Lecture 12: Time-Independent Perturbation Theory

Monday, February 10, 2020

Last time, we found that, for

$$H = H_0 + \lambda H_I$$

$$\Delta E_n = \left\langle \phi_n^{(0)} \middle| H_I \middle| \phi_n^{(0)} \right\rangle$$

and

$$\Delta \left|\phi_n\right\rangle == \sum_{m \neq n} \frac{\left\langle \phi_m^{(0)} \middle| H_I \middle| \phi_n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|\phi_m^{(0)}\right\rangle$$

Notice that we have switched the conventional indices from last lecture. Just use this from now on. The upper (0) means these are the unperturbed things.

What happens to this last equation if we have a degeneracy? Diagonalize the Hamiltonian such that

$$\langle m|H_I|n\rangle \propto \delta_{nm}$$

Let's say that $H_I = \bar{p} \cdot \vec{\mathbf{E}}$ where $\bar{p}$ is the dipole moment, which is the leading-order energy term for a hydrogen atom. If we put the electric field along the z-direction, the dipole moment will be $\bar{p} = -ez$ so

$$H_I = -ezE$$

Consider $n = 1$:

$$\Delta E_{n=1} = \langle 1,0,0|-ez|1,0,0\rangle\, E$$

$$\begin{gathered}
\langle 0,0|z|0,0\rangle = 0 \quad \text{since} \\
\pi^{-1} z \pi = -z \quad \text{and} \quad \pi\left|0,0\right\rangle = \pm\left|0,0\right\rangle \\
\langle 0,0|\pi\pi^{-1} z \pi\pi^{-1}|0,0\rangle = (\pm)\langle 0,0|-z|0,0\rangle(\pm) = -\langle 0,0|z|0,0\rangle = 0
\end{gathered}$$

where π is the parity operator.

For the higher states, we will use the fact that

$$\pi\left|l,m\right\rangle = (-1)^l\left|l,m\right\rangle$$

For $n = 2$, $l = 0, 1$, so

$$\Delta\left|\phi_{n=2}\right\rangle = \sum_{m,n} \frac{\langle m|z|n\rangle}{E_n - E_m} Ee\left|m\right\rangle$$

Now there are four degenerate states, $\{\left|0,0\right\rangle, \left|1,-1\right\rangle, \left|1,0\right\rangle, \left|1,+1\right\rangle\}$. We will now try to diagonalize the system in terms of these states. First,

$$\langle l,m|z|l'm'\rangle \propto \delta_{mm'}$$

$[L_z, z] = 0$ so $\langle lm|[L_z,z]|l'm'\rangle = 0$, so

$$0 = \langle lm|L_z z|l'm'\rangle - \langle lm|zL_z|l'm'\rangle = (m-m')\hbar\left[\langle lm|z|l'm'\rangle\right]$$

so $\Delta m = 0$ for $H_I \sim z$. Also, $\Delta l \neq 0$ since if the l's are the same, the states are orthogonal.

$l'm' \rightarrow$	(0,0)	(1,-1)	(1,0)	(1,1)
(0,0)	0	0	λ	0
(1,-1)	0	0	0	0
(1,0)	λ	0	0	0
(1,1)	0	0	0	0

We claim $\langle lm|z|l'm'\rangle = \langle l'm'|z|lm\rangle$ because the operators are all Hermitian. Now we need to diagonalize this. First we will change the order of the basis a bit:

$l'm' \rightarrow$	(0,0)	(1,0)	(1,1)	(1,-1)
(0,0)	0	λ	0	0
(1,0)	λ	0	0	0
(1,1)	0	0	0	0
(1,-1)	0	0	0	0

Let's now define $\xi_1 = \frac{1}{\sqrt{2}}\left[|0,0\rangle + |1,0\rangle\right]$ and $\xi_2 = \frac{1}{\sqrt{2}}\left[|0,0\rangle - |1,0\rangle\right]$, which are the eigenvectors of this matrix. Therefore, we can define a new basis $\{\xi_1, \xi_2, |1,1\rangle, |1,-1\rangle\}$ where

$$z = \begin{pmatrix} \hat{\lambda} & & & \\ & -\hat{\lambda} & & \\ & & 0 & \\ & & & 0 \end{pmatrix}$$

Referring back to our original equation for the perturbed energy, we can now see that these new states, ξ_1 and ξ_2 are not degenerate to $|1,1\rangle$ and $|1,-1\rangle$, but in fact have $\Delta E = \pm_{1,2}\hat{\lambda} = \pm 3a_0 E$ (the last equality requires the full calculation of the matrix element).

0.1 Selection Rules

For an operator O, what values of n, l, and m give

$$\langle nlm|O|n'l'm'\rangle \neq 0?$$

For example, in the case of $O = z$, we just showed that $\Delta m = 0$ using the fact that $[L_z, z] = 0$. For Δl, we need to use the fact that

$$\left[L^2, \left[L^2, z\right]\right] = 2\hbar^2\left\{z, L^2\right\}$$

Taking the matrix elements of both sides, we get a relationship between l and l'. The right-hand side gives us:

$$\langle nlm|2\hbar^2\left\{z, L^2\right\}|n'l'm'\rangle = (2\hbar^2)\hbar^2\left[(l'\,|l'+1\rangle) + (l\,|l+1\rangle)\right]\langle nlm|z|n'l'm'\rangle$$

The left-hand side gives

$$\begin{aligned}\langle nlm|L^2(L^2z - zL^2) - (L^2z - zL^2)L^2|n'l'm'\rangle = \hbar^2\langle nlm|z|n'l'm'\rangle\,&[(l(l+1))^2 \\ &- l(l+1)l'(l'+1) \\ &- l(l+1)l'(l'+1) \\ &+ (l'(l'+1))^2]\end{aligned}$$

These sides must be equal, so we can cancel the matrix elements and equate

$$(l+l')(l+l'+1)((l-l')^2 - 1) = 0$$

The possible solutions are $(l - l') = \pm 1$. We could also have $l = l' = 0$, but we previously ruled this out by using a parity argument. Therefore, $\Delta l = \pm 1$.