Hund's rules

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03/10/2022

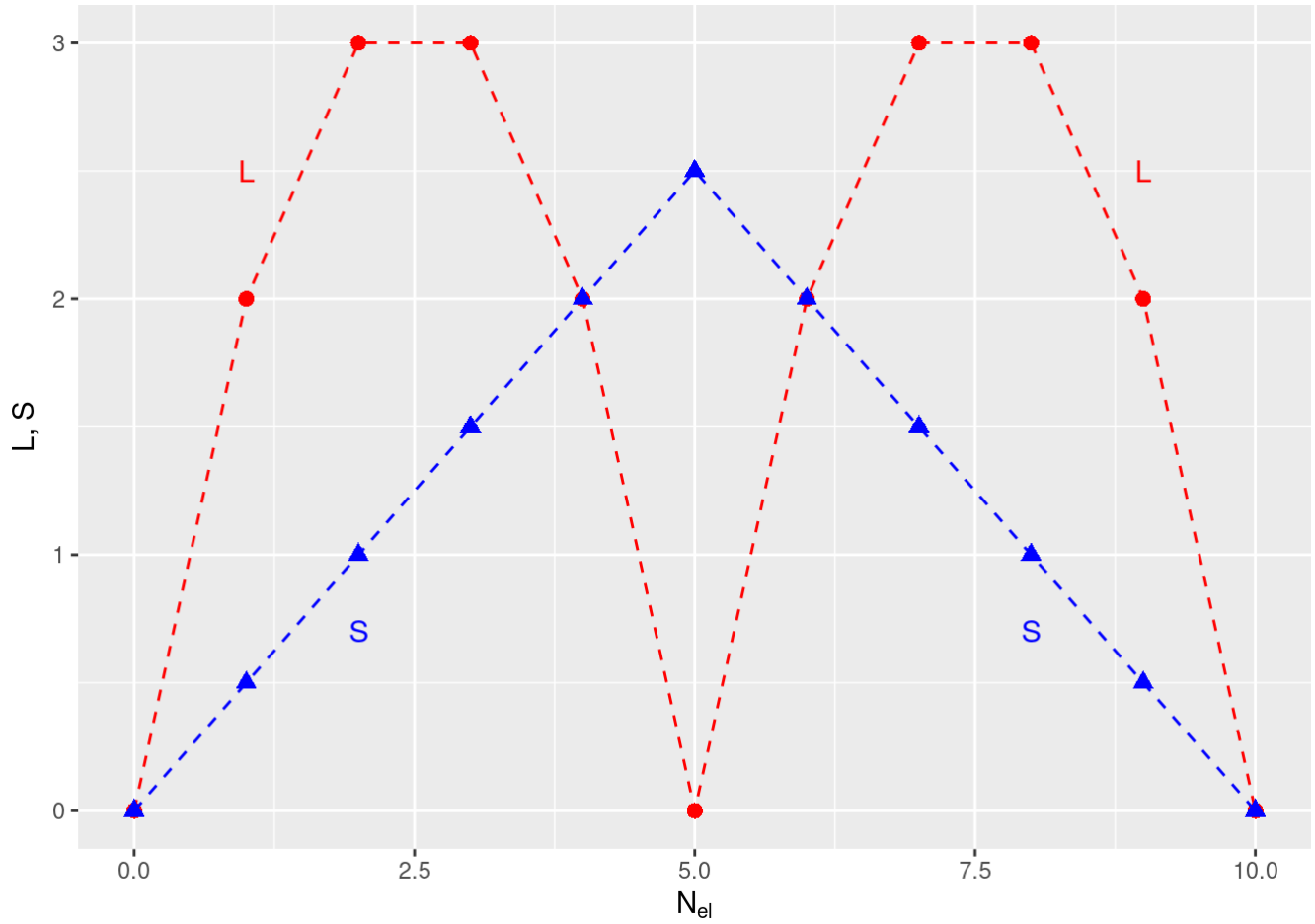
Proressive filling of the 3d shell

The first column in the file *shell_data.csv* gives the number of electrons that can be accommodated in a 3d shell. Fill the second and the third columns with the values of the total S and the total L compatible with the first two Hund's rules (the **default values** written in the file are obviously **not correct**), namely corresponding to the lower energy.

1. For which electronic configurations (3d)$^{n_{el}}$ (with n_{el} number of electrons) is L taking its minimal and maximal values?
   Answer
   L takes the minimal vaule $L = 0$ when the d shell is empty, half full $n_{el} = 5$, or totally full $n_{el} = 10$.
   L takes the maximal value $L = 3$ for $n_{el} = 2, 3, 7, 8$.

2. What can we say about the minimal and maximal values of S?
   Answer
   S increases progressively while filling the 3d shell till the shell is half full, when it takes the maximal value $S = 5/2$; from this point on, electrons are forced to pair to doubly occupy the same orbitals (Pauli principle) and S unavoidably starts decreasing; it vanishes when the shell becomes totally full.

The plot of the resulting S and L *versus* the number of electrons n_{el} will be automatically produced in the figure below:



He ground state… if electrons had no spin

Speculating how Nature would behave under unrealistic situations, sometimes, may help understand its laws more deeply.
Assuming that its electrons maintained the symmetry properties of fermions, what would be the ground-state of the He atom, if there were no spin coordinates?

1. • $(1s)^2$
2. • $(1s)^1(2s)^1$
3. • $(2p)^2$

Answer

Assuming that the total wave function of electrons still needed to be antisymmetric, the ground state of He would be $(1s)^1(2s)^1$. In fact, the pair of electrons would not be allowed to doubly occupy the $(1s)$ state because with two equivalent quantum numbers (n,l) no antisymmetric wave function could be built.

Consolidation assignment on spins 1/2

Express the four states of the multiplet $|3/2, M\rangle$ obtained by summing three spins one-half on the respective single-particle basis, i.e., $|m_1, m_2, m_3\rangle$, with $\hat{\mathbf{s}}_1 = \hat{\mathbf{s}}_2 = \hat{\mathbf{s}}_3 = 1/2$.

To this aim, apply successively the ladder operator $\hat{S}^+$ to the state $|--\!-\rangle$ in such a way that the whole subset $S = 3/2$ is spanned, as suggested below

$$\begin{aligned}
&\text{step 1:} \qquad |3/2,-1/2\rangle = N_{-}\hat{S}^{+}|3/2,-3/2\rangle = N_{-}\hat{S}^{+}|---\rangle \\
&\text{step 2:} \qquad |3/2,+1/2\rangle = N_{+}\hat{S}^{+}|3/2,-1/2\rangle \\
&\text{step 3:} \qquad |3/2,+3/2\rangle = N_{0}\hat{S}^{+}|3/2,+1/2\rangle
\end{aligned}$$

N_{-}, N_{+}, and N_0 are three (a priori) different normalization constants. For your convenience, we remind that

$$\hat{S}^{+} = \hat{S}^{x} + i\hat{S}^{y} = \left(\hat{s}_1^{x} + \hat{s}_2^{x} + \hat{s}_3^{x}\right) + i\left(\hat{s}_1^{y} + \hat{s}_2^{y} + \hat{s}_3^{y}\right) = \hat{s}_1^{+} + \hat{s}_2^{+} + \hat{s}_3^{+}$$

and that the ladder operators for spins $s = 1/2$ act as follows

$$\begin{aligned}
\hat{s}^{+}|+\rangle &= 0 \qquad & \hat{s}^{+}|-\rangle &= |+\rangle \\
\hat{s}^{-}|+\rangle &= |-\rangle \qquad & \hat{s}^{-}|-\rangle &= 0
\end{aligned}$$

which, for instance, implies

$$\begin{aligned}
\hat{s}_1^{+}|---\rangle &= |+--\rangle \\
\hat{s}_2^{+}|---\rangle &= |-+-\rangle \\
\hat{s}_2^{+}|+--\rangle &= |++-\rangle \\
&\dots
\end{aligned}$$

The four obtained states should be consistent with the Weyl theorem.

Answer
[SEE ATTACHED FILE]
Step 1

$$\begin{aligned}
|3/2,-1/2\rangle &= N_{-}\hat{S}^{+}|---\rangle \\
&\dots
\end{aligned}$$

INTRODUCTION TO MAGNETISM

Autumn Semester 2022

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Assignment 2

1. Orbital wave function of two p electrons

- The dimensionality of each multiplet of L is $2L+1$; the direct sum of those subspaces yelds $1+3+5$ for $L=0,1,2$ respectively.
- We know that the radial part of the spatial wave function is the same for both electrons $R_{2,1}(r_i)$ with $i=1,2$. As for the angular part, the state $|L=2, M=+2\rangle = |m_1=+1, m_2=+1\rangle$, or in the of spherical harmonics representation $Y_{1,+1}(\theta_1,\phi_1)Y_{1,+1}(\theta_2,\phi_2)$, is symmetric w.r.t. the exchange of the two electrons. With the help of a Clebsch-Gordan coefficients table one can verify that the other 4 states in the $L=2$ multiplet are symmetric w.r.t. the exchange of the two electrons as well. Knowing that the spin part of the wave fucntion is the spin triplet χ^{T} (symmetric w.r.t. the exchange $1 \leftrightarrow 2$), the angular part of the wave fucntion cannot be a state of the multiplet $L=2$.
- For $L=1$ multiplet, instead, using a Clebsch-Gordan coefficients table one can verify that

$$|L=1, M=+1\rangle = \frac{1}{\sqrt{2}}\left[Y_{1,+1}(\theta_1,\phi_1)Y_{1,0}(\theta_2,\phi_2) - Y_{1,0}(\theta_1,\phi_1)Y_{1,+1}(\theta_2,\phi_2)\right]$$
$$|L=1, M=0\rangle = \frac{1}{\sqrt{2}}\left[Y_{1,+1}(\theta_1,\phi_1)Y_{1,-1}(\theta_2,\phi_2) - Y_{1,-1}(\theta_1,\phi_1)Y_{1,+1}(\theta_2,\phi_2)\right]$$
$$|L=1, M=-1\rangle = \frac{1}{\sqrt{2}}\left[Y_{1,-1}(\theta_1,\phi_1)Y_{1,0}(\theta_2,\phi_2) - Y_{1,0}(\theta_1,\phi_1)Y_{1,-1}(\theta_2,\phi_2)\right]$$

  The spatial wave functions above are manifestly antisymmetric w.r.t. the exchange $1 \leftrightarrow 2$ and, thereore, compatible with a symmetric spin wave function χ^{T}.
- Generally, the relation $(\hat{\mathbf{L}})^2 = (\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2)^2 = (\hat{\mathbf{l}}_1)^2 + 2\,\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2 + (\hat{\mathbf{l}}_2)^2$ implies

$$\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2 = \frac{(\hat{\mathbf{L}})^2 - (\hat{\mathbf{l}}_1)^2 - (\hat{\mathbf{l}}_2)^2}{2}$$

  from which it follows that

$$\langle L, M|\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2|L, M\rangle = \frac{1}{2}\left[L(L+1) - l_1(l_1+1) - l_2(l_2+1)\right] = \frac{1}{2}L(L+1) - 2$$

  when $l_1 = l_2 = 1$. Thus, the scalar product $\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2$ takes three different eigenvalues associated with the three possible values of the modulus $L=0$, 1, 2 with the relative degeneracy deg = 1, 3, 5. As remarked at the first point of this assignment, the dimension of the Hilbert space is preserved passing from the basis $|l_1, m_1\rangle \otimes |l_2, m_2\rangle$ (3×3 basis kets) to $|L, M\rangle$ ($1+3+5$ basis kets).