Stationary State Perturbation Theory Examples PhL 2.9.09

I skipped all the examples while trying to focus on the complicated theory, but now it's time to look at these little examples. In retrospect, I think this was a very good way to proceed. I include the quasi section 13 here just since I skipped it the first time.

This is my last set of notes on Messiah's very excellent but not easy Chapter 16, and I have now read and annotated the entire chapter.

This chapter is the first in Messiah's Part Four on approximation methods, which begins with this quote: " If the dishes I offer you are badly prepared, it is less the fault of my cook that of the (food's) chemistry, which is still in its infancy". This from "The Roasting of Queen Pedauque" written in the 1800's by man of letters Anatole France (see online English text of this book). While the author was referring to the food of philosophy, Messiah is referring to the fact that the nice theoretical cuisine of QM is made problematic by the difficult details of doing actual calculations, "the chemistry", and such calculations he is hinting are still in their infancy. He was right in the sense that numerical work has certainly advanced since the 1960's, and no doubt so too have analytic methods.

CONTENTS

4. Ground state of He atom (p 690). 1
5. Coulomb Energy of Atomic Nuclei. (692). 1
7. Stark Effect for a Rigid Rotor. (695) 3
9. Atomic Levels in the Absence of Spin-Orbit Forces. (700) 4
10. Spin-Orbit Forces: LS and jj Coupling (700) 6
11. The Atom in LS Coupling: Splitting due to Spin-Orbital Coupling 6
12. Zeeman and Paschen-Bach Effects. 7
13. Symmetry of H and removal of degeneracy (709) 8
13. Quasi-degeneracy (711) 9

4. Ground state of He atom (p 690).

Consider a two electron atom in its ground state $(1S)^2$. We know the ground state to be just the product of identical simple expos about the same center, and then $\varepsilon_1 = \langle\varphi|V|\varphi\rangle$ which is (17). I skip details of the integral and accept (20) as the result. Then the table shows how good this simple first order SSPT really is for three different light 2-electron atom/ions. The starting state here is non-degenerate. The Coulomb interaction is repulsive of course, so the Coulomb perturbation raises the ground state energy in all cases. Accurate to on the order 2% or better.

5. Coulomb Energy of Atomic Nuclei. (692).

Preliminaries: Suppose $H_0|\varphi_i\rangle = E_i^0|\varphi_i\rangle$ and we list off all the states. Suppose some subset of these is degenerate and we say $H_0|\varphi_a,i\rangle = E_a^0|\varphi_a,i\rangle$ with degeneracy N. Suppose H_o is a rotational scalar, and suppose our only degeneracy is in the jm sense, so we have

$$H_0|jm,\alpha\rangle = E_j^0|jm,\alpha\rangle$$

and so N = (2j+1). These H_0 subspaces are orthogonal in that we know that

$$\langle j'm',\alpha'| H_0|jm,\alpha\rangle = 0 \qquad \text{if } j \neq j'$$

Even within one of the j subspaces, we know that

$$\langle jm',\alpha'| H_0|jm,\alpha\rangle = 0 \qquad \text{if } m \neq m'.$$

Now suppose V has this same symmetry! Suppose V too is a rotational scalar. Then we know that V cannot "link" states in different "subspaces" and for this purpose, we can think of jm and jm' as being different "subspaces" if m' ≠ m. Since neither H_0 nor even V can link these subspaces, each subspace is in effect a separate problem. The ε_1 energy correction is just going to be $\langle jm,\alpha|V|jm,\alpha\rangle$. In a true degeneracy problem, you have to solve $V|\varphi_i\rangle = \varepsilon_{1,i}|\varphi_i\rangle$ to find the right eigenkets because V in general wont be diagonal in your starting basis. But in this problem, V *is* diagonal in the starting basis if you use a jm type basis. So again, there is no problem computing $\langle jm,\alpha|V|jm,\alpha\rangle$. So the main point is that in a case like this, even though a subspace has 2j+1 degeneracy, with this kind of V we can just ignore the degeneracy and compute $\langle jm,\alpha|V|jm,\alpha\rangle$ which will be independent of m.

