Advanced Quantum Mechanics & Spectroscopy
(CHEM 7520)

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Week 10-11: Electronic spectroscopy of atoms and molecules

I. MANY-ELECTRON ATOMS: ELECTRONIC CONFIGURATIONS, ANGULAR MOMENTUM, SPIN

1) Now that we've discussed the foundations of electronic structure theory, we are in the position to apply this knowledge to electronic spectroscopy of atoms and molecules. We first turn our attention to the electronic structure of atoms. First, we refresh some results from the hydrogen atom problem. The ground-state electronic configuration of the H atom is $(1s)^1$. There are also unoccupied $2s$, $2p$, $3s$, $3p$, $3d$, etc orbitals. The H atom wavefunction is an eigenfunction of the one-electron orbital angular momentum operator $\hat{l}^2$, its projection along the axis of an applied external field $\hat{l}_z$, the one-electron spin operator $\hat{s}^2$, and its projection along the z-axis $\hat{s}_z$. This is a result of the fact that the Hamiltonian $\hat{H}$ commutes with $\hat{l}^2$, $\hat{l}_z$, $\hat{s}^2$, and $\hat{s}_z$. Thus, in addition to the principal quantum number n, each wavefunction is labeled using the l, m_l, s, and m_s quantum numbers. The quantum numbers satisfy the following property: $-l \leq m_l \leq l$ and $-s \leq m_s \leq s$. The H atom energy only depends on n. As a result, the $2s$ and $2p$ wavefunctions (or $3s$, $3p$, and $3d$) are energetically degenerate.

2) For the many-electron atoms, $\hat{H}$ no longer commutes with the one-electron operators $\hat{l}^2$, $\hat{l}_z$, $\hat{s}^2$, and $\hat{s}_z$, due to the presence of the electron-electron repulsion term. Instead, it commutes with the *total orbital angular momentum* operator $\hat{L}^2$, its *projection along the axis of an applied external field* $\hat{L}_z$, the *total spin* operator $\hat{S}^2$, and its *projection along the z-axis* $\hat{S}_z$. Thus, the wavefunction of a many-electron atom is an eigenfunction of all of these operators (in atomic units):

$$\hat{L}^2 |\Psi\rangle = L(L+1) |\Psi\rangle \tag{1}$$

$$\hat{L}_z |\Psi\rangle = M_L |\Psi\rangle \tag{2}$$

$$\hat{S}^2 |\Psi\rangle = S(S+1) |\Psi\rangle \tag{3}$$

$$\hat{S}_z |\Psi\rangle = M_S |\Psi\rangle \tag{4}$$

Hence, each atomic wavefunction can be labeled using the L, M_L, S, and M_S quantum numbers. As in the one-electron case, there is a similar relationship between these quantum numbers: $-L \leq M_L \leq L$ and $-S \leq M_S \leq S$. The $\hat{L}_z$ and $\hat{S}_z$ operators can be easily expressed in terms of the corresponding one-electron operators:

$$\hat{L}_z = \sum_i^N \hat{l}_z(i) \tag{5}$$

$$\hat{S}_z = \sum_i^N \hat{s}_z(i) \tag{6}$$

where the summation is performed over all N electrons. Expressions for the $\hat{L}^2$ and $\hat{S}^2$ in terms of $\hat{l}^2$ and $\hat{s}^2$ are more complicated.

$$\hat{L}^2 = \hat{L}_+\hat{L}_- + \hat{L}_z^2 - \hat{L}_z \tag{7}$$

$$\hat{S}^2 = \hat{S}_+\hat{S}_- + \hat{S}_z^2 - \hat{S}_z \tag{8}$$

where $\hat{L}_+$ and $\hat{L}_-$ ($\hat{S}_+$ and $\hat{S}_-$) are raising and lowering operators. Importantly, by making sure that $|\Psi\rangle$ is an eigenfunction of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$, we can greatly simplify the solution of the Schrödinger equation.

3) Our task now is to construct electronic wavefunctions for a given many-electron atom. We recall that any electronic wavefunction can be expanded in the basis of Slater determinants formed from a complete one-electron spin-orbital basis set. Thus, we will use Slater determinants to represent the atomic wavefunctions. For simplicity, we will assume that we always work with a complete one-electron basis set. Nevertheless, the results of our analysis will be applicable to finite basis sets as well.

