P4410 LECTURE 28

Next example of degenerate pert. theory: Spin-orbit interaction in hydrogen atom:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{r}, \quad \hat{H}' = \frac{2Z\mu_B^2}{r^3}\frac{\hat{\vec{L}}\cdot\hat{\vec{S}}}{\hbar^2}$$

Recall that the $\hat{H}_0$ eigenstate $|n\,l\,m_l\,m_s\rangle$ is not an eigenstate of $\hat{\vec{L}}\cdot\hat{\vec{S}}$ — it's related by Clebsch-Gordan coefficients. So in this case the $\hat{H}'$ is **not** already diagonal. But it's easy to diagonalize since we know $\hat{\vec{L}}\cdot\hat{\vec{S}}$ eigenstates are also $(\hat{\vec{L}}+\hat{\vec{S}})^2 = \hat{\vec{J}}^2$ eigenstates. So in the coupled basis, $\hat{H}'$ is diagonal!

$$\langle n\,l\,j\,m_j|\hat{\vec{L}}\cdot\hat{\vec{S}}|n\,l'\,j'\,m_j'\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\delta_{ll'}\delta_{jj'}\delta_{m_jm_j'}$$

So all we have to do is evaluate $\left\langle\frac{1}{\hat{r}^3}\right\rangle$ for these basis states. (See, ex. Liboff 10.48) radial integral:

$$\left\langle\frac{1}{\hat{r}^3}\right\rangle = \frac{2}{a_0^3 n^3 l(l+1)(2l+1)} \qquad a_0 \equiv \frac{\hbar^2}{\mu e^2}$$

μ ← reduced mass

$$\text{So } E^{(1)}_{nlj} = \langle nljm_j|\hat{H}'|nljm_j\rangle = \frac{(Z\alpha)^4}{2}\frac{mc^2}{n^3 l(l+\frac{1}{2})(l+1)}\frac{1}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

Note that for a given l, only two possible j values exist: $j = l \pm \frac{1}{2}$. For $l=0$, of course, $j=\frac{1}{2}$.

Now, note that the spin-orbit and the relativistic energy corrections are both of order $(Z\alpha)^4$, or $(Z\alpha)^2$ times the zeroth-order energy.

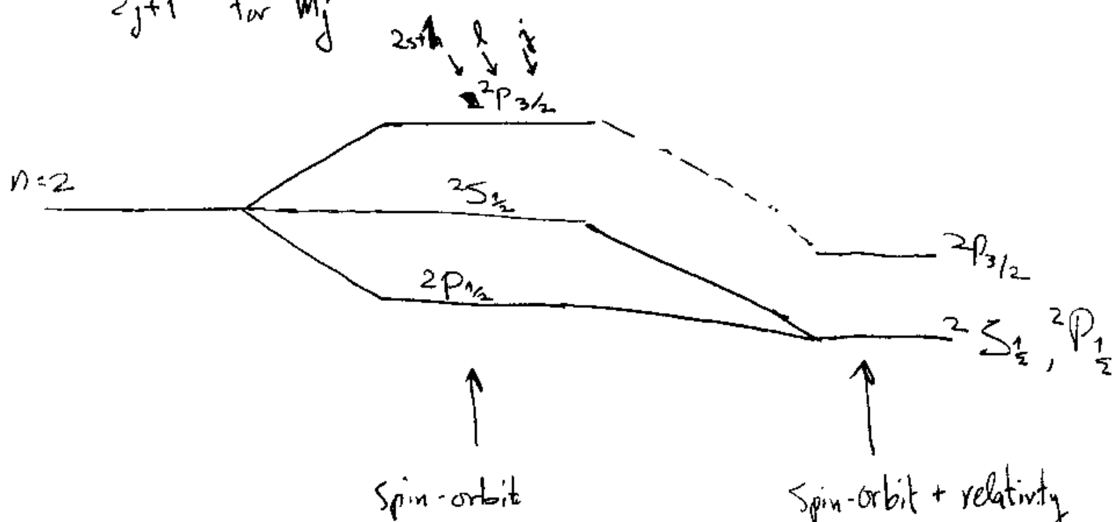
Note also that both perturbations are diagonal in the coupled basis! So we can combine the corrections for the full first-order fine structure energy:

$$E^{(1)} = -\frac{(Z\alpha)^4 mc^2}{2n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$$

To get this, look at relativistic correction and consider $l \to j+\frac{1}{2}$ and $l \to j-\frac{1}{2}$. This equation works in both cases! Note that degeneracy remains: l and m_j don't enter into the equation. Order of degeneracy is:

2 for l $(l = j \pm \frac{1}{2})$

$2j+1$ for m_j



Which agrees with experiment to order α^4.