \hat{z}\hat{p}_y = \hat{y}\hat{p}_z + \hat{p}_y\hat{z}$$

$$= \frac{m}{i\hbar}\left(\hat{y}[\hat{z},\hat{H}_0] + [\hat{y},\hat{H}_0]\hat{z}\right)$$

$$= \frac{m}{i\hbar}\left(\hat{y}\hat{z}\hat{H}_0 - \hat{H}_0\hat{y}\hat{z}\right)$$

So $<\Psi_m|\hat{y}\hat{p}_z + \hat{z}\hat{p}_y|\Psi_k>$

$$= -\frac{m}{i\hbar}\omega_{mk} <\Psi_m|\hat{y}\hat{z}|\Psi_k>$$

thus: $$<W_{EQ}> = \frac{e}{2i\hbar}\omega_{mk} <\Psi_m|\hat{y}\hat{z}|\Psi_k> B_0 \cos\omega t$$

For the selection rules we have:

$$\hat{y}\hat{z} \simeq \hat{r}^2\left(Y_{2,1}(\theta,\varphi) - Y_{2,-1}(\theta,\varphi)\right)$$

(because: $y = r\sin\theta\sin\varphi$

$z = r\cos\theta$

$Y_{2,\pm1} = (\ )\sin\theta\cos\theta\, e^{\pm i\varphi}$)

Hence ~~we can~~ l changes to $l+2$, l or $l-2$ while m changes to $m\pm1$. By changing the polarisation of the mag. field one also gets $m \to m\pm2$. Hence:

<u>EQ</u>: $\Delta l = 0, \pm2$; $\Delta m = 0, \pm1, \pm2$.

Photoelectric effect

As an application of electric dipole transitions, let us consider the photoelectric effect in Hydrogen.

We consider a Hydrogen atom in its ground state on which an electric dipole perturbation is applied. We would like to calculate the ionisation rate, which from Fermi's Golden Rule is given by:

$$dP_{E} = |\lambda \tilde{W}_{E0}|^2 \frac{\pi}{2\hbar} \delta(E - E_{1,0,0} - \hbar\omega)$$

where $E_{n,l,m}$ is the energy of the stationary state $\Psi_{n,l,m}$ and here $(n,l,m) = (1,0,0)$. E is the energy of the final state, which since it lies in the continuum can be approximated by a plane wave.

The perturbation is

$$\lambda W = \frac{e E_0}{m\omega} \hat{p}_z \sin\omega t = \lambda \tilde{W} \sin\omega t$$

Hence

$$\lambda \tilde{W} = \frac{eE_0}{m\omega} \hat{p}_z \quad \text{and}$$

$$\lambda \tilde{W}_{E0} = \frac{eE_0}{m\omega} \int \Psi_E^* \left(-i\hbar\frac{\partial}{\partial z}\right) \Psi_{1,0,0} \, d^3x$$

Here $\quad \psi_{1,0,0} = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$

$$\psi_E = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{x}} \qquad \text{where } \frac{\vec{p}^{\,2}}{2m} = E$$

Since $\hat{p}_z$ is Hermitian and ψ_E is an eigenstate,

$$\int \psi_E^* \hat{p}_z \psi_{1,0,0} = p_z \int \psi_E^* \psi_{1,0,0}$$

$$= p_z \cdot \frac{1}{\sqrt{\pi a_0^3}} \frac{1}{(2\pi\hbar)^{3/2}} \int e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}} e^{-r/a_0} d^3x.$$

The integral is easily evaluated:

$$\int e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}} e^{-r/a_0} d^3x =$$

$$\int_0^\infty r^2 dr \int_{-1}^{+1} d(\cos\theta) \int_0^{2\pi} d\varphi \; e^{-\frac{i}{\hbar} pr\cos\theta} e^{-r/a_0}$$

$$= 2\pi \int_0^\infty r^2 dr \cdot \frac{i\hbar}{pr}\left(e^{-\frac{ipr}{\hbar}} - e^{\frac{ipr}{\hbar}}\right) e^{-r/a_0}$$

$$= \frac{2\pi i\hbar}{p}\left(-\frac{\partial}{\partial a_0}\right)\int_0^\infty dr \left(e^{-\left(\frac{ip}{\hbar}+\frac{1}{a_0}\right)r} - e^{\left(\frac{ip}{\hbar}-\frac{1}{a_0}\right)r}\right)$$