4) Since $\hat{L}_z$ and $\hat{S}_z$ are just sums of the one-electron operators, any Slater determinant wavefunction is an eigenfunction of these operators. The corresponding eigenvalues are given as:

$$M_L = \sum_i^N m_{l_i} \tag{9}$$

$$M_S = \sum_i^N m_{s_i} \tag{10}$$

where m_{l_i} and m_{s_i} are the projections of the orbital angular momentum and spin along the axis of an applied external field for a spin-orbital ψ_i. Note that, in general, a Slater determinant is not an eigenfunction of $\hat{L}^2$ and $\hat{S}^2$. In fact, for many electronic states, the eigenfunctions of $\hat{L}^2$ and $\hat{S}^2$ are multi-determinant.

II. ATOMIC TERM SYMBOLS

1) In the absence of an external field, the energy of a many-electron atom depends on the total quantum numbers L and S and is $(2L+1)(2S+1)$-degenerate. It is convenient to represent each electronic state using a **term symbol**: ${}^{2S+1}L$, where $2S+1$ is the total spin multiplicity and L is the total orbital angular momentum labeled as S, P, D, F, G, ... for $L = 0, 1, 2, 3, 4, \ldots$, respectively.

2) An electronic configuration can correspond to one or several electronic states with specific L and S (i.e., term symbols). To determine the term symbols and the number of the $\hat{L}^2$ and $\hat{S}^2$ eigenfunctions, two rules can be used:
Rule 1: *For each Slater determinant with given values of M_L and M_S, there is an eigenfunction of $\hat{L}^2$ and $\hat{S}^2$ with $L \geq |M_L|$ and $S \geq |M_S|$.*
Rule 2: *The quantum number L satisfies the property: $L \leq \sum_i^N l_i$, where l_i are the orbital angular momenta of the individual orbitals $|\psi_i\rangle$. Similarly, for the spin quantum number we obtain: $S \leq \frac{N}{2}$.*

3) The simplest many-electron system is the helium atom. From the hydrogen atom energy level diagram, we expect the electronic configuration of the He atom to be $(1s)^2$. The electronic wavefunction can be expressed using a Slater determinant:

$$|\Psi_{\text{He}}\rangle = \mathscr{A}\,\psi_{1s}\alpha(1)\psi_{1s}\beta(2) \equiv \mathscr{A}\,1s\alpha(1)1s\beta(2) \tag{11}$$

For this wavefunction, $M_L = 0$ and $M_S = 0$. Note that the determinant $|\Psi_{\text{He}}\rangle$ is the only determinant that represents the $(1s)^2$ electronic configuration. Using the rules we stated earlier, we obtain: $0 \leq L \leq 0$, i.e. $L = 0$. For the spin, we obtain that $0 \leq S \leq 1$. Thus, the two possible term symbols for this electronic state are ${}^1S$ and ${}^3S$. However, according to rule 1, there is only one electronic state with $0 \leq S \leq 1$, since we were able to construct only one Slater determinant with $M_L = 0$ and $M_S = 0$. If this is the state with $S = 1$, there has to be a Slater determinant with $M_L = 0$ and $M_S = 1$. However, such Slater determinant ($\mathscr{A}\,1s\alpha(1)1s\alpha(2)$) is zero, due to the Pauli principle. We conclude that the Slater determinant $|\Psi_{\text{He}}\rangle$ corresponds to the state with a term symbol ${}^1S$.

