PROVING THE PARAMAGNETISM OF OXYGEN BY MOLECULAR MODELLING

Robson Fernandes de Farias
Universidade Federal do rio Grande do Norte, Cx. Postal 1664, 59078-970, Natal-RN, Brazil.
Email: robdefarias@yahoo.com.br

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_2), we conclude that such a molecule has no unpaired electrons and that O_2 is, consequently, a diamagnetic substance (see Figure 1).

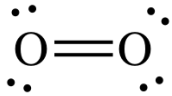

Fig. 1. Lewis structure for O_2

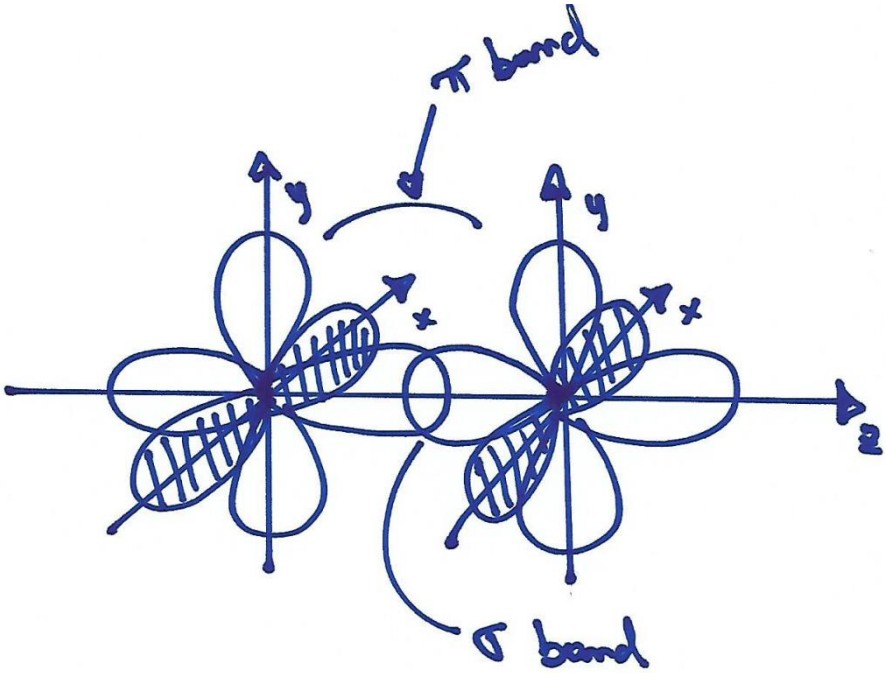

Fig. 2. Schematic representation of the σ and π bond formations in O_2, showing (for each oxygen atom) a filled p orbital and two p orbitals with one unpaired electron each

If we explain the formation of O_2 molecule by using VBT, the same result is obtained: O_2 has no unpaired electrons. Since the electron configuration of O is $1s^2 2s^2 2p^4$, the 2p level of each oxygen atom has 2 unpaired electrons. When two oxygen atoms approach each other, the

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 O_2 is paramagnetic, as some simple demonstrations [1] can easily show.

Molecular Orbital Theory (MOT) (generally introduced only in undergraduate classes) predicts, correctly, that O_2 is a paramagnetic substance, with two unpaired electrons (Figure 3).

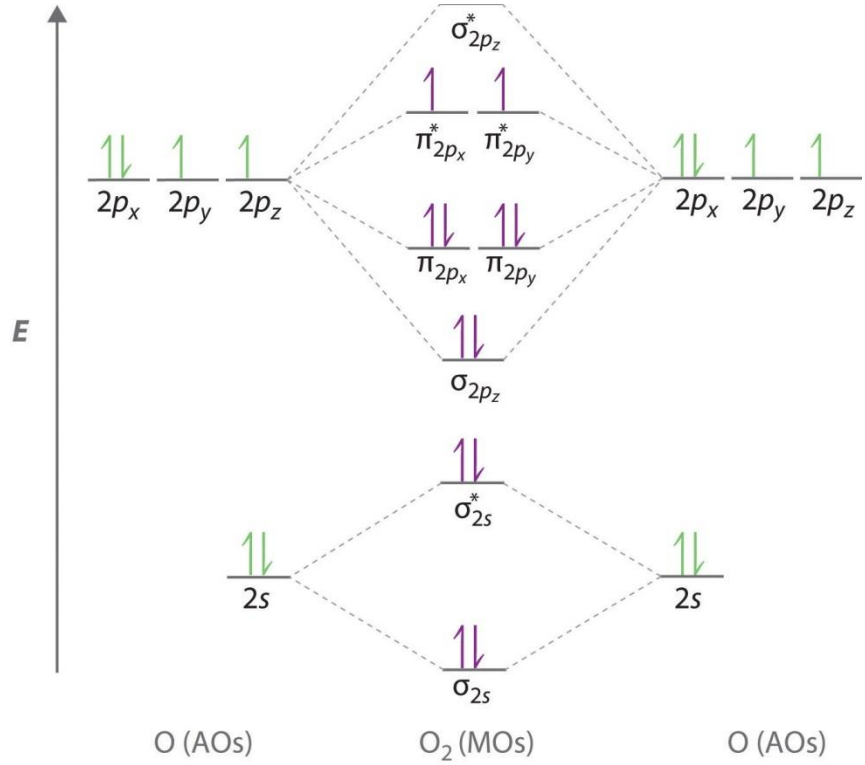

Fig. 3. Molecular Orbital diagram for O_2

The correct explanation/prediction of O_2 paramagnetism is one of the triumphs of MOT over VBT. Such facts, as well as the MO diagram for O_2 are presented in any college chemistry textbook [2]. But, how can we "prove", in the classroom, that O_2 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_{homo}, that is, the energy of the highest occupied molecular orbital and electron affinity, EA= -E_{lumo}, that is, the energy of the lowest unoccupied molecular orbital [4]. In fact, according to Koopman´s theorem [5], IE ≈ E_{homo}, and the theorem makes no claim about E_{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_{homo}) since, in the employed approximations, the lumo energy shows little correlation with the electron affinity [9].

Table 1. Experimental values for O_2 IE and EA, and calculated homo and lumo energies.

Parameter/Specie	O_2 (0 unpaired e^-)	O_2 (2 unpaired e^-)
IE/eV (exp)[a]	_	12.1 ± 0.1
EA/eV (exp)[b]	_	0.44 ± 0.10
E_{homo}/eV	8.27[c] 9.35[d]	10.82[c] 10.93[d]
E_{lumo}/eV	1.7[c] 3.24[d]	1.24[c] 2.99[d]

*[a]In 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; [b]In 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. [c]SE(PM6); [d] DFT/M06-2X/6-311-G**.*

Such agreement is a proof that molecular O_2 is, indeed, paramagnetic and also a proof that the number of unpaired electrons is two. In fact, O_2 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 E_{homo} (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 $^3\Sigma$ and $^1\Sigma$ forms [10].

REFERENCES

1. https://www.youtube.com/watch?v=Lt4P6ctf06Q. (accessed Dec 2017).
2. R. Chang, Chemistry, 10th Ed., McGraw Hill, New York, 2010.
3. Wavefunction Inc., Irvine, California, USA, 2016.
4. B.W. Pfennig, Principles of inorganic chemistry, Wiley, New Jersey, 2015.
5. T. Koopmans, Tjalling, *Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den einzelnen Elektronen eines Atoms*, Physica, 1 (1) (1934) 104.
6. http://webbook.nist.gov/cgi/cbook.cgi?ID=C7782447&Mask=20#Ion-Energetics. (accessed Dec 2017).
7. M. Grade, J. Wienecke, W. Rosinger, W. Hirschwald, *Electron impact investigation of the molecules SeS(g) and TeSe(g) under high-temperature equilibrium conditions*, **Ber. Bunsen-Ges. Phys. Chem.**, 87 (1983) 355.
8. T.O. Tiernan, R.L.C. Wu, *Thermochemical data for molecular negative ions from collisional dissociation thresholds*, **Adv. Mass Spectrom.**, 7A (1978), 136.
9. R.G. Parr, W. Yang, Density-functional theory of atoms and molecules, Oxford University Press, New York, 1989.
10. M. Laing, J. Chem. Ed., 66(6) (1989) 453.