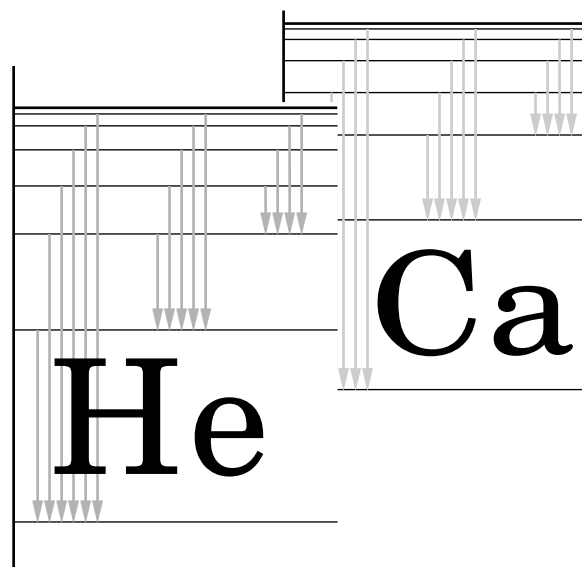


THE SPECTRUM OF HELIUM AND CALCIUM



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by
J. H. Hetherington

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Input Skills:

1. Explain the shell structure and electronic configuration of atoms (MISN-0-318).
2. State the $\Delta\ell$ and ΔJ selection rules for atomic transitions (MISN-0-314).

Output Skills (Knowledge):

- K1. Vocabulary: fine structure, spin singlet state, spin triplet state.
- K2. Sketch the energy level diagram for He (for one excited electron) and draw in the allowed transitions.
- K3. Sketch the energy level diagram for Ca (for one excited electron) and draw in the allowed transitions.
- K4. State the ΔS selection rule for atomic transitions.

Output Skills (Rule Application):

- R1. Given the electronic configurations for two inequivalent electrons, determine all possible states and write them in spectroscopic notation.
- R1. Sketch the energy level diagram for a given two-valence-electron atom (for one excited electron only) and draw in the allowed transitions.

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J. H. Hetherington

1. Introduction

A very satisfying aspect of the quantum theory of atoms is the rather complete classification of all the energy levels of atoms. From this we have a rather detailed understanding of the otherwise bewildering spectral lines that characterize each element.

This particular unit concerns atoms with two valence electrons. To a low approximation the two electrons can independently occupy Hydrogen-like levels. There are important differences from the hydrogen levels, however. First, the charge on the nucleus is different, and second, the electrons do interact to some extent, and, most importantly, the Pauli exclusion principle places restrictions on the quantum numbers of the two-electron states that can exist. allowed quantum numbers. requires that the two-electron state be antisymmetric under interchange of the two electrons.

2. Symmetries

2a. The Pauli Exclusion Principle. The Pauli exclusion principle says that only those states can exist which are antisymmetric under interchange of the two electrons. if the state stays the same when you exchange the two electron electrons, then it is “symmetric.” If the state changes sign when you exchange the two electrons, then the state is “anti-symmetric.” Thus exchange of the two electrons has the effect of multiplying the state by +1 if the state is symmetric, and multiplying it by -1 if the state is antisymmetric.

The Pauli principle “explains” why electrons cannot overlap in space and thus let all matter collapse. Although there are more sophisticated ways of expressing this principle, it stands by itself as an addendum to the other rules of quantum mechanics.

2b. Spin and Position. When you exchange one electron for the other you must exchange both their positions and their spins. In fact, the two-electron state is a product of the space and spin descriptions of the

two electrons and you can exchange their positions and spins separately! If exchanging their positions gives +1, then exchanging their spins must give -1 so that exchanging both produces a product that is -1. That is the requirement of the Pauli Exclusion Principle.

We conclude that a state which is symmetric under exchange of the electrons’ positions must be anti-symmetric under exchange of their spins. Similarly, a state which is anti-symmetric under position exchange must be symmetric under spin exchange.

