An unrestricted approach for the accurate calculation of the intermolecular potential of $(O_2)_4$: implications for the solid epsilon phase.

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Abstract

Oxygen in its elemental form shows a variety of magnetic properties in its condensed phases, in particular the epsilon solid phase loses its magnetism. These phenomena reflect the nature of the intermolecular forces present in the solid and the changes that arise with variations of pressure and temperature. In this study we use intermolecular potentials obtained with unrestricted *ab initio* methods to model the singlet state of the oxygen tetramer $((O_2)_4)$, which is the unit cell, consistent with the non-magnetic character of this phase. To do this, we perform an analysis of the coupled-uncoupled representations of the spin operator together with a pairwise approximation and the Heisenberg Hamiltonian. We start from unrestricted potentials for the dimer calculated at a high level as well as different DFT functionals and then apply a finite model to predict the properties of the epsilon phase. The results obtained in this way reproduce well the experimental data in the entire pressure range below 60 GPa. Additionally, we show the importance of calculating the singlet state of tetramer as opposed to previous DFT periodic calculations where the unrestricted description leads to a mixture of spin states and a poor comparison with the experiment. This point is crucial in the recent discussion about the coexistence of two epsilon phases: one where the identity of each O_2 with spin $S = 1$ is retained within the tetramer unit versus another at higher pressures where the tetramer behaves as a single unit with a closed shell character.

Introduction

The magnetism of oxygen and the very interesting characteristics exhibited by this molecule were studied by Gilbert N. Lewis in 1924. One of the most outstanding properties of oxygen is its paramagnetism in the liquid phase and its marked deviations to Curie's law.¹ In order to try to explain these deviations, Lewis proposed² the existence of molecular oxygen clusters, specifically dimers, which are mainly stabilized by weak van der Waals (vdW) forces. The characteristics of oxygen clusters cannot be explained only as a function of the intermolecular distance between the individual molecules or the relative orientations between them. An important role is played by the paramagnetic character of the O_2 molecule, in which we have two unpaired electrons, giving rise

to a triplet state ($S = 1$). The coupling between spin angular moments is responsible for the molecular oxygen dimer deviation from the typical behavior for vdW complexes.^{3, 4} These deviations are evident in all of oxygen phases, from the gas to the solid.⁵

The fact that the oxygen molecule is an open shell system means that, from a theoretical perspective, it is necessary to use unrestricted or restricted open shell methodologies.⁶ When considering clusters of oxygen molecules we find greater complexities and computational challenges even today. One of them arises from the spin coupling that characterizes the interaction between the constituent monomer triplets, for example in the dimer it implies that three intermolecular potentials are allowed, with singlet, triplet and quintet ($S = 0; 1; 2$) multiplicities. Correctly describing the formation of the dimer in its three spin states by theoretical methods is not trivial. Within a restricted methodology the $S = 0; 1$ states give rise to quasi-degeneracies which automatically invalidate the use of single reference methodologies.

For these reasons the theoretical studies carried out on the $O_2 - O_2$ system cover the use of multi reference *ab initio* methods,⁷⁻¹¹ for the study of its three corresponding spin states. Among these theoretical studies, those reported for the case of $S = 2$, at the RCCSD(T)¹⁰ level, stand out because for this multiplicity a single reference wave function is valid. For the cases of triplet and singlet multiplicities studies have been carried out through multireference methods¹¹ (MRCI) finding that this method does not provide the level of correlation necessary to describe with great precision the important dispersive forces that lead to binding in the dimer. For this reason, the use of hybrid methods^{9, 11} has been proposed in which the intermolecular singlet and triplet potentials are obtained by combining RCCSD(T) potentials of the quintet, which properly incorporate dispersion, with the energy differences between the singlet – quintet and triplet - quintet potentials, which are mainly due to exchange-effects calculated at the MRCI and CASPT2 levels. Throughout the manuscript we will refer to these hybrid methods as CC-PT2 and CC-MRCI.

Recently, our group obtained the interaction potentials of oxygen dimer, in 4 representative configurations (H,T,X,L).¹² These potentials were calculated through the use of Gaussian's "Antiferromagnetic Coupling" tool,¹³ with which it is possible to obtain interaction potentials using unrestricted methodology, and therefore at the high UCCSD(T) level. In that work we showed (through an analysis of the coupled-uncoupled representations of angular momentum) that the Antiferromagnetic (AF) and Ferromagnetic (F) state energies correlate with the energies of the $S = 1$ and $S = 2$ states, respectively, of the dimer (more details below). The results were shown as the most accurate obtained to date, due to the high level of correlation included in the UCCSD(T) calculations and the use of a complete basis set (CBS) extrapolation scheme. The interaction potential was also obtained for the $S = 0$ state, through the use of the Heisenberg Hamiltonian approximation obtaining an estimate of the exchange-coupling parameter J from the $S = 1$ and $S = 2$ states. The Heisenberg approximation is valid for most of the range of intermolecular distances modelled, therefore it was argued that the potential of the singlet state is probably the most accurate obtained to date.

However, the interest in oxygen unique properties are not ended in the dimer, but also extend to the liquid and solid phases.^{5, 14} In most of these phases, the molecular character remains, as expected, but a richness of magnetic characteristics appear, being oxygen the only one of the simple elements that in the solid phase presents an insulating and stable antiferromagnetic phase

in a wide range of pressure and temperature and that at higher pressure from 10 to 96 GPa, exhibits a striking phase, the epsilon phase, which becomes non-magnetic. One of the most interesting problems is the explanation of the structure and optical and magnetic properties of this phase, discovered in 1979 but the structure of which was not determined until 2006.^{15, 16} One of the particularities of this epsilon phase is the disappearance of the magnetic properties present in other phases. This manifestation is known as magnetic collapse and is consistent with a total spin equal to zero. The magnetic collapse occurs simultaneously with a sudden collapse of volume, a fact which was finally explained during the determination of the crystalline structure, by two independent X-ray diffraction studies,^{15, 16} which showed that the basic unit of the epsilon phase is composed of four molecules of O_2 (Figure 1). This tetramer structure is consistent with the experimental observation of the sudden reduction in volume by presenting intermolecular distances between 2.0 and 2.4 Å, significantly shorter than in previous phases, whose limit value is not less than 2.6 Å and usually are close to 3.0 Å at atmospheric pressure. Thanks to these studies,^{15, 16} the parameters of the unit cell of the epsilon phase are now available for a wide range of pressures and provide an important data set against which to compare theoretical models that describe the intermolecular forces present in the solid.

Figure 1. Tetramer structure as the unit cell of epsilon phase.

In 2011^{17, 18} a model study of the intra and inter tetramer distances dependence with pressure based on *ab initio* hybrid potentials for the dimer and tetramer, showed very good agreement with the experimental measurements^{15, 16} particularly in the lower pressure regime. An important feature was the softening of the repulsive wall in the tetramer singlet potential that could be related to the formation of an incipient chemical bond. Also, the energies and occupation numbers of the molecular orbitals arising from the π_g shells indicated the formation of bonding and anti-bonding combinations starting at an intermolecular distance of 3 Å but becoming clear only below 2.5 Å. Still for the relevant distances of the experiment, 2.0 – 2.4 Å, an important degree of multiconfigurational character remained. Using this same model but now exploring several DFT exchange-correlation functionals it was clearly shown¹⁹ that, even though the intermolecular potential of the singlet tetramer predicts an spurious minimum bound by chemical forces for all functionals, the repulsive wall can be adequately represented and since this is the key region for modeling the high pressure epsilon phase a reasonable description can be obtained. The very good results obtained with the application of this model and using *ab initio* hybrid potentials (CC-PT2 where the $S = 4$ state is calculated at RCCSD(T) level and the singlet-nonet splitting at CASPT2 level) for the dimer and tetramer will be used in our work as comparison.¹⁷

As evidence of the complexity of this phase, a recent study²⁰ has been published proposing that in the pressure range 8 to 96 GPa there are actually two phases with very similar structures, separated by a first-order phase transition at about 20 GPa. Both phases are consistent with the magnetic collapse of the epsilon phase, but present different behaviors in their local spin. In this study it is proposed that at pressures lower than 20 GPa, oxygen molecules retain their $S = 1$ character but establish antiferromagnetic correlations at short range. Subsequently, at pressures greater than 20 GPa, it is proposed that the identity of each O_2 in its $S = 1$ state has been lost and there are tetramers with a closed shell electronic structure. The authors also suggest that

evidence of the transition has been observed, at $T=20$ K and $P=25$ GPa, as a sharp splitting of a low frequency vibration.²¹ These results open again the debate and interest about this phase, motivating the realization of new studies in order to elucidate its intriguing properties.