The problem. So we have V as shown in (21), which involves quantities r_{ij} = distances = rotational scalars, so V is a rotational scalar. Messiah uses the notation $|\Phi_\mu^j\rangle$ to mean $|j\mu,\alpha\rangle$ for a strong-interaction state of the nucleus. The hadronic system has a rotationally scalar H_0 and we know we can denote it's states in this manner, though we might normally use I for the total spin of the nucleus instead of j (if we were named Levitt). So on top page 693 we see our $\langle jm,\alpha|V|jm,\alpha\rangle$matrix element written out where he assumes N nucleons in the nucleus. Well, he really has this:

$$\Phi_\mu^j(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n)$$

$$\langle jm,\alpha|V|jm,\alpha\rangle = \int dr_1 dr_2 ... dr_N \, \Phi_\mu^{j*}(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n) \, \Sigma_{i<j} \, e^2/r_{ij} \Phi_\mu^{j*}(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n)$$

where there are N nucleons, but only Z of them are protons so the $\Sigma_{i<j}$ is over protons. And of course roughly $e^2 = \lambda$, our smallness parameter. If you swap two proton spatial indices, each wavefunction negates since Fermions, but we then have an overall plus sign, so the integrand $\Phi^*\Phi$ is totally symmetric in the spatial coordinates. This means that each term i,j will have the same result so just add them together. The number of terms is Z(Z-1)/2 which is ways to pick a pair, (Z,2) = Z!/(Z-2)! 2! . Then the one term is

$$\int dr_1 dr_2 ... dr_N \, \Phi_\mu^{j*}(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n) \, e^2/r_{12} \Phi_\mu^{j*}(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n)$$

$$= \int dr_1 dr_2\, e^2/r_{12} \int dr_3 dr_4 \ldots dr_N\, |\Phi^2| \equiv \int dr_1 dr_2\, (e^2/r_{12})\rho(r_1, r_2)$$

where ρ is the overall probability of find electrons 1 and 2 at positions r1 and r2. A Pauli violating approximation is to assume that this is ρ(r1)ρ(r2) and then ρ is uniform inside a sphere. But now we have the same integral form we had on page 691 but a different function for ρ(1,2). You do the integral as in (19) and get result (25), where R is the nuclear radius.

So this then is the claimed shift of the nuclear ground state energy when you "turn on" the Coulomb repulsion of the protons. Suppose you have two nuclei in the same hadronic state -- same number of nucleons, so (Z,N) in some spin state jμ. It seems reasonable to assume that if you flipped all the isospin states of all N nucleons, the ground energy should be the same, apart from the changed Coulomb interaction. So you could measure the ground state difference (Z,N) and (N-Z,N) maybe by some sort weak interaction decay that changes a proton to a neutron (measure energy of the emitted particles). Then you could compare this to $\varepsilon_1(Z,N) - \varepsilon_1(N-Z,N)$ from two Coulomb calculations. He says this works out in a reasonable way, but there is no reference. Note that j used above is real angular momentum, not isospin, even if you call it I.

7. Stark Effect for a Rigid Rotor. (695)

In this problem, $H_0 = \mathbf{L}^2/2I$ and this is the angular analog of the free particle $\mathbf{P}^2/2m$. It applies in the real world situation for molecules (say diatomic) where you can ignore vibrations because those levels might be widely spaced relative to the rotational levels. So in this problem, we imagine a diatomic molecule and it rotates and we ignore the vibrational levels, AND we assume it has an fixed electric dipole moment and we then slap the thing in a z-axis E field which is going to try to line up the dipoles. The E field is treated as a SSPT perturbation, and then this is a "Stark Effect" example (would be Zeeman for a B field situation, a completely different problem).