2c. Spin Symmetries. When the both electrons have $m_s = 1/2$, we write the state as $\begin{pmatrix} 1 & 1 \\ 2 & 2 \end{pmatrix}$ or, more succinctly, as $(\uparrow\uparrow)$. When the first electron has $m_s = (1/2)$ and the second has $m_s = -1/2$, we write the state as $(\uparrow\downarrow)$. Then there are three *symmetric* spin states:

$$S = 1, M_S = +1: (\uparrow\uparrow)$$

$$S = 1, M_S = 0: \frac{1}{\sqrt{2}} [(\uparrow\downarrow) + (\downarrow\uparrow)]$$

$$S = 1, M_S = -1: (\downarrow\downarrow)$$

These are called the “triplet” states of two electrons because there are three of them. There is one *antisymmetric* spin state:

$$S = 0, M_S = 0: \frac{1}{\sqrt{2}} [(\uparrow\downarrow) - (\downarrow\uparrow)]$$

and of course this is called the “singlet” state of the two electrons. The two square roots of 2 are needed only for making numerical calculations, so they need not concern you here.

▷ In each line above, exchange the spin of electron 1 with the spin of electron 2 everywhere in that line. See for yourself that each line is either symmetric or anti-symmetric under the exchange.

2d. Space Symmetry. Each of the two electrons can have an ℓ value that is any integer, so the total L can also be any integer. States with even L are symmetric in exchange of the electrons’ positions, while states with odd L are antisymmetric. Thus the symmetric states are, in spectroscopic notation: S, D, G , etc. The anti-symmetric states are: P, F , etc.

2e. Combining Space and Spin. Since even- L states of two electrons are symmetric, the electrons' spins must be in the antisymmetric state:

$$L = 0, S = 0$$

$$L = 2, S = 0$$

...

while for odd- L states the spins must be in a symmetric state:

$$L = 1, S = 1$$

$$L = 3, S = 1$$

...

3. Helium

3a. Helium and the Pauli Principle. In the case of helium the nuclear charge is $+2e$ which makes the levels have lower energy than they would have in hydrogen.

When Helium is in the ground state both electrons are in the $1S$ state ($n = 1, \ell = 0$). Since both have $\ell = 0$, total $L = 0$. Thus the state is symmetric under position exchange and hence is anti-symmetric under spin exchange: $S = 0$.

3b. He Energy Level Diagram. In Fig.1 the ground state corresponds to both electrons being in the $2s$ state (s^2 configuration). As noted above, the Pauli exclusion principle does not allow more than one such level. And it must be the $S = 0$ combination of the two spins of the electron.

The lowest two of the excited states in Fig.1 are both of the $1s2s$ configuration. Since the two electrons are inequivalent, i.e. they are in different states of n and/or ℓ , the Pauli principle allows their spins to combine into either $S = 1$ or $S = 0$. Because there is a selection rule $\Delta S = 0$ (which is not completely rigorous as we will see below), these levels (singlet, i.e. $S = 0$, and triplet, i.e. $S = 1$) are separated on the energy level diagram since only a few spectral lines result from transitions from triplet to singlet or *vice versa*.

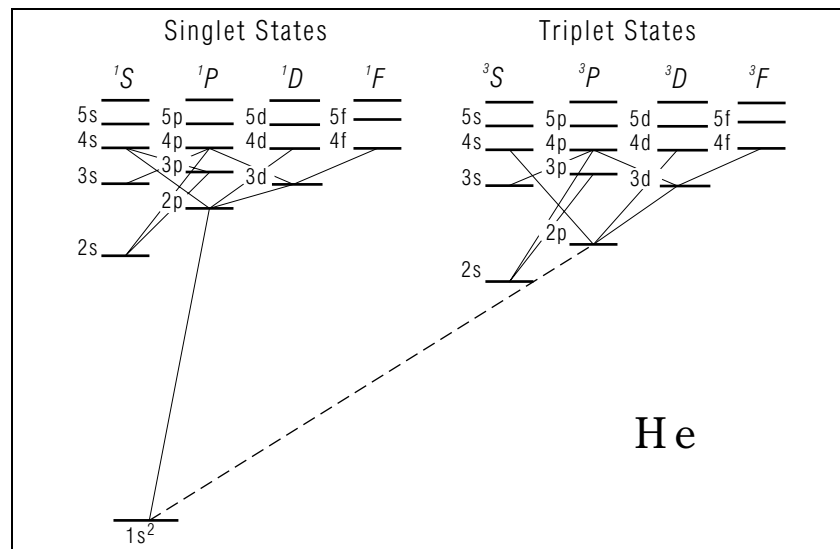


Figure 1. Some energy levels of He, with an allowed and a forbidden transition to the ground state.

