**Stark & Zeeman Interaction**

Now I want to investigate the Hamiltonian of an atom in an electric and magnetic field. First I look at a single atom in such a field, and then generalize to a dielectric/dimagnetic material in such a field. Finally I’ll include the field in H as well.

**H for an Atom (in an external EM field)**

Going to start from a place a little more complicated than usual. Going back to the EM folder/Least Action principle file, we would see that the Hamiltonian for an atom’s electrons and EM field ….. all in an *external* field, is (e is negative for electron):



[this is kinetic energy of electrons in atom + interaction potential energy of electrons in atom + external potential energy of electrons in atom] where the sum is over all electrons in our atom (and we’re presuming nucleus is fixed for simplicity). And **A** = **A**b + **A**f, and **B** = **B**b + **B**f, where the subscript b stands for ‘bound charge’, i.e., the charges in the atom, while f stands for ‘free charge’, which are those responsible for the external fields. **A**f and φf would be considered known. Note that if we’re considering an atom which is within a dielectric or something, then the free charges would comprise all the charges, free or bound, that reside around and within all the other atoms in the dielectric. So Af, and φf, would be the bulk interstitial vector potential and electric potential respectively. We’ve also filled in the spin term, which is a quantum update not included in the original EM Hamiltonian. Now if we want H for just the particles, regardless of their associated fields, then we have to fill in what the fields are, in terms of the particles’ positions. But first a simplification: for an atom, we generally ignore the contributions of the electrons’ magnetic fields, as being insignificant next to their electric fields. So that means we can neglect **A**b and **B**b = ∇×**A**b. So,



Now we’ll recall from that same (EM folder – Least Action) file how we saw that ∫dτ Eb2 just reduces to the electrostatic potential energy between all the charges. So then we have:



(sum is over all electrons in atom) where **A**f is the external magnetic vector potential, φf(**r**) is the external electric potential, and V is the Coulomb potential (well first V is from nucleus, and second V is interelectron repulsion). Since the free fields typically vary spatially on a much larger scale than an atomic diameter, we can take the fields to be constant. In this case we can write:



So then we have:



includes the single particle potentials felt by each electron from the nucleus, as well as the interelectron repulsion. Guess I’ll subsume all the Coulomb potentials into a single VCFA(**r**).



This can be written as, keeping in mind we’re dealing with operators here, which don’t necessarily commute:



where ⊥2 is the position operator (squared) projected onto a plane perpendicular to **B** (for instance it’s 2 + 2 if **B** is in z direction). And in the last line, I used the property that **A**·(**B**×**C**) can be cyclically permuted – for scalars anyway. But it (evidently) works for these two non-commuting operators too. Have to verify this later, but it also worked out when we did the single particle in magnetic field earlier. So then we have:



So we have:



The first extra term models the paramagnetic response, where the net magnetic moment is trying to align with the magnetic field, and the second governs the usually weaker diamagnetic response, where the moment is trying to anti-align. Out to second order in Bf, we can say that the energy levels are (using perturbation theory):



where |n> is an eigenstate of the HDFA. Most of the time we’ll be interested in evaluating this for states |n> close to the ground state. Remember from the Hund’s Rules file, that the lowest lying states are given by Hund’s rule, and take the form |n> = |LTSTJTmJT>. Evaluating the matrix products between such states can be assisted with the Wigner-Eckert theorem. In this context it says,



(note primes on the right mJT) where



is the Lande´ g-factor. Not going to bother proving this g formula, but we did demonstrate it to be true for L (ℓ) arbitrary, and s = 1/2 in the Quantum Mechanics/Time-Independent/Zeeman file. There are proofs that don’t look too bad online. Okay, here’s the one in Ashcroft & Mermin. So consider following manipulations. We can write that expression above, and then dot both sides and sum over m´JT:



Now the <mJt´JT|**J**|JTmJT> matrix element is diagonal in JT, so we could extend the sum over the JT quantum numbers without cost, and write:



Now within the fixed LTST subspace the set of eigenstates spanning all JTmJT values is complete. So within this subspace, we can say,



Therefore, we have:



Now:



So now we can say,



This simplifies, filling in g = 2,



So there we go. Well with this in hand, now we can write,



(can’t replace LT + gST with gLJT in the second term unless |i> is one of |LTSTJTm´JT>, but it will typically also have different J´T values as well, which would invalidate that replacement) Anyway. If we can stop at first order in B, then we can say:



We’ll note that this is precisely the form of δEn that we got for the single atom, just with an updated g 🡪 gL. We’ll note that if the orbital is filled, or ½ filled -1 (like Carbon), then gL = 0 (or maybe just JT = 0, in which case allowed values of mJT are zero) , in which case there is only a diamagnetic response. Otherwise, we’ll get a paramagnetic + diamagnetic response. Usually the former is strongest.

**Physical Magnetic Dipole Moment**

As discussed in the free particle-in-magnetic field file (Quantum Mechanics/Time-Independent file), the *physical* magnetic dipole moment is,



(where γ = e/2m, **L**(phys)i = **r** × **v**phys(i) = **r** × (**p**-e**A**)/m). The second equality seems to depend on using the symmetric gauge. For instance, consider, for a single electron, and **B**f = Bf.



And the magnetic moment would be:



w/o spin, and with spin,



As can see, this matches up with -∂H/∂Bf for single particle, and will as well when we generalize to any number particle. We can also recognize the electric dipole moment operator,



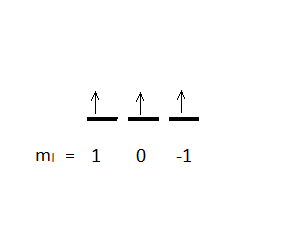
And so we *could* write this as:



For paramagnets (atoms where JT ≠ 0), we can usually neglect the r⊥2 term in the smallish B limit. An important implicit requirement for this is that as B shrinks (and thereby B2 shrinks below B), r⊥2 does not itself get larger. And it wouldn’t, thanks to the Coulomb potential coming from the atom’s nucleus. That should keep the electrons bound to the atom and r⊥ to around an atomic radius. But if the orbital is filled, or ½ filled -1, then JT = 0, in which case all mJT = 0, and in which case there is *only* a diamagnetic response. So it would certainly not be neglectable. This is the case for Carbon, for instance. Its diamagnetic response is the reason for frogs being suspended in magnetic fields. But we also cannot neglect the diamagnetic part of the dipole moment if we’re dealing with free electrons in a metal. That’s because as B2 << B, r⊥2 actually grows, because the free electrons in a metal are only held into any sort of orbit by the magnetic field itself, and so as it shrinks, the radius of their orbit increases. And so turns out that the diamagnetic contribution to the dipole moment is comparable to the paramagnetic contribution in the small B limit for a metal (technically just a clean metal, as if there are impurities present, then these the electrons can’t complete these large cyclotron orbits)

**Example**

What are the lowest lying eigenstates of, say, Phosphorus? Well, the electron configuration of P is [Ne]3s23p3. It’s got 15 electrons, including 3 in the 3p orbital, which we label as |n=3,ℓ=2,mℓms>. Then first 12 would fill the 1s, 2s, 2p, and 3s subshells/orbitals. Then the three electrons left would occupy the 3p subshell and would have quantum numbers ℓ = 1, s = ½. Max ST would be all spin up ST = 3/2. We can draw the suborbitals:



Max LT would 0. JT = 3/2, and then we have 4 mjT states left corresponding mJT = -3/2, -1/2, 1/2, 3/2. And this ground state multiplet would be termed 4S3/2. Taking the ground state of the atom to be E = 0, with the magnetic field turned off, the energy levels of these states would be:



where |n> = |LTSTJTmJT> is one of those states in the ground state multiplet.

We can work this out the expectation.



where,



We can take **J**T and **B**f to point in the z-direction. So this comes to:



where in the last line we restored a factor of ℏ that we need for units’ sake. In a 3T field, the lowest energy state would be:

