1) Identify the terms for the micro-states associated with 1 valence electron in a d-shell and 1 valence electron in a p shell for an isolated atom.

The number of microstates is given by \( \frac{n!}{e!(n-e)!} \), where \( n \) is the number of electron “slots” and \( e \) is the number of electrons.

\[
\frac{10!}{1!(9!)} \frac{6!}{1!(5!)} = 60 \text{ microstates}
\]

\[\begin{array}{cccccc|c}
+2 & +1 & 0 & -1 & -2 & +1 & 0 & -1 & \text{Total States} \\
\hline
? & ? & L = 3; \ ^3F = 21 \text{ microstates} & 21 \\
? & ? & L = 3; \ ^1F = 7 \text{ microstates} & 28 \\
? & ? & L = 2 – Previously Found \ ^3F & 28 \\
? & ? & L = 2 – Previously Found \ ^1F & 28 \\
? & ? & L = 2; \ ^3D = 15 \text{ microstates} & 43 \\
? & ? & L = 2; \ ^1D = 5 \text{ microstates} & 48 \\
? & ? & L = 1 – Previously Found \ ^3F & 48 \\
? & ? & L = 1 – Previously Found \ ^1F & 48 \\
? & ? & L = 1 – Previously Found \ ^3D & 48 \\
? & ? & L = 1 – Previously Found \ ^1D & 48 \\
? & ? & L = 1; \ ^3P = 9 \text{ microstates} & 57 \\
? & ? & L = 1; \ ^1P = 3 \text{ microstates} & 60 \\
? & ? & L = 0 – Previously Found \ ^3F & 60 \\
? & ? & L = 0 – Previously Found \ ^1F & 60 \\
? & ? & L = 0 – Previously Found \ ^3D & 60 \\
? & ? & L = 0 – Previously Found \ ^1D & 60 \\
? & ? & L = 0 – Previously Found \ ^3P & 60 \\
? & ? & L = 0 – Previously Found \ ^1P & 60 \\
\end{array}\]

The terms are \(^3F, \ ^1F, \ ^3D, \ ^1D, \ ^3P \& \ ^1P\).
2) The following two electron wavefunctions are for the excited state of the Helium atom with an electronic configuration of 1s\(^2\)2s\(^1\):

\[
\Psi = (1/\sqrt{2})[(\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1))]((\alpha(1)\alpha(2))
\]

\[
\Psi = (1/\sqrt{2})[(\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1))]((\beta(1)\beta(2))
\]

\[
\Psi = (1/\sqrt{2})[(\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1))((\alpha(1)\beta(2) - \alpha(2)\beta(1))
\]

\[
\Psi = (1/\sqrt{2})[(\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1))((\alpha(1)\beta(2) + \alpha(2)\beta(1))
\]

Why do we have to represent the two electron wavefunctions as super-positions (sums and minuses) of one electron wavefunctions?

Demonstrate that all of the wavefunctions obey the Pauli principle.

Identify which of the wavefunctions represent the triplet state and which represent the singlet state. Explain your choices (a vector diagram of triplet state electron spin angular momentum may be helpful).

We know that the electrons are in the two orbitals represented by the wavefunctions: \(\psi_{1s}\) and \(\psi_{2s}\). The possible cases are \(\psi_{1s}(1)\psi_{2s}(2)\) and \(\psi_{1s}(2)\psi_{2s}(1)\) but the electrons are indistinguishable despite our labels, we cannot determine the actual case that occurs, therefore we use superposition, the sum and difference of the two cases to represent the possible outcomes: \(\Psi = \psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)\)

To obey the Pauli principle the wavefunctions must be antisymmetric with respect to exchange of any two electrons: \(\Psi(1,2) = -\Psi(2,1)\).

\(\Psi(1,2) = (1/\sqrt{2})[\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)]((\alpha(1)\alpha(2))
\]

\(\Psi(2,1) = (1/\sqrt{2})[\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)]((\alpha(2)\alpha(1))
\]

\(= (1/\sqrt{2})[-\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{2s}(2)]((\alpha(2)\alpha(1))] = -\Psi(1,2)\)

Obey the Pauli principle, the orbital component of the wavefunction is antisymmetric with respect to electron exchange.

\(\Psi(1,2) = (1/\sqrt{2})[\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)]((\beta(1)\beta(2)) = -\Psi(2,1)\)

\(\Psi(1,2) = (1/\sqrt{2})[\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)]((\alpha(1)\beta(2) + \alpha(2)\beta(1)) = -\Psi(2,1)\)

Both of these 2-electron wavefunctions obey the Pauli principle, the orbital component of the wavefunction is antisymmetric with respect to electron exchange.

\(\Psi(1,2) = (1/\sqrt{2})[\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)]((\alpha(1)\beta(2) - \alpha(2)\beta(1))
\]

\(\Psi(2,1) = (1/\sqrt{2})[\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)]((\alpha(2)\beta(1) + \alpha(1)\beta(2))
\]

\(= (1/\sqrt{2})[\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)]((\alpha(1)\beta(2) + \alpha(2)\beta(1)) = -\Psi(1,2)\)

Obey the Pauli principle, the spin component of the wavefunction is antisymmetric with respect to electron exchange. The orbital component of the wavefunction is symmetric with respect to electron exchange.

The wavefunctions that have orbital components that are antisymmetric to electron exchange represent the three allowed orientations of the electron spin angular momentum with respect to an axis that are found in the triplet state.

These are \(\alpha(1)\alpha(2), \alpha(1)\beta(2) + \alpha(2)\beta(1)\) and \(\beta(1)\beta(2)\). Each spin-function is a vector that is one unit long but they have different projections onto the axis. The singlet state is represented by the wavefunction that has the spin component that is antisymmetric with respect to electron exchange: \(\alpha(1)\beta(2) + \alpha(2)\beta(1)\). There is only one possible orientation of the singlet.
3) Show that the sp\(^2\)-hybrid orbitals formed on an atom are normalized.

Show that the sp\(^2\)-hybrid orbitals formed on an atom are orthogonal.

\[ \Psi_1 = (1/\sqrt{3})\psi_s + (\sqrt{2}/3)\psi_{px} \]
\[ \Psi_2 = (1/\sqrt{3})\psi_s - (1/\sqrt{6})\psi_{px} + (1/\sqrt{2})\psi_{py} \]
\[ \Psi_3 = (1/\sqrt{3})\psi_s - (1/\sqrt{6})\psi_{px} - (1/\sqrt{2})\psi_{py} \]

Normalization:
\[ \Psi_1^* \Psi_1 \, d\tau = (1/\sqrt{3})^2 \psi_s^2 + (\sqrt{2}/3)^2 \psi_{px}^2 = 1 \]
\[ \Psi_2^* \Psi_2 \, d\tau = (1/\sqrt{3})^2 \psi_s^2 - (1/\sqrt{6})^2 \psi_{px}^2 + (1/\sqrt{2})^2 \psi_{py}^2 = 1 \]
\[ \Psi_3^* \Psi_3 \, d\tau = (1/\sqrt{3})^2 \psi_s^2 - (1/\sqrt{6})^2 \psi_{px}^2 - (1/\sqrt{2})^2 \psi_{py}^2 = 1 \]

Orthogonality:
\[ \Psi_1^* \Psi_2 \, d\tau = \chi((1/\sqrt{3})\psi_s + (\sqrt{2}/3)\psi_{px})((1/\sqrt{3})\psi_s - (1/\sqrt{6})\psi_{px} + (1/\sqrt{2})\psi_{py}) \, d\tau = 0 \]
\[ \Psi_2^* \Psi_3 \, d\tau = \chi((1/\sqrt{3})\psi_s - (1/\sqrt{6})\psi_{px} + (1/\sqrt{2})\psi_{py})((1/\sqrt{3})\psi_s - (1/\sqrt{2})\psi_{py} - (1/\sqrt{6})\psi_{px}) \, d\tau = 0 \]

Again the 1-electron atomic orbital wavefunctions are normalized and orthogonal.

4) Sketch the molecular orbital diagrams for the following:
N₂, O₂, F₂, C₂, OF, NO, CN

a) Determine the bond order and paramagnetism for each case.

Paramagnetic molecules have unpaired electrons.

b) Which species will become more stable if an electron is added?

c) Which species will become more stable if an electron is removed?

The MO diagrams for diatomic molecules are shown below. The diagram on the left is for all molecules to the right of O₂ and the diagram on the right is for O₂ and F₂.

N₂ (10 valence e⁻'s): Use the diagram on the left.

  Bond Order = (8 -2)/2 = 3, 0 unpaired electrons.
  Will become less stable if e⁻ is added into π⁺ orbital, LUMO.
  Will become less stable if e⁻ is removed from π⁻ orbital, HOMO.

O₂ (12 valence e⁻'s): Use the diagram on the right.

  Bond Order = (8 -4)/2 = 2, 2 unpaired electrons.
  Will become more stable if e⁻ is added into partially filled π⁺ orbital.
  Will become more stable if e⁻ is removed from partially filled π⁻ orbital.

F₂ (14 valence e⁻'s): Use the diagram on the right.

  Bond Order = (8 -6)/2 = 1, 0 unpaired electrons.
  Will become less stable if e⁻ is added into σ⁺ orbital, LUMO.
  Will become more stable if e⁻ is removed from σ⁻ orbital, HOMO.

C₂ (8 valence e⁻'s): Use the diagram on the left.

  Bond Order = (6 -2)/2 = 2, 0 unpaired electrons.
  Will become more stable if e⁻ is added into σ⁻ orbital, LUMO.
  Will become more stable if e⁻ is removed from partially filled σ⁻ orbital.

OF (13 valence e⁻'s): Use the diagram on the right.

  Bond Order = (8 -5)/2 = 1.5, 1 unpaired electrons.
  Will become less stable if e⁻ is added into partially filled σ⁺ orbital.
  Will become more stable if e⁻ is removed from partially filled σ⁻ orbital.

NO (11 valence e⁻'s): Use the either diagram.

  Bond Order = (8 -3)/2 = 2.5, 1 unpaired electrons.
  Will become more stable if e⁻ is added into partially filled π⁺ orbital.
  Will become less stable if e⁻ is removed from partially filled π⁻ orbital.

CN (9 valence e⁻'s): Use the diagram on the left.

  Bond Order = (7 -2)/2 = 2.5, 1 unpaired electrons.
  Will become more stable if e⁻ is added into partially filled σ⁻ orbital.
  Will become less stable if e⁻ is removed from partially filled σ⁻ orbital.
5) Generate the secular determinant matrix for the $\pi$ system of the oxalate ion ($\text{C}_2\text{O}_4^{2-}$) using simplified Huckel theory with the same Coulomb integrals for the carbon and oxygen atoms and one resonance integral. Use the scheme shown here:

\[
\begin{pmatrix}
\alpha & \beta & \beta & 0 & 0 \\
\beta & \alpha & 0 & 0 & \beta \\
\beta & 0 & \alpha & 0 & 0 \\
\beta & 0 & 0 & \alpha & 0 \\
0 & \beta & 0 & 0 & \alpha \\
0 & \beta & 0 & 0 & \alpha
\end{pmatrix}
\]

The eigenvalues associated with the matrix are:
\[
\alpha, \alpha, \alpha + \beta, \alpha - 2\beta, \alpha + 2\beta, \alpha - \beta
\]

Describe the nature of the orbitals associated with these energies. Relate these features to the Lewis structure shown above. Discuss what features of the Lewis structure are reflected in these eigenvalues and what features are not.

The two orbitals with eigenvalues of $\alpha$ are non-bonding orbitals. There is no overlap between neighboring atoms which would give rise to a resonance integral or $\beta$ term in the energy.

Since the integrals represented by $\alpha$ & $\beta$ are negative quantities, the eigenvalues $\alpha + \beta$ & $\alpha + 2\beta$ are the energies of bonding orbitals and are at lower energy than the eigenvalues $\alpha - \beta$ & $\alpha - 2\beta$ which are the energies of anti-bonding orbitals and are found at higher energy.

The Lewis structure shows two oxygen atoms with equivalent unshared pairs of electrons that should be part of the $\pi$ system. This is consistent with the degenerate $\alpha$ eigenvalues that were found.

The Lewis structure shows two equivalent $\pi$ bonds. This is inconsistent with the non-degenerate eigenvalues that were found for the bonding orbitals.
Assign eigenvalues to each of the diagrams. Explain the assignment with respect to the nature of each orbital shown. How are these orbitals a better reflection of the nature of the bonding in the molecule than the Lewis structure given the nature of the eigenvalues?

Starting at the top left: Bonding Orbital, no nodal planes (change of phase) very stable, low energy. Energy = $\alpha + 2\beta$.

Top Right: Anti-Bonding Orbital, nodal planes between all atoms (change of phase) very unstable, high energy. Energy = $\alpha - 2\beta$.

Middle Left & Middle Right: Non-Bonding Orbitals, no overlap between O & C atoms as no C orbital contribution. Energy = $\alpha$.

Bottom Left: Anti-Bonding Orbital (C-O) with some Bonding (C-C) character. Bonding character stabilizes the orbital, not as high energy as the other anti-bonding orbital. Energy = $\alpha - \beta$.

Bottom Right: Bonding Orbital (C-O) with some Anti-Bonding (C-C) character. Anti-Bonding character destabilizes the orbital, not as low energy as the other bonding orbital. Energy = $\alpha + \beta$.

The molecular orbitals contain all of the atoms of the pi system. There are two non-equivalent bonding orbitals that are compatible with the two unequal low-energy eigenvalues. There are two degenerate non-bonding orbitals that only contain O atom contributions and are the lone-pairs that are expected to be found on the O atoms.

MO theory represents the delocalized nature of the bonding in the oxalate anion better than valence bond theory which requires the introduction of resonance in order to accurately represent the molecule. Two Lewis structures are required but only one set of molecular orbitals.

\[
\begin{array}{c}
\text{O}^- \\
\text{O} \\
\text{O}^-
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}^-
\end{array}
\]