Time Independent Perturbation Theory Contd.

Intrinsic Perturbations of the H atom

The eigenstates to the unperturbed hydrogen atom hamiltonian can be written as $|nlm_l m_s^{(e)} m_s^{(p)}>$ with $n \geq 1$, $0 \leq l \leq n-1$, $-l \leq m_l \leq l$, $m_s^{(e)} = \pm 1/2$ and $m_s^{(p)} = \pm 1/2$. These quantum numbers completely specify the state of the Hydrogen atom. Often, the proton spin and even the electron spin are suppressed when writing down these states, but they are of course always there implicitly. Ignoring the spin of the proton for now, we can label the eigenstates with

$$|nlm_l m_s^{(e)}>$$

In the following, we will discuss two additions to the hydrogen atom Hamiltonian:

Relativistic corrections
The kinetic energy $T_k \neq \frac{P^2}{2m}$, instead

$$T_k = \sqrt{m^2 c^4 + p^2 c^2} - mc^2$$

$$= mc^2 \left(\sqrt{1 + \frac{P^2}{m^2 c^2}} - 1 \right) = mc^2 (1 + \frac{P^2}{2m^2 c^2} - \frac{1}{8}\frac{P^4}{m^4 c^4} \ldots - 1)$$

$$\approx \frac{P^2}{2m} - \underbrace{\frac{P^4}{8m^3 c^2}}_{H_p}$$

This part of H_p is very small at normal velocities (it is suppressed versus the leading term in the kinetic energy by a factor $\frac{1}{4} v^2/c^2$).

LS Coupling
The electron has a magnetic moment $\mu = \gamma \mathbf{S}$ that interacts with the external magnetic field the electron "sees" in its own rest frame where the proton is moving (and, as any moving charge, will produce a magnetic field). This gives a second term due to interaction the angular momentum and spin of the electron as:

$$H_p = \frac{e^2}{2m^2 c^2 r^3} \mathbf{S_e} \cdot \mathbf{L_e}$$

The scalar product can be expressed as

$$\mathbf{S_e} \cdot \mathbf{L_e} = \frac{(\mathbf{S}+\mathbf{L})^2 - \mathbf{L}^2 - \mathbf{S}^2}{2} = \frac{\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2}{2}$$

If we rewrite the eigenstates in terms of eigenstates to $\mathbf{J}^2, \mathbf{L}^2, \mathbf{S}^2$, we can "automatically" diagonalize the perturbing Hamiltonian (and evaluate its matrix elements).

Total angular momentum:

$$\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2$$

For the electron $s = \frac{1}{2}$; $\mathbf{S^2}$ has eigenvalue $\frac{3}{4}\hbar^2$.

We rewrite the state in terms of eigenfunctions to $\mathbf{J}^2$ as

$$|nljm_j> \text{ with } \begin{cases} l & \text{orbital angular momentum quantum number} \\ j, m_j & \text{eigenstate to } \mathbf{J}^2, J_z \end{cases}$$

Rules for angular momentum addition:

$$j = \begin{cases} l + \frac{1}{2} \\ l - \frac{1}{2} & \text{if } l \geq 1 \end{cases}$$

So that

$$|n, l, j, m_j >= \sum_{m_l, m_s} < l, m_l, \frac{1}{2} m_s | j, m_j > |n, l, m_l, m_s^{(e)} >$$

The sum goes over all possible states that can contribute (only the ones for which the C.G.C are not zero, i.e. $m_j = m_l + m_s$).

Relativistic corrections to the hydrogen atom energies

The two relativistic additions to the Hydrogen wave function are a correction of the kinetic energy expression and spin orbit interaction.

$$H_p = -\frac{1}{8}\frac{p^4}{m^3 c^2} + \frac{e^2}{4m^2 c^2 r^3}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{L}^2)$$

with $\mathbf{L}_e.\mathbf{S}_e = \frac{\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{L}^2}{2}$

Kinetic Part

The correction to the kinetic energy can be rewritten as

$$-\frac{1}{8}\frac{P^4}{m^3c^2} = -\frac{1}{2mc^2}(\frac{P^2}{2m})^2$$

$$= -\frac{1}{2mc^2}(H_o + \frac{e^2}{r})^2 = -\frac{1}{2mc^2}\left(H_o^2 + \frac{H_o e^2}{r} + \frac{e^2 H_o}{r} + \frac{e^4}{r^2}\right)$$

This part of the perturbing Hamiltonian acts only on the radial part of the wave function (it is rotationally symmetric) and therefore only depends on the quantum numbers n, l. Therefore, we can pick either $|nlm_l m_s^{(e)}>$ or $|n, l, j, m_j>$ as our basis states. Out of laziness, we list them as $|n, l, m>$ below. Furthermore, for the same reason, this part of H_p is already diagonal in l and therefore we do not need to change the basis of eigenfunctions of the unperturbed hydrogen atom Hamiltonian.