The fact that weak intermolecular forces determine the existence of oxygen clusters together with their characteristic quasi-degeneracies mentioned previously, means that it is difficult to achieve a correct description of these through the computational methods currently available, except for the very smallest ones. This is of particular interest in the case of studies in condensed phases where most of the time density functional methods are used. Although significant progress has been made in the description of weak interactions, the problem of quasi-degeneracies at distances relevant to the simulation of properties of the condensed phase remains. Many studies have been conducted for this system,²²⁻²⁴ taking into account the tools provided by DFT, among them one in which the performance of DFT periodic studies with local basis sets for the epsilon phase is noteworthy.²⁵ In these studies, the methodology followed does not manage to reproduce certain structural parameters of the cell (such as the change of the intra- and inter $(O_2)_4$ distances with pressure) in the lower pressure regime, compared to the experimental results.^{15, 16} On the other hand, further studies were performed by the same authors, but using in this case unrestricted DFT,²⁶ motivated by the possible treatment with this methodology of quasi-degeneracies. Unfortunately, the new results present greater differences with the experiment than the restricted variant, with PBE, PBE0 and B3LYP being the functionals used in the mentioned studies.^{25, 26} As we will illustrate, a problem with that approach is that the correct singlet state for the tetrameric unit is not properly represented in the unrestricted density, which actually corresponds to a mixture of several spin states.

In the present work we will reproduce the parameters of the epsilon phase unit cell as a function of pressure, through the pairwise interaction model developed in Ref. 17, 18 using the potentials obtained for the dimer¹² at the high level UCCSD(T), and also using different unrestricted DFT functionals (PBE, PBE0, M062X, B3LYP) most of which were used in periodic DFT calculations already mentioned. We will establish comparisons with the results obtained within this model¹⁷ using the dimer and tetramer potentials obtained at the CC-PT2 level, as well as with experimental X-ray results.¹⁵ Additionally, we will perform an analysis, starting from the coupled-uncoupled representations between spin angular moments of oxygen, in order to correctly model the singlet state of the tetramer, consistent with the antiferromagnetic character of the epsilon phase.

Methodology

It is necessary to mention more details regarding the Antiferromagnetic Coupling procedure available in Gaussian 09. In this procedure the initial orbitals of the UHF step are obtained in separate fragment calculations (one for each O_2) that are later combined in a single set and orthogonalized. This treatment can be applied to any system with open shell structure whose antiferromagnetic state is defined by specifying the z component of the spin of each electron in a given monomer and where the total number of α electrons ($S_z = 1/2$) is equal to the total number of β electrons ($S_z = -1/2$). The treatment to include the electron correlation is made with the unrestricted methodology in standard form.

In ferromagnetic coupling, for the dimer, both fragments (monomers) have $S_z = 1$, while in antiferromagnetic coupling one of the monomers has $S_z = 1$ and the other $S_z = -1$. The ferromagnetic state energy coincides with that of the quintet state for oxygen dimer, while there is uncertainty regarding which state energy the antiferromagnetic calculation approximates, it does not correlate with the singlet, contrary to what might be expected. In order to be able to clarify this aspect, it is necessary to analyze the system according to the angular momentum coupled-uncoupled schemes and establish an analogy between the uncoupled representation and the unrestricted methodology used in the *ab initio* calculations. For further details consult Ref. 12 where it is shown that: the AF and F state energies calculated with the *ab initio* unrestricted methodology correlate with the energies of the $S = 1$ and $S = 2$ dimer states, respectively. A more complicated issue is the correlation between their wavefunctions. For simplicity in writing we will mention this energy correlation in the rest of the manuscript without making this precision on every occasion.

The study that we developed on the epsilon phase can be understood in a clearer way, if we divide it in four consecutive steps:

a) **Study of the role of many-body interactions.**

Due to the doubling of the size of the system, from oxygen dimer to tetramer, it is not feasible to perform wave function calculations of the same quality as for the dimer¹² (UCCSD(T)-CBS). Furthermore, as will be shown below the problem of spin-contamination for the antiferromagnetic state of the tetramer is more severe than for the dimer.

As an alternative to the problem introduced by the increase in the size of the system, we have the application of a model of pairwise interactions (starting from the dimer) and then it is necessary to analyze the role played by the many-body interactions in the accurate description of the tetramer potentials. In order to test the approximation, we can compare with *ab initio* calculations at a lower level of theory as described below.

These calculations of the tetramer were made, as for the dimer, with the Gaussian09 program, through its antiferromagnetic coupling tool. The unit cell $(O_2)_4$ of the epsilon phase is formed, as already mentioned, by 4 molecules of O_2 , each one in its triplet state. In the case of the tetramer, for the purposes of calculation specification, three different combinations of individual spins are possible for this system: Antiferromagnetic **AF1**, alternating the individual spins between the four molecules of the tetramer: +1 -1 +1 -1 (Figure 2 i); **AF2**, differentiating it from the previous one by the arrangement between its individual spins: +1 +1 -1 -1 (Figure 2 ii); and Ferromagnetic **F** where the individual spins are arranged so that we have the maximum multiplicity: +1 +1 +1 +1 (Figure 2 iii).

Figure 2. Scheme for the configurations of the antiferromagnetic and ferromagnetic calculations in the oxygen tetramer. Each black circle represents an O_2 molecule perpendicular to the plane of this surface. i) AF1 coupling ii) AF2 coupling iii) F coupling.

The pairwise interaction model, establishing all possible combinations between pairs of molecules, is summarized in equations [1-3] for the three tetramer calculations performed. Based on the spin coupling of the dimer, combination between two molecules with the same spin projection value correlate to the quintet (q), while coupling of two oxygen molecules with opposite spin correlate with the triplet (t), denoting in brackets the side of the square or the corresponding diagonal.

$$\text{AF1} \quad V_{\text{tetramer}} = 4V_t(\text{side}) + 2V_q(\text{diagonal}) \quad [1]$$

$$\text{AF2} \quad V_{\text{tetramer}} = 2V_q(\text{side}) + 2V_t(\text{side}) + 2V_t(\text{diagonal}) \quad [2]$$

$$\text{F} \quad V_{\text{tetramer}} = 4V_q(\text{side}) + 2V_q(\text{diagonal}) \quad [3]$$

b) Spin expectation value for $(O_2)_4$ in the *ab initio* Antiferromagnetic calculation.

It is necessary to clarify that just as the antiferromagnetic calculation for the dimer does not approximate a singlet state energy but rather a triplet, it is important to analyze the case of the tetramer.

In the two AF variants calculated for $(O_2)_4$ we obtain, from the calculations at UHF level, an expectation value $\langle S^2 \rangle = 4.2$, very distant from the $S = 0$ needed to model the epsilon phase, and even more, this value cannot be assigned with a given spin state, but rather illustrates the high degree of spin contamination. At DFT level the problem remains, with $\langle S^2 \rangle$ values that differ from UHF by less than 5%. On the other hand, and also similar to what happens for the state of maximum multiplicity of the dimer, the Ferromagnetic calculation of $(O_2)_4$ corresponds with the expected $S = 4$ nonet state, showing in the calculation a value of $S^2 = 20.2$ with only a slight contamination for both UHF and DFT calculations.

The spin values obtained as a result of the antiferromagnetic calculations are supported by the analysis that we perform for $(O_2)_4$ in Appendix A. In this analysis we use the already mentioned analogy between the uncoupled representations of angular momentum with the unrestricted methodologies. In this way we evaluate the expectation value of $\hat{S}^2 (\langle s_1, s_2, s_3, s_4; m_1, m_2, m_3, m_4 | \hat{S}^2 | s_1, s_2, s_3, s_4; m_1, m_2, m_3, m_4 \rangle)$ for the AF combinations of the $(O_2)_4$ system. The value obtained in both cases is 4. As we can see, the expectation value of S^2 according to the proposed analysis corresponds to the value of S^2 obtained from the *ab initio* calculation, the latter showing, however, a small degree of additional spin contamination ($S^2 = 4.2$).

c) How do we obtain the $(O_2)_4$ singlet state?

As we just mentioned, the results obtained for the oxygen tetramer through the antiferromagnetic coupling tool do not correspond to a pure spin state. Due to the magnetic

collapse characteristic of the epsilon phase, it is necessary to model adequately the oxygen tetramer singlet state. To obtain the singlet state for $(O_2)_4$, we performed an analysis similar to that developed in the dimer,¹² through the coupled-uncoupled angular momentum representations. To do this, we have to obtain the matrix of the potential operator in the uncoupled base and then diagonalize it. Below we describe the steps involved in more detail.

