A BRIEF INTRODUCTION TO MOLECULAR ORBITAL THEORY OF SIMPLE POLYATOMIC MOLECULES FOR UNDERGRADUATE CHEMISTRY STUDENTS

Ione M. Baibich*
Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre - RS, Brasil
Ian S. Butler
Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

Received on 18/7/11; accepted on 14/2/12; published on web on 15/6/12

A simple, four-step method for better introducing undergraduate students to the fundamentals of molecular orbital (MO) theory of the polyatomic molecules H\textsubscript{2}O, NH\textsubscript{3}, BH\textsubscript{3} and SiH\textsubscript{4} using group theory is reported. These molecules serve to illustrate the concept of ligand group orbitals (LGOs) and subsequent construction of MO energy diagrams on the basis of molecular symmetry requirements.

Keywords: molecular orbital theory; ligands group orbitals; molecular symmetry.

INTRODUCTION

Undergraduate students often have great difficulty understanding the molecular orbital (MO) theory for non-linear, polyatomic molecules. Most inorganic chemistry textbooks address the MOs of simpler polyatomic molecules without using molecular symmetry or group theory. Typically, only in later chapters of textbooks is the concept of ligand group orbitals (LGOs) and application of group theory in the MO approach introduced, and even then chiefly for transition metal compounds.\textsuperscript{1-3} To better appreciate LGOs, it is important to understand that the orbitals of the ligands cannot be treated independently, because they transform under the symmetry operations of the molecular point group concerned. We describe here a relatively straightforward, stepwise method by which undergraduate students can better understand the benefits of MO theory in inorganic chemistry. Nowadays, in many universities throughout the world, undergraduate students are introduced to group theory on physical chemistry courses before embarking on inorganic chemistry courses.

RESULTS AND DISCUSSION

We are assuming here that the students understand the principles of point group symmetry and know how to identify the basic symmetry elements for a molecule: principal rotation axis and other rotation axes, planes of symmetry, center of symmetry (or inversion center), rotation-reflection axes and identity. In addition, we assume that students know how to classify a molecule according to its particular point group and are aware that reducible representations represent the symmetries of specific molecular properties, in our case, the valence orbitals.\textsuperscript{4} It is also assumed that the basic principles of molecular orbital (MO) theory for diatomic molecules which students have seen in earlier courses are understood along with the fact that molecular orbitals are linear combinations of atomic orbitals. These linear combinations occur when the symmetries of the atomic orbitals are the same and the orbitals are close in energy. Finally, the students are taken to fully understand the differences between bonding, antibonding and nobonding molecular orbitals. Four representative polyatomic molecules will be considered in this paper, namely: H\textsubscript{2}O, NH\textsubscript{3}, BH\textsubscript{3} and SiH\textsubscript{4}.

Example 1: H\textsubscript{2}O

The point group of H\textsubscript{2}O is C\textsubscript{2v}. The symmetries of the valence orbitals of the central O atom can readily be obtained from the C\textsubscript{2v} character table. The symmetries of s orbitals are always given by the totally symmetric irreducible representations in character tables, while symmetries of p orbitals are obtained from the 3\textsuperscript{rd} column of the character tables in which the x, y and z Cartesian coordinate axes are indicated. The d orbitals can be identified from the 4\textsuperscript{th} column of the character table as the binary products of the Cartesian coordinates (z\textsuperscript{2}, xy, etc.). To obtain the symmetries of the LGOs of H\textsubscript{2}O, we need to know that the C\textsubscript{2} principal rotation axis is about the z-axis containing the O atom. In order to find the reducible representations for the LGOs, the following well-known group theoretical reduction formula is used:

\[
\alpha_j = \frac{1}{h} \sum_R g(R) X_i(R) X_j(R)
\]

where \(\alpha_j\) is the number of times the \(j\)-th irreducible representation appears in the reducible representation, \(h\) is the order of the group, \(R\) represents the symmetry operation, \(g\) is the order of the class, \(X_i(R)\) is the irreducible representation character in \(R\) and \(X_j(R)\) is the reducible representation character in \(R\). The orbitals that are going to combine linearly must have the same symmetry and be close in energy. The actual energy levels for individual molecules are readily obtained from experimental measurements, such as by photoelectron spectroscopy.