4) For the lithium atom with electronic configuration $(1s)^2(2s)^1$, the wavefunc-

tion can be represented using two Slater determinants:

$$|\Psi_{\text{Li}}\rangle = \mathscr{A} 1s\alpha(1)1s\beta(2)2s\alpha(3) \qquad M_L = 0,\ M_S = \frac{1}{2} \tag{12}$$

$$|\Psi_{\text{Li}}\rangle = \mathscr{A} 1s\alpha(1)1s\beta(2)2s\beta(3) \qquad M_L = 0,\ M_S = -\frac{1}{2} \tag{13}$$

Since we only need $|M_L|$ and $|M_S|$ to determine term symbols, we don't need to consider the configuration with $M_L = 0,\ M_S = -\frac{1}{2}$. We observe that there is only one determinant with $M_L = 0,\ M_S = \frac{1}{2}$. The possible values of L and S are: $L = 0$; $S = \frac{1}{2},\ \frac{3}{2}$. Therefore, the possible term symbols are: ${}^2S$ and ${}^4S$. Since a determinant with $M_S = \frac{3}{2}$ is zero, we conclude that the only possible electronic state for the configuration $(1s)^2(2s)^1$ is ${}^2S$.

5) For all of the states that we've dealt so far, we were able to represent the electronic wavefunction using a single Slater determinant. From this analysis, we can expect that the Hartree-Fock theory works well for the ground states of the helium and lithium atoms. This is supported by the results from the full CI computations, which demonstrate that the electronic wavefunction is dominated by a single determinant.

6) We also note that the electrons that occupy closed electronic shells (e.g., $(1s)^2$) do not make non-zero contributions to M_L, M_S, L, and S. Therefore, when determining the term symbols, these closed electronic shells can be omitted from the analysis. This also suggests that atoms that have the same open-shell configurations and different number of closed-shell orbitals will have the same term symbols (i.e., $(1s)^1 \equiv (1s)^2(2s)^1 \equiv (1s)^2(2s)^2(2p)^6(3s)^1 \equiv \ldots$).

7) For the beryllium atom, the ground-state electronic configuration is $(1s)^2(2s)^2$. The electronic wavefunction can be represented using a single Slater determinant:

$$|\Psi_{\text{Be}}\rangle = \mathscr{A} 1s\alpha(1)1s\beta(2)2s\alpha(3)2s\beta(4) \tag{14}$$

Since there is only one determinant possible for this electronic configuration and all electronic shells are filled, the corresponding term symbol is ${}^1S$. In addition to this Slater determinant, the exact wavefunction of the Be atom has a significant contribution from the ${}^1S$ state arising from the excited-state electronic configuration $(1s)^2(2p)^2$.

8) For the boron atom, the ground-state electronic configuration is $(1s)^2(2s)^2(2p)^1$. The electronic wavefunction can be represented using the following Slater deter-

minants:

$$|\Psi_\mathrm{B}\rangle = \mathscr{A}[\mathrm{core}^4]2p_{+1}\alpha(5) \qquad M_L = 1,\ M_S = \frac{1}{2} \tag{15}$$

$$|\Psi_\mathrm{B}\rangle = \mathscr{A}[\mathrm{core}^4]2p_{0}\alpha(5) \qquad M_L = 0,\ M_S = \frac{1}{2} \tag{16}$$

$$|\Psi_\mathrm{B}\rangle = \mathscr{A}[\mathrm{core}^4]2p_{-1}\alpha(5) \qquad M_L = -1,\ M_S = \frac{1}{2} \tag{17}$$

In addition to these three determinants, there are three more determinants with $M_S = -\frac{1}{2}$. Using the rules we have discussed above, we obtain that these determinants correspond to the ${}^2P$ electronic state.

9) A quicker algorithm for determining term symbols can be formulated as follows:

(a) Determine the range of all possible L and S values using rule 2 as: $0 \le L \le \sum_i^N l_i$ and $0 \le S \le \frac{N}{2}$.

(b) Start with the largest M_S value. Decrease M_S until the smallest non-negative value. For each M_S value:

  i. Start with the largest M_L value. Decrease M_L until the smallest non-negative value. For each combination of M_L and M_S:

    A. Write all possible Slater determinants.

    B. Determine all possible term symbols using rule 1 for $L \ge M_L$ and $S \ge M_S$.

10) Using this algorithm, for the carbon atom in the ground-state $(1s)^2(2s)^2(2p)^2$ electronic configuration, we obtain the following term symbols: ${}^3P$, ${}^1D$, and ${}^1S$.

