Problem Set 2
Due Thursday, October 1, 2009

Problems from Cotton: Chapter 4: 4.6, 4.7;  Chapter 6: 6.2, 6.4, 6.5

Additional problems:

(1) Consider the $D_{3h}$ point group and use a coordinate system wherein the $z$-axis is coincident with the $C_3$ axis and the $x$- and $y$-axes lie perpendicular to the $C_3$ axis.

(a) Construct matrices for each symmetry operation (i.e., construct a representation) using three $p$ orbitals that sit on the origin as a basis:

\[
\begin{bmatrix}
1 \\
0 \\
0
\end{bmatrix} ; \quad \begin{bmatrix}
0 \\
1 \\
0
\end{bmatrix} ; \quad \begin{bmatrix}
0 \\
0 \\
1
\end{bmatrix}
\]

(b) Construct a representation using five $d$ orbitals that sit on the origin as a basis:

\[
\begin{bmatrix}
1 \\
0 \\
0
\end{bmatrix} ; \quad \begin{bmatrix}
0 \\
1 \\
0
\end{bmatrix} ; \quad \begin{bmatrix}
0 \\
0 \\
1
\end{bmatrix} ; \quad \begin{bmatrix}
0 \\
1 \\
0
\end{bmatrix} ; \quad \begin{bmatrix}
0 \\
0 \\
1
\end{bmatrix}
\]

(c) By examining the representations you constructed in parts a and b, confirm that properties that divide the symmetry operators into classes are obeyed. Also, discuss the general form of any subblock structure you can identify.

(2) To account for the nonlinear and anisotropic nature of the Zeeman splitting induced in a paramagnetic molecule by an applied magnetic field, $\mathbf{H}$, an effective Hamiltonian is defined that includes a so-called $g$-tensor:

\[
\mathbf{H}_{\text{eff}} = \mu_B \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} = \mu_B \begin{bmatrix}
H_x & H_y & H_z
\end{bmatrix} \begin{bmatrix}
g_{xx} & g_{xy} & g_{xz} \\
g_{yx} & g_{yy} & g_{yz} \\
g_{zx} & g_{zy} & g_{zz}
\end{bmatrix} \begin{bmatrix}
S_x \\
S_y \\
S_z
\end{bmatrix}
\]

For a molecule with one unpaired electron, for example, this expression accounts for dependence of the splitting of the spin-up and spin-down spin states on the direction of the applied magnetic field with respect to the molecular coordinate system. (Anisotropy occurs because the electron may have some orbital magnetic moment that ‘adds to’ or ‘subtracts from’ the spin magnetic moment and the orbital magnetism depends on the shape of the molecule.) Were there no anisotropy in the $g$-tensor, the matrix would be diagonal, with $g_{xx} = g_{yy} = g_{zz} = g_e = 2.0023…$ and the Zeeman splitting would be independent of the applied field direction. Similarly, an induced electric dipole moment, $\mathbf{\mu}$, also depends on the angle that the applied electric field, $\mathbf{E}$, makes with the molecular axes. This is quantified in the molecule’s polarizability tensor, $\mathbf{\alpha}$:

\[
\begin{bmatrix}
\mu_x \\
\mu_y \\
\mu_z
\end{bmatrix} = \begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix} \begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
\]
Because the electronic distribution of the bonding electrons in a molecule is not isotropic, the induced dipole does not generally align with the direction of the applied field. Both \( \mathbf{g} \) and \( \alpha \) are examples of second-rank tensors and their forms must obey certain symmetry constraints. Let’s use the label \( \mathbf{A} \) to represent a general second-rank tensor; \( \mathbf{A} \) is a \( 3 \times 3 \) matrix. If we apply a symmetry operation to a molecule, we move it to a physically indistinguishable position, and the form of \( \mathbf{A} \) must be unchanged. Therefore, the \( 3 \times 3 \) matrix representing a symmetry operation, \( \mathbf{R} \), must commute with \( \mathbf{A} \):

\[ \mathbf{AR} = \mathbf{RA} \Rightarrow \mathbf{A} = \mathbf{R}^{-1} \mathbf{A} \mathbf{R}. \]