3c. Fine splitting. The 3P levels in Fig.1 are actually each split into three levels because $S = 1$ can add to $L = 1$ to give total angular momentum $J = 0, 1, 2$. Similarly, the 3D levels are split into three levels with $J = 1, 2, 3$. The 3S levels, even though they are called “triplet,” are not split in this way because $S = 1$ can add to $L = 0$ in only one way, and gives $J = 1$. In the same way, all the singlet levels are unsplit because $S = 0$ adds to L to give only one J , which is $J = L$.

You should determine all the possible J subscripts that can be applied to the spectroscopic notation heading the various columns of Fig. 1.

3d. Electromagnetic translations. Note that in Fig.1 electromagnetic transitions are shown by lines connecting different levels. The $\Delta L = \pm 1$ rule and the $\Delta S = 0$ rule are compatible with all of the lines shown except for the dashed line from the 2^3P level to the 1^1S level. This dashed line violates $S = 0$ but a high concentration of atoms in this level (although it is not the lowest level of the triplet states, many atoms excited to a higher triplet level decay to this state by allowed transitions shown on the diagram), and the large energy available for the decay (transition rate depends on the difference in energy levels in the transition), overcome the prohibition given by the $\Delta S = 0$ rule, which is not absolute

anyway.

3e. Collisional De-excitation. It is interesting to ask how an atom that reaches the 2^3S level of He can ever be de-excited. Will it remain in that state forever? No, because in a gas the atom will bump into other atoms and it can deexcite by converting its stored energy into kinetic energy of motion of the two atoms. Note that He in this state should be quite chemically active until it returns to the ground state.

4. Calcium

4a. Spectrum of Ca. Another atom with two electrons in a closed s -shell is calcium. As one would expect from its greater chemical reactivity, the lowest excited states of Ca are substantially lower than the lowest excited states of He. [For example, the 2^3S level of He is at 19.8 eV compared to the lowest level of Ca, 4^3S , at 1.88 eV.] The spectrum of Ca is somewhat similar to that of He in that singlet and triplet excited systems exist. In addition, in calcium we have bound states where both of the s electrons are excited. In Figure 2 we show an energy level diagram of Ca.

4b. Singlet states. Look at the first four columns of Fig. 2. They are labeled 1S , 1P , 1D , 1F , respectively. These are levels where one electron is in the $4s$ state and the other electron is in some other state with the spins adding to zero angular momentum, $S = 0$. The ground state is among these levels and is at the bottom of the first column. It has two electrons in the $4s$ state ($4s^2$). [The “core” electrons, i.e. those filling the $1s$, $2s$, $2p$, $3s$, $3p$ levels, are ignored because a great deal of energy would be required to remove these electrons and no important excited states of un-ionized Ca involves this kind of excitation. However, the x -ray spectrum of Ca would involve ionized (usually) Ca with one electron removed from the core. We will not be concerned with core excitations in this unit.]

4c. Energy units. The vertical axis in Fig. 2 is in units of 10^{-3} cm^{-1} ; if you wish to translate this into electron volts, merely multiply the vertical coordinate by 0.124. For example, the 1.88 eV mentioned above, when divided by 0.124, is 15.2 — which is about the location of the lowest excited state in Fig. 1.