The first task is to solve the H_0 problem and the solution kets are $|\ell m\rangle$ with energies $E_\ell = (\hbar^2/2I)\ell(\ell+1)$ which is pretty obvious. Then take $V = -dE\cos\theta$ and then our perturbation theory efforts are going to involve matrix elements of the form $V_{\ell\ell'} = \langle \ell' m'|V|\ell m\rangle$. This is a 3D problem so we have the full ℓm to think about. But from a spherical tensor operator point of view, $V \sim z = r\cos\theta$ is (1,0) and then the Wigner-Eckhart theorem tells us at once that

$$\langle \ell' m'|\, z\, |\ell m\rangle = \langle \ell' m'|T^{(1,0)}|\ell m\rangle = (-1)^{1-\ell+\ell'}\, (2\ell'+1)^{1/2} \langle \ell' \,||\, z \,||\, \ell\rangle \langle 10;\ell m|\ell' m'\rangle$$

$$= \delta_{m',m}\, (-1)^{1-\ell+\ell'}\, (2\ell'+1)^{1/2} \langle \ell' \,||\, z \,||\, \ell\rangle \langle 10;\ell m|\ell' m\rangle$$

Next, parity tells us that $\langle \ell \,||\, z \,||\, \ell\rangle = 0$, so the only possible terms have $\ell' = \ell \pm 1$. The CG coefficient would also allow for $\ell' = \ell$ since it only knows about rotations, not parity. We are using the W-E theorem not to compute these matrix elements, but just to show that most matrix elements are 0.

Before continuing, we have to ask about the degeneracy situation again. Each level has $2\ell+1$ different values of m, so has degeneracy except for $\ell=0$. But just as in the first example above, states with different m values never couple (see WET above), so you can treat each one as an independent state. This says that you can ignore the $2\ell+1$ degeneracy and do this problem as if there were no degeneracy.

So the ε_1 matrix element $\langle \ell m|V|\ell m\rangle = 0$ right off the bat from parity.

The ε_2 formula is $\langle \ell m|VQ_{ao}V|\ell m\rangle$ as seen in (29) page 694 since all lower $\varepsilon_i = 0$. Normally such a sum is infinite in terms, going over the whole perp space, but here that sum becomes very finite:

$$\varepsilon_2 = \langle \ell m|V\Sigma_{\ell' \neq \ell\ m'}|\ell' m'\rangle\langle \ell' m'|V|\ell m\rangle/(E_\ell - E_{\ell'}) = \Sigma_{\ell' \neq \ell\ m'}\langle \ell m|V|\ell' m'\rangle\langle \ell' m'|V|\ell m\rangle/(E_\ell - E_{\ell'})$$

$$= \Sigma_{\ell' \neq \ell}\langle \ell m|V|\ell' m\rangle\langle \ell' m|V|\ell m\rangle/(E_\ell - E_{\ell'})$$

$$= \langle \ell m|V|\ell+1 m\rangle\langle \ell+1 m|V|\ell m\rangle/(E_\ell - E_{\ell+1}) + \langle \ell m|V|\ell-1 m\rangle\langle \ell-1 m|V|\ell m\rangle/(E_\ell - E_{\ell-1})$$

Messiah then plugs in for the energy denominators, and then uses the following fascinating result that I never saw before

$$\langle \ell m|\cos\theta|\ell-1 m\rangle = [\ (\ell^2 - m^2) / (4\ell^2-1)\ ]^{1/2}$$

where θ is a coordinate space operator, not a number! See separate notes on "spherical harmonics and C-G coefficients" for a detailed derivation of this result and of Messiah B.90. When the dust settles, we get ε_2 as shown in (34) page 697 and now we have some m-dependence (m^2) of the energy levels of our rigid rotor. So whereas we had $(2\ell+1)$ degeneracy when we start off, with the perturbation we end up with $\ell+1$ split-apart levels. The pair of levels with the same |m| stays degenerate. The splitting distance is proportional to m^2 and so is not even. This certainly has spectroscopy implications. You might make a Stark MRI machine and identify molecules by the spectrum splittings here which I would guess could be put in the RF range. I see nothing on the web about such a device. You would have to have E field gradients. Probably hard to make a very large E field and not kill the patient! You could only see rotations of polar groups.