Using this expression, we can find the symmetry constraints on the form of \( \mathbf{A} \) for an \( O_h \)-symmetry molecule. Let’s start with a \( C_2 \) rotation along the \( z \)-axis:

\[
\mathbf{A} = C_2^{-1}(z) \mathbf{A} C_2(z)
\]

\[
\begin{bmatrix}
A_{xx} & A_{xy} & A_{xz} \\
A_{yx} & A_{yy} & A_{yz} \\
A_{zx} & A_{zy} & A_{zz}
\end{bmatrix} = \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix}
A_{xx} & A_{xy} & A_{xz} \\
A_{yx} & A_{yy} & A_{yz} \\
A_{zx} & A_{zy} & A_{zz}
\end{bmatrix} = \begin{bmatrix}
A_{xx} & A_{xy} & A_{xz} \\
A_{yx} & A_{yy} & A_{yz} \\
-A_{zx} & -A_{zy} & A_{zz}
\end{bmatrix}
\]

Comparing the first and last forms enables us to conclude \( A_{zx} = A_{zy} = A_{xz} = A_{yz} = 0 \).

Applying the same procedure with the \( C_2(x) \) or \( C_2(y) \) rotations, we conclude that \( A_{yx} = A_{xy} = 0 \), too. So far then, we know

\[
\mathbf{A} = \begin{bmatrix}
A_{xx} & 0 & 0 \\
0 & A_{yy} & 0 \\
0 & 0 & A_{zz}
\end{bmatrix}
\]

Finally, we can use one of the \( C_3 \) rotations:

\[
\mathbf{A} = C_3^{-1}(x) \mathbf{A} C_3(x)
\]

\[
\begin{bmatrix}
A_{xx} & 0 & 0 \\
0 & A_{yy} & 0 \\
0 & 0 & A_{zz}
\end{bmatrix} = \begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & 0 & 0
\end{bmatrix} \begin{bmatrix}
A_{xx} & 0 & 0 \\
0 & A_{yy} & 0 \\
0 & 0 & A_{zz}
\end{bmatrix} = \begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & 0 & 0
\end{bmatrix} \begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
0 & 0 & A_{xx}
\end{bmatrix} = \begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
0 & 0 & A_{xx}
\end{bmatrix}
\]

\[
A_{yy} = A_{zz} \quad \Rightarrow \quad \mathbf{A} = \begin{bmatrix}
A_{xx} & 0 & 0 \\
0 & A_{yy} & 0 \\
0 & 0 & A_{zz}
\end{bmatrix} \equiv \begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

In \( O_h \) then, all second rank tensors (like \( \mathbf{g} \)-tensors and polarizabilities) are isotropic (diagonal with identical elements). **Finally, your problem: find the general form of second-rank tensors for molecules that are (a) \( D_{3h} \), (b) \( D_{2h} \), and (c) \( C_{2h} \).**
(3) Class Operators. For any point group, we can define operators called \textit{class operators} that are formed by summing point group operators within each class and dividing by the number of operators in the class. For example, for the $D_{3h}$ group we have six class operators (draw, for example, the symmetry elements for the cyclo-propenium cation): (Note that each sum is divided by the number of operators in the class.)

(a) Using the multiplication properties of the point group operations, \textit{construct a multiplication table based on class operators} (i.e., Fill in the table. A multiplication table for $D_{3h}$ will be handy!):

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$\Omega_E$</th>
<th>$\Omega_3$</th>
<th>$\Omega_{2\perp}$</th>
<th>$\Omega_h$</th>
<th>$\Omega_S$</th>
<th>$\Omega_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega_E$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Omega_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Omega_{2\perp}$</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Omega_h$</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Omega_S$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Omega_v$</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

If you have correctly filled in the table, you can immediately \textit{confirm} that each of these operators commutes with the others, in other words, (definition: $[A, B] = AB - BA$):

$[\Omega_3, \Omega_{2\perp}] = [\Omega_3, \Omega_h] = [\Omega_3, \Omega_S] = [\Omega_3, \Omega_v] = [\Omega_{2\perp}, \Omega_h] = [\Omega_{2\perp}, \Omega_S] = [\Omega_{2\perp}, \Omega_v] = [\Omega_h, \Omega_S] = [\Omega_h, \Omega_v] = [\Omega_S, \Omega_v] = 0$