4d. Triplet states. The second four columns of Fig. 2 are labeled 3S , 3P , 3D , 3F , respectively. These are the triplet states, and are analogous to the singlet states but with $S = 1$. Note that there is a triplet state

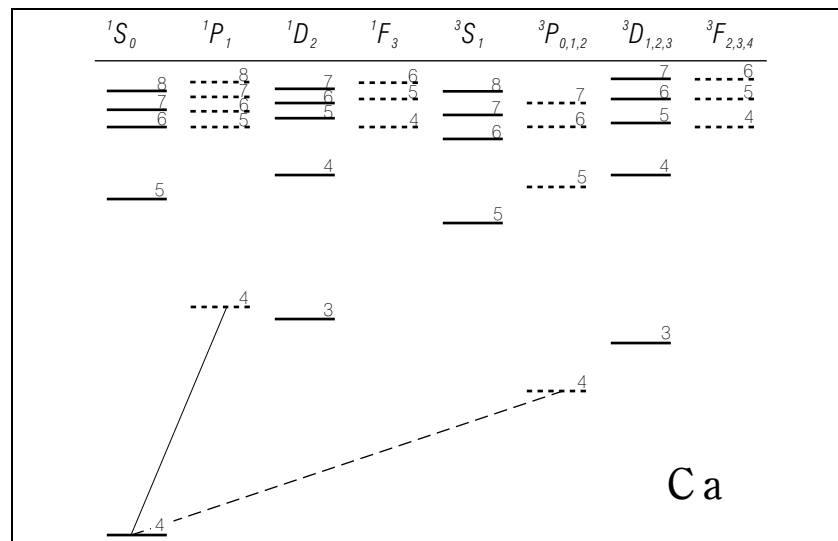


Figure 2. An energy-level diagram for Ca I. The ground state and states with one excited electron are shown on the left side of the diagram, those with two excited electrons on the right side. When one electron is excited, the other is still $4s$ and hence has $\ell = 0$. For those levels, the total L is just the ℓ of the excited electron so only those quantum numbers are shown.

for every singlet state except for the ground state. In this case, because both electrons are in the same state (n 's and ℓ 's the same), only the $S = 0$ state is permitted by the Pauli exclusion principle. The next nine columns, labeled 1S , 1P , 1D , 1F , 3S , 3P , 3D , 3F , 3G , are singlet and triplet states, but with both electrons excited. Notice that each level is described by the configuration of both electrons, as well as by the spectroscopic notation at the bottom of the column. [If you have not already done so, read the description in the figure caption so you can determine the complete configuration of each of the “regular” excited states as well.] One of the lowest levels of the two excited electron states is incorrectly labeled. Can you determine which one it is? If it is not incorrect, you should expect to find another lower level that is not shown.

4e. Notes on the Ca Spectrum.

- a. Note that some two excited electron states have energy higher than the ionization energy of the atom. These states can decay by ionization; i.e., by ejecting one electron and having the other electron return to the ground state.
- b. Note that in columns where more than one J -value is indicated, each level actually is a multiplet of three levels. This splitting is too small to be shown.
- c. Note that the lowest two excited electron levels must have at least one electron in either the $4p$ or $3d$ level because these lie substantially below the next ($5s$) possible level. In fact, the lower two electron levels are found to have both electrons in one or the other of these two levels.
- d. The $S = 0$ selection rule is not absolute so that just as in He a low lying triplet level makes a radioactive, (i.e., emitting a photon), transition to the ground state.
- e. How many $4p^2$ states do you find? What is their total L ? Should there be more L values?
- f. Are the triplet levels generally below the equivalent singlet levels in Ca?

Acknowledgments

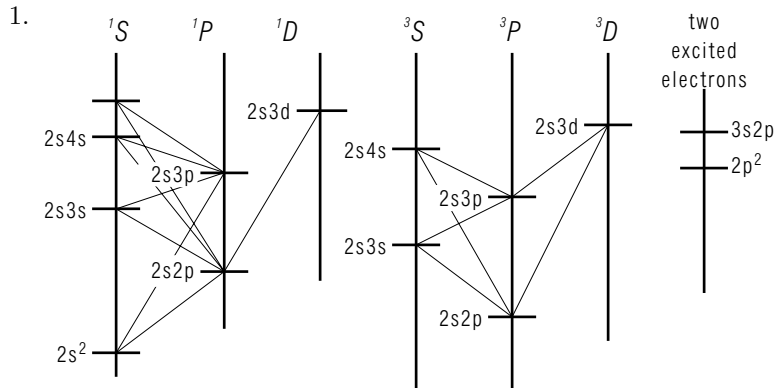
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PROBLEM SUPPLEMENT

Note: Problems 5 and 6 also occur in this module's *Model Exam*.