9. Atomic Levels in the Absence of Spin-Orbit Forces. (700)

This is a dense action-packed little section. I went back and read the referenced section 14.12. The idea of the central field approximation is that you pretend each electron moves in a common potential created by all the electrons. This would then account for shielding. No formulas are given in that section for what potential you might use for this purpose. The Ham is then as shown page 701. It is just the sum of a Ham for each separate electron. For a multi-electron atom (ie, for atoms), you need to make one of those Slater Determinant things to make an overall solution wavefunction which has the right Pauli anti-symmetry properties, and this is discussed elsewhere in this book.

The exact potential for an atom is given by the first term in (40), while the central potential model is shown in A. The exact problem is insoluble he says back in 14.12. So now the perturbation theory idea is this: treat the difference between the exact and the central field model Hams as a perturbation which here he just calls V_1 . Then see where you can get with this! We are going to try to diagonalize V_1 and break the degeneracy that the central potential model usually gives.

Symmetry is a big issue here.

(1) both H and H_C are spin-invariant (since they don't even mention spins). This suggests that S^2 and S_z are good quantum numbers for state labeling. So: invariant under spin rotations. We are also invariant under normal rotations because everything in either Ham is a scalar. So this means L^2 and L_z can also be

labels, and finally J^2 and J_z can be labels as well, again, for either the full H or for H_C (and V_1 since it is the difference between these two). Write a state then as $|\gamma LSM_LM_S\rangle$ where γ is "other". We then know that

$\langle|\gamma L'S'M_L'M_S'|\ V_1|\gamma LSM_LM_S\rangle = \delta$ on all these labels as shown 702 A

For example, you could say $[L_3,V_1] = 0$, then sandwich around it and get

$(M_L' - M_L)\ \langle|\gamma L'S'M_L'M_S'|\ V_1|\gamma LSM_LM_S\rangle = 0$

so $M_L' = M_L$. But the other thing is that there is no dependence on these M_L values. I am always slow on the uptake on this. Here is a proof:

$a_+ \equiv L_+ / c_+ \qquad\qquad c_+ = \sqrt{\ell(\ell+1) - m(m+1)} \qquad\qquad$ //+ is that of m+1

$a_+^\dagger = L_+^\dagger / c_+ = L_-/c_+$

$a_+^\dagger a_+ = L_-L_+ / c_+^2$

$a_+^\dagger a_+|\ell m\rangle = L_-L_+|\ell m\rangle / c_+^2 = [\ \ell(\ell+1)-m(m+1)]\ |\ell m\rangle / c_+^2 = |\ell m\rangle$

So we then know that $a_+|\ell m\rangle = |\ell m+1\rangle$. Then

$\langle\ell m+1|V|\ell m+1\rangle = \langle\ell m|\ a_+^\dagger V\ a_+|\ell m\rangle = \langle\ell m|\ V\ a_+^\dagger a_+|\ell m\rangle = \langle\ell m|\ V|\ell m\rangle$

and that is why the matrix element is the same for any value of m. So, our reduced matrix element shown in A depends only on L and S.

Carbon atom example: put 2 electrons in the $2p^2$ there are (6,2) = 15 ways. All are allowed if one is spin up and one spin down. What can we do with our two electrons? Spin can be S=1 or S=0. Each has L=1, so can have L = 2,1,0 which in spectroscopic notation means D,P,S, so we get the 6 cases he lists off in B. We know S=1 is sym, and we know P is antisym. So ^{3}P is overall antisym. Notation $^{2S+1}$L sort of. The other two L values require S = 0, hence list is reduced to that shown in B. If we look at the degeneracy of each of the notations in B, we get 9+1+5 = 15.

Why is this the same as we got with our $\binom{6}{2} = 15$ count? Just saying there are 6 states already us making use of the Pauli Principle, because we only have 3 orbital P states and we are saying we can only put 2 into each of these to get 6. So the 15 here is a Pauli number, and we have merely reorganized that list to come up with linear combinations all of which are overall antisymmetric.

