Discussion 4 solutions by Eli Charlton

1. For the four closed-shell electrons in the 1s²2s² shells of Be,
   (a) \( L = 0 \Rightarrow \mathbf{L} = S, \ S = 0 \) and \( L = 0 \Rightarrow J = 0 \).
   Altogether, this means that the Be term symbol is \( 2S+1L_J = 'S_0' \).

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

\[
\hat{\mathbf{L}} = \begin{pmatrix} \hat{\mathbf{l}}^x \\
\hat{\mathbf{l}}^y \\
\hat{\mathbf{l}}^z 
\end{pmatrix} \quad \text{for electron 1}
\]
\[
\hat{\mathbf{L}} = \begin{pmatrix} \hat{\mathbf{l}}^x \\
\hat{\mathbf{l}}^y \\
\hat{\mathbf{l}}^z 
\end{pmatrix} \quad \text{for electron 2}
\]

Since \( \hat{\mathbf{l}}^2 = \hat{\mathbf{l}}^x \hat{\mathbf{l}}^x + \hat{\mathbf{l}}^y \hat{\mathbf{l}}^y + \hat{\mathbf{l}}^z \hat{\mathbf{l}}^z \) and \( \hat{\mathbf{l}}^z \) commute, we can find simultaneous eigenstates \( \vert l_1, m_1 \rangle \) that obey
\[
\hat{\mathbf{l}}^z \vert l_1, m_1 \rangle = m_1 \vert l_1, m_1 \rangle
\]
\[
\hat{\mathbf{l}}^2 \vert l_1, m_1 \rangle = \hbar^2 L(l_1 + 1) \vert l_1, m_1 \rangle
\]

And same thing for operators \( \hat{\mathbf{l}}^2 = \hat{\mathbf{l}}^x \hat{\mathbf{l}}^x + \hat{\mathbf{l}}^y \hat{\mathbf{l}}^y + \hat{\mathbf{l}}^z \hat{\mathbf{l}}^z \) and \( \hat{\mathbf{l}}^z \) with states \( \vert l_2, m_2 \rangle \).

Since the two valence electrons of C are in the p orbital, we know that \( l_1 = l_2 = 1 \).

From the properties of angular momentum
operators and their eigenstates, we know that

\[ m_{l_1} = -l_1, -l_1 + 1, \ldots, l_1 - 1, l_1 \]

\[ = -l_1, 0, l_1 \]

\[ m_{l_2} = -l_2, -l_2 + 1, \ldots, l_2 - 1, l_2 \]

\[ = -l_2, 0, l_2 . \]

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, \( \hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2 \) and \( \hat{L}^\alpha \) commute and have simultaneous eigenstates \( |L, M_L \rangle \)

\[ \hat{L}^2 |L, M_L \rangle = \hbar^2 L (L+1) |L, M_L \rangle \]

\[ \hat{L}^\alpha |L, M_L \rangle = \hbar M_L |L, M_L \rangle. \]

Since \( \hat{L}^\alpha \) are total (orbital) angular momentum operators, their possible eigenvalues are constrained by the individual angular momentum eigenvalues.
In particular, for \( \hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 \), the possible values for \( L \) are
\[
L = \left| \hat{L}_1 - \hat{L}_2 \right|, \ldots, \hat{L}_1 + \hat{L}_2.
\]
(\( \in \) steps of 1)

So, for \( \hat{L}_1 = \hat{L}_2 = 1 \), \( L \) 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 \( \langle L, M_L \rangle \), we get
\[
L = 0, M_L = 0 : \quad 10, 0, 0
\]
\[
L = 1, M_L = -1, 0, 1 : \quad 11, -1, 11, 0, 11, +1
\]
\[
L = 2, M_L = -2, -1, 0, +1, 2 : \quad 12, -2, 12, -1, 12, 0, 12, +1, 12, +2
\]

which is 9 states. The \( \langle L_1, M_{L_1} \rangle \) and \( \langle L, M_L \rangle \) states both span the same 9-dimensional vector space.
(d) Using the Clebsch-Gordan table, we get that