$$= \frac{8\pi a_0^3}{\left[1+\left(\frac{p}{\hbar}a_0\right)^2\right]^2}$$

Putting in all the constants, we have:

$$\lambda \tilde{W}_{E_0} = \frac{eE_0}{m\omega} \cdot \frac{p_z}{\sqrt{\pi a_0^3}} \cdot \frac{1}{(2\pi\hbar)^{3/2}} \cdot \frac{8\pi a_0^3}{\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^2}$$

$$= \frac{eE_0}{m\omega} \frac{p_z}{\pi}\left(\frac{2a_0}{\hbar}\right)^{3/2} \frac{1}{\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^2}$$

Hence Fermi's Golden Rule gives:

$$\frac{d}{dt} P_{1,0,0\to E} = \frac{\pi}{2\hbar}\left(\frac{eE_0}{m\omega}\right)^2\left(\frac{p_z}{\pi}\right)^2\left(\frac{2a_0}{\hbar}\right)^3 \cdot \frac{1}{\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^4}$$

$$\times\ \delta(E_p - E_{1,0,0} - \hbar\omega)$$

$$\downarrow$$

$$\delta\left(\frac{p^2}{2m} - E_{1,0,0} - \hbar\omega\right)$$

$$= \frac{m}{p}\,\delta\left(p - \sqrt{2m(E_{1,0,0}+\hbar\omega)}\right)$$

Now we can integrate over $d^3p = p^2\,dp\,d\Omega$ which sets $p = \sqrt{2m(E_{1,0,0}+\hbar\omega)}$. Of course $p_z = p\cos\theta$ with p as above and θ is the angle between the polarisation of $\vec{A}$ (the vector field) which we have chosen along $\vec{e}_z$, and the outgoing momentum

Thus,

$$\frac{d}{dt}\Delta P_{1,0,0\to d\Omega} = \left(\frac{eE_0}{m\omega}\right)^2 \frac{m}{2\pi\hbar}\, p \cdot p_z^2 \cdot \left(\frac{2a_0}{\hbar}\right)^3 \frac{1}{\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^4}$$

$$= \frac{4a_0^3 e^2 E_0^2}{m\pi\omega^2\hbar^4} \frac{p^3 \cos^2\theta}{\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^4} d\Omega$$

where $p = \sqrt{2m(E_{1,0,0}+\hbar\omega)}$.

Note that we have integrated over all $|\vec{p}|$ but the δ-fn in the Golden Rule made sure the only $\vec{p}$ that contribute are those for which $\frac{\vec{p}^2}{2m} = E_{1,0,0} + \hbar\omega$.

The total ionization rate is:

$$\mathcal{J}_{1,0,0} = \frac{d}{dt}\Delta P_{1,0,0\to \text{all}} = \underbrace{\int \sin\theta\, d\theta\, d\varphi \cos^2\theta}_{4\pi/3}$$

$$\times\ 4a_0^3\left(\frac{e_0 E_0}{\omega}\right)^2 \frac{1}{m\pi\hbar^4} \cdot \frac{p^3}{\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^4}$$

$$\boxed{\mathcal{J}_{1,0,0} = \frac{16a_0^3}{3m\hbar^4}\left(\frac{eE_0}{\omega}\right)^2 \frac{p^3}{\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^4}}$$

From the ionisation rate $\mathcal{J}_{1,0,0}$ we can define the energy absorption rate:

$$\frac{dE_{abs}}{dt} = \hbar\omega . \mathcal{J}_{1,0,0}$$

The incident energy (in units where $c=1$) ~~to~~ per unit area is $\frac{|E_0|^2}{8\pi}$.

Then the <u>cross-section</u> σ is defined as absorption rate divided by incident energy per unit area, ie:

$$\sigma = \frac{\hbar\omega \mathcal{J}_{1,0,0}}{|E_0|^2/8\pi} = \frac{128\pi e^2 (a_0 p)^3}{3m\hbar^3\omega\left[1+\left(\frac{pa_0}{\hbar}\right)^2\right]^4}$$

In the limit $a_0 p \gg \hbar$, this simplifies to:

$$\sigma \simeq \frac{128\pi e^2}{m\omega}\left(\frac{\hbar}{pa_0}\right)^5$$