Discussion 4 solutions

by Eli Chertkov

① For the four closed-shell electrons in the $1s^2 2s^2$ shells of Be,

(a) $L=0 \Rightarrow \mathcal{L}=S$, $S=0$ and $L=0 \Rightarrow J=0$.

Altogether, this means that the Be term symbol is

$$^{2S+1}\mathcal{L}_J = {}^1S_0 .$$

(b) For each of the two valence electrons of Carbon, there is a set of orbital angular momentum operators:

$$\hat{\ell}_1^x, \hat{\ell}_1^y, \hat{\ell}_1^z \quad \text{for electron 1}$$
$$\hat{\ell}_2^x, \hat{\ell}_2^y, \hat{\ell}_2^z \quad \text{for electron 2.}$$

Since $\hat{\ell}_1^2 = \hat{\ell}_1^{x2} + \hat{\ell}_1^{y2} + \hat{\ell}_1^{z2}$ and $\hat{\ell}_1^z$ commute, we can find simultaneous eigenstates $|\ell_1, m_{\ell_1}\rangle$ that obey

$$\hat{\ell}_1^2 |\ell_1, m_{\ell_1}\rangle = \hbar^2 \ell_1 (\ell_1+1) |\ell_1, m_{\ell_1}\rangle$$
$$\hat{\ell}_1^z |\ell_1, m_{\ell_1}\rangle = \hbar m_{\ell_1} |\ell_1, m_{\ell_1}\rangle .$$

And same thing for operators $\hat{\ell}_2^2 = \hat{\ell}_2^{x2} + \hat{\ell}_2^{y2} + \hat{\ell}_2^{z2}$ and $\hat{\ell}_2^z$ with states $|\ell_2, m_{\ell_2}\rangle$.

Since the two valence electrons of C are in the p orbital, we know that $\ell_1 = \ell_2 = 1$.

From the properties of angular momentum

(1con) operators and their eigenstates, we know
(bcon) that $m_{l_1} = -l_1, -l_1+1, \ldots, l_1-1, l_1$

$$= -1, 0, 1$$

$$m_{l_2} = -l_2, -l_2+1, \ldots, l_2-1, l_2$$

$$= -1, 0, 1.$$

So, we have $3^2 = 9$ possible states for the two C electrons:

$$|l_1 m_{l_1}\rangle |l_2 m_{l_2}\rangle \equiv |m_{l_1}, m_{l_2}\rangle$$

$$= |-1,-1\rangle, |-1,0\rangle, |-1,1\rangle,$$
$$|0,-1\rangle, |0,0\rangle, |0,1\rangle,$$
$$|1,-1\rangle, |1,0\rangle, |1,1\rangle.$$

(c) The operators $\hat{L}^\alpha = \hat{l}_1^\alpha + \hat{l}_2^\alpha$ for $\alpha = x, y, z$ are another set of angular momentum operators. Again, $\hat{L}^2 = \hat{L}^{x2} + \hat{L}^{y2} + \hat{L}^{z2}$ and $\hat{L}^z$ commute and have simultaneous eigenstates $|L, M_L\rangle$

$$\hat{L}^2 |L, M_L\rangle = \hbar^2 L(L+1) |L, M_L\rangle$$
$$\hat{L}^z |L, M_L\rangle = \hbar M_L |L, M_L\rangle.$$

Since $\hat{L}^\alpha$ are total (orbital) angular momentum operators, their possible eigenvalues are constrained by the individual angular momenta eigenvalues.

l_{con} In particular, for $\hat{L}^\alpha = \hat{l}_1^\alpha + \hat{l}_2^\alpha$, the possible
(L_{con}) values for L are

$$L = |l_1 - l_2|, \ldots, l_1 + l_2 .$$

(in steps of 1)

So, for $l_1 = l_2 = 1$, L can take the values

$$L = 0, 1, 2 .$$

For a particular L, the values of M_L are

$$M_L = -L, -L+1, \ldots, L-1, L .$$

If we list all the possibilities for $|L, M_L\rangle$, we get

$L=0, M_L=0$: $|0,0\rangle$

$L=1, M_L=-1,0,+1$: $|1,-1\rangle, |1,0\rangle, |1,+1\rangle$

$L=2, M_L=-2,-1,0,+1,2$: $|2,-2\rangle, |2,-1\rangle, |2,0\rangle, |2,+1\rangle, |2,+2\rangle$

which is 9 states. The $|m_{l_1}, m_{l_2}\rangle$ and $|L, M_L\rangle$ states both span the same 9-dimensional vector space.