Now,

$$H_o|nlm >= -Ry(\frac{1}{n^2})|nlm >$$

To calculate the change in energy to 1st order, we have to evaluate the following matrix elements:

$$< nlm|(H_o^2 + \frac{H_o e^2}{r} + \frac{e^2 H_o}{r})|nlm >= \frac{Ry^2}{n^4} - \frac{2Ry}{n^2} < nlm|(\frac{e^2}{r})|nlm >$$

and

$$< nlm|(\frac{e^4}{r^2})|nlm > .$$

Taking

$$< nlm|(\frac{e^2}{r})|nlm >= \frac{2Ry}{n^2}$$

(the expectation value for the potential energy is twice that for the total energy) we get for the total correction

$$= -\frac{1}{2mc^2}\left[-\frac{3Ry^2}{n^4} + < nlm|(\frac{e^4}{r^2})|nlm >\right]$$

Now we evaluate the last part, using a somewhat tricky "detour":

The Hamiltonian is written as

$$H_o = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)$$

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The solutions can be expressed in terms of the quantum numbers k, l, m with $n = k + l + 1$ - they are (associated Laguerre) polynomials of degree k multiplied with r^l and the angular momentum eigenstates Y_{lm}, with eigenvalues $E_{kl} = -Ry/(k+l+1)^2$. Now let's pretend that we can treat l like a continuous variable and ask the question "what happens if we increase l by a tiny amount λ?" First of all, the energy will change by an amount

$$\delta E_{kl} = \frac{\partial E_{kl}}{\partial l}\lambda = -2\frac{-Ry}{(k+l+1)^3}\lambda = 2\frac{Ry}{n^3}\lambda. \tag{1}$$

We can think of this change as being due to a change in the Hamiltonian itself,

$$H_0 \to H_0 + \delta H = H_0 + \frac{\partial H_0}{\partial l}\lambda = H_0 + \hbar^2\frac{2l+1}{2mr^2}\lambda \tag{2}$$

Using our knowledge about perturbation theory, we can therefore conclude that the change in energy, δE_{kl}, is the first order correction due to the "perturbing Hamiltonian" δH_0:

$$\delta E_{kl} = 2\frac{Ry}{n^3}\lambda = <nlm|(\delta H_0)|nlm> = \hbar^2\frac{2l+1}{2m}\lambda<nlm|\frac{1}{r^2}|nlm> \tag{3}$$

Therefore, we conclude that

$$<nlm|(\frac{e^4}{r^2})|nlm> = 2\frac{Ry}{n^3}\frac{2me^4}{\hbar^2(2l+1)} = \frac{4Ry^2}{n^3(l+\frac{1}{2})} \tag{4}$$

(note $Ry = me^4/2\hbar^2$).

We end up with

$$<nlm|H_p|nlm> = \frac{Ry^2}{2mc^2}(\frac{3}{n^4} - \frac{4}{n^3(l+\frac{1}{2})})$$

Fine Structure Part

Since the previous result does not depend on our choice for the basis states (as long as they are eigenfunctions to L^2), we can evaluate the second part of H_P by choosing the eigenstates $|n, l, j, m_j>$ which diagonalize the LS term and thus the complete perturbing Hamiltonian.