The system $(O_2)_4$, being composed of 4 oxygen molecules each with spin equal to one ($s_1 = s_2 = s_3 = s_4 = 1$) allows, according to the Clebsch-Gordan rules, spin couplings with values $S = 4; 3; 2; 1$ and 0 , being the last one the state that describes the non-magnetic character in the epsilon phase. A system of these characteristics allows to build 3^4 states in the coupled or uncoupled representations. Due to the size of the matrix generated for this number of states and to make it easier to handle, we take into consideration the fact that the $M_S = 0$ component is present in all spin multiplicities. Furthermore, the potential matrix is block-diagonal in the M_S quantum number. Due to this, the construction and corresponding diagonalization of the potential matrix of the $M_S = 0$ component states, is sufficient to obtain the energies of all the spin states in particular the $S = 0$ state. In order to assign spin value to these eigenvectors one can apply the matrix representation of the total spin (S^2) in the uncoupled representation. In this way we know that the ground state corresponds to $S = 0$ and there are no crossings with other spin states for the range of geometries explored.

We proceed then to express the potential $V(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4)$ using a pairwise decomposition and for the pair interaction we use Heisenberg's Hamiltonian ($\mathcal{H}_{int} = V_{sa} - 2J\mathbf{S}_i \cdot \mathbf{S}_j = V_{sa} - J(\mathbf{S}_{ij}^2 - S_i^2 - S_j^2)$). Taking into account the spin operators of $\mathcal{H}_{int}$ the evaluation of the potential matrix elements $\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | V | m'_{s1}, m'_{s2}, m'_{s3}, m'_{s4} \rangle$ is reduced to the evaluation of spin operator matrix elements, in particular $\langle m_{si}, m_{sj} | \mathbf{S}_{ij}^2 | m'_{si}, m'_{sj} \rangle$. The calculations are simplified by using the orthonormality properties of the basis and matrix transformations associated with changes of basis. The details of the procedure are presented in Appendix B.

d) Model for the energy of the epsilon phase.

The study of the epsilon phase will be approached through the application of a model,^{17,18} which, as we have mentioned, has already been used with favorable results using the *ab initio* hybrid interaction potentials.

The unit cell of this model is represented in Figure 3. The clusters of $(O_2)_4$ are arranged along a 2D layer and the interatomic distances of the O_2 are kept fixed ($1.21 \text{ \AA}$). As we can see from Figure 3, several degrees of freedom are considered, such as the lattice parameters a and b (which differ in magnitude and are perpendicular to each other), the intra- and intercluster distances (d and D respectively) and the α angle of the rhombus formed by the four O_2 molecules with their axes arranged perpendicular to the layer. The lattice parameters are taken from Fujihisa et al¹⁵, where they were determined as functions of pressure from X-ray diffraction experiments. Thus, in this model, the variable pressure is included indirectly through a and b . From the atomic positions observed at 11.4 GPa and reported in detail in Ref.15, the rhombus angle is estimated ($\alpha = 81.4^\circ$); this value is kept fixed since no pressure dependence of this angle was reported. Furthermore, it is assumed that at a given pressure, the center of mass of the clusters remain fixed

and in positions determined by the a and b parameters and that all clusters vary in size (length of d) at the same time.

Figure 3: Model of the unit cell of the epsilon phase. The O_2 bond axes are perpendicular to the plane formed by $a - b$ and the $(O_2)_4$ clusters form rhombuses with $\alpha = 81.4^\circ$. The central $(O_2)_4$ cluster has six nearest neighbors: the four clusters at the corners of the unit cell plus other two just above and below the center of the unit cell (only their O_2 molecules closest to the central cluster are here depicted).

In this way, at each pressure, it is possible to establish the energy per $(O_2)_4$ cluster as a sum of intra- and inter-clusters contributions:

$$E(d) = V^{intra}(d) + 1/2 \sum_i V_i^{inter}(d) \quad [4]$$

where V^{intra} is the potential of the $(O_2)_4$ tetramer in its singlet state and V_i^{inter} represents the interaction of the central cluster of Figure 3 with a neighbor i , and where the factor $1/2$ is introduced to avoid a double counting of these inter-cluster energies. Each $(O_2)_4$ cluster has six first neighbors and the corresponding V_i^{inter} is given as a sum of $O_2 - O_2$ potentials for molecules belonging to different clusters. Distances between these molecules have been obtained as functions of a, b, α and d , and from them, the dimer potentials are evaluated. In particular, the so-called inter-cluster distance D , which will be further compared with the experimental determinations, is given as:

$$D = \left[\left(\frac{a}{2} - d \cos\left(\frac{\alpha}{2}\right) \right)^2 + \left(\frac{b}{2} - d \sin\left(\frac{\alpha}{2}\right) \right)^2 \right]^{1/2} \quad [5]$$

In practice we have only considered the $O_2 - O_2$ energies corresponding to short $O_2 - O_2$ distances, specifically, those that are indicated by dashed lines in Figure 3, as the contributions coming from more distant pairs are negligible. As for the $O_2 - O_2$ potential, we use a spin averaged potential because the non-magnetic character of the epsilon phase suggests the spin-dependence has been washed out.¹⁷ In summary, it is possible to evaluate the evolution of the cluster energy in the epsilon phase as a function of the mentioned variables, introducing potentials calculated at the high level UCCSD(T), for the oxygen dimer and tetramer.

Then the procedure to follow consists of: given the parameters a and b for each value of pressure (taken from Ref. 15), the positions of the center of mass of the oxygen clusters are defined. With this specification of the unit cell, the evolution of the energy of the cell is studied, as given by eq.[4], and determined by V^{intra} and V_i^{inter} . The values of the distances d_m (and D_m ,

obtained from Eq.[5]) that minimize the energy of the cell for each pressure value are thus calculated. We will proceed, later, to compare with experimental values¹⁵ of d_m and D_m .

Calculation specifications for $(O_2)_4$

The tetramer $(O_2)_4$ was calculated at UMP2/AVTZ level as well as at the UPBE, UPBE0, UB3LYP and UM062X level with AVQZ basis set and Superfine integration grid (SFG). The grid of distances used for the supermolecule varying the side of the square that is formed by the centers of mass of the oxygen molecules, was from 15 Å to 1.4 Å in 68 steps of 0.2 Å. This was done for the two AF (Figure 2 i) and ii)) and F combinations (Figure 2 iii). The BSSE error was removed through the counterpoise procedure.²⁷

On the other hand, to apply the already mentioned pairwise interaction model and compare it with the supermolecule calculation, it was necessary to extend with respect to previous calculations⁸ the grid of distances between the centers of mass of two oxygen molecules, in order to satisfy the geometric specificities between the sides and the diagonal of the tetramer. The grid finally used was consistent with a diagonal variation of 21.21 Å to 1.98 Å in 68 steps. Two sets of calculations for the dimer interaction potentials were performed. In order to test the validity of the pairwise approximation for the tetramer we performed UMP2/AVTZ calculations whereas to obtain the final singlet state of the tetramer coming from diagonalization of the potential matrix UCCSD(T)/AVQZ were used.

Results

Oxygen dimer and tetramer

We start with a comparison of the performance of interaction potentials obtained using DFT with our previous¹² accurate results for the dimer in Figure 4. The results are shown for the H conformation in the $S = 1$ and $S = 2$ states. One important objective is to establish comparisons with previous periodic calculations,^{25, 26} and this justifies the selection of the functionals used. Additionally, we also use the M062X functional, which is known to include²⁸ “dispersion-like” or “medium range correlation energy” emphasizing its applicability for equilibrium geometries rather than a proper long-range treatment.

As we can observe, the greatest discrepancies between the analyzed functionals and the accurate UCCSD(T)/AVQZ results are found for the triplet state. For this state, the functional UPBE0 gives hardly any attractive interaction, while the UB3LYP is repulsive for all the distance grid modeled. Although adding dispersion corrections would improve the results specially in the longer range, we did not pursue this option since we wanted to make a comparison with previous periodic calculations^{25, 26} that did not include them either, considering that for the epsilon phase the distances fall in the repulsive region of the interaction ($R < 2.5$ Å). On the other hand, the UPBE functional gives completely incorrect values, both in depth and position of the potential well. Apparently, the introduction of HF exchange is critical to properly represent the important exchange interactions in this state of the system. The case of M06-2X deserves special mention in

the sense that it clearly provides the best comparison with UCCSD(T) results, very good comparison in the longer range but loses accuracy in the shorter range indicating the difficulty in describing exchange-effects. In previous studies of the epsilon phase (Refs 20, 25) it has been mentioned that GGA functionals tend to underestimate the associated band gaps. We have calculated the HOMO-LUMO gap associated with the π_g orbitals of the dimer and find the values 0.639, 0.468, 0.443 and 0.422 Hartree for UHF, M06-2X, PBE0 and PBE, respectively.

In the case of UM062X, the differences in the potential well in relation to the UCCSD(T)/AVQZ level, are of 1.4 and 3.7 meV for the $S = 1$ and $S = 2$ states respectively (see Table 1). The behavior in the dimer will have, within the model used, a direct incidence on the results for the tetramer and the solid phase. Results for distances between 2 Å to 2.8 Å, approximately, are especially relevant for our purpose. For a more precise comparison, we present in Table 1 the values of the interaction potential at the equilibrium distance, and at 2.2 Å, this corresponding to a typical intratetramer distance between oxygen molecules in the epsilon phase around 20 GPa, for all the analyzed calculation levels. As mentioned before¹⁹ we notice that even though the hybrid functionals have very large relative errors in the equilibrium region their predictions improve noticeably in the repulsive region, relevant for the epsilon phase. In this respect we notice that the values of the intratetramer distance d_m are in the interval 2.0 – 2.4 Å whereas those of the intertetramer distances D_m cover larger values 2.4 – 2.8 Å, where larger deviations in the DFT potentials can be seen in Figure 4. This point will be further discussed below when presenting the results of our structural model.

Figure 4: Dimer interaction potentials for H conformation in their $S = 1$ and $S = 2$ spin states, at the UCCSD(T)/AVQZ level. Comparison with the UBPE, UPBE0, UB3LYP and UM062X functionals, with AVQZ basis set.

Table 1: Interaction energies (meV) at the equilibrium distance and at 2.2 Å, for $(O_2)_2$ H conformation, in $S = 1$ and $S = 2$ states, at the UCCSD(T), UM062X, UPBE, UPBE0 and UB3LYP levels with AVQZ basis set. For the purely repulsive UB3LYP functional we show energy values at distances where the equilibrium distances are located at the UCCSD(T) level.

$V(\text{meV}) / R(\text{\AA})$	$S = 1$	$S = 2$	$S = 1$	$S = 2$
UCCSD(T)	-19.9/3.2	-13.1/3.4	408.4/2.2	919.0/2.2
UM062X	-18.5/3.2	-9.4/3.6	386.2/2.2	907.8/2.2
UPBE	-32.3/2.2	-4.9/3.8	-260.7/2.2	1015.8/2.2
UPBE0	-6.2/3.4	-2.9/3.8	364.8/2.2	992.4/2.2

UB3LYP	65.7/3.2	113.0/3.4	368.2/2.2	1048.0/2.2
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Beyond spin multiplicities, the spin average potential is a parameter of importance within our model. We observe in the V_{sa} , that the differences presented for the $S = 1$ state are significantly washed out due to the smaller discrepancy in the description of the $S = 2$ state. Still, the smallest differences with respect to UCCSD(T) continue to be those of the UM062X functional for longer distances (see Figure 5 and Table 2). At distances less than $2.2 \text{ \AA}$ there is a remarkable similarity in the behavior of UCCSD(T), UM062X, UPBE0 and UB3LYP, this last one with larger deviations.

Figure 5: Spin average dimer potential (V_{sa}) for H conformation, at UCCSD(T)-AVQZ level and its comparison with UBPE, UPBE0, UB3LYP and UM062X functionals with AVQZ basis set.

Table 2: Spin average dimer potential (V_{sa}) for H conformation, at UCCSD(T)/AVQZ level and its comparison with UBPE, UPBE0, UB3LYP and UM062X functionals with AVQZ basis set at two intermolecular distances, relevant for long and short range interactions.

$V_{sa} \text{ (meV)}$	$R = 3.4 \text{ \AA}$	$R = 2.2 \text{ \AA}$
UCCSD(T)	-15.6	663.7
UM062X	-12.5	647.0
UPBE	-8.5	491.7
UPBE0	-2.9	678.6
UB3LYP	9.9	708.1

We have also calculated the exchange-coupling constant appearing in the Heisenberg Hamiltonian: J . Together with V_{sa} it determines all the relevant interaction energies and as such it is useful to compare the values obtained with different methods (Figure 6 and Table 3). For details about its evaluation we refer the reader to Ref. 12. As observed in the description of the dimer $S = 1$ state, PBE shows the largest deviations compared with UCCSD(T) overestimating the value of J . Also, we point out that the best estimates from DFT approximations are provided by M06-2X and

PBE0 the former in the shorter range and the latter at longer intermolecular distances. The failure of PBE can be associated with inaccuracies in the treatment of exchange which are clearly improved by the hybrid functionals through addition of HF exchange. A more detailed comparison is given in Table 3 where the same conclusions are reached but one can see that important differences appear for $R = 2.6 \text{ \AA}$ with deviations of roughly 25% from the better performing functionals compared with UCCSD(T).

Figure 6: Exchange-coupling constant (J) for the H conformation, at UCCSD(T)-AVQZ level and its comparison with UBPE, UPBE0, UB3LYP and UM062X functionals with AVQZ basis set. We show the absolute values of J plotted in logarithmic scale.

Table 3: Exchange-coupling constant (J) for the H conformation, at UCCSD(T)/AVQZ level and its comparison with UBPE, UPBE0, UB3LYP and UM062X functionals with AVQZ basis set at three intermolecular distances.

$J \text{ (meV)}$	$R = 2.2 \text{ \AA}$	$R = 2.6 \text{ \AA}$	$R = 3.0 \text{ \AA}$
UCCSD(T)	-127.7	-25.2	-5.5
UM062X	-130.4	-31.1	-7.9
UPBE	-262.0	-58.5	-13.4
UPBE0	-156.9	-32.7	-7.2
UB3LYP	-169.9	-36.6	-8.4

An aspect of vital importance is being able to determine the role that the many body interactions play in the reproduction of the tetramer interaction potential. This analysis can be done for the calculated *ab initio* combinations (AF1, AF2 and F) and comparing them with the interaction potentials obtained through the use of pairwise approximations, eqs. [1-3].

In Figure 7 we show a comparison at the UMP2/AVTZ level between the $(O_2)_4$ tetramer in the AF and F combinations and the results obtained using the pairwise approach at the same calculation level.

We observe that the many body interactions are fairly small for the AF1 and AF2 combinations in most of the analyzed range of distances. Differences less than 3 *meV* between supermolecule vs pairwise approximation are observed for distances greater than 2.6 $\text{\AA}$, which represents a percentage error of 1% or less. At distances of 2.6 $\text{\AA}$ and shorter, the differences begin to be greater than 6 *meV*, representing however at this point a percentage error of only 4%. These percentage errors reach 10% at 1.8 $\text{\AA}$. On the other hand, for F combination the percentage error

is even less than for the AF combinations, reaching 10 % until 1.4 Å in agreement with previous studies^{17, 29} which already indicated that for the highest multiplicity the pair-wise approximation is excellent. It is also worth mentioning that for the lower spin combinations the present unrestricted results indicate a smaller role of the many-body interactions compared with supermolecular restricted calculations^{17, 29} and this may reflect the fact that the unrestricted calculations localize orbitals in each O_2 molecule making the calculation more akin to a pair-wise description whereas in the restricted methodology molecular orbitals are fully delocalized in the supermolecule.

We show in Table 4 the interaction energies at distances of the potential well and at 2.2 Å, obtained through the supermolecule calculation or applying the pairwise interaction model.

Figure 7: Comparison Supermolecule vs pairwise approximations at UMP2/AVTZ level, for AF and F combinations.

Table 4: Interaction energies at equilibrium distances and at 2.2 Å for $(O_2)_4$ supermolecule vs pairwise approximation, for AF and F combinations. Results at UMP2/AVTZ level.

	Supermolecule		Pairwise approximation	
	$V(\text{meV}) / d_m(\text{\AA})$		$V(\text{meV}) / d_m(\text{\AA})$	
AF1	-99.7/3.2	1672.6/2.2	-99.3/3.2	1734.3/2.2
AF2	-82.6/3.2	2583.3/2.2	-82.3/3.2	2617.3/2.2
F	-70.6/3.4	3506.4/2.2	-70.5/3.4	3548.5/2.2

Similar results to those shown in Figure 7 are observed when establishing the same comparisons at other levels (UPBE, UPBE0, UB3LYP, UM062X).

