Spectroscopic terms

I. Consider Phosphorus.

1. What is its electronic structure?
2. How much microstates does it have?
3. Write the microstates possible $|M_S, M_L>$ pairs.
4. What is the fundamental state? The next excited states?

Consider now the spin-orbit coupling.

5. Write the fundamental state. The first exited state.
6. Place all states on an energy diagram knowing that the spin-orbit coupling constant is $103 cm^{-1}$.
7. Can you draw a conclusion on the population of these states at room temperature?

II. Do the same analysis for cobalt +II ($\zeta = 500\ cm^{-1}$), iridium +III ($\zeta = 4000\ cm^{-1}$), europium + III ($\zeta = 1300\ cm^{-1}$), thulium +II ($\zeta = 1200\ cm^{-1}$) and uranium + V ($\zeta = 1900\ cm^{-1}$).

Note: $\zeta = \lambda/2S$

The crystal field typical values are given as follow.

Cobalt: between 20 000 and 40 000 cm^{-1}.

Iridium: between 5000 and 10 000 cm^{-1}.

Europiu : between 500 and 750 cm^{-1}.

Thulium: between 500 and 750 cm^{-1}.

Uranium: between 1000 and 2000 cm^{-1}.

III. Conclude on the fundamental state and the first excited states in presence of ligands around the metal center.

1. For each of the following configurations, construct a microstate table and reduce the table to its constituent free-ion terms. Identify the lowest-energy term for each.

a. p^3

b. p^1d^1 (as in a $4p^1\ 3d^1$ configuration)

2. For each of the lowest-energy (ground state) terms in problem 1. , determine the possible values of *J*. Which *J* value describes the state with the lowest energy?

3. An excited state of calcium has the configuration [Ar]$4s^13d^1$. For an s^1d^1 configuration, do the following:

a. Prepare a microstate table, showing each microstate.

b. Reduce the table to its free ion terms.

c. Determine the lowest-energy term.

4. The outer electron configuration of the element cerium is d^1f^1 . For this configuration, do the following:

a. Construct a microstate table.

b. Reduce this table to its constituent free-ion terms (with labels).

c. Identify the lowest-energy term (including *J* value).

5. There is such a thing as an s^1f^1 configuration! This can occur, for example, in an excited state of a Pr^{3+} ion. For an s^1f^1 configuration, do the following:

a. Construct a microstate table, showing clearly the relevant quantum numbers of each electron in each microstate.

b. Reduce this table to its constituent free-ion terms (with labels).

c. Identify the lowest-energy term (including *J* value).

6. For each of the following free-ion terms, determine the values of *L*, M_L, *S*, and M_S:

a. $2D$ (d^3)

b. $3G$ (d^4)

c. $4F$ (d^7)

7. For each of the free-ion terms in Problem 6. , determine the possible values of *J*, and decide which is the lowest in energy.