An unrestricted approach for the accurate calculation of the interaction potentials of open-shell monomers: the case of $O_2 - O_2$

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Abstract

The properties of molecular oxygen including its condensed phases continue to be of great relevance for the scientific community. The richness and complexity of their associated properties stem from the fact that it is a very stable diradical. Its open-shell nature leads to low-lying multiplets with total electronic spin $S = 0, 1, 2$ in the case of the dimer, $(O_2)_2$, and the accurate calculation of their intermolecular potentials represents a challenge to *ab initio* electronic structure methods. In this work we present intermolecular potentials calculated at a very high level, thus competing with the most accurate restricted potentials obtained to date. This is accomplished by drawing on an analogy between the coupled and uncoupled representations of angular momentum and restricted vs unrestricted methodologies. The $S = 2$ state can be well represented by unrestricted calculations in which the spins of the unpaired electrons are aligned in parallel; however for the state where they are aligned in antiparallel fashion it would seem the total spin is not well defined i.e. the well-known spin contamination problem. We show that its energy corresponds to that of the $S = 1$ state and perform unrestricted coupled cluster calculations for these two states. Then we obtain the $S = 0$ state through the Heisenberg Hamiltonian and show that this is very reliable in the well region of the potentials. We make extensive comparisons with the best restricted potentials (Bartolomei, *et al Phys. Chem. Chem. Phys.*, 10, 1-7, 2008) and with reliable experimental determinations, a very good agreement is globally found.

Introduction

The study of weakly bound molecular complexes continues to be an area of great interest in both basic and applied science. The development of powerful optical resolution techniques, molecular beam state of the art technology and ultracold conditions provide a wealth of detailed information on the nature of intermolecular forces, collision dynamics and spectroscopy.¹⁻² In parallel, the development of highly accurate theoretical methods to interpret and make new predictions in a virtuous feedback loop has propelled the field to new heights constantly pushing the known boundaries of this field. In the case of the molecular oxygen dimer there has been recent

interest in its role as a collision-complex on the chemistry of the Earth's atmosphere,³⁻⁴ radiation budget⁵ and climate⁶ as well as in the interstellar media.⁷ Knowledge of the interaction potential is also of relevance in the study of the condensed phases of oxygen⁸⁻¹⁰ where in recent years the study of the change in the nature of the intermolecular forces in solid oxygen as a function of pressure and the properties of the epsilon phase have been highly debated.¹¹⁻¹³

Even though significant efforts have been devoted to the detailed experimental and theoretical characterization of the $(O_2)_2$ ground and excited states,^{4, 14-28} an accurate determination of its fundamental properties remains challenging. From molecular beam collision experiments¹⁸, a reasonable estimation of the isotropic radial coefficients for the dimer interaction has been obtained; however deriving from experimental measurements related anisotropic components that determine the angular dependence of the interaction or the splitting between the spin multiplets is much more difficult²⁵ (this issue will be further discussed in the Results and Discussion section). From high resolution spectroscopy¹⁶ the geometry of the minimum has been accurately determined; however an accurate determination of its binding energy remains elusive as has been discussed in detail in our previous work.²⁶ Next we discuss difficulties in the theoretical treatments.

The proper description of the electronic structure of the molecular oxygen dimer is a challenging task since it involves the interaction of two open-shell molecules in the $^3\Sigma_g^-$ (triplet) ground state leading to three distinct interaction potential energy surfaces with total electronic spin $S = 0, 1$ and 2 . If one uses restricted methodologies then in the case of the quintet state ($S = 2$), the HF reference is well-defined and one can perform highly accurate RCCSD(T)²⁹ or SAPT³⁰ calculations of the interaction potential in a straightforward fashion. **When applicable these methods are widely considered as the golden standard to compare with.** However, when one considers the triplet ($S = 1$) or singlet ($S = 0$) states the near-degeneracy of the valence π_g^* shells together with their partial occupation requires the use of multiconfigurational methodology. The main attractive component for these dimers arises from dispersion forces which cannot be accurately computed with truncated CI or CASPT2 approaches; the first one is not size consistent and compared with CCSD(T) cannot recover correlation at a sufficiently high level whereas the second one overestimates dispersion due to the uncoupled treatment of monomer polarizabilities.³¹ On the other hand the crucial exchange interactions responsible for the splittings between multiplet states can be adequately calculated with these methods as shown in Ref. 24. In that work so-called hybrid potentials were obtained by combining the $S = 2$ intermolecular potential computed at RCCSD(T) level with splittings for the $S = 0$ and $S = 1$ states calculated at two levels: MRCI and CASPT2. In this way it was possible to circumvent the evaluation of dispersion with multiconfigurational methods and obtain fairly accurate potentials for the three multiplicities. In addition, it was proposed in this study, based on MRACPF calculations which improve the size inconsistency problems of the MRCI estimates,²⁴ that the MRCI and CASPT2 hybrids provide an indicator of the upper and lower limits, respectively, of the interaction energy of the dimer, so that more accurate results should lie in the intermediate energy region between the MRCI and CASPT2-hybrids.