If a set of operators mutually commutes, then they share a common set of eigenfunctions. In this $D_{3h}$ example, let us consider $\Phi$ to be an arbitrary eigenfunction of $\Omega_E$, $\Omega_3$, $\Omega_{2\perp}$, $\Omega_h$, $\Omega_S$, and $\Omega_v$ with eigenvalues $\lambda_E$, $\lambda_3$, $\lambda_{2\perp}$, $\lambda_h$, $\lambda_S$, and $\lambda_v$, respectively. First, since $\Omega_E = E$ is just the identity operator, it is clear that $\lambda_E = 1$ for \textit{any} eigenfunction $\Phi$. Symbolically,

$\Omega_E \Phi = 1 \cdot \Phi; \quad \Omega_3 \Phi = \lambda_3 \cdot \Phi; \quad \Omega_{2\perp} \Phi = \lambda_{2\perp} \cdot \Phi; \quad \Omega_h \Phi = \lambda_h \cdot \Phi; \quad \Omega_S \Phi = \lambda_S \cdot \Phi; \quad \Omega_v \Phi = \lambda_v \cdot \Phi$

(c) Using the multiplication table and the fact that all the class operators mutually commute, you can \textit{establish all the possible sets of eigenvalues for the class operators}. Relationships between the $\lambda$'s follow from the relationships between the $\Omega$'s. It is easy to check that \textit{one} acceptable set of eigenvalues is $\lambda_E = \lambda_3 = \lambda_{2\perp} = \lambda_h = \lambda_S = \lambda_v = 1$. The other sets of possible eigenvalues can be worked out using the multiplication table.

\textbf{Example:} If one has a set of mutually commuting operators, \textit{then any algebraic relation that is true of the operators must also be true of the eigenvalues of the operators}. For example, suppose that operators $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ all mutually commute. Further suppose that we know the following multiplication table:
Let us consider $\Phi$ to be an arbitrary eigenfunction of $A$, $B$, and $C$ with eigenvalues $\lambda_A$, $\lambda_B$, and $\lambda_C$, respectively. Inspection of the multiplication table shows that $A$ is just the identity operator, therefore it is clear that $\lambda_A = 1$, always. Symbolically, we can write

$$A \Phi = 1 \cdot \Phi \quad B \Phi = \lambda_B \cdot \Phi \quad C \Phi = \lambda_C \cdot \Phi$$

Using the multiplication table, we can write,

$$B^2 \Phi = \frac{1}{2}(A + B) \Phi \quad \therefore \quad \lambda_B^2 = \frac{1}{2}(1 + \lambda_B)$$

which has the solutions $\lambda_B = -\frac{1}{2}, 1$. Also,

$$C^2 \Phi = \frac{1}{3}(A + 2B) \Phi \quad \therefore \quad \lambda_C^2 = \frac{1}{3}(1 + 2\lambda_B)$$

Remember, the equations involving the eigenvalues are true only because $A$, $B$, and $C$ mutually commute. We can conclude that the possible eigenvalues are

$$\begin{align*}
\lambda_B &= 1 \quad \text{and} \quad \lambda_C = \pm 1 \\
\lambda_B &= -\frac{1}{2} \quad \text{or} \quad \lambda_C = 0
\end{align*}$$

To summarize, we can construct a table with three distinct possible sets of eigenvalues (labeled $\Gamma_1, \Gamma_2, \Gamma_3$):

<table>
<thead>
<tr>
<th></th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>1</td>
<td>-\frac{1}{2}</td>
<td>0</td>
</tr>
</tbody>
</table>

Your task is to repeat the above procedure for the $D_{3h}$ class operators.]

