PROVING THE PARAMAGNETISM OF OXYGEN
BY MOLECULAR MODELLING

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ABSTRACT

The present work describes how molecular modelling (semi-empirical and density functional theory-DFT approach) can be used to prove that molecular oxygen is paramagnetic, with two unpaired electrons. [African Journal of Chemical Education—AJCE 8(2), July 2018]
INTRODUCTION

Since high school, students are familiar with Lewis structures and Valence Bond Theory (VBT). If we simply write the Lewis structure for molecular oxygen (O\textsubscript{2}), we conclude that such a molecule has no unpaired electrons and that O\textsubscript{2} is, consequently, a diamagnetic substance (see Figure 1).

Fig. 1. Lewis structure for O\textsubscript{2}

![Lewis structure for O2](Image)

If we explain the formation of O\textsubscript{2} molecule by using VBT, the same result is obtained: O\textsubscript{2} has no unpaired electrons. Since the electron configuration of O is 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{4}, the 2p level of each oxygen atom has 2 unpaired electrons. When two oxygen atoms approach each other, the

Fig. 2. Schematic representation of the σ and π bond formations in O\textsubscript{2}, showing (for each oxygen atom) a filled p orbital and two p orbitals with one unpaired electron each

![Schematic representation of bond formations in O2](Image)
respective unpaired electrons of each atom, are paired with each other, forming a σ and a π bond, resulting in zero unpaired electrons (Figure 2).

However, it is well known that O₂ is paramagnetic, as some simple demonstrations [1] can easily show.

Molecular Orbital Theory (MOT) (generally introduced only in undergraduate classes) predicts, correctly, that O₂ is a paramagnetic substance, with two unpaired electrons (Figure 3).

![Molecular Orbital diagram for O₂](image)

*Fig. 3. Molecular Orbital diagram for O₂*

The correct explanation/prediction of O₂ paramagnetism is one of the triumphs of MOT over VBT. Such facts, as well as the MO diagram for O₂ are presented in any college chemistry textbook [2]. But, how can we “prove”, in the classroom, that O₂ has, indeed, two unpaired electrons?
The present work described how molecular modelling can be used to prove that molecular oxygen is paramagnetic, with two unpaired electrons. Such an approach can be a useful tool in the classroom for both general chemistry and inorganic chemistry classes.

**METHODOLOGY**

Molecular oxygen (O\(_2\)) was modelled by using Spartan’16 [3], with two possibilities: zero and two unpaired electrons. The calculations were performed by using two approach/levels of theory: Semi-Empirical (PM6) and DFT/M06-2X/6-311-G**.

As is well known from hard and soft acid-base theory, ionization energy, IE = \(E_{\text{homo}}\), that is, the energy of the highest occupied molecular orbital and electron affinity, \(EA= -E_{\text{lumo}}\), that is, the energy of the lowest unoccupied molecular orbital [4]. In fact, according to Koopman’s theorem [5], \(IE \approx E_{\text{homo}}\), and the theorem makes no claim about \(E_{\text{lumo}}\) energy. A similar theorem exists in density functional theory (DFT).

Hence, the calculated homo and lumo energies were compared with \(O_2\) experimental values for IE and EA [6-8].

**RESULTS AND DISCUSSION**

The obtained results are summarized in Table 1. As can be verified, only the calculated values for \(O_2\) with two unpaired electrons are in good agreement (specially the IE) with the experimental values. In fact, we must pay attention only in the IE values since (\(E_{\text{homo}}\)) since, in the employed approximations, the lumo energy shows little correlation with the electron affinity [9].
Table 1. Experimental values for O2 IE and EA, and calculated homo and lumo energies.

<table>
<thead>
<tr>
<th>Parameter/Specie</th>
<th>O₂ (0 unpaired e⁻)</th>
<th>O₂ (2 unpaired e⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IE/eV (exp)ᵃ</td>
<td></td>
<td>12.1 ± 0.1</td>
</tr>
<tr>
<td>EA/eV (exp)ᵇ</td>
<td></td>
<td>0.44 ± 0.10</td>
</tr>
<tr>
<td>Eₕomo/eV</td>
<td>8.27ᶜ</td>
<td>10.82ᶜ</td>
</tr>
<tr>
<td></td>
<td>9.35ᵈ</td>
<td>10.93ᵈ</td>
</tr>
<tr>
<td>Eₗumol/eV</td>
<td>1.7ᶜ</td>
<td>1.24ᶜ</td>
</tr>
<tr>
<td></td>
<td>3.24ᵈ</td>
<td>2.99ᵈ</td>
</tr>
</tbody>
</table>

ᵃIn Ref. 5, there are several reported experimental values for IE, all of them very close to each other. The value employed here is from Ref. 6; ᵇIn Ref. 5, there are several reported experimental values for EA, all of them very close to each other. The value employed here is from Ref. 7. ᶜSE(PM6); ᵈDFT/M06-2X/6-311-G**.

Such agreement is a proof that molecular O₂ is, indeed, paramagnetic and also a proof that the number of unpaired electrons is two. In fact, O₂ with two unpaired electrons (triplet form) is only one of the three forms of oxygen [10], considering the possible distributions of electrons in the MO diagram, and the most stable (less energetic) one. The difference between the calculated Eₕomo (DFT/M06-2X/6-311-G** approach, for example) = 10.93-9.35 = 1.58 eV = 152.4 kJmol⁻¹ is the energetic difference between ³Σ and ¹Σ forms [10].

REFERENCES