For H\textsubscript{2}O, we therefore have:

**Step 1.** Identification of the point group symmetry of the molecule: C\textsubscript{2v}.

**Step 2.** Determination of the symmetries of the valence orbitals of the central atom.

From the C\textsubscript{2v} character table (Table 1), the s valence orbital has \(\alpha_s\) symmetry, while the symmetries of the p valence orbitals are

<table>
<thead>
<tr>
<th>C\textsubscript{2v}</th>
<th>E</th>
<th>C\textsubscript{2}</th>
<th>(\sigma) ((xz))</th>
<th>(\sigma') ((yz))</th>
<th>(x^2, y^2, z^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{1}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(\sigma)</td>
</tr>
<tr>
<td>A\textsubscript{2}</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>(R_z) X\textsubscript{2}</td>
</tr>
<tr>
<td>B\textsubscript{1}</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>(x, R_z) Y\textsubscript{2}</td>
</tr>
<tr>
<td>B\textsubscript{2}</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>(y, R_z) Y\textsubscript{2}</td>
</tr>
</tbody>
</table>

* e-mail: ione@iq.ufrgs.br
A brief introduction to molecular orbital theory

identified as: $p_z$, $a_1$; $p_x$, $b_1$ and $p_y$, $b_2$ (N.B. Lower-case letters are used to represent the irreducible representations).

**Step 3.** Identification of the symmetries of the LGOs for the H atoms of H$_2$O. To achieve this, the internal coordinates for the σ bonds ($\sigma_i$ and $\sigma_j$) in Figure 1 must be considered. In the four examples examined in this paper, the orbitals of the H atoms in the molecular orbital diagrams are referred to as “ligand group orbitals” which are symmetry - adapted H atomic orbitals. The reducible representations for the LGOs are given by the number of internal coordinates ($\sigma$) that do not move when each of the different symmetry operations is applied.

<table>
<thead>
<tr>
<th>$\Gamma_{\text{red}}$</th>
<th>E</th>
<th>2C$_x$</th>
<th>3σ$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>$\frac{1}{4}[(1 \times 2 \times 1) + (1 \times 0 \times 1) + (1 \times 0 \times 1) + (1 \times 2 \times 1)] = 1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_2$</td>
<td>$\frac{1}{4}[(1 \times 2 \times 1) + (1 \times 0 \times 1) + (1 \times 0 \times -1) + (1 \times 2 \times -1)] = 0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_3$</td>
<td>$\frac{1}{4}[(1 \times 2 \times 1) + (1 \times 0 \times -1) + (1 \times 0 \times 1) + (1 \times 2 \times -1)] = 0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_4$</td>
<td>$\frac{1}{4}[(1 \times 2 \times 1) + (1 \times 0 \times -1) + (1 \times 0 \times -1) + (1 \times 2 \times -1)] = 1$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus, the symmetries of the LGOs for H$_2$O are $a_1 + b_2$.

**Step 4.** Construction of the energy level diagram for H$_2$O. Figure 2 illustrates the MO energy diagram for H$_2$O. The students know that linear combinations of the central atom atomic orbitals and the LGOs have to be accomplished with orbitals with the same irreducible representations and that, in the four examples being considered in this paper, the orbitals have the energy requirements to combine. For more advanced students, some papers that deal with more detailed energy calculations are suggested.$^{7,8}$ (Comment: it should be noted it is an approximation to state that $a_1$, and $b_2$ ligand orbitals have the same energies.)

Considering the number of electrons in the various orbitals:

- Bond order of H$_2$O = $\frac{1}{2}(4 - 0) = 2$
- Bond order of O-H = 2/2 = 1

We use the approximation that two orbitals combine to form two new orbitals, such that the $a_i$ orbital which originates from the $p_z$ oxygen orbital is represented as shown above and not as a linear combination of all the $a_i$ orbitals in the molecule. This orbital is lowered in energy as a result of interaction with other orbitals of the same symmetry.

