



Evolution of the atomic structure and the magnetism of small oxygen clusters



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ABSTRACT

Motivation for the present theoretical study has been provided by the experimental production of molecular oxygen clusters, and by the observation of an antiferromagnetic ordering of the localized molecular spins in the low temperature α -phase of solid oxygen. We have studied small $(O_2)_n$ clusters with $n = 2, 3$ and 4, by performing unrestricted Møller–Plesset (UMP2) calculations. Focusing on magnetic states showing localized molecular spins, emphasis is placed on the analysis of the evolution of the magnetic behavior as the cluster size increases, and as the geometric arrangement of the oxygen molecules changes for fixed cluster size. Though the clusters treated are small, fingerprints of the cooperative antiferromagnetism known to occur in the low temperature phase of solid oxygen are already visible in the small clusters.

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1. Introduction

The oxygen molecule, O_2 , in its ground state is a paramagnetic molecule with a net spin $S = 1$. Solid oxygen combines the properties of a molecular crystal and those of a magnetic system, producing an interesting material [1]. The low-temperature phase of solid oxygen is the only antiferromagnetic insulator consisting of a single element. Solid oxygen forms three crystalline phases at normal atmospheric pressure, α , β and γ phases, and three high pressure phases [1]. The low-temperature α -phase is stable below 23.9 K and has a monoclinic crystal structure. It shows orientational ordering of the O_2 molecules, in which the molecular axes are collinear and perpendicular to the planes of the close-packed (001) layers. The structure of the intermediate β phase, stable between 23.9 and 43.8 K, is rhombohedral, with the same simple orientational structure as the α phase. The γ phase, with cubic structure and orientational disorder, is stable between 43.8 and 54.4 K. In the α phase, the spins of the O_2 molecules order in a long-range antiferromagnetic structure which is commensurate with the lattice. Instead, the γ phase is paramagnetic, as well as the liquid phase above it, and the magnetic structure of the intermediate β phase is complex.

Molecular oxygen clusters $(O_2)_n$ with sizes up to $n = 70$ have been produced by the expansion of oxygen through a nozzle into vacuum [2–4]. For the mass analysis, the clusters are first crossed

by an electron beam to charge the clusters. However, the process of electron attachment leads to evaporation of O_2 molecules from the original cluster.

Theoretical studies of oxygen clusters have been performed by several groups. Molecular oxygen clusters $(O_2)_n$ are characterized by weak van der Waals bonding between the oxygen molecules. The cluster $(O_2)_2$ has been studied by ab initio methods, mainly with the objective of developing intermolecular O_2 – O_2 interaction potentials. Applying first order exchange intermolecular perturbation theory, van der Avoird and coworkers [5,6] have calculated potential energy surfaces (PES) for singlet, triplet and quintet spin states, and have used those PES to study properties of the solid phases [7]. It was shown in these works that the lowest energy state of $(O_2)_2$ corresponds to a configuration with the two molecular axes parallel and the molecular spins antiferromagnetically coupled. The dependence of the exchange coupling parameter with the relative orientation of the two molecules was also studied. Bussery and Wormer [8] added dispersion corrections. More recently, Bartolomei et al. [9] combined Coupled Cluster (CC) and Configuration Interaction (CI) methodologies to calculate the PES for the singlet and triplet spin multiplicities. The same group has studied some particular states of the trimer $(O_2)_3$, and the tetramer $(O_2)_4$ clusters [10,11]. Also, cyclic clusters, like O_4 , O_6 , O_8 , O_{12} , have been studied [12–16]. It is well-established that these cyclic clusters all lie significantly higher in energy than the appropriate numbers of separated oxygen molecules, and the purpose of some of these works has been to investigate if those cyclic clusters are local minima in the potential energy surface and to find the corresponding barriers for dissociation into oxygen molecules.

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The CC and CI methods represent the most accurate options to calculate the electronic structure of small molecules and clusters. However, these methods become difficult to apply to large molecules or large clusters. This is due to the substantial computational demands (storage memory and computational time) associated to the optimization of the geometries, a process in which the electronic structure of the molecule or cluster has to be recalculated many times, that is, for many intermediate geometric configurations. Our intention is to investigate the magnetic structure of molecular $(\text{O}_2)_n$ clusters and its evolution towards the magnetism of the bulk solid. For this purpose we use the Møller–Plesset (MP2) method [17]. The computational demands of this method are smaller and this would permit the study of larger clusters.

As mentioned above, the low temperature phase of solid oxygen is a molecular solid in which the spin magnetic moments of the O_2 molecules present a long range order antiferromagnetic configuration. Motivated by this property we have analyzed the arrangement of the magnetic moments in the $(\text{O}_2)_2$, $(\text{O}_2)_3$ and $(\text{O}_2)_4$ clusters with the purpose of investigating the evolution of the magnetic arrangement as the cluster grows in size. We find that oxygen molecules with a given spin orientation tend to be surrounded by molecules of the opposite spin orientation. Of course, some frustrations of the antiparallel spin ordering occur because of the small number of molecules in the cluster, but the trend to produce an antiferromagnetic solid is already imprinted in the small clusters.