One may consider an unrestricted approach since it simplifies the near-degeneracy problems found in restricted approaches by localizing orbitals and specifying the z -component of the electronic spin in each fragment. Furthermore, with this methodology it is possible to include electron correlation at the UCCSD(T) level and thus to carry out very accurate calculations of the intermolecular potentials. Two cases for the spin

couplings have to be considered: a) Ferromagnetic coupling in which both molecules have $m_s = +1$ (parallel arrangement) b) “Antiferromagnetic” coupling in which the first molecule has $m_s = +1$ and the second one $m_s = -1$ (antiparallel arrangement). The ferromagnetic state coincides with the quintet state of the restricted calculations. However, the case of the “antiferromagnetic” state is less clear. In a previous theoretical study³² of molecular oxygen clusters, using unrestricted methodology and motivated by the properties of the low temperature α solid phase, Cabria *et al* point out that indeed the ferromagnetic states of $(O_2)_n$ clusters ($n = 2 - 4$) have well-defined total spin with only marginal spin contamination but, on the contrary, the “antiferromagnetic” states do not correspond to pure spin states. Perhaps this well-known spin contamination problem is one of the reasons there have been very few unrestricted studies of oxygen clusters. In this respect it is worth mentioning the important work on spin-contamination and the application of spin-projection techniques to alleviate it by the group of Schlegel.³³

The problem of treating strongly correlated magnetic systems has been of great interest to the electronic structure community for quite some time and many important contributions have been made.³⁴⁻³⁶ For a comprehensive review see Ref. 35 and for more recent work with a good introduction Ref. 34. In particular we would like to briefly mention the seminal work of Noodleman³⁷ where it is shown that using a single determinant wavefunction it is possible to obtain explicit energy expressions for the broken symmetry (BS) state and states with well-defined spin S . In his derivation second-order perturbation approximations are used and special emphasis is put on the overlap between the magnetic orbitals which can be used as a variational parameter to optimize both BS and states with spin S . In this way he related the energy of the BS state with those of well-defined spin and by invoking the Heisenberg Hamiltonian he can express the energies in terms of the exchange-coupling constant J . Alternatively, he shows that J is proportional to the energy difference between the maximum multiplicity state and the BS state at the single determinant level. Finally, he concludes that the Heisenberg Hamiltonian will be valid if the overlap between magnetic orbitals is small and can be treated as a perturbation. Our approach is similar to that of Noodleman with the particularity that for two $s = 1$ molecules, the energy of the BS state corresponds to that of the triplet state of the dimer. An important difference in our approach is that we go beyond the single determinant description to include correlation at a very high level (UCCSD(T)) and the problem of spin contamination is shown to be minimized.

In this work we present an analysis on the nature of the “antiferromagnetic” state for the dimer using an analogy between the well-known coupled and uncoupled representations of angular momentum with restricted and unrestricted methodologies, respectively. We show that the BS state energy can be used to directly and accurately approximate the energy of the triplet state. Together with the Heisenberg Hamiltonian^{20, 38} this allow us to obtain intermolecular potentials of the three spin multiplicities at UCCSD(T) level. The methodology could be applied to other interesting problems where interactions among $s = 1$ atoms or molecules are involved.

