Physics 742 – Graduate Quantum Mechanics 2

Solutions to Chapter 12

9. [15] A hydrogen atom in some combination of the $n = 2$ states is placed in an electric field which adds a perturbation $W = \frac{1}{2}\lambda\left(X^2 - Y^2\right)$ where λ is small. Ignore any spin-orbit or hyperfine splitting of the hydrogen atom; *i.e.*, treat all $n = 2$ states of hydrogen as perfectly degenerate before W is included.

(a) [8] Find all non-vanishing matrix elements $\langle 2l'm'|W|2lm\rangle$ for this interaction.

Since our wave functions for hydrogen are given in spherical coordinates, our first step is to rewrite this expression in spherical coordinates. We have

$$W(\mathbf{r}) = \tfrac{1}{2}\lambda\left(x^2 - y^2\right) = \tfrac{1}{2}\lambda r^2 \sin^2\theta\left(\cos^2\phi - \sin^2\phi\right) = \tfrac{1}{2}\lambda r^2\sin^2\theta\cos(2\phi)$$
$$= \tfrac{1}{4}\lambda r^2 \sin^2\theta\left(e^{2i\phi} + e^{-2i\phi}\right)$$

We now need to calculate

$$\langle 2l'm'|W|2lm\rangle = \tfrac{1}{4}\lambda\int_0^\infty r^2 dr r^2 R_{2l'}(r) R_{2l}(r)\int d\Omega \sin^2\theta\left(e^{2i\phi} + e^{-2i\phi}\right) Y_{l'}^{m'}(\theta,\phi)^* Y_l^m(\theta,\phi)$$

The final integral will be non-vanishing only if the powers of $e^{i\phi}$ can be arranged to cancel. Since Y_l^m is proportional to $e^{im\phi}$, this only happens if $m - m' = \pm 2$, which in turn demands that m and m' both be ± 1 and of opposite sign, which also guarantees that $l = l' = 1$. So the only cases we need to consider are

$$\langle 2,1,-1|W|2,1,1\rangle = -\frac{1}{4}\left(\frac{\sqrt{3}}{2\sqrt{2\pi}}\right)^2 \int_0^\infty r^2 dr r^2 R_{21}^2(r)\int d\Omega\sin^2\theta\left(e^{2i\phi} + e^{-2i\phi}\right)e^{2i\phi}\sin^2\theta$$

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Performing the ϕ-integration, we realize these formulas are identical, and substituting in our radial wave functions, they become

$$\langle 2,1,-1|W|2,1,1\rangle = \langle 2,1,1|W|2,1,-1\rangle = -\frac{3\cdot 2\pi}{32\pi}\lambda\frac{1}{24a_0^5}\int_0^\infty r^2 dr r^2 r^2 e^{-r/a_0}\int_0^\pi \sin^5\theta\, d\theta$$
$$= -\frac{\lambda}{32\cdot 4a_0^5}6!a_0^7\cdot 2\int_0^1\left(1 - z^2\right)^2 dz = -\frac{45}{4}\lambda a_0^2\left(1 - \tfrac{2}{3} + \tfrac{1}{5}\right) = -6\lambda a_0^2$$

(b) [7] Find the perturbed eigenstates and eigenenergies of the n = 2 states to zeroth and first order in λ respectively.

The full four by four $\tilde{W}$ matrix is

$$\tilde{W} = \begin{pmatrix} \langle 200|W|200\rangle & \langle 200|W|210\rangle & \langle 200|W|211\rangle & \langle 200|W|21-1\rangle \\ \langle 210|W|200\rangle & \langle 210|W|210\rangle & \langle 210|W|211\rangle & \langle 210|W|21-1\rangle \\ \langle 211|W|200\rangle & \langle 211|W|210\rangle & \langle 211|W|211\rangle & \langle 211|W|21-1\rangle \\ \langle 21-1|W|200\rangle & \langle 21-1|W|210\rangle & \langle 21-1|W|211\rangle & \langle 21-1|W|21-1\rangle \end{pmatrix}$$

$$= -6\lambda a_0^2 \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

It is clear that the first two states, to this order in perturbation theory, are unperturbed, so they are still eigenstates

$$|200\rangle, |210\rangle; \quad E_{200} = E_{211} = \varepsilon_2 = -\frac{k_e^2 e^4 m}{8\hbar^2}$$

To find the remaining two states, we need to diagonalize the submatrix

$$\tilde{W}' = -6\lambda a_0^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

We've encountered this matrix enough that we should know it by heart by now. The states and corresponding energies will be

$$|\pm\rangle = \tfrac{1}{\sqrt{2}}\left(|211\rangle \pm |21-1\rangle\right) \quad E_\pm = \varepsilon_2 + w_\pm = -\frac{k_e^2 e^4 m}{8\hbar^2} \mp 6\lambda a_0^2$$