1. Write Slater determinant wavefunctions for the 1s2s states of the He atom.

Things to consider:

1) there are just 2 e⁻'s, so each Slater determinant can be 2x2 only and expand to just 2 terms.

2) the possible spin-orbitals to use to make Slater determinants are:
   1sₓ, 1sᵧ, 2sₓ, 2sᵧ  i.e. 4 possible combinations.

Two of the triplets are easy:

\[ \frac{1}{\sqrt{2}} \begin{pmatrix} 1s(1) & 1s(2) \\ 2s(1) & 2s(2) \end{pmatrix} \]

\[ \frac{1}{\sqrt{2}} \begin{pmatrix} 1s(1) & 1s(2) \\ 2s(1) & 2s(2) \end{pmatrix} \]
The singlet & 3rd triplet involve a total of 4 terms each, so they are obviously linear combinations of 2 determinants:

\[ \Phi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi(1) \alpha(1) & \psi(2) \alpha(2) \\ 2\psi(1) \beta(1) & 2\psi(2) \beta(2) \end{vmatrix} \]

\[ \Phi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi(1) \beta(1) & \psi(2) \beta(2) \\ 2\psi(1) \alpha(1) & 2\psi(2) \alpha(2) \end{vmatrix} \]

Comparing the expanded determinants with the singlet + third triplet wavefunctions,

\[ 4_{\text{singlet}} = \frac{1}{\sqrt{2}} \left[ \Phi_1 - \Phi_2 \right] \]

\[ 4_{\text{triplet-3}} = \frac{1}{\sqrt{2}} \left[ \Phi_1 + \Phi_2 \right] \]
(2) Find all possible RS term symbols. Assuming Hund's Rules apply, find the ground state.

Assuming the circled ground state below:

\[ \text{L} = 1, \text{S} = \frac{1}{2}, \text{J} = \frac{3}{2}, \frac{1}{2} \]

Levels: \( ^2P_{\frac{3}{2}}, ^2P_{\frac{1}{2}} \)

so min J is ground state.

(a) \( 1s^2 2s^2 2p \)

\[ \begin{align*}
L_1 &= 1 & \Rightarrow & & L_1 = 1 \\
S_1 &= \frac{1}{2} & \Rightarrow & & S_1 = \frac{1}{2} \\
L_2 &= 2 & \text{and} & & L_2 = 1, 2, 3 \\
S_2 &= \frac{1}{2} & \text{and} & & S_2 = \frac{1}{2}, 0
\end{align*} \]

\( ^2P_{\frac{3}{2}}, ^2P_{\frac{1}{2}} \)

(b) \[ \text{[Ne]} \, 3s^2 3p^3 \text{d} \]

\[ \begin{align*}
L_1 &= 1 & \Rightarrow & & L_1 = 3, 2, 1 \\
L_2 &= 2 & \text{and} & & L_2 = 3, 2, 1 \\
S_1 &= \frac{1}{2} & \Rightarrow & & S_1 = 1, 0 \\
S_2 &= \frac{1}{2} & \text{and} & & S_2 = \frac{1}{2}, 0
\end{align*} \]

\( ^3F_4, ^3D_3, ^3P_1, ^1F_3, ^3P_2, ^3D_2, ^3D_1, ^1D_2, ^3P_1 \)
(c) \([\text{Ar}] 4s^2 3d^9 4p\)

\[
\begin{align*}
    \ell_1 &= 2  & L &= 3, 2, 1 \\
    \ell_2 &= 1 \\

    a_1 &= \frac{1}{2}  & S &= 1, 0 \\
    a_2 &= \frac{1}{2}
\end{align*}
\]

- all terms & levels identical to 2b

ground state though might be \(^3F_4\) although
this is ambiguous in this case.

(d) \([\text{Kr}] 5p 4f\)

\[
\begin{align*}
    \ell_1 &= 1  & L &= 4, 3, 2 \\
    \ell_2 &= 3 \\

    a_1 &= \frac{1}{2}  & S &= 1, 0 \\
    a_2 &= \frac{1}{2}
\end{align*}
\]

- \(^3G, ^3F, ^3D, ^1G, ^1F, ^1D\)

\[
\begin{align*}
    L=4, S=1 & : J = 5, 4, 3 \\
    L=3, S=1 & : J = 4, 3, 2 \\
    L=2, S=1 & : J = 3, 2, 1 \\
    L=1, S=0 & : J = X
\end{align*}
\]
3. Determine the levels and number of states

(a) \( 4F \)  \( L=3, \ S=3/2 \)

\[ J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2} \]

\# states = \( 25 + 1 = 10 + 8 + 6 + 4 = 28 \) states

(b) \( 1S \)  \( L=0, \ S=0 \)

\[ J = 0 \]

\# states = 1

(c) \( 3p \)  \( L=1, \ S=1 \)

\[ J = 2, 1, 0 \]

\# states = \( 5 + 3 + 1 = 9 \)

(d) \( 2D \)  \( L=2, \ S=1/2 \)

\[ J = \frac{5}{2}, \frac{3}{2} \]

\# states = \( 6 + 4 = 10 \)
(4) Predict the ground state term symbols

**Hint**: use Hund’s rules

(a) \(1s^2 2s^2 2p^6 3s\)

- one electron in a 3s orbital

\[
\begin{align*}
S &= \frac{1}{2} = S \\
L &= 0 = L \\
J &= \frac{1}{2} = J
\end{align*}
\]

\(2S_{1/2}\) only possibility

(b) \([Ar] 4s^2 4p^3\)

- 3 electrons in a 4p subshell

\[
\text{max } S: \text{ all 3 with same spin} \\
a_1 = a_2 = a_3 = \frac{1}{2} \Rightarrow S = \frac{3}{2}
\]

\[
\text{max } L: \text{ there is only one way to put the 3 s’s in the 4p where they have the same spin:}
\]

\[
\begin{array}{ccc}
1 & 1 & 1 \\
1 & 0 & 1
\end{array}
\]

so \(m_l = 0\)

\[
\begin{array}{c}
4 \left( S_{3/2} \right)
\end{array}
\]

\(\therefore L = 0, J = \frac{3}{2}\)
(c) \([\text{Ar}] 4s^2 3d^{10}\)

This is like a rare gas configuration.

\[
\begin{array}{|c|}
\hline
\text{1s} \\
\hline
\end{array}
\]

(d) \([\text{Kr}] 5s^2 4d^2\)

- 2 electrons in a d subshell

\[\text{max } S : \text{ both } e^-'s \text{ w/ same spin } S = 1\]

\[\text{max } L \]

\[
\begin{array}{|c|c|c|c|}
\hline
m_e & -2 & -1 & 0 & 1 & 1 & 2 & m_l = 3 \\
\hline
L & 3 & 3 & 3 & 3 & 3 & 3 & \text{so } J = 4, 3, 2 \\
\hline
\end{array}
\]

\[\therefore S = 1, \ L = 3 \quad \text{so } J = 4, 3, 2\]

Shell is < \(\frac{1}{2}\) filled \(\Rightarrow \) \(3F_2\)
(5) The atom trial function: \( \Phi = e^{-\alpha (r_1^2 + r_2^2)} \)

(i) Complete expression for the trial energy

in atomic units,

\[ \hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_1 r_2} \]

\[ d\tau_1 = r_1^2 \sin \theta_1 \, dr_1 \, d\theta_1 \, d\phi_1 \]
\[ d\tau_2 = r_2^2 \sin \theta_2 \, dr_2 \, d\theta_2 \, d\phi_2 \]

\[ E_{\text{trial}} = \int_{r_1=0}^{\infty} \int_{\theta_1=0}^{\pi} \int_{\phi_1=0}^{2\pi} \int_{r_2=0}^{\infty} \int_{\theta_2=0}^{\pi} \int_{\phi_2=0}^{2\pi} e^{-\alpha (r_1^2 + r_2^2)} \hat{H} e^{-\alpha (r_1^2 + r_2^2)} \, d\tau_1 \, d\tau_2 \]

\[ = \int_{r_1=0}^{\infty} \int_{\theta_1=0}^{\pi} \int_{\phi_1=0}^{2\pi} \int_{r_2=0}^{\infty} \int_{\theta_2=0}^{\pi} \int_{\phi_2=0}^{2\pi} -2 \alpha (r_1^2 + r_2^2) \, d\tau_1 \, d\tau_2 \]

(5) \( E_{\text{trial}} = \frac{11}{4} \alpha - \frac{11}{2} \sqrt{\alpha} \)

optimal \( \alpha: \) \( \frac{\partial E_{\text{trial}}}{\partial \alpha} = 0 = \frac{11}{4} - \frac{11}{4} \alpha^{-1/2} \)

\( \alpha = 1 \)

optimal \( E: \) \( \frac{11}{4} (1) - \frac{11}{2} \sqrt{1} = -\frac{11}{4} \) a.u.

\( = -74.8 \text{ eV} \)

(expt.: -79.0 eV)