If you have worked out all the possible sets of eigenvalues, you should get five more solutions that do not contradict the multiplication table you initially constructed. Write down a table with six distinct possible sets of eigenvalues (labeled $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5$, and $\Gamma_6$):

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$\lambda_E$</th>
<th>$\lambda_3$</th>
<th>$\lambda_{2 \perp}$</th>
<th>$\lambda_h$</th>
<th>$\lambda_S$</th>
<th>$\lambda_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_5$</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_6$</td>
<td></td>
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</tr>
</tbody>
</table>
(d) Take the z-axis to be the $C_3$ axis. Show that each of the following orbitals, centered at the origin is an eigenfunction of the class operators and assign each to one of these 6 sets: $p_x$, $p_y$, $p_z$ orbitals; $d_{x^2-y^2}$, $d_{z^2}$, $d_{xy}$, $d_{xz}$, $d_{yz}$ orbitals.

(e) You should be able to see obvious similarities between the eigenvalue table and character tables for the $D_{3h}$ group (or any group you wanted to work through). Exploiting these similarities and using facts from lecture and/or outside reading, give an informative, coherent discussion of the implications of this problem. Your discussion should touch upon at least the following:

(i) the relationships between the number of commuting operators, the number of irreducible representations, and the number of class operators;

(ii) the connection between “quantum numbers” and symmetry;

(iii) the relationship between symmetry operators and the Hamiltonian operator.

(4) (a) Derive complete matrices for all the irreducible representations of the $D_{3h}$ point group. Construct a table in which each of the symmetry operations is listed across the top and each of the representations forms a separate row (your table should look like a character table, except that matrices appear instead of just the characters). Hint: The “matrices” for one-dimensional IR’s are trivial. For higher dimensional representations it is easier to choose a convenient set of functions that must form a basis for the irreducible representation; various atomic orbitals located on the origin can sometimes be helpful – see the character table.

(b) Use your table to give one example of each of the properties discussed in lecture:

(i) Vectors formed from matrix elements from the $m$th rows and $n$th columns of different irreducible representations are orthogonal

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{mn}]^* = 0 \text{ if } i \neq j$$

(ii) Such vectors formed from different row-column sets of the same irreducible representation are orthogonal and have magnitude $h/l_i$:

$$\sum_i l_i^2 = l_1^2 + l_2^2 + l_3^2 + \cdots = h$$

(iii) The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group, that is,

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)_{m'n'}]^* = (h/l_i) \delta_{mm'} \delta_{nn'}$$

(iv) The sum of the squares of the characters in any irreducible representation equals $h$, the order of the group:

$$\sum_R [\chi_i(R)]^2 = h$$

(v) The vectors whose components are the characters of two different irreducible representations are orthogonal, that is,
\[ \sum_{R} \chi_i(R) \chi_j(R) = 0 \text{ when } i \neq j \]

(vi) Matrices in the same class have equal characters
(vii) The number of irreducible representations of a group is equal to the number of classes in the group.

(5) Diborane, B\(_2\)H\(_6\), is a prototypical molecule on which the concept of the 2c-2e bond, so familiar from organic chemistry, is wholly inadequate. This molecule dramatically illustrates that the valence ideas that are familiar from the study of covalent organic molecules are inadequate for treating the broader range of covalent molecules.

(a) What irreducible representations (IRs) are spanned by the reducible representation built up from the four terminal B-H \( \sigma \) bonds? (Use the coordinate system shown throughout this problem.)

(b) What IRs would be spanned by 4 \( \sigma \) bonds that might be naively thought to form the B\(_2\)H\(_2\) ring? (Note: Such bonds cannot be present if only diborane has too few electrons to form them.)

(c) What IRs are spanned by the two “sp\(^2\)-hybrid” orbitals directed from the BH units into the center of the B\(_2\)H\(_2\) ring (one of which is shown above)? What IRs are spanned by the two “\( \pi \)-lone-pair” orbitals (one of which is shown above)? What IRs are spanned by the two bridging hydrogen 1s orbitals?

(d) Construct a qualitative MO diagram using these six orbitals and whatever electrons are not used by the molecule in the four terminal B-H \( \sigma \) bonds.

(e) As noted in (b), diborane has an insufficient supply of electrons to form four B-H \( \sigma \) bonds in the B\(_2\)H\(_2\) ring. What first row element A would have enough electrons that we could reasonably draw a diborane-like A\(_2\)H\(_6\) structure and interpret all the lines as 2c-2e bonds? What do you conclude about the “reasonableness” of such a structure from this symmetry analysis?