Answer any THREE of the four questions. You may work a fourth problem for extra credit. All work will be graded but no total grade will exceed 80 points.

1. A. (10 points) Give a concise statement of Hund’s three rules.
   
   First rule: The lowest energy state belonging to a configuration has maximum S.
   Second Rule: Of the states of maximum spin, the lowest term has maximum L.
   Third Rule: The lowest J-state of the lowest term is the one with maximum J for a more than half-filled shell and minimum J for less than half-filled shell.
   None of the Hund’s rules apply to any but the lowest energy term belonging to a configuration.

B. (10 points) State the definition of a vector operator.

   \[ [A_i, B_j] = \epsilon_{ijk} \hbar B_k \]

C. (10 points) If \( B \) and \( C \) are vector operators with respect to \( A \), then what do you know about matrix elements of \( B \cdot C \) in the \( |AM_A\rangle \) basis?

   \( B \cdot C \) is scalar with respect to \( A \), therefore
   
   \[ \langle A' M'_A | B \cdot C | A M_A \rangle = \delta_{A'A} \delta_{M'_A M_A} \langle A | B \cdot C | A \rangle \]
   independent of \( M_A \).

D. (5 points) The atomic spin-orbit Hamiltonian has the form

   \[ H^{SO} = \sum_i \xi(r_i) \hat{t}_i \cdot \hat{s}_i \]

Classify \( H^{SO} \) as vector or scalar with respect to \( J, L, \) and \( S \). State whether \( H^{SO} \) is diagonal in the \( |JM_JLS\rangle \) or \( |LM_LSM_S\rangle \) basis.

   \( H^{SO} \) is scalar, vector, vector with respect to \( J, L, S \). \( H^{SO} \) is diagonal with respect to \( J \) and \( M_J \) but not \( L \) and \( S \) in the \( |JM_JLS\rangle \) basis but diagonal in nothing in the \( |LM_LSM_S\rangle \) basis.
2. Consider the following multiplet transition array:

<table>
<thead>
<tr>
<th>Lower State (L'', L''')</th>
<th>J</th>
<th>?</th>
<th>?</th>
<th>?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(180)</td>
<td>(16)</td>
<td>(0)</td>
<td></td>
</tr>
<tr>
<td>? 16934.63</td>
<td>48.15</td>
<td>16982.78</td>
<td>64.20</td>
<td>17046.98</td>
</tr>
<tr>
<td></td>
<td>50.51</td>
<td>50.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper State</td>
<td>?</td>
<td>17033.29</td>
<td>64.17</td>
<td>17097.46</td>
</tr>
<tr>
<td>(L', S')</td>
<td>63.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>?</td>
<td>(310)</td>
<td>17160.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Intensities are in parentheses above transition frequencies in cm\(^{-1}\); line separations in cm\(^{-1}\) are given between relevant transition frequencies.

A. (10 points) Use the Landé interval rule

\[ E(L, S, J) - E(L, S, J - 1) = \zeta(nLS)J \]

to determine \( J' \) and \( J'' \) values. Rather than list the \( J' \) and \( J'' \) assignments of each line, only list \( J' \) and \( J'' \) for the line observed to be most intense and for the line observed to be least intense.

Consider upper state term separations first

\[
\frac{E(J_{\text{MAX}}) - E(J_{\text{MAX}} - 1)}{E(J_{\text{MAX}} - 1) - E(J_{\text{MAX}} - 2)} = \frac{J_{\text{MAX}}}{J_{\text{MAX}} - 1} = \frac{63.10}{50.50} = \frac{5}{4}
\]

Upper state \( J \) ranges 5\( \leftrightarrow \)3

Lower state:

\[
\frac{J_{\text{MAX}}}{J_{\text{MAX}} - 1} = \frac{64.18}{48.15} = \frac{4}{3}
\]

lower state \( J \) ranges 4\( \leftrightarrow \)2

Most intense line 17160.56 cm\(^{-1}\) in \( J'' = 4 \leftrightarrow J' = 5 \)

Least intense line 17046.98 cm\(^{-1}\) in \( J'' = 4 \leftrightarrow J' = 3 \)

B. (10 points) Use the range of \( J' \) and \( J'' \) and the intensity distribution (i.e., that the most intense transition is not \( \Delta J = 0 \)) to determine the term symbols \( ^{2S+1}L \) for the upper and lower states. Assume \( \Delta S = 0 \).

Range of \( J \) implies either \( S = 1, L' = 4, L'' = 3 \) or \( L = 1, S' = 4, S'' = 3 \)

The second possibility is \( \Delta S \neq 0 \) forbidden.

Upper state is \(^3G\), Lower state is \(^3F\).
C. (5 points) Is the upper state regular (highest J at highest term energy) or inverted (highest J at lowest term energy)? Is the lower state regular or inverted? [Partial energy level diagrams might be helpful here.]

\[
\begin{array}{c|c|c|c|c}
\text{Energy} & J = 5 & J’ = 3 & J” = 4 \\
\hline
3G & 17160.56 & 3G & 17046.98 \\
3F & 17046.98 & 3F & 16934.63 \\
\end{array}
\]

upper state regular \hspace{1cm} lower state inverted

3. A. (5 points) List the L-S terms that arise from the \((ns)(np)^2\) and \((ns)^2(np)\) configurations. [HINT: \((np)^2\) gives \(1S, 3P, 1D\); to get \(sp^2\) couple an \(s\) electron to these three states.]

\[
\begin{align*}
(ns)(np)^2 & \rightarrow 2S, 2P, 4P, 2D \\
(ns)^2(np) & \rightarrow 2P^o
\end{align*}
\]

B. (5 points) Which configuration gives rise to odd terms and which to even?

\[
\begin{align*}
(ns)(np)^2 & \text{ is even because } \Sigma \ell_i = 2 \\
(ns)^2(np) & \text{ is odd because } \Sigma \ell_i = 1
\end{align*}
\]

C. (5 points) List the electric dipole allowed transitions between terms of the \(sp^2\) and \(s^2p\) configurations. (Ignore fine-structure splitting of L-S terms into J-states.)

\[
\begin{align*}
2S & \rightarrow 2P^o \\
2P & \rightarrow 2P^o \\
2D & \rightarrow 2P^o \text{ are the allowed transitions.}
\end{align*}
\]

D. (10 points) Construct qualitative energy level diagrams on which you display all allowed \(J’’-J’\) components of \(2P^o - 2S, 2P^o - 2P,\) and \(2P^o - 2D\) transitions. Indicate which \(J’’-J’\) line you would expect to be strongest for each of these three transitions.
4. (25 points) Calculate transition probabilities for the two transitions

\[
\begin{align*}
\text{n}_{\text{snp}} \, ^1P_{10}^{0} & \rightarrow \text{(np)}^{2} \, ^1S_{00} \\
\text{n}_{\text{snp}} \, ^1P_{10}^{0} & \rightarrow \text{(np)}^{2} \, ^1D_{20}
\end{align*}
\]

given the following information:

\[
\begin{align*}
^1P_{10}^{0} & = |J = 1, M_J = 0, L = 1, S = 0\rangle \\
& = \frac{1}{\sqrt{2}}|s^0- p^0^+| - \frac{1}{\sqrt{2}}|s^0^+ p^0^-| \\
^1S_{00} & = |J = 0, M_J = 0, L = 0, S = 0\rangle \\
& = \frac{1}{\sqrt{3}}|p^1^- p - 1^+| - \frac{1}{\sqrt{3}}|p^1^+ p - 1^-| + \frac{1}{\sqrt{3}}|p^0^+ p^0^-| \\
^1D_{20} & = |J = 1, M_J = 1, L = 0, S = 0\rangle \\
& = \frac{1}{\sqrt{6}}|p^1^+ p - 1^-| - \frac{1}{\sqrt{6}}|p^1^- p - 1^+| + \frac{2}{\sqrt{6}}|p^0^+ p^0^-|
\end{align*}
\]

The electric dipole transition moment operator, \( \mu \), does not operate on spin coordinates, is a one-electron operator, and is a vector with respect to \( \ell \). \( n_{\text{snp}} \rightarrow \text{(np)}^{2} \) transitions are \( \Delta \ell = +1 \) processes. The relevant \( \Delta \ell = +1 \) matrix elements, as given by the Wigner-Eckart theorem for vector operators are

\[
\begin{align*}
\langle n, \ell = 1, m_\ell = 1 | \frac{1}{2} (\mu_+ + \mu_-) | n, \ell = 0, m_\ell = 0 \rangle &= -\frac{1}{\sqrt{2}} \mu_+(ns) \\
\langle n, \ell = 1, m_\ell = 0 | \mu_+ | n, \ell = 0, m_\ell = 0 \rangle &= \mu_+(ns) \\
\langle n, \ell = 1, m_\ell = -1 | \frac{1}{2} (\mu_+ + \mu_-) | n, \ell = 0, m_\ell = 0 \rangle &= +\frac{1}{\sqrt{2}} \mu_+(ns)
\end{align*}
\]

where \( \mu_+(ns) \) is the reduced matrix element \( \langle np | \mu | ns \rangle \).
Since $\mu$ is a one electron operator, the two-electron Slaters must match for one spin-orbital and must have identical spin in the other. This means we need only consider part of $^1S_{00}$ and $^1D_{20}$.

$^1S_{00} \rightarrow \frac{1}{\sqrt{3}} |p0^+ p0^-|$

$^1D_{20} \rightarrow \frac{2}{\sqrt{6}} |p0^+ p0^-|$ because the $|p1^+ p - 1^-|$ and $|p1^- p - 1^+|$ Slaters differ from the $|s0^- p0^+|$ and $|s0^+ p0^-|$ Slaters by two spin-orbitals.

So we do not even need to evaluate matrix elements to get the ratio of transition probabilities

$$\frac{^1P^{\circ}_{10} - ^1S_{00}}{^1P^{\circ}_{10} - ^1D_{20}} = \frac{\left(\frac{1}{\sqrt{3}}\right)^2}{\left(\frac{2}{\sqrt{6}}\right)^2} = \frac{1}{2}$$

Actually evaluating matrix elements gives

$$\left[ \langle ^1P^{\circ}_{10} | \mu | ^1S_{00} \rangle \right] = \frac{1}{\sqrt{6}} \left[ \langle s0^- p0^+ | \mu | p0^+ p0^- \rangle - \langle s0^+ p0^- | \mu | p0^+ p0^- \rangle \right]$$

$$= \frac{1}{\sqrt{6}} \left[ -\mu_+(ns) - \mu_+(ns) \right] = -\frac{2}{\sqrt{6}} \mu_+(ns)$$

Probability is $|\langle 1|\mu|2 \rangle|^2 = \frac{2}{3} |\mu_+(ns)|^2$ for $P^\circ - S$

$= \frac{4}{3} |\mu_+(ns)|^2$ for $P^\circ - D$

Show all your work including false starts. If you are unable to express the transition probabilities in terms of $\mu_+(ns)$, lavish partial credit will be given for the ratio of transition probabilities

$$\frac{^1P^{\circ}_{10} - ^1S_{00}}{^1P^{\circ}_{10} - ^1D_{20}}$$