Now, since our two electrons don't *have* any other labels, a state is just $|LSM_LM_S\rangle$. We don't have to diagonalize in the $\gamma\gamma'$ sense implied by A, so he says we *are* diagonal therefore. For each item in the list C, we have a diagonal matrix element which is our ε_1 in effect. So things split into 9+5+1 degeneracy, starting off from all 15 being degenerate. That is to say, we expect to see 9+5+1 based on our symmetry arguments. Some of these could in theory be degenerate so you might have 9+6, say. But you could not possibly have 3+6+5+1, for example. So we use symmetry here to compute the expected degeneracy, then we have to actually install the H_0 wavefunctions to compute the exact ε_1 diagonal elements.

We have of course so far ignored the L•S spin orbit coupling which we know arises from the Dirac equation. This is evident looking at our (4) on page 701. So in what we have done to this point, we get for carbon the columns (a) and (b) of the figure. In this case Hund says triplet is more stable because S = 1 for 2 electrons is sym, so spatial is antisym and this keeps electrons apart and reduces the repulsion energy. For more than 2 electrons, this same Hund idea applies but you have to go look at D.18 for the Young Tableau discussion of how that all works.

To summarize: for carbon, we started with 15 degenerate states and used only symmetry arguments to show that the first order ε_1 splitting for our V_1 results in a 9+5+1 degeneracy situation. In theory we could have calculated the ε_1 . We found in this problem that V_1 was already diagonal, so we did not have to actually solve the level 1 EV problem. But this example does fit into degenerate SSPT section.

10. Spin-Orbit Forces: LS and jj Coupling (700)

Preliminaries. I am confused once again by the idea of $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Think of this as just a generic addition of two angular momentum operators like $\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$. My first question: is this plus sign even meaningful? And if so, what does it mean?

Well, this caused me to go off and write out all the gory details in " Addition of angular momenta.doc" which is stored in physics/angular momentum. I had to get into two different kinds of direct products (not so much direct sums), and I think I got it all nailed. In that write-up, at the end I give summaries of L-S and j-j coupling and I won't repeat them here.

The new (to me) idea is that you are first applying one perturbation in first order, and then to degenerate multiplets that survive that, you apply a second first order perturbation. It is as if you had two different smallness λ variables. In smaller atoms, one perturbation is stronger than the other and then L-S coupling is used. For very large Z, you have the reverse situation and j-j coupling works better.

This material is at the very heart of the field of interest called "atomic physics". You learn a great amount just from "the symmetries of the problem". It is this general notion that gets carried over into the newer field of "elementary particle physics" which I am supposed to know something about. You can see how far behind I am when I don't even know what $\mathbf{J} = \mathbf{L} + \mathbf{S}$ means in regular atomic physics.

The figure on page 703 shows the situation for carbon with two valence electrons, which is Messiah's case study in this section. The first perturbation V_1 without the spin stuff takes you from column (a) to column (b). Then the second perturbation V_2 takes you do column (c). The levels can in theory be computed using the approximation methods we are talking about in this chapter, and can also be measured experimentally by photon absorption and emission, modulo the usual "selection rules" for such.

Messiah is not diving way down into atomic physics details here. His main point is to show how you deal with the combination of perturbation theory and degeneracy, and this is the theory that he just presented in section 8.

11. The Atom in LS Coupling: Splitting due to Spin-Orbital Coupling.

This is mainly just a rehash of what we did in the last section and what I did in all my notes for LS. The main act here is to show that you can replace $\Sigma_i \mathbf{L}^{(i)} \bullet \mathbf{S}^{(i)}$ by $\mathbf{L} \bullet \mathbf{S}$ using a WET argument (Wigner Eckhart Theorem), if you are willing to add an overall unknown constant he calls A. This gives result (45) on page 705. Then from the usual formula we can compute the various matrix elements of V_2 (the spin orbit perturbation you apply second). We want to do this of course in our reorganized $|LSJM_J\rangle$ states and we get the result (46) on page 706, where A still appears. You would then have to go off to do some

actual calculation work to compute "A". Once you know its sign, you can know the ordering of the splittings in the right column of the figure. Formula (46) shows that larger J has larger positive energy and that is exactly what we see in the picture. In fact, the ratios of the splitting gaps should all be given by this formula (46). I remember something like this in the Levitt boom on NMR, but think it was something with the nuclear spin. Perhaps the very same idea.

