**Stark/Zeeman Effect**

Let’s take a look at some examples,

**Stark Effect**

Let’s consider a Hydrogenic atom in an external electric field, **E** (if atom were part of substance, then this field would basically be the bulk interstitial field, i.e., the sum of the truly external field and the fields of the other N – 1 particles), not to be confused with energy eigenvalue E. Ignoring the relativistic effects we analyzed last time (or maybe presuming that the effect of the **E** field is bigger), the Hamiltonian would be:



where e is the absolute value of the electron charge. We found the eigenstates/values of Hatom to be:



and we’d like to calculate the perturbative corrections to these energy eigenvalues when we have this electric field present. The perturbative corrections are given by:



where n in this formula runs over all indices nℓmℓms, and En(0), |ψn(0)> are just the associated Hydrogenic energies and states. And V1 = e**E**·**r**. For point of application let’s focus on Lithium. It has 3 electrons. According to the central field approximation (later), each electron will feel a net potential of 3 protons + 2 other electrons. Thus the potential each electron feels is the same as a single hydrogen nucleus. And so at the most basic level, the states these electrons can occupy are just those of a hydrogen atom as well. Further, according to the Pauli-Exclusion principle (later too), the ground state can be approximated by filling these three electrons into the lowest energy states available to them. Thus the first two would go into the n = 1 shell. The second would go somewhere in the n = 2 shell. The central field approximation has more to say about where this electron would go, but to a good-enough level of approximation, let’s just say that it could go anywhere. This shell has two subshells s and p, and is all total 2 + 6 = 8-fold degenerate. We can ignore spin, though, since the V1 perturbation doesn’t interact with it. And so we’re effectively just 1 + 3 = 4-fold degenerate. So then work out the energy corrections we have to diagonalize V1 with respect to this degenerate subspace. So we need to calculate:



Without loss of generality, let’s say **E** = Ez**k**. Then we must calculate,



Many of these elements are zero. Recall discussion of parity:



So ℓ+ℓ´ must be odd. In our context that means ℓ and ℓ´ must be different or else it’s zero. But there are more zero elements than just these. Now consider the effects of rotational symmetry. Consider a rotation about the z-axis, by amount θ. Then we have:



Since this must be true for all θ, we must have mℓ = m´ℓ. So now we have just two (one) guys to calculate.



I’m not going to calculate it, but let’s just say it’s z0. Could probably use Time Reversal Symmetry arguments to prove that it’s a real number too? Then our 4×4 matrix is:



Definitely pays to use symmetry arguments to figure out what’s zero first. Eigenvalues are, expanding determinant along the bottom row:



These two eigenvalues will be two-fold degenerate each. So our new energy levels, within the n = 2 shell would be:



Won’t bother finding the new eigenstates. But we’d expect the two with lower energy to describe the electron orbit shifting against the field lines, and the ones with higher energy shifting along the field lines. The 2-fold degeneracy of each energy level probably is accounted for in the different ways the electron can traverse its orbit (CCW or CW). And this makes sense because since Lz operator commutes with z operator (implicitly implied by fact that z-rotation operator doesn’t change z), the eigenstates of V1 = eEzz ought to be eigenstates of Lz too. Seems like doing spectroscopy in an ambient electric field would provide a good way to measure electric field strengths.

**Zeeman Effect**

Now let’s consider the effect of a magnetic field on the energy levels. The Hamiltonian will now go to:



This is **A** would be the external **A** for an isolated atom; if its part of a substance, then the sum of whatever **A** external to the substance there is + the **A** due to the other N – 1 atoms. We worked this out somewhat when we analyzed the behavior of a free electron in a magnetic field. In that symmetric gauge file, we posited that:



which reduced our H to (using units with ℏ = 1):



(e is absolute value of electron charge) Oh I guess we also presumed **B** to be pointing in the z-direction. We’ll add spin to our electron, which will bring this to:



Typically ignore the diamagnetic term (proportional to B2) since we’re only going out to first order in B anyway (as mentioned elsewhere, I think we can be sure the B2 term is smaller because while small B would make x2 + y2 larger, in the free particle case, here we have a confining potential which precludes that, and so the B2 term should unequivocally get smaller), and just say:



But wait, Lz and Sz already commute with H­atom. So we know what these levels are. Energies are:



This formula is appropriate for relatively large magnetic fields (say above 1 T or so), which dominate the fine-structure corrections. In this context, this result is called the Paschen-Back correction. If the magnetic fields are weaker than this, then we should really use the fine-structure approximate eigenbasis to evaluate the magnetic field splitting. Okay so let’s include the fine-structure perturbation to H as well,



Approximate eigenstates of unperturbed H0 (including the fine structure corrections) are the |nℓsjmj> guys, which is degenerate w/r to the mj eigenvalue. So we need the linear combination of these guys which diagonalizes γ(Lz + gSz)B. Turns out it is still |nℓsjmj> so we’re good (will explicitly verify this to be true for our case below). So the first order correction to the energy would just be:



To evaluate this expectation, I think we need to use our result from the J-eigenfunctions file (s = ½):



(the top sign is for j = ℓ + s, the bottom for j = ℓ - s) Then filling this in, and allowing the matrix elements to be non-diagonal to see that non-diagonal elements will vanish:



So the elements are diagonal. And now proceeding with the diagonals.



So then our energies are:



So we can say,



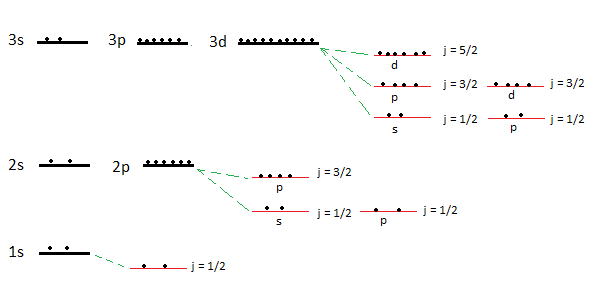
where gL is the Lande´ g-factor. There is another way to write gL, though, in a way which may be generalized to non s = ½ spin values. It is:



Can verify it’s the same for our case s = ½ at least.



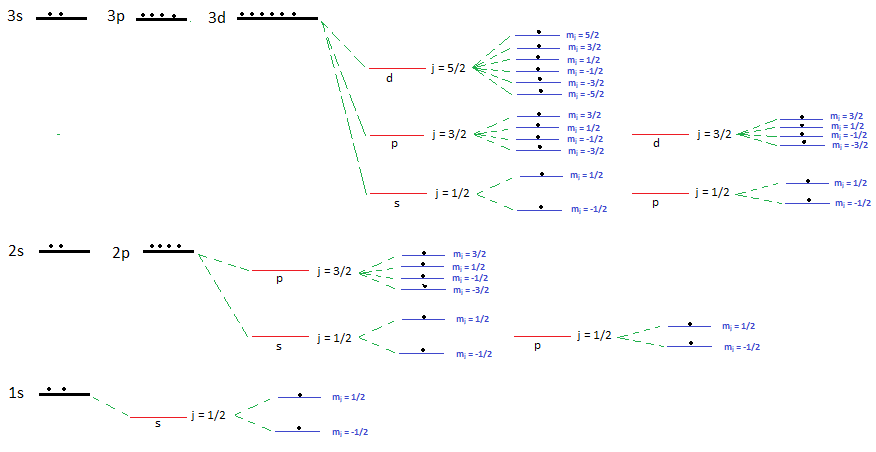
So it is the same. Going back to our energy levels in the fine structure file,



we see that degeneracy of our levels will be lifted – since even ones with same j values (but different ℓ’s) will have their degeneracy lifted because they have each different gL’s. The gL’s are:



And so our new picture would look like:



**Example**

Assuming we can still use first order perturbation theory, what’s the change in ground state energy of an electron in the ground state of a Hydrogen atom in a 1 T magnetic field? Note we’ll have to restore a factor of ℏ in the Zeeman effect term. So,



Well α = 1/137 or so, En(0) = -13.6 eV, and g = 2 about. So filling in our info,



(remember e is negative here) So the change in energy is roughly:

