Physics 4261: Lectures for week 4

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4.1 Slater determinants

This week we are going to try to cover both the alkalis, and the LS coupling scheme. The order will be slightly different than the book. The first thing we are going to do is write down the Hamiltonian for a multi-electron atom.

$$\hat{H} = \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_i} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}.$$

The solution is going to be a wavefunction of the form,

$$\Psi\left(\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_N}\right).$$

Now, of utmost importance is that the wavefunction be antisymmetric with respect to exchange of any two electrons. Of course, spin exists, so we can have spatially symmetric but spin-antisymmetric wavefunctions too. We obviously have a big space of wavefunctions to look through, so it's helpful to make some approximations to make things easier. In fact, it's essential to do so. A particularly useful sub-class of wavefunctions are called Slater determinants, constructed as follows:

$$\Psi\left(\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_N}\right) = \det \begin{pmatrix} \psi_1(\mathbf{r_1}) & \psi_1(\mathbf{r_2}) & \cdots & \psi_1(\mathbf{r_N}) \\ \psi_2(\mathbf{r_1}) & \psi_2(\mathbf{r_2}) & \cdots & \psi_2(\mathbf{r_N}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r_1}) & \psi_N(\mathbf{r_2}) & \cdots & \psi_N(\mathbf{r_N}) \end{pmatrix}$$

These are essentially product wavefunctions, only with the correct symmetry enforced. In fact exchange of particles is a symmetry of the Hamiltonian. Supposing we ignore interactions between the electrons, we would get a ground state with the lowest N wavefunctions (again, counting spin), each with one electron. Then we have the famous "building up" principle of chemistry. This turns out to be a reasonable picture in some ways, but misses some other points.

4.2 Hartree-Fock method

How to proceed using a wavefunction composed of Slater determinants? The basic theoretical tool is called the Hartree-Fock method, and it is based on the variation method. It's kind of a chemist's thing, but we need to learn it anyway. As you recall the variational method is a technique to solve for approximated wavefunctions in a restricted space, by choosing the wavefunction with the minimum expectation value of the energy,

$$E_0^{\text{var}} = \min \langle \psi | \hat{H} | \psi \rangle \ .$$

Now clearly $E_0^{\text{var}} \geq E_0$. If ψ includes all possible wavefunctions, then the variational method will be exact. This can be shown with the calculus of variations. If ψ is restricted to Slater determinants, this leads to a set of self-consistent equations, which are best thought of iteratively.

Let's ask, what is the expectation of energy in the simple "building up" state ψ_B.

$$\langle \psi_B | \hat{H} | \psi_B \rangle = \sum_i E_i + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{<ij>} \langle \psi_B | \frac{1}{r_{ij}} | \psi_B \rangle \ ,$$

$$\langle \psi_B | \hat{H} | \psi_B \rangle = \sum_i E_i + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{<ij>} \int \int |\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + \text{exchange.}$$

Now we are considering the state ψ_1 variationally. It appears to see an "effective" potential, given by

$$V_{\text{eff}} = \frac{-Ze^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{e^2}{4\pi\epsilon_0} \sum_{i=2}^{N} \int |\psi_i(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} d^3r'.$$

In the full Hartree-Fock method, we would have to include a Slater determinant, and then we would generate additional terms, called the exchange energy, of the form,

$$E_{\text{exchg}} = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{<ij>} \int \int \psi_i^*(r) \psi_j^*(r') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i(r') \psi_j(r) d^3r d^3r'.$$

However, we are going to ignore those terms for now, in which case this potential is nothing more than the nuclear potential, plus the potential given by the other electrons, assuming them to be classical charge distributions. In a full Hartree-Fock, which we won't really do, we would start with the initial guess for the wavefunctions, say assuming no interaction. Then, we update the effective potential (and exchange terms) to include the charge of the other electrons, and re-solve for the new wavefunctions (which has to be done numerically as the modified potential is too difficult to do analytically). Then we put those update wavefunctions in to define a new potential, and iterate, and finally we hope it converges to some unique value.

4.3 Central-field approximation

Now, to make our lives even easier, we are going to simplify even more. We are going to say that the effective potential is a function of r only, so that the effective central-field potential has the form $V_{\text{CF}}(r)$. We can then easily define the central-field $E_{\text{CF}}(r) = \frac{\partial}{\partial R} V_{\text{CF}}(r) \hat{\mathbf{r}}$. We can make some observations about the central field. For small r, we have that

$$E_{\text{CF}}(r) \rightarrow \frac{Ze}{4\pi\epsilon_0 r^2} \hat{\mathbf{r}},$$

because there are no electrons really close to the nucleus. For large r, we have

$$E_{\text{CF}}(r) \rightarrow \frac{e}{4\pi\epsilon_0 r^2}\hat{\mathbf{r}},$$

because all of the electrons except this one are close in to the nucleus, so it just looks like an ion with charge $+e$. A huge benefit to the central-field is that we don't need to recompute angular eigenfunctions, we still get to use the $Y_{l,m}$! Therefore, we only need to worry about the radial equation, and we can still simply number the states with each value of l, so it still makes sense to talk about, for example, a $3d$ state in lithium.

4.4 The special thing about alkalis

Hydrogen had pretty simple wavefunctions, but for spectroscopy it's pretty awful, because the Lyman lines are all in the deep UV where air absorbs light and it's really difficult to make light. Furthermore, if I excite hydrogen, I can get "stuck" in the $2s$ states, because those are metastable. Another aspect is that the excited states can be ionized by absorption of Lyman α radiation. The alkalis from lithium onward, however, don't have any of these problems. By blocking the $1s$ state, the outermost electron has it's lowest state as $2s$, so there are no metastable states. Also, the $2p$ state lies less than half-way to ionization, so subsequent ionization is not an issue. This makes the alkalis everyone's go to atom for spectroscopy.

4.5 The quantum defect

A good rule of thumb for the alkali levels is to take the Rydberg formula, and simply add an offset to the principle quantum number n, called the quantum defect:

$$E(n,l) = \frac{-hcR_\infty}{(n-\delta_l)^2}.$$

The quantum defect roughly captures the effects of the inner electrons. Hence the dependence on l, as the higher l wavefunctions do not probe the region near the nucleus nearly as much. We can then define the effective quantum number $n^* = n - \delta_l$. This ends up in the range of 1.5 to 2 for the alkalis.

4.6 Spin-orbit coupling in alkalis

Because the alkali structure is so similar to hydrogen, the spin-orbit coupling can be computed in basically the same way. So we have $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, etc. To quantify the magnitude of the effect, recall that for hydrogen-like atoms the spin-orbit splitting is given by

$$\Delta E_{\text{s-o}} = \frac{Z^4\alpha^2 hcR_\infty}{n^3 l(l+1)}.$$

The modified form for the alkalis is

$$\Delta E_{\text{s-o,alkali}} = \frac{Z^2\alpha^2 hcR_\infty}{(n^*)^3 l(l+1)},$$

here, we made the same replacement of the quantum defect, and also we used the power Z^2 to interpolate between Z^4 dependence of the hydrogen-like ion (relevant near zero where the spin-orbit coupling is big), and Z^0 dependence of a singly-charge atom (relevant far away and useful to determine the energy).

4.7 Relative intensites

Since we are moving into some spectroscopy, let's consider a simple rule for transition strengths. This is to say that the total strength of all absorption or emission lines between two states is proportional to the degeneracy of the state. This comes from the fact that the strength in the non-spin orbit coupled case all these lines are the same, and the spin-orbit coupling is a weak perturbation (usually). So an equilibrium situation involves equal populations of all the m_j levels, and hence the total transition strength will be proportional to the degeneracy.

4.8 Angular momentum couplings

Imagine an atom with more than one valence electron (e.g. carbon). There are now two orbital angular momenta, **l**, $\mathbf{l}_1$ and $\mathbf{l}_2$, and two spins, $\mathbf{s}_1$, and $\mathbf{s}_2$. We need to figure out how to add all of these up to make the total angular momentum **J**. There are two basic ways: either add the orbital angular momenta to make **L**, and all spins to make. I will now attempt to motivate the interactions which lead to these couplings.

4.9 Spin interactions and LS coupling

Let's come back to the notion of the exchange interaction between a pair of particles:

$$E_{\text{exchg}} = -\frac{e^2}{4\pi\epsilon_0}\int\int \psi_1^*(r)\psi_2^*(r')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_1(r')\psi_2(r)d^3rd^3r'.$$

The minus sign comes from our Slater determinant, because we must be an a totally antisymmetric wavefunction with respect to Fermion exchange. However, we have to consider spin. In fact, if we have different spins, we can be in a totally anti-symmetric spin wavefunction, but a totally symmetric spatial wavefunction. For example,

$$|1s1s\uparrow\downarrow\rangle - |1s1s\downarrow\uparrow\rangle\ ,$$

is symmetric spatially and antisymmetric with spin. This configuration does not generate an exchange term, because the exchange flips the spin. We can also consider other states, like

$$|1s2s\uparrow\uparrow\rangle - |2s1s\uparrow\uparrow\rangle\ .$$

In this case, the spatial wavefunction is anti-symmetric, and the Pauli exclusion principal keeps the two identical spins apart. Of course we can also have

$$|1s2s\uparrow\downarrow\rangle - |2s1s\downarrow\uparrow\rangle\ ,$$

which has no exchange term. However, this is really a superposition of two states with opposite exchange integrals:

$$|(1s2s - 2s1s)(\uparrow\downarrow + \downarrow\uparrow)\rangle + |(1s2s + 2s1s)(\uparrow\downarrow - \downarrow\uparrow)\rangle$$

The point of all this is that the total spin of the system, **S**, matters. Similar arguments exist for the total angular momentum. For example, with two electrons in a d orbital, the interaction may depend on whether they are in states with the same value of m (for example, both in $m = 2$), versus one in $m = 2$ and the other in $m = 0$. Thus I expect **L**, the total orbital angular momentum operator, to matter. Absent any spin-orbit coupling, I therefore expect $\mathbf{L}^2$ and $\mathbf{S}^2$ to commute with the Hamiltonian, so that different values of S and L will give different energies. Now is when things are going to get really fun. Spin-orbit coupling does exist, but let's say it's small compared with the electrostatic terms. The spin-orbit Hamiltontian is

$$H_{\text{s-o}} = \beta_1 \mathbf{s}_1 \cdot \mathbf{l}_1 + \beta_2 \mathbf{s}_2 \cdot \mathbf{l}_2.$$

Now, to do perturbation theory we need to know the expectation of the operator $\mathbf{s}_1$ in the state **S**. It turns out, due to something called the Wigner-Eckart theorem, that the expectation value of any vector operator is proportional to the vector **S**, since this is the only vector that can be defined. Thus, prefactors aside, the two spin-orbit terms lead to just one proportional to $\mathbf{L} \cdot \mathbf{S}$. Here is the basic procedure to put everything together:

1. Figure out the configuration (i.e. $1s^2 2s^2 2p^1 3p^1$).

2. Figure out what the possible values of L and S are. In this case, we have L is the sum of two spin 1 particles, so $L = 0, 1, 2$. $S = 0, 1$.

3. Now couple the values of S and L to make J.

4. If the electrons are in the same state (i.e. $1s^2 2s^2 2p^2$), we need to figure out which combinations of L and S are allowed by the anti-symmetrization. I find it helpful to start with the largest possible value of L_z, the total angular momentum, and within that the biggest S_z. You can count total states and use the n choose k formula to find the total size of the Hilbert space. Then subtract out the configurations as you find them. So biggest is $L_z = 2$, which forces $L = 2$, $S = 0$. Then $L_z = 1$, which has four ways, one from $L = 2$ is used up by three more from $L = 1$, $S = 1$. Then finally $L_z = 0$, which has 5 ways, 4 we counted already, and the fifth must be $L = 0$, $S = 0$.

5. These states are represented by a term symbol ${}^{2S+1}L_J$, where L is usually a capital letter S, P, D, etc. So carbon has ${}^1D_2$, ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1S_0$, and these are pronounced "singlet D two", "triplet P two", etc.

4.10 The jj coupling scheme

In the previous, we coupled orbital angular momenta to make L before adding spin-orbit coupling because it was assumed spin-orbit is a weaker effect. This is true for light atoms but less so for heavy ones, and particularly for atoms in different sub-shells. Let's talk about the $nsnp$ configuration. If we did LS coupling, we'd have $L = 1$ obviously, and we'd have $S = 1$ or $S = 0$. So we'd have ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, and ${}^1P_1$. Now if we do jj coupling, we first add together spin and orbit in the s state, which leaves $j_1 = 1/2$. Then we have two values of j_2, namely $j_2 = 3/2$ and $j_2 = 1/2$. This gives us two states written as $(1/2, 1/2)$ and $(1/2, 3/2)$. The adding the total angular momentum gives $(1/2, 1/2)_0$, $(1/2, 1/2)_1$, $(1/2, 3/2)_1$, and $(1/2, 3/2)_2$. Note that there are always the same number of each J state, just in different terms! Also, note that the $(1/2, 1/2)_1$ and $(1/2, 3/2)_1$ both include some amount of spin singlet and triplet. This is important, as there is no perfect LS scheme, in reality all couplings fall somewhere in between the LS and jj limits, in the intermediate coupling scheme. So a little bit of ${}^1P_1$ can mix with ${}^3P_1$, which allows so-called intercombination transitions. Since electric dipoles do not affect spin, we cannot move between singlet and triplet otherwise. So, ${}^3P_1$ states have a weak intercombination transition, whereas ${}^3P_0$ and ${}^3P_2$ states are extremely long lived.

4.11 The interval rule

Back in the LS scheme, we finally add L and S together to make J. The value of the $\mathbf{L} \cdot \mathbf{S}$ term comes out as $2\mathbf{L} \cdot \mathbf{S} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2$. This can tell us about the spacing of the levels: level J is spaced apart from level $J - 1$ by an amount $J(J + 1) - (J - 1)J = 2J$. So the spacing between $J = 2$ and $J = 1$ is twice that between $J = 1$ and $J = 0$. This is called the interval rule. Note that it does not apply in the intermediate coupling scheme, so this is a way to check how well the LS coupling applies.

4.12 Hyperfine splitting

Thus far we have only considered the nucleus as being an electric charge. However, the nucleus also carries a spin, as does the electron. The nucleus interacts with the magnetic field by the formula

$$-g_I \mu_N \mathbf{I} \cdot \mathbf{B},$$

where $\mu_N = \mu_B m_e / M_p$, and g_I is a fudge factor that we leave to nuclear physicists to figure out. This moment can couple to the magnetic field produced by the electron. Let's make a simple estimation, assuming the nucleus is fixed. We have two ways to do this. For s states, we don't worry about magnetic field produce by the orbital angular momentum of the electron, and only worry about the electron's spin. In this case we consider only the region very near the nucleus, as the nucleus itself is extremely small. Considering the electron's wavefunction to define a magnetization density

$$\mathbf{M} = -g_s \mu_B \mathbf{s} |\psi(r)|^2.$$

Now, from E&M, we know that inside a uniformly magnetized sphere, we have a field $\mathbf{B} = 2/3\mu_0\mathbf{M}$. This same argument shows zero field in the empty region of a hollow sphere (analogous to, but not the same as, the zero field inside a hollow charged sphere). Thus, we get an electron field of

$$\mathbf{B}_e = -\frac{2}{3}\mu_0 g_s \mu_B |\psi(0)|^2 \mathbf{s},$$

leading to a hyperfine interaction

$$H_{\text{HFS}} = g_I \mu_N \frac{2}{3} \mu_0 g_s \mu_B |\psi(0)|^2 \mathbf{I} \cdot \mathbf{s}.$$

Now let's make some gestures in the direction of the case $l \neq 0$. In this case, the field of the electron can be computed from the formula,

$$\mathbf{B}_e = \frac{\mu_0}{4\pi} \left\{ \frac{-e\mathbf{v} \times \mathbf{r}}{r^3} - \frac{\boldsymbol{\mu}_e - 3(\boldsymbol{\mu}_e \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}}{r^3} \right\},$$

where the first term is the orbital magnetic field (Biot-Savart law) and the second term is the magnetic dipole of the spin. At this point, we wave our hands, and argue that all of these terms depend on μ_B and $1/r^3$, and the angular momentum, so we get some interaction (to do it right we would be doing some difficult angular integrals)

$$\begin{aligned} H_{\text{HFS}} &\propto g_I \mu_N \mu_0 \mu_B \left\langle \frac{1}{r^3} \right\rangle \mathbf{I} \cdot \mathbf{J}, \\ H_{\text{HFS}} &= A \mathbf{I} \cdot \mathbf{J}. \end{aligned}$$

With $l = 0$, we had $\mathbf{J} = \mathbf{s}$, so in fact the interaction will always involve $\mathbf{I} \cdot \mathbf{J}$. Like fine structure, we have a $1/r^3$ dependence, but we lack a dependence on the nuclear charge Z, instead depending on nuclear moment. Therefore, we expect a Z dependence instead of a Z^2 dependence. This is a pretty crude approximation, but something to keep in mind, and in general it's true that high-Z atoms have more hyperfine splitting. Note also that the interval rule should apply to hyperfine splitting, although interactions which are higher powers of $\mathbf{I} \cdot \mathbf{J}$ are also allowed if we consider quadrupolar nuclei.

4.13 Other nuclear effects

The nucleus has other small effects on the electronic structure. These sometimes lead to isotope shifts, for example between hydrogen and deuterium, but isotope shifts are present in nearly all species. One of these effects is of course the reduced mass effect. Another effect is nuclear size, which gives a small correction to the Coulomb potential at short range. For hydrogen, and highly charge hydrogen-like atoms, these effects can be quantified because exact results for transitions can be calculated.