**Example 2: NH$_3$**

**Step 1.** The point group of NH$_3$ is C$_3v$.

**Step 2.** The symmetries of the 2s and 2p orbitals of N are $a_1$ and $a_1 + e$, respectively.

**Step 3.** The symmetries of the LGOs are represented as three vectors along the NH bond axes:

$G_{\text{red}} = 2 \times C_3 \times V (xz) \times V (yz)$

$\Gamma_{\text{red}} = a_1 + e$

**Step 4.** The MO energy diagram for NH$_3$ is shown in Figure 3.

The energy of the central $a_1$ orbital is lowered by interactions with other orbitals of the same symmetry in the approximation that we are using, as explained above.

Bond order of NH$_3$ = $\frac{1}{2}(6 - 0) = 3$

Bond order of N-H: 1

**Example 3: BH$_3$**

**Step 1.** The point group of BH$_3$ is D$_3h$.

**Step 2.** The symmetries of the 2s and 2p orbitals of B are $a_1'$ and $e'$ + $a_2''$, respectively.

**Step 3.** The symmetries of the LGOs are given by:

<table>
<thead>
<tr>
<th>$\Gamma_{\text{red}}$</th>
<th>E</th>
<th>2C$_2$</th>
<th>3S$_z$</th>
<th>3σ$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Therefore, the symmetries of the LGOs for BH$_3$ are $a_1' + e'$.

**Step 4.** The energy level diagram for BH$_3$ is shown in Figure 4.

Bond order of BH$_3$ = $\frac{1}{2}(6 - 0) = 3$
Bond order of B-H: 1

(N.B. Chemically, BH$_3$ is actually a H-bridged dimer, B$_2$H$_6$, but it is easier for the students to understand the approach for the simpler BH$_3$ species.)
At this stage, we ask the students what is required for NH$_3$ (a Lewis base) and BH$_3$ (a Lewis acid) to react together to form the 1:1 adduct NH$_3$·BH$_3$. The answer is that the BH$_3$ molecule must distort from D$_3h$ to C$_3v$ symmetry, so that its LUMO orbitals (which are empty and higher in energy) will have the same symmetries as do the HOMO orbitals (which are full and lower in energy) of NH$_3$. Only then, will it be possible for the LUMO and HOMO orbitals to combine linearly to form two new molecular orbitals thereby producing the adduct (Figure 5).

Example 4: SiH$_4$

Step 1. The point group of SiH$_4$ is T$_d$.
Step 2. The symmetries of the 3s and 3p orbitals of Si are $a_1$ and $t_2$, respectively.
Step 3. The symmetries of the LGOs are given by:

<table>
<thead>
<tr>
<th>$\Gamma_{red}$</th>
<th>E</th>
<th>8C$_s$</th>
<th>3C$_2$</th>
<th>6S$_1$</th>
<th>6C$_{3v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{red}$</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Therefore, the symmetries of the LGOs for SiH$_4$ are $a_1 + t_2$.
Step 4. The MO energy level diagram for SiH$_4$ is shown in Figure 6.

CONCLUSIONS

In order to render our group theoretical method for producing MO energy diagrams easier for undergraduate students to follow, we have constructed the following stepwise general approach:

Step 1. Identify the point group symmetry of the molecule
Step 2. Determine the symmetries of the valence orbitals of the central atom from the character table
Step 3. Find the symmetries of the LGOs
Step 4. Construct the MO energy level diagram.

This algorithm is entirely consistent with Taber’s well-known pedagogical approach to chemical education.

ACKNOWLEDGEMENTS

I. M. Baibich thanks CNPq (Brazil) for financial support. I. S. Butler gratefully acknowledges a NSERC InterAmerica Collaborative Grant for travel assistance between Canada and Brazil. We thank S. Wolke for the Figures.

REFERENCES

9. Taber, K. S.; Chemical Education: Research and Practice in Europe 2001, 2, 123.