As we have already mentioned, it is not possible to model the $(O_2)_4$ singlet state with the antiferromagnetic methodology and the AF combinations describe a mixture of spin states. However, to obtain this state is of vital important due to the non-magnetic character of the epsilon phase of solid oxygen. This is also a challenge for unrestricted descriptions in periodic calculations²⁶ where the same type of spin mixing will occur since the basic unit for the calculation is the tetramer.

A comparison between AF1, AF2 and the lowest singlet state is shown in Figure 8 at the UCCSD(T)/CBS level, all of them obtained with the pairwise interaction procedure. We observe the importance of achieving a correct description of the singlet state of the oxygen tetramer, this being the deepest in energy of the three combinations. Similar results are observed at the DFT level of theory. The differences noticeably increase at shorter distances as evidenced in Table 5. This is especially relevant when comparing the reported results of DFT periodic studies,²⁶ in which precisely these combinations, AF1 and AF2, were used.

Figure 8: Comparison of $(O_2)_4$ interaction potential, between AF1, AF2 and lowest singlet state, obtained by pairwise interaction and potential matrix diagonalization, at the UCCSD(T)/CBS level.

Table 5: Interaction energies at equilibrium distances and at 2.2 Å for the AF1, AF2 and lowest singlet state for $(O_2)_4$, obtained by pairwise interaction, at the UCCSD (T)/CBS level.

Pairwise	$V(\text{meV}) / d_m (\text{\AA})$	
AF1	-93.3/3.2	1544.7/2.2
AF2	-72.7/3.2	2535.1/2.2
Lowest singlet	-108.3/3.0	1035.2/2.2

In Figure 9 we show the behavior of the $(O_2)_4$ lowest singlet state at different levels of calculation. As expected, the results of the UPBE functional are completely inconsistent with respect to the others. Except for the UPBE functional, the remaining results are close to each other in the region of longer distances, but they differ markedly in the short distances. We observe that the repulsive wall is most pronounced for the functional UM062X, followed by UCCSD(T), while the behaviors of UPBE0 and UB3LYP are shallower and very similar. The slope of the curves in the repulsive zone of the potential has a direct impact on the results found for the solid phase. A more marked repulsive wall implies that it is more difficult to achieve compression in the solid phase subjected to high pressures, an aspect that we will comment on below.

Figure 9: Comparison of the $(O_2)_4$ lowest singlet, obtained through the pairwise approximation and potential matrix diagonalization, at different levels of calculation, and using AVQZ basis set.

Epsilon Phase

We start the discussion of results using the best justified potentials i.e. those corresponding to the singlet states of the tetramer with the aim of comparing with experiment and also contrast the different electronic structure methods used to obtain them. In Figure 10 we show the results of the referred model for the epsilon phase,^{17, 18} using the interaction potentials of the $(O_2)_4$ lowest singlet state, obtained by pairwise interaction, at the UCCSD(T), UPBE, UPBE0, UB3LYP, UM062X levels and the previous¹⁷ CC-PT2 potentials.

As we can see the d_m and D_m distances values obtained with UM062X and UCCSD(T), are in good agreement with the experimental results in the whole range of pressures shown, though a better description is observed below 60 GPa. Also the agreement is better for UCCSD(T) for the most part of the pressure range explored and this reflects some of the limitations we already noticed earlier concerning the UM062X description of the interaction potential in the repulsive region. The differences above 60 GPa, correspond to d_m values close to 2 Å. This is directly related to what was mentioned before for the tetramer: at distances less than 2 Å the errors of applying a pairwise model begin to show. This can be contrasted with the CC-PT2 approach where a very good

description is seen in the whole range of pressures and where no pairwise approximations were applied.

On the other hand, the UPBE0 and UB3LYP functionals are in very good agreement with the experiment in the low pressure area, up to pressures close to 35 GPa corresponding to d_m values of 2.1 Å, approximately. With increasing pressure, the calculated values quickly deviate from the experiment. Once again this is a direct reflection of the behavior in the tetramer for distance values less than 2.1 Å, high up in the repulsive wall, both functionals are very similar to each other and less repulsive than UCCSD(T), translating into lower d_m values in the epsilon phase.

In the case of the UPBE functional, a particular behavior is found again. The results observed for the dimer are clearly reflected in the solid phase: values completely deviated from the experimental results in all the analyzed pressure range, presenting d_m values consistent with the underestimation that this functional gives for the $O_2 - O_2$ interaction energies.

A comparison of the solid phase results between the different calculation methods can be understood by analyzing the potential curves of the $(O_2)_4$ (Figure 9), in the repulsive zone. We see that the most repulsive potentials coincide with the highest values of d_m and therefore the lowest values of D_m , for a given pressure value. For this reason, the region where the UM062X potential becomes steepest ($R < 2.3$ Å) correspond with those results in the solid phase with the highest d_m values, for a given value of pressure. The same analysis can be done for the rest of the results.

Figure 10: Pressure dependence of d_m and D_m parameters for oxygen epsilon phase at UCCSD(T), UM062X, UPBE, UPBE0 and UB3LYP, all with AVQZ basis set and their comparison with experimental results.¹⁵ We also show the CC-PT2 results from Ref. 17.

These results also show, within our model, the importance and need to use interaction potentials that are capable of reproducing, the characteristics of the dimer system.

Another aspect to emphasize, although it has already been mentioned, is the importance of adequately modeling the singlet state that represents the non-magnetic nature of the epsilon phase. The differences observed for the tetramer between the lowest singlet state with the AF1 and AF2 combinations are also notable when modeling the epsilon phase. In Figure 11 we show the results, for UCCSD(T)/AVQZ potentials that correspond to the AF1, AF2 combinations and the lowest singlet state used above. We can see how the d_m and D_m values for the AF1 and AF2 combinations are far from the experimental results, much more than those of the lowest singlet state. It is also worth mentioning that the observed behavior for the AF1 and AF2 combinations resembles the periodic calculations²⁶ in the sense that the d_m and D_m values become much closer to each other and in between the experimental results. This suggests that an important limitation of the unrestricted periodic calculations is the proper description of the singlet state and not so much the use of an unrestricted approach for the electronic structure. This is important because the failure of the unrestricted periodic approach could be taken as an indication of the need to use a closed-shell restricted description for the tetramer when in fact the problem is properly dealing

with the total spin of the system. This point bears on the recent proposal²⁰ of two epsilon phases, one with open-shell character in the lower pressure regime and a closed-shell for higher pressures.

Figure 11: Pressure dependence of the d_m and D_m parameters for the oxygen epsilon phase in the lowest singlet state and AF1, AF2 combinations of $(O_2)_4$. Results obtained at the UCCSD(T)/AVQZ level using a pairwise approach. Comparison with experimental data.¹⁵

Conclusions

In this work we have presented a study of the epsilon phase of solid oxygen, through the use of a previously reported finite model in which we use unrestricted potentials for the oxygen dimer and tetramer. We show that the AF states of the oxygen tetramer calculated with the Gaussian Antiferromagnetic Coupling methodology do not correlate with the characteristic singlet state of the monomeric unit of the epsilon phase, in fact they represent a mixture of several non-zero spin states. Through an analysis of the coupled-uncoupled representation and using the Heisenberg approximation it was possible to construct the potential matrix in the uncoupled base, from its diagonalization we obtain the energy of all the spin states of $(O_2)_4$, in particular the desired singlet state which represents the ground state of the tetramer.

We made comparisons with DFT periodic results, reported in previous studies. We demonstrate the importance of using exchange-correlation functionals that include HF exchange in order to correctly model the behavior of oxygen in its different aggregates (dimer, tetramer and solid phase). Furthermore, the importance of using the correct singlet potentials for the tetramer within any model of the epsilon phase was highlighted. This is of special relevance for unrestricted periodic calculations where it will be difficult to avoid the spin-contamination problem and the corresponding predictions will be strongly affected by this problem. This same point also bears on the recent debate²⁰ regarding the coexistence of two epsilon phases, the one at lower pressures being described by antiferromagnetic coupling in the tetramer with each O_2 keeping its $S = 1$ character as opposed to the higher pressure phase where the tetramer acquires a closed-shell electronic structure.

The results obtained for the epsilon phase, using unrestricted potentials and through the application of the already mentioned pairwise interaction model, are in good correspondence with the experimental results, for pressures below 60 GPa. In this way, we were able to obtain results for the epsilon phase, starting from potentials for the dimer, calculated at a high level (UCCSD(T)).

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Data availability

The data that supports the findings of this study are available from the corresponding authors upon reasonable request

Appendix

Appendix A: Expectation value of $\hat{S}^2$ for AF combinations of $(O_2)_4$.