Let $|a> = |n, l, j, m_j>$

$$\mathbf{S}^2|a> = \hbar^2 s(s+1) = \frac{3\hbar^2}{4}|a>$$

$$\mathbf{L}^2|a> = \hbar^2 l(l+1)$$

$$\mathbf{J}^2|a> = \hbar^2 j(j+1)|a>; j = (l \pm \frac{1}{2})$$

For the case $l + \frac{1}{2}$

$$\mathbf{J}^2 = \hbar^2 (l + \frac{1}{2})(l + \frac{3}{2}) = \hbar^2 (l^2 + 2l + \frac{3}{4})$$

For the case $l - \frac{1}{2}$

$$\mathbf{J}^2 = \hbar^2 (l - \frac{1}{2})(l + \frac{1}{2}) = \hbar^2 (l^2 - \frac{1}{4})$$

And we have

$$2\mathbf{L}\mathbf{S}|a> = \hbar^2 l|a> \quad (\text{for } j = l + \frac{1}{2})$$

$$2\mathbf{L}\mathbf{S}|a> = \hbar^2 (-l - 1)|a> \quad (\text{for } j = l - \frac{1}{2})$$

To find the 1st order change in energy, we only have to calculate

$$< n, l, j, m_j | H_p | n, l, j, m_j >$$

The only thing that remains to figure out is the $\frac{1}{r^3}$ term and only n and l affect the matrix element of this term. I am running out of steam and simply quote the result (see Shankar's exercise 17.3.4 if you want to derive this yourself):

$$< n, l, j, m_j | H_p^{LS} | n, l, j, m_j > = \frac{e^2}{2m^2c^2} \frac{1}{a_o^3 n^3 l(l+\frac{1}{2})(l+1)} \times \frac{\hbar^2}{2} \begin{cases} l & \text{if } j = l + \frac{1}{2} \\ -(l+1) & \text{if } j = l + \frac{1}{2} \end{cases}$$

$$< n, l, j, m_j | H_p^{LS} | n, l, j, m_j > = \begin{cases} \frac{e^2}{4m^2c^2} \frac{\hbar^2}{a_o^3 n^3 (l+\frac{1}{2})(l+1)} & \text{if } j = l + \frac{1}{2} \\ -\frac{e^2}{4m^2c^2} \frac{\hbar^2}{a_o^3 n^3 l(l+\frac{1}{2})} & \text{if } j = l - \frac{1}{2} \end{cases}$$

For example, if $l = 1$, we get six degenerate eigenstates of H_0 for every value of n. After "turning on" the perturbation due to $L \cdot S$ coupling, we get 4 states with $j = 1 + 1/2$ which are raised in energy and 2 states with $j = -1/2$ which are lowered in energy by double that amount (so that the average energy is still the same as the unperturbed one).

Knowing that

$$a_o = \hbar^2/me^2; \quad Ry = \frac{me^4}{2\hbar^2} = \frac{mc^2\alpha^2}{2}; \quad \alpha = \frac{e^2}{\hbar c}$$

and replacing these into the constants for H_p we have

$$\frac{e^2}{4m^2c^2} \frac{\hbar^2}{a_o^3 n^3} = \frac{mc^2\alpha^4}{4n^4} n$$

for the LS term and

$$\frac{Ry^2}{2mc^2} \left(\frac{3}{n^4} - \frac{4}{n^3(l+\frac{1}{2})}\right) = \frac{mc^2\alpha^4}{8n^4}\left(3 - \frac{4n}{l+\frac{1}{2}}\right)$$

for the kinetic term.

Adding the 2 parts of the perturbing Hamiltonian we get

$$\frac{mc^2\alpha^4}{8n^4} \times \left(3 + 2n\frac{1 - 2(l+1)}{(l+\frac{1}{2})(l+1)}\right) = \frac{mc^2\alpha^4}{8n^4}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) \quad \text{for } j = l + \frac{1}{2}$$

This turns out to be the same as

$$\frac{mc^2\alpha^4}{8n^4} \times \left(3 + 2n\frac{-1 - 2(l)}{l(l+\frac{1}{2})}\right) = \frac{mc^2\alpha^4}{8n^4} \times \left(3 - \frac{4n}{j+\frac{1}{2}}\right) \quad \text{for } j = l - \frac{1}{2}$$

The total energy change due to both effects is thus

$$\frac{mc^2\alpha^4}{8n^4}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)$$

meaning it is still degenerate in l but depends on j.

We can see that the fractional change in energy is equal to

$$E_n \times \frac{\alpha^2}{n^2}\left(\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right)$$

which is suppressed by the (small) factor $\frac{\alpha^2}{n^2}$, which justifies that even to first order the perturbative approximation must be quite good.