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(d) Using the Clebsch-Gordon table, we get that

($|m_{\ell_1}, m_{\ell_2}\rangle$ states)

(i)
$$\left.\begin{aligned} |2,2\rangle_{L,M} &= |1,1\rangle \\ |2,1\rangle_{L,M} &= \frac{1}{\sqrt{2}}|1,0\rangle + \frac{1}{\sqrt{2}}|0,1\rangle \end{aligned}\right\} L=2$$

$$\left.\begin{aligned} |1,1\rangle_{L,M} &= \frac{1}{\sqrt{2}}|1,0\rangle - \frac{1}{\sqrt{2}}|0,1\rangle \\ |1,0\rangle_{L,M} &= \frac{1}{\sqrt{2}}|1,-1\rangle - \frac{1}{\sqrt{2}}|-1,1\rangle \end{aligned}\right\} L=1$$

$$|0,0\rangle_{L,M} = \frac{1}{\sqrt{3}}|1,-1\rangle - \frac{1}{\sqrt{3}}|0,0\rangle + \frac{1}{\sqrt{3}}|-1,1\rangle \,.\Big\} L=0$$

(ii) Written in terms of $|m_{\ell_1}, m_{\ell_2}\rangle$, we can see that

$|2,2\rangle_{L,M}$, $|2,1\rangle_{L,M}$, and $|0,0\rangle_{L,M}$ $\quad (L=2,0)$

are symmetric and

$|1,1\rangle_{L,M}$ and $|1,0\rangle_{L,M}$ $\quad (L=1)$

are antisymmetric under exchange of electrons 1 and 2.

This agrees with the rules stated in the problem.

(2) For the two p electrons of C, $l_1 = l_2 = 1$.

(a) Since they are both electrons, they have spin 1/2. So $s_1 = s_2 = 1/2$.

For $l_1 = l_2 = 1$, total L can take on the values $L = |l_1 - l_2|, \ldots, l_1 + l_2$

$= 0, 1, 2.$

Likewise, for $s_1 = s_2 = 1/2$, total S can take on the values $S = |s_1 - s_2|, \ldots, s_1 + s_2$

$= 0, 1.$

Again by the same logic, total J can take on the values $J = |L - S|, \ldots, L + S$.

The possibilities (and their term symbols $^{2S+1}\mathcal{L}_{J\pi}$) are

$L=0, S=0, J=0 \Rightarrow {}^1S_0$ $({}^1S)$

$L=0, S=1, J=1 \Rightarrow {}^3S_1$ $({}^3S)$

$L=1, S=0, J=1 \Rightarrow {}^1P_1$ $({}^1P)$

$L=1, S=1, J=0,1,2 \Rightarrow {}^3P_0, {}^3P_1, {}^3P_2$ $({}^3P)$

$L=2, S=0, J=2 \Rightarrow {}^1D_2$ $({}^1D)$

$L=2, S=1, J=1,2,3 \Rightarrow {}^3D_1, {}^3D_2, {}^3D_3$ $({}^3D)$

(2 con) Ignoring J, we get the six term
(a con) symbols ^1S, ^3S, ^1P, ^3P, ^1D, ^3D.

But some of these represent states that are symmetric under exchange of electrons 1 and 2. These are not valid fermionic states since fermionic states must be antisymmetric under exchange.

Consider the states $|L, S\rangle$ corresponding to the ^{2S+1}L term symbol. These states are products of an orbital angular momentum part and a spin-part.

By the logic of the previous problem, the largest L (or S) states are symmetric under exchange and then the lower L (or S) states alternate symmetric/antisymmetric as you decrease L (or S).

For example, in our case

$L=2 \to$ symmetric
$L=1 \to$ antisymmetric
$L=0 \to$ symmetric.