For the AF1 combination, the state can be described as: $|1, -1, 1, -1\rangle$ using the notation $|m_{s1}, m_{s2}, m_{s3}, m_{s4}\rangle$, ignoring in each case the $s_{1;2;3;4} = 1$ for simplicity of notation.

We want to know the value of $\hat{S}^2$, for which we use the following relation:

$$\begin{aligned}\hat{S}^2 &= (\hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \hat{S}_4)^2 \\ &= \hat{S}_1^2 + \hat{S}_2^2 + \hat{S}_3^2 + \hat{S}_4^2 + 2(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_4)\end{aligned}\quad [1]$$

In order to evaluate $\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | \hat{S}^2 | m_{s1}, m_{s2}, m_{s3}, m_{s4} \rangle$ we use:

$$\begin{aligned}&\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | \hat{S}^2 | m_{s1}, m_{s2}, m_{s3}, m_{s4} \rangle \\ &= \langle m_{s1} | \hat{S}_1^2 | m_{s1} \rangle + \langle m_{s2} | \hat{S}_2^2 | m_{s2} \rangle + \langle m_{s3} | \hat{S}_3^2 | m_{s3} \rangle + \langle m_{s4} | \hat{S}_4^2 | m_{s4} \rangle \\ &\quad + 2(\langle m_{s1} m_{s2} | \hat{S}_1 \hat{S}_2 | m_{s1} m_{s2} \rangle + \langle m_{s1} m_{s3} | \hat{S}_1 \hat{S}_3 | m_{s1} m_{s3} \rangle \\ &\quad + \langle m_{s1} m_{s4} | \hat{S}_1 \hat{S}_4 | m_{s1} m_{s4} \rangle + \langle m_{s2} m_{s3} | \hat{S}_2 \hat{S}_3 | m_{s2} m_{s3} \rangle \\ &\quad + \langle m_{s2} m_{s4} | \hat{S}_2 \hat{S}_4 | m_{s2} m_{s4} \rangle + \langle m_{s3} m_{s4} | \hat{S}_3 \hat{S}_4 | m_{s3} m_{s4} \rangle)\end{aligned}\quad [2]$$

Where:

$$\langle m_{s1} | \hat{S}_1^2 | m_{s1} \rangle = \langle m_{s2} | \hat{S}_2^2 | m_{s2} \rangle = \langle m_{s3} | \hat{S}_3^2 | m_{s3} \rangle = \langle m_{s4} | \hat{S}_4^2 | m_{s4} \rangle = 2 \quad [3]$$

So it remains to evaluate the elements $2\langle m_{si}, m_{sj} | \hat{S}_i \hat{S}_j | m_{si}, m_{sj} \rangle$.

Given that:

$$\hat{S}_{ij}^2 = \hat{S}_i^2 + \hat{S}_j^2 + 2\hat{S}_i\hat{S}_j \quad [4]$$

$$2\hat{S}_i\hat{S}_j = \hat{S}_{ij}^2 - (\hat{S}_i^2 + \hat{S}_j^2) \quad [5]$$

Using the eq.[5] and taking into account that in the interaction between two O_2 molecules with parallel spins $\hat{S}_i\hat{S}_j = \frac{6-2-2}{2} = 1$, while in the case of antiparallel spins $\hat{S}_i\hat{S}_j = \frac{2-2-2}{2} = -1$.

In this way the evaluation of $\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | \hat{S}^2 | m_{s1}, m_{s2}, m_{s3}, m_{s4} \rangle$ remains:

$$\begin{aligned}&\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | \hat{S}^2 | m_{s1}, m_{s2}, m_{s3}, m_{s4} \rangle \\ &= 2 + 2 + 2 + 2 + 2(-1 + 1 - 1 - 1 + 1 - 1) = 4\end{aligned}\quad [6]$$

Being 4 the expectation value of S^2 for the supermolecule $(O_2)_4$ in its AF1 combination, using the uncoupled representation. An analogous analysis can be performed for the combination AF2, obtaining the same result. As we can see, the expectation value of S^2 according to the proposed analysis corresponds to the value of S^2 obtained from the AF coupling calculation, the latter showing, however, a small degree of additional spin contamination ($S^2 = 4.2$).

Appendix B: Evaluation of the potential $V(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4)$ using the Heisenberg Hamiltonian, for $(O_2)_4$.

We construct the 19 uncoupled states of $(O_2)_4$ consistent with $M_s = 0$, employing the notation $|m_{s1}, m_{s2}, m_{s3}, m_{s4}\rangle$, ignoring in each case the $s_{1;2;3;4} = 1$ for simplicity of notation. Let us point out that representing the state $|1; 1; -1; -1\rangle$ is in our notation equivalent to $|1, 1; 1, 1; 1, -1; 1, -1\rangle$.

$$\begin{array}{ll}
 |1; 1; -1; -1\rangle & |0; -1; 0; 1\rangle \\
 |1; 0; -1; 0\rangle & |0; -1; 1; 0\rangle \\
 |1; 0; 0; -1\rangle & |-1; -1; 1; 1\rangle \\
 |1; -1; -1; 1\rangle & |-1; 0; 1; 0\rangle \\
 |1; -1; 1; -1\rangle & |-1; 0; 0; 1\rangle \\
 |1; -1; 0; 0\rangle & |-1; 1; 1; -1\rangle \\
 |0; 1; 0; -1\rangle & |-1; 1; -1; 1\rangle \\
 |0; 1; -1; 0\rangle & |-1; 1; 0; 0\rangle \\
 |0; 0; 1; -1\rangle & |0; 0; 0; 0\rangle \\
 & |0; 0; -1; 1\rangle
 \end{array} \quad [1]$$

We proceed then to evaluate the potential $V(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4)$ using Heisenberg's Hamiltonian ($\mathcal{H}_{int} = V_{sa} - 2J\mathbf{S}_a \cdot \mathbf{S}_b = V_{sa} - J(S^2 - S_a^2 - S_b^2)$), and thus approximating to a pairwise interaction.

$$\begin{aligned}
 V(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) = & (V_{sa_{12}} + V_{sa_{13}} + V_{sa_{14}} + V_{sa_{23}} + V_{sa_{24}} + V_{sa_{34}}) \\
 & - 2(J_{12}S_1S_2 + J_{13}S_1S_3 + J_{14}S_1S_4 + J_{23}S_2S_3 + J_{24}S_2S_4 + J_{34}S_3S_4)
 \end{aligned} \quad [2]$$

Where V_{sa} is a potential averaged in the spin and J is the exchange coupling constant:

$$V_{sa} = \frac{[V_{|S=1\rangle} + V_{|S=2\rangle}]}{2} \quad [3]$$

$$J = \frac{[V_{|S=1\rangle} - V_{|S=2\rangle}]}{4}. \quad [4]$$

Taking into account the expression of the Heisenberg Hamiltonian we proceed to evaluate the elements $\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | V | m'_{s1}, m'_{s2}, m'_{s3}, m'_{s4} \rangle$ and this can be considerably simplified by using the orthonormality properties of the base. It is necessary to differentiate within this pairwise approximation, whether the interactions are along the side of the tetramer or to the diagonal (See Figure 2). Interactions at distances corresponding to the side will occur between pairs of molecules i-j: 1-2; 2-3; 3-4; 4-1; while interactions on the diagonal will be between molecules 1-3 and 2-4.

The relationships established and their demonstration can be seen, for some specific cases in the form of $\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | V | m'_{s1}, m'_{s2}, m'_{s3}, m'_{s4} \rangle$, starting from the eq. 2 of this Appendix and the following relations:

$$(S_i + S_j) \cdot (S_i + S_j) = S_i^2 + S_j^2 + 2S_i S_j = S_{ij}^2 \quad \text{and} \quad S_i \cdot S_j = \frac{1}{2}(S_{ij}^2 - S_i^2 - S_j^2)$$

- Diagonal case: $\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | V | m_{s1}, m_{s2}, m_{s3}, m_{s4} \rangle$

$$\begin{aligned} & \langle \mathbf{1}, \mathbf{1}, -\mathbf{1}, -\mathbf{1} | V | \mathbf{1}, \mathbf{1}, -\mathbf{1}, -\mathbf{1} \rangle \\ &= \left(V_{sa12} - \frac{J_{12}}{2} [\langle 1, 1 | S_{12}^2 | 1, 1 \rangle - \langle 1 | S_1^2 | 1 \rangle - \langle 1 | S_2^2 | 1 \rangle] \right) \langle -1 | -1 \rangle \langle -1 | -1 \rangle + \\ & \left(V_{sa13} - \frac{J_{13}}{2} [\langle 1, -1 | S_{13}^2 | 1, -1 \rangle - \langle 1 | S_1^2 | 1 \rangle - \langle -1 | S_3^2 | -1 \rangle] \right) \langle 1 | 1 \rangle \langle -1 | -1 \rangle + \\ & \left(V_{sa14} - \frac{J_{14}}{2} [\langle 1, -1 | S_{14}^2 | 1, -1 \rangle - \langle 1 | S_1^2 | 1 \rangle - \langle -1 | S_4^2 | -1 \rangle] \right) \langle 1 | 1 \rangle \langle -1 | -1 \rangle + \\ & \left(V_{sa23} - \frac{J_{23}}{2} [\langle 1, -1 | S_{23}^2 | 1, -1 \rangle - \langle 1 | S_2^2 | 1 \rangle - \langle -1 | S_3^2 | -1 \rangle] \right) \langle 1 | 1 \rangle \langle -1 | -1 \rangle + \\ & \left(V_{sa24} - \frac{J_{24}}{2} [\langle 1, -1 | S_{24}^2 | 1, -1 \rangle - \langle 1 | S_2^2 | 1 \rangle - \langle -1 | S_4^2 | -1 \rangle] \right) \langle 1 | 1 \rangle \langle -1 | -1 \rangle + \\ & \left(V_{sa34} - \frac{J_{34}}{2} [\langle -1, -1 | S_{34}^2 | -1, -1 \rangle - \langle -1 | S_3^2 | -1 \rangle - \langle -1 | S_4^2 | -1 \rangle] \right) \langle 1 | 1 \rangle \langle 1 | 1 \rangle \end{aligned}$$

Given that $\langle m_i | m_j \rangle = 1$ if and only if $i = j$; on contrary $\langle m_i | m_j \rangle = 0$

$$\begin{aligned} & \langle \mathbf{1}, \mathbf{1}, -\mathbf{1}, -\mathbf{1} | V | \mathbf{1}, \mathbf{1}, -\mathbf{1}, -\mathbf{1} \rangle \\ &= V_{sa12} - \frac{J_{12}}{2} [\langle 1, 1 | S_{12}^2 | 1, 1 \rangle - 4] + V_{sa13} - \frac{J_{13}}{2} [\langle 1, -1 | S_{13}^2 | 1, -1 \rangle - 4] \\ &+ V_{sa14} - \frac{J_{14}}{2} [\langle 1, -1 | S_{14}^2 | 1, -1 \rangle - 4] + V_{sa23} - \frac{J_{23}}{2} [\langle 1, -1 | S_{23}^2 | 1, -1 \rangle - 4] \\ &+ V_{sa24} - \frac{J_{24}}{2} [\langle 1, -1 | S_{24}^2 | 1, -1 \rangle - 4] + V_{sa34} - \frac{J_{34}}{2} [\langle -1, -1 | S_{34}^2 | -1, -1 \rangle - 4] \end{aligned}$$

In this way, for diagonal elements

$$\begin{aligned} \langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | V | m_{s1}, m_{s2}, m_{s3}, m_{s4} \rangle &= V_{sa12} - \frac{J_{12}}{2} [\langle m_1, m_2 | S_{12}^2 | m_1, m_2 \rangle - 4] \\ &+ V_{sa13} - \frac{J_{13}}{2} [\langle m_1, m_3 | S_{13}^2 | m_1, m_3 \rangle - 4] + V_{sa14} - \frac{J_{14}}{2} [\langle m_1, m_4 | S_{14}^2 | m_1, m_4 \rangle - 4] \\ &+ V_{sa23} - \frac{J_{23}}{2} [\langle m_2, m_3 | S_{23}^2 | m_2, m_3 \rangle - 4] + V_{sa24} - \frac{J_{24}}{2} [\langle m_2, m_4 | S_{24}^2 | m_2, m_4 \rangle - 4] \\ &+ V_{sa34} - \frac{J_{34}}{2} [\langle m_3, m_4 | S_{34}^2 | m_3, m_4 \rangle - 4] \end{aligned}$$

- Elements that differ in 2 m_s values

$$\begin{aligned} \langle 1, 1, -1, -1 | V | 1, 0, -1, 0 \rangle &= \left(V_{sa12} - \frac{J_{12}}{2} [\langle 1, 1 | S_{12}^2 | 1, 0 \rangle - \langle 1 | S_1^2 | 1 \rangle - \langle 1 | S_2^2 | 0 \rangle] \right) \langle -1 | -1 \rangle \langle -1 | 0 \rangle + \\ &\left(V_{sa13} - \frac{J_{13}}{2} [\langle 1, -1 | S_{13}^2 | 1, -1 \rangle - \langle 1 | S_1^2 | 1 \rangle - \langle -1 | S_3^2 | -1 \rangle] \right) \langle 1 | 0 \rangle \langle -1 | 0 \rangle + \\ &\left(V_{sa14} - \frac{J_{14}}{2} [\langle 1, -1 | S_{14}^2 | 1, 0 \rangle - \langle 1 | S_1^2 | 1 \rangle - \langle -1 | S_4^2 | 0 \rangle] \right) \langle 1 | 0 \rangle \langle -1 | -1 \rangle + \\ &\left(V_{sa23} - \frac{J_{23}}{2} [\langle 1, -1 | S_{23}^2 | 0, -1 \rangle - \langle 1 | S_2^2 | 0 \rangle - \langle -1 | S_3^2 | -1 \rangle] \right) \langle 1 | 1 \rangle \langle -1 | 0 \rangle + \\ &\left(V_{sa24} - \frac{J_{24}}{2} [\langle 1, -1 | S_{24}^2 | 0, 0 \rangle - \langle 1 | S_2^2 | 0 \rangle - \langle -1 | S_4^2 | 0 \rangle] \right) \langle 1 | 1 \rangle \langle -1 | -1 \rangle + \\ &\left(V_{sa34} - \frac{J_{34}}{2} [\langle -1, -1 | S_{34}^2 | -1, 0 \rangle - \langle -1 | S_3^2 | -1 \rangle - \langle -1 | S_4^2 | 0 \rangle] \right) \langle 1 | 1 \rangle \langle 1 | 0 \rangle \\ \langle 1, 1, -1, -1 | V | 1, 0, -1, 0 \rangle &= V_{sa24} - \frac{J_{24}}{2} [\langle 1, -1 | S_{24}^2 | 0, 0 \rangle] \end{aligned}$$

In this way: If $|m_{s1}, m_{s2}, m_{s3}, m_{s4}\rangle$ and $|m'_{s1}, m'_{s2}, m'_{s3}, m'_{s4}\rangle$ differ in 2 m_s values, the evaluation remains:

$$\begin{aligned} \langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | V | m'_{s1}, m'_{s2}, m'_{s3}, m'_{s4} \rangle &= V_{sa_{ij}} - \frac{J_{m_{si}, m_{sj}}}{2} [\langle m_{si}, m_{sj} | S_{ij}^2 | m'_{si}, m'_{sj} \rangle] \end{aligned}$$

where: m_{si}, m_{sj} are the elements that differ from m'_{si}, m'_{sj} respectively.

- Elements that differ for 3 or 4 m_s values.

Due to the orthogonality of the elements $\langle m_{si} | m_{sj} \rangle$, the matrix elements than differ in more than two m_s values are zero, due to the potential operator depends only of two molecules at the same time.

In this way if $|m_{s1}, m_{s2}, m_{s3}, m_{s4}\rangle$ and $|m'_{s1}, m'_{s2}, m'_{s3}, m'_{s4}\rangle$ differ in 3 or 4 m_s values, then $V\langle m_{s1}, m_{s2}, m_{s3}, m_{s4} | V | m'_{s1}, m'_{s2}, m'_{s3}, m'_{s4} \rangle = 0$.

- There are no elements of the base that differ in only one element, due to the restriction of $\sum m_{si} = 0$

The problem is reduced to the evaluation of the elements $\langle m_{si}, m_{sj} | S_{ij}^2 | m'_{si}, m'_{sj} \rangle$, based on the information of J and V_{sa} , for the side and diagonal of the tetramer. The evaluation of the elements S_{ij}^2 remains.

Taking into account that $S^2 |S; M_s\rangle = S(S+1) |S; M_s\rangle$, $S^2 = 0; 2$ and 6 for the $|0; 0\rangle, |1; 0\rangle$ and $|2; 0\rangle$ coupled states respectively. We construct the corresponding matrices from the uncoupled states arranged in the order of the vector of Eq [5]:

$$\begin{bmatrix} |1,1; 1,1\rangle \\ |1,1; 1,0\rangle \\ |1,1; 1,-1\rangle \\ |1,0; 1,1\rangle \\ |1,0; 1,0\rangle \\ |1,0; 1,-1\rangle \\ |1,-1; 1,1\rangle \\ |1,-1; 1,0\rangle \\ |1,-1; 1,-1\rangle \end{bmatrix} \quad [5]$$

We proceed to build the S^2 matrix in the uncoupled base, through the corresponding base change $A^T S^2 A$, where:

$$A = \begin{bmatrix} 0 & 0 & 1/\sqrt{3} & 0 & -1/\sqrt{3} & 0 & 1/\sqrt{3} & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{6} & 0 & \sqrt{2/3} & 0 & 1/\sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad [6]$$

$$S^2 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 6 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 \end{bmatrix} \quad [7]$$

$$A^T S^2 A = \begin{bmatrix} 6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 4 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 2 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 4 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 \end{bmatrix} \quad [8]$$

Eq. 8 shows the S^2 matrix in the uncoupled base. In this way it is possible to evaluate the potential, starting from the previous expressions and to construct its corresponding matrix in the uncoupled base from whose diagonalization, as we mentioned, we obtain all the spin states of $(O_2)_4$.

References:

1. Kittel, C., *Introduction to solid state physics*. 8th ed.; Wiley: Hoboken, NJ, 2005; p 680.
2. Lewis, G. N., The magnetism of oxygen and the molecule O_4 . *J. Am. Chem. Soc.* **1924**, 46 (9), 2027-2032.
3. Pauling, L., *The nature of the chemical bond*. 3er ed.; Ithaca, N.Y., 1960.
4. Aquilanti, V.; Ascenzi, D.; Bartolomei, M.; Cappelletti, D.; Cavalli, S.; Vítores, M. d. C.; Pirani, F., Molecular Beam Scattering of Aligned Oxygen Molecules. The Nature of the Bond in the O_2 - O_2 Dimer. *J. Amer. Chem. Soc.* **1999**, 121, 10794-10802.
5. Freiman, Y. A.; Jodl, H. J., Solid oxygen. *Phys. Rep.* **2004**, 401 (1), 1-228.
6. Jensen, F., *Introduction to Computational Chemistry (Second Edition)*. John Wiley & Sons Ltd: The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, 2007.
7. Carmona-Novillo, E.; Bartolomei, M.; Hernández, M. I.; Campos-Martínez, J.; Hernández-Lamonedá, R., *Ab initio* rovibrational structure of the lowest singlet state of O_2 - O_2 . *J. Chem. Phys.* **2012**, 137 (11), 114304.

8. Bartolomei, M.; Carmona-Novillo, E.; Hernández, M. I.; Campos-Martínez, J.; Hernández-Lamonedá, R., Global *ab initio* potential energy surfaces for the $O_2(^3\Sigma_g^-)+O_2(^3\Sigma_g^-)$ interaction. *J. Chem. Phys.* **2010**, *133* (12), 124311.
9. Bartolomei, M.; Hernández, M. I.; Campos-Martínez, J.; Carmona-Novillo, E.; Hernández-Lamonedá, R., The intermolecular potentials of the O_2-O_2 dimer: a detailed *ab initio* study of the energy splittings for the three lowest multiplet states. *Phys Chem Chem Phys* **2008**, *10* (35), 5374-80.
10. Bartolomei, M.; Carmona-Novillo, E.; Hernández, M. I.; Campos-Martínez, J.; Hernández-Lamonedá, R., Accurate *ab initio* intermolecular potential energy surface for the quintet state of the $O_2(^3\Sigma_g^-)-O_2(^3\Sigma_g^-)$ dimer. *J. Chem. Phys.* **2008**, *128* (21), 214304.
11. Hernández-Lamonedá, R.; Bartolomei, M.; Hernández, M. I.; Campos-Martínez, J.; Dayou, F., Intermolecular Potential of the O_2-O_2 Dimer. An *ab Initio* study and comparison with Experiment. *J. Phys. Chem. A* **2005**, *109* (11587).
12. Valentín-Rodríguez, M. A.; Bartolomei, M.; Hernández, M. I.; Campos-Martínez, J.; Hernández-Lamonedá, R., An unrestricted approach for the accurate calculation of the interaction potentials of open-shell monomers: The case of O_2-O_2 . *J. Chem. Phys.* **2020**, *152* (18), 184304.
13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; X. Li, M. C., A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox *Gaussian 09*, 2009.
14. Freiman, Y. A.; Jodl, H. J.; Crespo, Y., Solid oxygen revisited. *Phys. Rep.* **2018**, *743* (1), 1-55.
15. Fujihisa, H.; Akahama, Y.; Kawamura, H.; Ohishi, Y.; Shimomura, O.; Yamawaki, H.; Sakashita, M.; Gotoh, Y.; Takeya, S.; Honda, K., O_8 Cluster Structure of the Epsilon Phase of Solid Oxygen. *Phys. Rev. Lett.* **2006**, *97* (8), 085503.
16. Lundegaard, L. F.; Weck, G.; McMahon, M. I.; Desgreniers, S.; Loubeyre, P., Observation of an O_8 molecular lattice in the epsilon phase of solid oxygen. *Nature* **2006**, *443* (201).
17. Bartolomei, M.; Carmona-Novillo, E.; Hernández, M. I.; Pérez-Ríos, J.; Campos-Martínez, J.; Hernández-Lamonedá, R., Molecular oxygen tetramer $(O_2)_4$: Intermolecular interactions and implications for the ϵ solid phase. *Phys. Rev. B* **2011**, *84* (9), 092105.
18. Bartolomei, M.; Carmona-Novillo, E.; Hernández, M. I.; Pérez-Ríos, J.; Campos-Martínez, J.; Hernández-Lamonedá, R., Erratum: Molecular oxygen tetramer $(O_2)_4$: Intermolecular interactions and implications for the ϵ solid phase [Phys. Rev. B *84*, 092105 (2011)]. *Phys. Rev. B* **2013**, *87* (17), 179906.

19. Bartolomei, M.; Pérez-Ríos, J.; Carmona-Novillo, E.; Hernández, M. I.; Campos-Martínez, J.; Hernández-Lamonedá, R., Can density functional theory methods be used to simulate the epsilon phase of solid oxygen? *Chem. Phys. Lett.* **2014**, 592 (170).
20. Crespo, Y.; Fabrizio, M.; Scandolo, S.; Tosatti, E., Collective spin 1 singlet phase in high-pressure oxygen. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, 111 (29), 10427-10432.
21. Carter, W. B.; Schiferl, D.; Lowe, M. L.; Gonzales, D., New phase of oxygen at high pressure and low temperature. *J. Phys. Chem.* **1991**, 95 (6), 2516-2519.
22. Neaton, J. B.; Ashcroft, N. W., Low-energy linear structures in dense oxygen: implications for the epsilon phase. *Phys. Rev. Lett.* **2002**, 88 (20), 205503.
23. Oganov, A. R.; Glass, C. W., Crystal structure prediction using *ab initio* evolutionary techniques: Principles and applications. *J. Chem. Phys.* **2006**, 124 (24), 244704.
24. Ma, Y.; Oganov, A. R.; Glass, C. W., Structure of the metallic *Phys. Rev. B* **2007**, 76 (6), 064101.
25. Ochoa-Calle, A. J.; Zicovich-Wilson, C. M.; Hernández-Lamonedá, R.; Ramírez-Solís, A., Understanding the ϵ and ζ High-Pressure Solid Phases of Oxygen. Systematic Periodic Density Functional Theory Studies Using Localized Atomic Basis. *J. Chem. Theory Comput.* **2015**, 11 (1195).
26. Ramírez-Solís, A.; Zicovich-Wilson, C. M.; Hernández-Lamonedá, R.; Ochoa-Calle, A. J., Antiferromagnetic vs. non-magnetic ϵ phase of solid oxygen. Periodic density functional theory studies using a localized atomic basis set and the role of exact exchange. *Phys. Chem. Chem. Phys.* **2017**, 19 (4), 2826-2833.
27. Van-Duijneveldt, F. B.; Van-Duijneveldt-Van-de-Rijdt, J. G. C. M.; Van-Lenthe, J. H., State of the Art in Counterpoise Theory. *Chem. Rev.* **1994**, 94 (1873-1885).
28. Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, 120 (1), 215-241.
29. Hernández-Lamonedá, R.; Pérez-Ríos, J.; Carmona-Novillo, E.; Bartolomei, M.; Campos-Martínez, J.; Hernández, M. I., Properties of the molecular oxygen trimer from pairwise additive interactions. *Chem. Phys.* **2012**, 399, 80-85.

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