12. Zeeman and Paschen-Bach Effects.

These "effects" are always done in perturbation theory, so apropo for Messiah to present them here.

Zeeman Effect. We start with the usual H' from BD page 13 which arises from the relativistic Dirac theory of the electron, but which also has a semi-classical derivation. We assume that we start with an atomic problem where we have some J multiplet he calls $|E_o JM\rangle$ of degeneracy (2J+1). The WET tells us (48) since both objects are "vectors" that J rotates, and this defines g, the Lande factor. Then we do our ε_1 calculation and at once get page 708 A, and we find that the degeneracy is fully split into a set of equally spaced levels, 2J+1 of them. You can compute g just from angular momentum fiddling, and the result is in (50), I did it all. We imagine first doing perhaps L-S coupling, so our states are really $|E_o LS\ JM\rangle$, so our J manifold is within some larger LS manifold, and that is where you get your L and S to put into the formula for g. So, our theory not only tells us that things are equally spaced, it tells us the exact amount of the spacing. We could apply this to the $^3P_2$ shown on page 703 figure, and our 5 levels would be split equally and we would have L=1 S=1 J=2 so g = 1 + (6+2-2)/(2*6) = 1 + 1/2 = 3/2 and the exact spacing would be $g\mu_B$ according to our theory here. In this section, the implication is that you do your LS process, and then treat the B field as a third perturbation smaller than everything in LS.

Paschen-Back Effect. If the B field is large, we treat the perturbations in this order:

1) V_1 2) then B field 3) then spin-orbit V_2 (usually ignored)

So this says we use the LS states that result from the V_1 perturbation alone, and then the B field perturbation calculation is totally trivial because we know how to take a matrix element of $L_z + 2S_z$ in the LS basis, and the result is that the splitting is $-\mu_B B (M_L + 2M_S)$. We could apply this to the ^3P sitting in our page 703 figure with its 9 degenerate states and L = 1 and S = 1. So what values do we get?

M_L	M_S	$(M_L + 2M_S)$
1	1	3
1	0	1
1	-1	-1
0	1	2
0	0	0
0	-1	-2
-1	1	1
-1	0	-1
-1	-1	-3

So we see in this case that our 9 states split into 1 + 1 + 2 + 1 + 2 + 1 + 1, so some degeneracy remains for the +1 and -1 values. (This may be an example of "accidental" degeneracy, I am not sure.)

You could now consider doing the spin-orbit perturbation to these results, and maybe you will split those two pairs of degenerate states. Messiah does not carry this out.

13. Symmetry of H and removal of degeneracy (709)

The general idea discussed here is that the full H has some smaller symmetry group than H_0. Let's look back now at some of the previously presented examples.

(1) In the Zeeman Effect, H_0 has SO(3) and representations are D^J of size 2J+1. When you turn on the B field which picks out a spatial direction, the full H in this case only has symmetry SO(2) which group has only 1-dimensional *irreducible* representations (see PDF on same). The SO(3) representation has kets |JM> of good quantum numbers, while the SO(2) has kets |M> where only M is "good". If you take a J representation of SO(3), it is irreducible with respect to SO(3), but it is reducible *with respect to SO(2*), that is Messiah's point here. What exactly does this mean? Suppose J = 1. It means this

$$D^{J=1}(SO3) = D(SO2) \oplus D(SO2) \oplus D(SO2)$$

My group theory is quite rusty right now, but I think the above is true. Now since H_0 has the full SO3 symmetry, the three SO2 representation shown above all have the same energy. That is, the |jm> kets have the same energy for all 2j+1 values of m. But under H which has only SO2 symmetry, the three representations on the right above can have (and in general will have) different energies, and the role that j plays in |jm> for SO3 is now played by m in |m> for SO2. \