2. Method

In order to describe the weak interaction between the O_2 molecules we have performed unrestricted (that is, spin polarized) Møller–Plesset (UMP2) calculations [17], implemented in the Gaussian 09 code [18]. Calculations with different correlation-consistent (cc) basis sets of increasing size, aug-cc-pVXZ, with X = D, T, Q and 5 [19–23] have been performed and compared. This family of basis sets contains diffuse functions, which are necessary to reproduce correctly the weak interactions between the oxygen molecules. The calculations were done self-consistently with a total energy convergence tolerance of 2.7×10^{-5} eV. Clusters of two, three and four O_2 molecules have been studied, and the optimizations started with different initial geometries and relative orientations of the molecular axes.

Because we are interested in studying the evolution of the magnetism in the clusters, and the connection to the antiferromagnetic arrangement of spins in the α -phase of solid oxygen, for every cluster geometry and orientation of the axes we have investigated different magnetic configurations: a ferromagnetic order with all the molecular spins pointing in the same direction, and several arrangements with some spins pointing in the up direction and the others pointing in the opposite, down direction. This means that we have to take the solid state-like approach, that is, we are interested in states having localized spins in the molecules of the cluster. This is easy in the ferromagnetic case, because this state

corresponds to the state of highest spin multiplicity. For non-ferromagnetic configurations, with up and down spins, the calculations have been done in two steps. In the first step we have divided the cluster into fragments, each fragment being an oxygen molecule with its corresponding charge and spin, and we have generated wavefunction guesses for each one of those fragments. Then we have combined them together into a wavefunction guess of the cluster, and used it to perform the SCF UMP2 calculations. The optimizations of the cluster geometries were run until the forces on the atoms were lower than 0.023 eV/Å. Frequency analysis has been performed and the results guarantee that the structures are minima in the potential energy hypersurface.

As indicated above, the ferromagnetic state should correspond to the maximum spin multiplicity, and we have confirmed this point. For instance, in the ferromagnetic configuration of the $(\text{O}_2)_2$ cluster, the value of $\langle S^2 \rangle$ is 6.1, already very close to 6.0, and the spin contamination is drastically reduced by using the method of annihilation of the first contaminant [24–26]. In that case $\langle S^2 \rangle = 6.0038$. Similar reductions occur for larger clusters: from 12.147 to 12.0063 in the highest spin state of $(\text{O}_2)_3$, and from 20.191 and 20.0085 in the highest spin state of $(\text{O}_2)_4$. On the other hand, non-ferromagnetic configurations do not correspond to pure spin states, and this is a consequence of the localization of the up and down spins on the different molecules of the cluster. But these are the states of interest to make the connection with the antiferromagnetic solid.

The calculations for the smallest cluster, $(\text{O}_2)_2$, served to investigate the performance of the four basis sets, the aug-cc-pVXZ basis sets with X = D, T, Q and 5. It is observed that the smallest basis set, the aug-cc-pVDZ basis set, is enough to give the main trends. For this reason, for the larger molecular clusters we have employed the aug-cc-pVDZ basis set. However we have also used the aug-cc-pVTZ basis set in selected cases to obtain quantitatively more accurate values for different properties. The binding energies of the smallest cluster, $(\text{O}_2)_2$, have been corrected for the basis set superposition errors using the counterpoise, cp, method [27–29]. The binding energies with and without the cp corrections are different, but their trends are the same. Hence, for larger clusters we have used the expensive cp method only for some particular cases of interest.

3. Cluster of two oxygen molecules, $(\text{O}_2)_2$

Four geometries, shown in Fig. 1, have been investigated in the case of a cluster formed by two oxygen molecules. Three of those configurations, the linear, parallel and T-shape configurations, are planar, that is, the axes of the two molecules lie on a common plane. The two axes are perpendicular in the T-shape configuration. In the cross configuration, the two axes are also perpendicular but do not lie on a common plane; that is, the cross configuration is three-dimensional. For each of those four configurations we have studied two magnetic arrangements: one with the spins of the

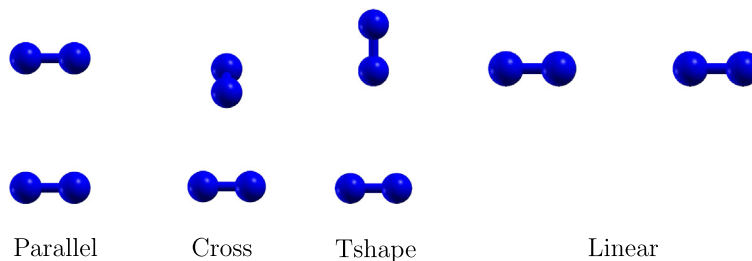


Fig. 1. Four studied geometries of the molecular cluster $(\text{O}_2)_2$: Parallel, cross, T-shape and linear.

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