1. Make a rough sketch of the lowest excited energy level you would expect to find for Be (ground state is $1s^2 2s^2$).
2. Two electrons are in the $2p3d$ configuration. In what spectroscopic states would you expect these to be found?
3. Show the allowed transition you expect on your diagram for problem (1).
4. A two valence electron atom is in the 3D_1 state. From which of the following configurations could this state have been formed?
 - a. $2s2p$
 - b. $3d3p$
 - c. $5g3p$
 - d. $3d4d$
 - e. $2p3p$
5. Two electrons are in the $4d5p$ configurations. What are the possible spectral terms that can be formed from this state? Give complete descriptions, including the J value.
6. Sketch the energy levels (single excited electron) for Sr. The ground state configuration is $5s^2$ and all lower are levels filled.

Brief Answers:



Note the order of levels. We expect the general order of levels of low lying states to be given by the generalized level diagram of Unit 318. Also, we would expect on experience the triplet to lie below the corresponding singlet levels somewhat. We might expect, on the basis of experience with Ca, some two excited electron levels. In truth, we expect them to be split into singlet and triplet and somewhat split in energy, depending on the L value of the state, but without firm guidelines we have simply drawn these as a single levels with configuration labeling.

2. $\ell_1 = 1, \ell_2 = 2 \Rightarrow L = 1, 2, 3$ and $s_1 = s_2 = \frac{1}{2} \Rightarrow S = 0, 1$.

so we have $^1P, ^1D, ^1F, ^3P, ^3D, ^3F$.

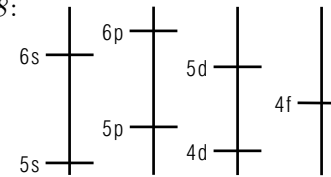
And, if we wish to consider the problem of total J , we have $^1P_1, ^1D_2, ^1F_3, ^3P_{0,1,2}, ^3D_{1,2,3}, ^3F_{2,3,4}$.

3. See figure in Problem (1) answer. We would suspect that it would be possible to find a spectral line from the $2s2p\ ^3P$ state to the ground state in analogy with Ca and He. However, it does violate $\Delta S = 0$, so we leave it out.

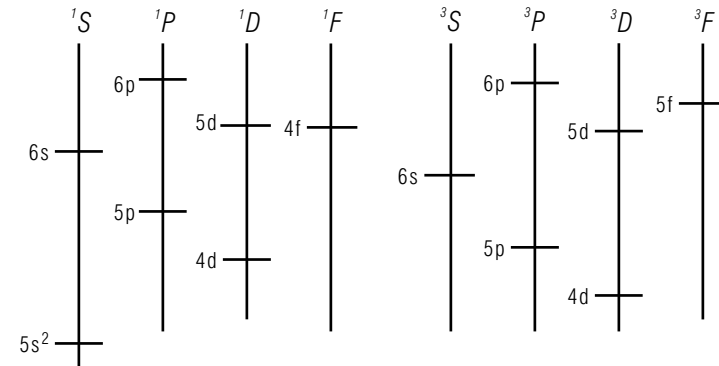
4. b, d, e

5. $^1P_1, ^1D_2, ^1F_3, ^3P_{0,1,2}, ^3D_{1,2,3}, ^3F_{2,3,4}$.

6. First, write down the relevant part of the diagram from MISN-0-318:



From the above diagram we can construct:



Note that the configuration of the excited electron is shown. The triplet levels are slightly lower than the singlet ones. Spectroscopic notation is across the top.

MODEL EXAM

1. See Output Skills K1-K4 in this module's *ID Sheet*. The actual exam may include one or more of these skills, or none.
2. Sketch the energy levels (single excited electron) for Sr. The ground state configuration is: $5s^2$ and all lower levels filled. [Note that to answer this question you will need to know the general level scheme given in Unit 318.]
3. Two electrons are in the $4d5p$ configurations. What are the possible spectral terms that can be formed from this state? Give complete descriptions, including the J value.

Brief Answers:

1. See this module's text.
2. See this module's *Problem Supplement*, Problem 6.
3. See this module's *Problem Supplement*, Problem 5.