(called a "triplet")
$S=1 \to$ symmetric
$S=0 \to$ antisym.
(called a "singlet")

The only way to get antisymmetric $|L,S\rangle$ states is by multiplying symmetric and antisymmetric

(2 con) states together. This happens when

(a con)

$L = 0$ or 2 (sym.) and $S = 0$ (antisym.)

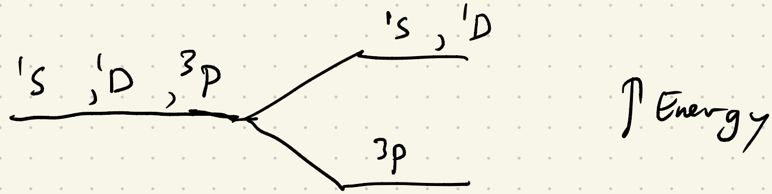
OR $L = 1$ (antisym.) and $S = 1$ (sym.)

These states correspond to the 3 term symbols

^1S, ^1D and ^3P.

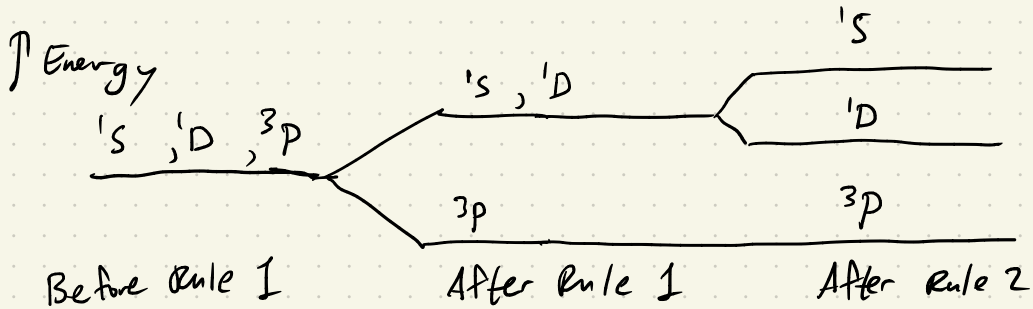
(b) Hund's rules tell you how to order the $|S, L, J\rangle$ states in energy. Rule 1 tells you which S have lower energy. Rule 2 tells you which L have lower energy. Rule 3 tells you which J have lower energy.

Rule 1 says maximize S. The largest possible S we can pick is $S=1$, so ^3P states are lowest in energy and ^1S and ^1D are higher in energy. Let's draw an energy level diagram to describe what Hund's Rule 1 told us:



Before Rule 1 After Rule 1

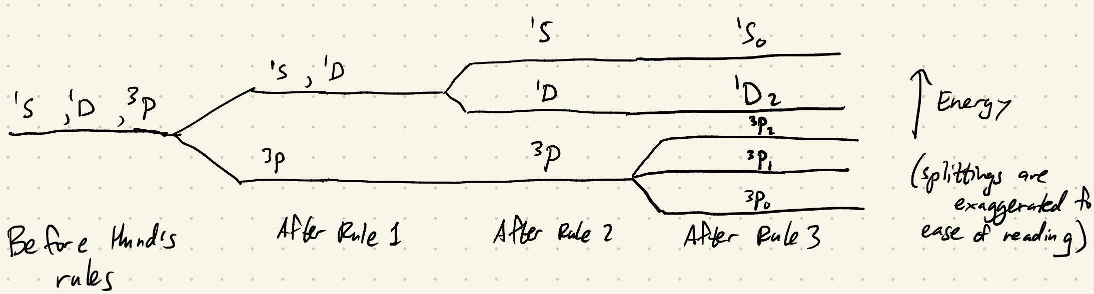
(2 cont) (c) Rule 2 tells us to maximize L. This means that ^1D (with $L=2$) is lower in energy than ^1S (with $L=0$). The diagram becomes:



(d) Rule 3 tells us to minimize J if the shell is less than half full (which it is since 2 out of 6 electrons in the "p-shell" are filled).

This means that lower J states have lower energy.

The diagram then becomes:



This agrees with the neutral carbon (C I) entry in the NIST Atomic Spectra Database.