(2) Here is a another example that is slightly different in nature. In the LS coupling plan, before V_2 is turned on, think of H_0 as including V_1. The states at this point are $|LS;M_LM_S\rangle$ which is representation $D^{L\otimes S}$ of SO3, and in *this* example this happens to be a *reducible* representation of SO3. H_0 is invariant under this reducible representation of SO3, so degeneracy is (2L+1)(2S+1). We know we write this as

$$D^{L\otimes S} = \Sigma_{\oplus}\, D^J \qquad \text{and } H_0 \text{ (at this point, which includes } V_1)$$

where the D^J are *irreducible* representations of SO3. But until V_2 is turned on, all these D^J submanifolds will have the same energy. When V_2 is turned on, the full H no longer has $D^{L\otimes S}$ symmetry, and has only D^J symmetry within each of the D^J submanifolds of $D^{L\otimes S}$, so now the individual D^J split apart in energy. I think you might say that before V_2 is turned on, we have SO(3) ⊗ SO(3) symmetry with generators being the L and S vectors. But after V_2 is turned on, we have only SO(3) with J as generator.

(3) Another example was the Stark rigid rotor. H_0 had SO(3) symmetry with L as generator vector. An electric field reduces you to SO(2), so this situation is similar to that of the Zeeman effect above. However, in this case the results still show some symmetry since ±m states are still degenerate. This means that the full H still has some residual symmetry, and that would be parity. Somehow the initial symmetry group is SO(3)⊗P for H_0 and the final group is SO(2)⊗P for the full H with E field turned on.

(4) Another example was our He atom on page 690. The H_0 has no r_{12} term so you might say it has the symmetry SO(3)⊗SO(3) with generator vectors L_1 and L_2 for the two electrons. When the r_{12} perturbation is turned on, the full-H symmetry is SO(3) with total vector L as generator. I think in this

example it was always assumed that S = 0 (orthohelium), so L and J are always the same, so we were able to simply ignore spin. Messiah only talked about the ground state which had no degeneracy to start with, so in this example we simply saw this ground state move up due to the r_{12} repulsion term. But you see it has the similar notion of "perturbation reduces symmetry and thus reduces degeneracy".

Three extra points that Messiah makes:

(1) The symmetry group of H is always a "subgroup" of the symmetry group of H_0.

(2) The reduced symmetry of the full H applies to all orders of perturbation theory.

(3) You might not *see* the expected degeneracy reduction in first or second order perturbation theory, but eventually you will see it at some order. In the Stark rotor, we had to go to second order to see it.

This section reminds me of what a carefully crafted book Messiah is! I pay a price for reading pieces of it out of order, but that is OK. Here all the examples previously presented are shown to fit into this generalized symmetry framework, for example, but that was not mentioned until the examples were duly presented with no mention of groups.

13. Quasi-degeneracy (711)

In the case that two subspaces of H_o with energies E_a^0 and E_b^0 are so close that perturbation theory makes no sense, there is a way to still do perturbation theory, and these manifolds are called "quasi" degenerate. You replace them with one manifold of the average of the two energies, but then you correct for this in the perturbation term where you then add to V what is shown in page 712 B. We know that V is small since we are doing perturbation theory, and the extra terms are also small because we assumed a and b were close together so the distance of each from the average E_α^0 is small.

Here is an example. In Paschen-Back above we had this batting order:

1) V_1 2) then B field 3) then spin-orbit V_2 (usually ignored)

You could think of this differently. Think of doing 1 and 3 together, but then you realize that the spin-orbit splittings are smaller than the B field perturbation, so you are in the quasi situation. So combine the spin-split states together with some average energy, then do the B field perturbation. But then when you are done, you should apply the spin-orbit perturbation correction along with the extra terms shown in B.

I think Saxon combines quasi into his 2-state degeneracy discussion from the start, which caused me some confusion when I was reading it.