Methodology

Coupled-uncoupled schemes. Antiferromagnetic coupling

We want to illustrate how the coupled and uncoupled representations of angular momentum³⁹⁻⁴⁰ can be used to great advantage to analyze the calculations performed with unrestricted methodology and relate them to those pertaining to a restricted approach. Let $\mathbf{s}_a$ and $\mathbf{s}_b$ be the spin operators of the monomers, and $\mathbf{S} = \mathbf{s}_a + \mathbf{s}_b$, the total electronic spin. We follow the standard notation for coupled [1] and uncoupled [2] representations,

$$|SM\rangle \quad [1]$$

$$|s_a m_a, s_b m_b\rangle \quad [2]$$

where M, m_a and m_b are the corresponding numbers for the spin projections. For two oxygen molecules each in the ground electronic state, $s_a = s_b = 1$, arising from the half-filled π_g orbitals, the state of the compound system can have total spin $S = 0, 1$ and 2.

An analogy can be established between the uncoupled basis representation above and *ab initio* unrestricted calculations where basis functions are localized at the fragments (monomers) and therefore, a value for the spin component z on each monomer (m_a, m_b) can be assigned. We wish to find out the expressions for the matrix elements of the $O_2 - O_2$ potential energy using the uncoupled representation. First, since the total spin and its projection commute with the electronic Hamiltonian, it is given in the coupled representation by a diagonal matrix with elements labelled as $V_{|S,M\rangle}$. After using the transformation between the coupled and the uncoupled basis, the potential energy matrix in the uncoupled representation becomes a block diagonal matrix, with blocks labelled by $M = m_a + m_b$, as described in more detail in the Appendix A. Except for the matrix elements between $(m_a, m_b) = (+1, +1)$ or $(m_a, m_b) = (-1, -1)$ states, which are identical to the potential of the quintet state, $S = 2$, [expectation](#) values of the potential energy in the remaining uncoupled states are given as a linear combination of the eigen-energies $V_{|S,M\rangle}$.

A simpler picture is attained if the system is described by the well-known Heisenberg Hamiltonian, eq. [3],

$$\mathcal{H}_{int} = V_{sa} - 2J\mathbf{s}_a \cdot \mathbf{s}_b = V_{sa} - J(S^2 - s_a^2 - s_b^2) \quad [3]$$

where V_{sa} is a spin-independent energy, also known as spin-averaged potential and J is the exchange coupling parameter. Both quantities depend on the intermolecular distance R , as well as the relative orientation of the two monomers. Note that if J is positive, then the $S = 2$ state is favored (ferromagnetic coupling) whereas if J is negative then the $S = 0$ state is favored (antiferromagnetic coupling). As explained below care must be taken with the use of the term antiferromagnetic, here we use it in its proper definition implying an $S = 0$ state.

Within this model, the eigenstates are given as:

$$\begin{aligned} V_{|S=0\rangle} &= V_{sa} + 4J \\ V_{|S=1\rangle} &= V_{sa} + 2J \\ V_{|S=2\rangle} &= V_{sa} - 2J \end{aligned} \quad [4]$$

Using these energies, now depending on V_{sa} and J , the potential energy matrix in the uncoupled representation becomes simplified (see Eq.(4) of the Appendix A). Notably, the triplet state energy equal to $V_{sa} + 2J$ happens to be the same as:

$$\langle 1, \pm 1, 1, \mp 1 | \mathcal{H}_{int} | 1, \pm 1, 1, \mp 1 \rangle = V_{sa} + 2J \quad [5]$$

i.e., the expectation value of the (broken-symmetry) state $|s_a m_a, s_b m_b\rangle = |1, +1, 1, -1\rangle$ (or $|1, -1, 1, +1\rangle$).

Concluding, only the expectation values of the potential energy in the $|s_a m_a, s_b m_b\rangle = |1, \pm 1, 1, \mp 1\rangle$ and the $|s_a m_a, s_b m_b\rangle = |1, \pm 1, 1, \pm 1\rangle$ states, corresponds to the energies of the triplet $V_{|S=1\rangle}$ and quintet $V_{|S=2\rangle}$ states respectively. It is also worth noticing that the expectation value of S^2 for the $|1, \pm 1, 1, \mp 1\rangle$ uncoupled states is equal to 2 i.e the same as a pure triplet state.

This result suggests that the energy calculated at the unrestricted level with an “antiferromagnetic” coupling option (antiparallel spins) provides a good approximation of the energy of the triplet state of the complex. As detailed in the Appendix A), we have checked that this conclusion holds even considering a further order^{35, 41} in the Heisenberg Hamiltonian.

The issue of spin-contamination in coupled-cluster calculations has been discussed since their first implementation in the unrestricted formalism, a good summary and references to original work has been given by Stanton.⁴² It has been found that molecular properties calculated at the coupled-cluster level are quite insensitive to the choice of orbitals, particularly, UHF and ROHF references lead to very similar results even in cases where spin-contamination is non-negligible. Interestingly the reason is not related to a spin purification of the wavefunction (actually even for a ROHF reference the fact that the excitation operator T does not commute with S^2 leads to spin-contamination at the coupled-cluster level⁴³) but rather to an invariance of the coupled-cluster energy to spin-contamination of the wavefunction. As has been analyzed by Schlegel⁴⁴ in the case of UCCSD it can be shown that the energy is invariant to elimination of any single spin contaminant. This opens the door for an accurate determination of the interaction potentials with unrestricted methodology as illustrated in the next sections.

Computational details

The potential energy surfaces for the $S = 1$ and $S = 2$ states are calculated at the UCCSD(T) level with augmented correlation consistent basis sets⁴⁵⁻⁴⁸ and complete basis set (CBS) extrapolations.⁴⁹⁻⁵¹ For various relative orientations of the molecules, detailed below, the intermolecular distance R is varied from 2.5 to 5.0 Å in steps of 0.1 Å. These unrestricted calculations were made through the Gaussian⁵² “antiferromagnetic” implementation. In this procedure the initial guess orbitals for the UHF step are obtained in separate fragment calculations (one for each O_2) which are then combined into a single set and orthogonalized. This is directly related to the well-known treatment of proper dissociation⁵³⁻⁵⁴ in the H_2 molecule using a UHF wavefunction with initial orbitals localized in each hydrogen atom. It really corresponds to the usual procedure that guarantees that the lowest energy solution of the UHF equations, which corresponds with the broken-symmetry (BS) solution, is obtained. However the treatment can be applied in general to any system with an open-shell electronic structure and the “antiferromagnetic” state is completely defined by specifying the z component of the spin for each electron and the fact that the number of alpha ($s_z = 1/2$) and beta ($s_z = -1/2$) electrons are equal (in this sense analogous to

the simple closed-shell case). In our case one of the O_2 molecules has 9 electrons with alpha spin and 7 electrons with beta spin whereas the second O_2 has 7 electrons with alpha spin and 9 electrons with beta spin. Treatment of electron correlation now proceeds with the standard unrestricted methodology and as mentioned above we perform UCCSD(T) calculations. In our case the $S = 2$ state is approximated with the ferromagnetic coupling where both fragments (monomers) have $m_a = m_b = 1$ and for the $S = 1$ state with the “antiferromagnetic” coupling where for one monomer $m_a = +1$ and for the other $m_b = -1$.

It is interesting to contrast the case of $O_2 - O_2$ with that of the much simpler H_2 regarding the properties of the UHF BS solutions. In both cases at long range the exchange interactions disappear and the corresponding BS multiplet states become degenerate. However important differences between both cases appear already at the monomer level, where for O_2 we observe differences between the UHF and ROHF descriptions, the first one leading to a lower energy and with associated spin contamination of the wavefunction. One can speculate whether in the shorter range of the $O_2 - O_2$ interaction the UHF and ROHF solutions will converge in analogy with the H_2 case. In order to test this, we performed CASSCF calculations with 4 active electrons in the corresponding 4 π_g^* orbitals to verify whether a single configuration wavefunction is obtained when decreasing sufficiently the intermolecular distance. Indeed, we found that this happens for intermolecular distances smaller than 2 Å. The transformation from multi to single configuration can be understood as due to significant overlap between the π_g^* orbitals leading to bonding and antibonding combinations thus favoring double occupancy of the bonding orbitals. However, this region of the interaction corresponds to high energies along the repulsive wall. A comparison of the UHF BS and ROHF energies indicate that the first one is still much lower in energy and thus, in contrast to the H_2 case, no unification of the solutions occur. This can be understood in terms of the original difference between the UHF and ROHF solutions for the monomer and the fact that in the dimer the BS solution retains an open-shell character even at short distances and the unpaired electrons lead to different exchange interactions with spin-orbitals of different spin. In contrast for the much simpler H_2 case the monomer is a one-electron system where no difference between UHF and ROHF descriptions arise and the fact that H_2 possesses only two electrons of different spin allows convergence of restricted and unrestricted solutions.

The basis set superposition error was eliminated using the counterpoise procedure.⁵⁵ For the CBS extrapolation⁴⁹⁻⁵¹ we use the relations:

$$E_{corr}(X) = E_{corr}(\infty) + cX^{-3} \quad [6]$$

$$c = \frac{E_{corr}(X_2) - E_{corr}(X_1)}{\frac{1}{X_2^3} - \frac{1}{X_1^3}} \quad [7]$$

$$E_{corr}(\infty) = E_{corr}(X_1) - \frac{c}{X_1^3} \quad [8]$$

Our best estimate of $E_{corr}(\infty)$ was obtained by extrapolation of the AVTZ / AVQZ basis sets, being AVTZ(X_1) and AVQZ(X_2). It is necessary to point out that the extrapolation scheme is only applied to the correlation contribution to the total energy;

as is well-known, the convergence of the HF energy is much faster and the AVQZ level should be close to the CBS limit.

Expectation values of the electronic spin were monitored throughout the calculations. This is a standard procedure to analyze possible spin contamination and we use it here to obtain relevant information on this problem. In this way, the expectation value of S^2 for the O_2 monomer is equal to 2.049, indicating only a minor spin contamination of the expected triplet state. Regarding the total spin of the complex in the “antiferromagnetic” coupling, $(m_a, m_b) = (\pm 1, \mp 1)$, it is obtained $\langle S^2 \rangle = 2.0984$, mostly corresponding to a triplet state of the complex, as expected, although it presents a modest degree of spin contamination at the UHF level. Finally, for the calculation of the quintet state (parallel spins) the expectation value of S^2 was found to be 6.0974.

As mentioned above, a direct calculation of the singlet state with unrestricted calculations is not possible. In this work, the Heisenberg Hamiltonian is invoked for estimating the energies of the singlet state (Eq. [4]), by using V_{sa} and J as obtained from the UCCSD(T)-CBS triplet and quintet energies:

$$V_{sa} = \frac{[V_{|S=1\rangle} + V_{|S=2\rangle}]}{2} \quad [9]$$

$$J = \frac{[V_{|S=1\rangle} - V_{|S=2\rangle}]}{4}. \quad [10]$$

Accuracy of this procedure for the calculation of the singlet state is discussed in the Results and Discussion section.

Finally due to the strong multireference character of the system when using restricted methodology we have monitored the T1 diagnostic⁵⁶⁻⁵⁷ in test calculations of the antiferromagnetic state, even though one expects that with the unrestricted approach these problem should be bypassed. At the equilibrium geometries of the H, T, X and L configurations the value we obtain is 0.018 in all cases (rounding up to two figures). This value lies below the accepted cut-off of 0.02 where highly accurate results should be expected. The test also indicates a very weak geometry dependence of the diagnostic. We also monitored the convergence properties of the coupled-cluster calculations in order to compare the more standard $S = 2$ case with the antiferromagnetic BS state. For all geometries explored near their minimum energy values the required number of iterations is only slightly higher in the case of the BS state. However, for shorter intermolecular distances in the repulsive region up to 50% more iterations are required in the case of the BS state.

Geometries and Spherical Harmonic Expansion of the Potential Energy Surface

In this article we will present a detailed comparison of the present unrestricted calculations with previous accurate restricted RCCSD(T)²⁹ and multireference hybrid²⁴ results, specifically, for the four basic configurations of the dimer, i.e., H (parallel), L (linear), T (T-shaped) and X (crossed), which are shown in Fig. 1.

Fig. 1. Oxygen dimer conformations. a) Parallel H b) linear L c) T shape
d) cross shape X

In addition, the interaction potential can be represented as a spherical harmonic expansion:²⁰

$$V(R, \theta_a, \theta_b, \phi) = 4\pi \sum_{L_a L_b L} V^{L_a L_b L}(R) Y_{L_a L_b}^{L 0}(\theta_a, \theta_b, \phi) \quad [11]$$

$$Y_{L_a L_b}^{L 0}(\theta_a, \theta_b, \phi) = (2L + 1)^{\frac{1}{2}} \sum_m (-)^{L_a - L_b} \begin{pmatrix} L_a & L_b & L \\ m & -m & 0 \end{pmatrix} Y_{L_a m}(\theta_a \phi_a) Y_{L_b - m}(\theta_b \phi_b) \quad [12]$$

where θ_a, θ_b are the angles formed between the intermolecular vector and the intramolecular vector of each monomer, ϕ is the torsional angle, $Y_{L_a m}$ and $Y_{L_b - m}$ are spherical harmonics and $(:::)$ are 3- j Wigner symbols. The first term V^{000} in Eq. [11] represents the isotropic component of the interaction, while the remaining terms describe the anisotropy.

It is possible to obtain a more compact representation of the PES, using only four terms in the spherical harmonic expansion (eq.[11]). This is the minimum number of terms that are needed to characterize the four basic configurations of the dimer (Figure 1). Since O_2 is a homonuclear molecule, only even coefficients contribute in the expansion:

$$V(R, \theta_a, \theta_b, \phi) = 4\pi \{ V^{000}(R) + V^{202}(R) [Y_{20}^{20}(\theta_a, \theta_b, \phi) + Y_{02}^{20}(\theta_a, \theta_b, \phi)] + V^{220}(R) Y_{22}^{00}(\theta_a, \theta_b, \phi) + V^{222}(R) Y_{22}^{20}(\theta_a, \theta_b, \phi) + \dots \} \quad [13]$$

An optimal procedure to determine the isotropic term on the basis of calculations of the potential at selected configurations (9 total) was devised by Koide and Kihara (KK).⁵⁸ In Table 1 we present the orientations and we will refer to this approach as the KK procedure. In a sense it is a generalization of the four-term expansion mentioned before to a more accurate nine term representation. Later on, this analysis was extended for the calculation of other terms,⁵⁹ where it was demonstrated that V^{202} and V^{404} can be obtained with the same level of precision, in comparison with the isotropic one, starting from the KK conformations. This conclusion was based on a comparison with a very accurate representation of the quintet state, based on calculations at 65 different geometries and involving 29 radial terms²⁹ obtained from numerical integration over the angular coordinates.

Table 1: Geometry parameters for KK conformations.

Notation	Geometry parameters (θ_a, θ_b, ϕ)
H	$\frac{\pi}{2}; \frac{\pi}{2}, 0$
T	$0; \frac{\pi}{2}; 0$
X	$\frac{\pi}{2}; \frac{\pi}{2}; \frac{\pi}{2}$
L	$0; 0; 0$
zd	$0; \theta_0; 0$
xd	$\frac{\pi}{2}; \theta_0; \frac{\pi}{4}$
dd	$\theta_0; \theta_0; 0$
dd'	$\theta_0; \theta_0; \frac{\pi}{2}$
dd''	$\theta_0; \theta_0; \pi$

In these studies,⁵⁸⁻⁵⁹ it was demonstrated that the expressions for the coefficients V^{000} and V^{202} from KK conformations, are those collected in the following equations:

$$V^{000} = \frac{1}{25} \left(\frac{8}{9} V_H + \frac{16}{9} V_T + \frac{8}{9} V_X + \frac{4}{9} V_L + 4V_{zd} + 8V_{xd} + \frac{9}{4} V_{dd} + \frac{9}{2} V_{dd'} + \frac{9}{4} V_{dd''} \right) \quad [14]$$

$$V^{202} = \frac{1}{\sqrt{5}} \left(-\frac{8}{63} V_H + \frac{4}{315} V_T - \frac{8}{63} V_X + \frac{22}{315} V_L + \frac{13}{35} V_{zd} - \frac{16}{35} V_{xd} + \frac{9}{140} V_{dd} + \frac{9}{70} V_{dd'} + \frac{9}{140} V_{dd''} \right) \quad [15]$$

These are the expressions that will be used in this study for the calculation of V^{000} and V^{202} coefficients, using both, the UCCSD(T)-CBS and the hybrids potentials.

Results and Discussion

In this article, we will make an extensive comparison of our unrestricted results with the accurate restricted RCCSD(T),²⁹ the multireference hybrid potentials²⁴ as well as with some experimental results. The Results section has been organized in the following subsections: I: Interaction energies II: Radial terms III: Exchange-Coupling parameter.