\[(i)\]
\[12,2 \rangle_{LM} = \frac{1}{\sqrt{2}} |11,1\rangle \quad \{ L = 2 \}
\]
\[12,1 \rangle_{LM} = \frac{1}{\sqrt{2}} |11,0\rangle + \frac{1}{\sqrt{2}} |10,1\rangle \quad \{ L = 2 \}
\]
\[11,1 \rangle_{LM} = \frac{1}{\sqrt{2}} |11,0\rangle - \frac{1}{\sqrt{2}} |10,1\rangle \quad \{ L = 1 \}
\]
\[11,0 \rangle_{LM} = \frac{1}{\sqrt{2}} |11,-1\rangle - \frac{1}{\sqrt{2}} |10,-1\rangle \quad \{ L = 0 \}
\]
\[10,0 \rangle_{LM} = \frac{1}{\sqrt{3}} |10,-1\rangle - \frac{1}{\sqrt{3}} |10,0\rangle + \frac{1}{\sqrt{3}} |10,1\rangle \quad \{ L = 0 \}
\]

(ii) Written in terms of \(|m_1, m_2\rangle\), we can see that

\[12,2 \rangle_{LM}, 12,1 \rangle_{LM}\), and \[10,0 \rangle_{LM}\) (\(L=2,0\))

are symmetric and

\[11,2 \rangle_{LM}\) and \[11,0 \rangle_{LM}\) (\(L=1\))

are antisymmetric under exchange of electrons 1 and 2.

This agrees with the rules stated in the problem.
For the two \( p \) electrons of \( C \), \( l_1 = l_2 = 1 \).

(a) Since they are both electrons, they have spin \( \frac{1}{2} \).
So, \( s_1 = s_2 = \frac{1}{2} \).

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 \( s_1 = s_2 = \frac{1}{2} \), 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) are

\[
\begin{align*}
L = 0, S = 0, J = 0 & \Rightarrow \ 'S_0 \quad (^1S ) \\
L = 0, S = 1, J = 1 & \Rightarrow \ 'S_1 \quad (^3S ) \\
L = 1, S = 0, J = 1 & \Rightarrow \ 'P_1 \quad (^1P ) \\
L = 1, S = 1, J = 0, 1, 2 & \Rightarrow \ 'P_0, \ 'P_1, \ 'P_2 \quad (^3P ) \\
L = 2, S = 0, J = 2 & \Rightarrow \ 'D_2 \quad (^1D ) \\
L = 2, S = 1, J = 1, 2, 3 & \Rightarrow \ 'D_1, \ 'D_2, \ 'D_3 \quad (^3D )
\end{align*}
\]
Ignoring \( \mathcal{J} \), we get the six term symbols \( 'S, 3S, 'P, 3P, 'D, 3D \).

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 \( L \) 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 \( \nu \) (called a "triplet")

\[
\begin{align*}
L = 2 & \rightarrow \text{symmetric} \quad S = 1 \rightarrow \text{symmetric} \\
L = 1 & \rightarrow \text{antisymmetric} \quad S = 0 \rightarrow \text{antisymmetric} \\
L = 0 & \rightarrow \text{symmetric} \quad S \rightarrow \text{antisymmetric}
\end{align*}
\]

The only way to get antisymmetric \( |L, S\rangle \) states is by multiplying symmetric and antisymmetric
These states correspond to the 3 term symbols $\ ^1S,$ $\ ^1D$ and $\ ^3P.$

(b) Hund's rules tell you how to order the $1S, L, \ J \ J$ 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:

```
\begin{tikzpicture}
    \node (S) at (0,0) {$\ ^1S,$ $\ ^1D,$ $\ ^3P$}
        child { node (D) {$\ ^1S,$ $\ ^1D$} }
        child { node (P) {$\ ^3P$} }
    \draw [->] (S) -- (D);
    \draw [->] (S) -- (P);
\end{tikzpicture}
```

Before Rule 1 \hspace{2cm} After Rule 1
(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:

\[
\begin{align*}
\text{\( ^1S, ^1D, ^3P \)} & \quad \text{\( ^1S, ^1D \)} \\
\text{Before Rule 1} & \quad \text{After Rule 1} & \quad \text{After Rule 2}
\end{align*}
\]

(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:

\[
\begin{align*}
\text{\( ^1S, ^1D, ^3P \)} & \quad \text{\( ^1S, ^1D \)} & \quad \text{\( ^1S \)} & \quad \text{\( ^1S_0 \)} \\
\text{Before Hund's rules} & \quad \text{After Rule 1} & \quad \text{After Rule 2} & \quad \text{After Rule 3}
\end{align*}
\]

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