11) To determine which of these states is the ground state, we can use **Hund's rules**:
Hund's rule 1: *For a given electronic configuration, the term with the largest spin multiplicity* ($2S+1$) *has the lowest energy.*
Hund's rule 2: *For the specific spin multiplicity, the term with the largest L has the lowest energy.*
Note that Hund's rules generally hold for the ground-state electronic configuration, but are often violated for the excited-state configurations.

12) We can predict the energy ordering for the states of the carbon atom arising from the $(1s)^2(2s)^2(2p)^2$ electronic configuration as: ${}^3P < {}^1D < {}^1S$.

13) The above algorithm can be used to determine the term symbols when electrons occupy the same electronic shell. If an electronic configuration contains two open electronic shells, two electrons occupying two different shells cannot occupy the same spin-orbital. In this case, we do not need to worry about the Pauli principle and can use rules for adding angular momenta to determine the term symbols. The rules state that *two systems with angular momenta* L_1*,* S_1 *and* L_2*,* S_2 *couple to a system with L and S defined by the following equations:* $|L_1 - L_2| \leq L \leq (L_1 + L_2)$ *and* $|S_1 - S_2| \leq S \leq (S_1 + S_2)$.

14) As an example, consider electronic configuration $(2s)^1(2p)^1$. The first shell $(2s)^1$ gives rise to the term symbol ^2S. The second shell corresponds to ^2P. Using the rules for adding angular momenta: $^2S \otimes {}^2P = {}^1P \oplus {}^3P$.

15) Evaluation of term symbols for electronic shells that are more than half-filled can be simplified by taking advantage of the *particle-hole equivalence*. The following electronic configurations have the same term symbols: $(s)^n \equiv (s)^{2-n}$, $(p)^n \equiv (p)^{6-n}$, $(d)^n \equiv (d)^{10-n}$, etc.

III. SPIN-ORBIT COUPLING, SELECTION RULES IN ATOMIC SPECTROSCOPY

1) We discussed that an electronic configuration corresponds to, in general, multiple states characterized by specific values of L and S. Each value of L is the result of the coupling of the electrons' orbital angular momenta. Similarly, each value of S is the result of the coupling of the electrons' spin angular momenta. Since S and L are just two different types of angular momenta, they can couple too. This interaction (known as spin-orbit coupling) is much weaker, but it can be observed in the experiment and becomes stronger for heavier elements.

2) When $\hat{L}$ and $\hat{S}$ couple, their quantum numbers are no longer good quantum numbers. When spin-orbit interaction is not too strong, we can describe it using the so-called L-S coupling scheme (or Russell-Saunders coupling scheme). In this scheme, we introduce the **total angular momentum operator** $\hat{J}$ and its quantum number J. For given L and S, the possible values of J are: $|L - S| \leq J \leq (L + S)$. As a result of the spin-orbit coupling, the electronic energy depends on the values of J. This gives rise to splitting of the terms characterized by the ^{2S+1}L symbols into **levels** characterized by the $^{2S+1}L_J$ symbols.

3) The energy ordering of the levels can be predicted using the third Hund's rule:

Hund's rule 3: *For a given term $^{2S+1}L_J$, in an atom with a half-filled subshell or less, the level with the lowest value of J lies lowest in energy. If the shell is more than half-filled, the level with the highest value of J is lowest.*

4) What are the selection rules in the absorption spectra of many-electron atoms? They are governed by the the conservation of the angular momenta. Recall that a photon carries one unit of angular momentum. As a result, the allowed electronic transitions in many-electron atoms should satisfy the following requirements (dipole approximation):

- Must involve one electron that must change its orbital angular momentum $\Delta l = \pm 1$. Thus, electronic transitions between terms corresponding to the same electronic configuration are not dipole-allowed.
- Must not change the total orbital angular momentum by more than one unit: $\Delta L = 0, \pm 1$.
- Must not change the total angular momentum by more than one unit: $\Delta J = 0, \pm 1$.
- Must not change the total spin: $\Delta S = 0$.

There are some exceptions to the selection rules listed above:

- Transitions between $L = 0$ and $L' = 0$ are not allowed.
- Transitions between $J = 0$ and $J' = 0$ are not allowed.
- As the spin-orbit interaction increases, the spin selection rule ($\Delta S = 0$) becomes less firm.