I. Interaction Energies

A comparison between our best results UCCSD(T)-CBS with the hybrid potentials are shown in Fig.2, for the two spin states that are calculated directly (triplet and quintet), as well as for the singlet state calculated through the exchange-coupling constant J and V_{sa} (Eqs. 4, 9 and 10).

We expect the description of the triplet state with the unrestricted methodology to be the most accurate to date given that both electron correlation and basis set completeness has been treated at a higher level than in previous restricted approaches. It is reassuring to find that in the case of the triplet state the potential lies between the two previous restricted hybrid approaches. As mentioned in the Introduction, one conclusion of the restricted hybrid study²⁴ was that the MRCI and CASPT2 hybrid potentials yield upper and lower bounds, respectively. Similar behavior is seen for the singlet state which is the most difficult to estimate and where the larger differences were seen in the case of the hybrid potentials.

It is worth noting that previous calculations of the $O_2 - O_2$ rovibrational structure in the singlet state²⁶ found that the ground state has a rectangular (H) geometry and that the associated rotational constants obtained using the MRCI or the CASPT2 hybrid potentials bracketed the spectroscopy determination of Biennier et al.¹⁷ The fact that the present singlet potential for the H geometry lies between the two hybrid potentials suggests that using the present procedure for the calculation of the interaction would lead to an even closer agreement with the observed structure.

Fig.2: Interaction potentials for the H, T, X, L oxygen dimer geometries, in its three spin states, at UCCSD(T)-CBS level. Comparison with RCCSD(T),²⁹ hybrid-CASPT2²⁴ and hybrid-MRCI methods.²⁴

The case of the linear configuration deserves special mention since the unrestricted potentials, specially the triplet, does not lie between the hybrid approximations but are slightly less attractive. In part, the origin for this behavior can be seen when comparing the unrestricted and restricted potentials for the quintet state where again the unrestricted approach leads to slightly less attractive potentials. Still the differences are very small, on the order of 0.62 meV or less in the potential well region. In general, the

consistency between the high-level restricted calculations and our current unrestricted ones, shows that the current uncertainty in the potentials for the molecular oxygen dimer is very small. For a more precise comparison, the values of the interaction energy in the potential well are shown in Table 2 for the different methods that have been discussed.

Notice that in the case of the X configuration, due to the negligible overlap between the π_g^* orbitals, the spin-exchange effects are very small leading to nearly-degenerate multiplets.

In order to have an estimation of the accuracy of the present singlet state, whose calculation has involved the Heisenberg Hamiltonian approximation, we have used the hybrid-MRCI and hybrid-CASPT2 singlet potentials of Ref. 24 and an error is computed by comparison with those potentials recalculated using the same procedure followed here, that is, through J and V_{sa} , obtained from the $S = 1$ and $S = 2$ hybrid potentials (eqs. 4, 9 and 10). As expected, it is found that the error decreases monotonically with distance. For the T and L conformations the errors in the singlet calculation are less than 10% for the entire range of R (2.5 to 5 Å), whereas for the X conformation, this happens in the range from 3 to 5 Å. For these three conformations errors less than 1% are found in the neighborhood of their respective wells. The H conformation presents the most stringent test where errors below 10% are found for values of R greater or equal to 2.8 Å but for the equilibrium geometry, the largest errors in the Heisenberg approximation are observed for the hybrid-CASPT2 data, with a value of 4.7%. We also noticed that the Heisenberg approximation leads to more attractive wells.

The largest errors are found in the region of the repulsive wall as expected, indicating the breakdown of Heisenberg's approximation when the exchange-repulsion term is dominant and in consonance with previous results reported in Ref. 24. These very small percentage errors indicate the reliability of Heisenberg's approximation for the calculation of the singlet state particularly around the potential well. Given the small differences found in the behavior of the hybrid MRCI and CASPT2 approaches it is reasonable to assume that our UCCSD(T) calculations will have similar deviations from the Heisenberg Hamiltonian prediction. For this reason, we can say that our unrestricted estimate of the singlet state is probably, as is the case of the triplet, the most accurate for this system to date.

We notice that a recent *ab initio* study of triplet states⁶⁰ based on explicitly correlated MRCI+Q calculations provide binding energies for the H conformation in its equilibrium geometry ($R = 3.18$ Å) which are smaller than those presented in Table 2. For example, using their larger active space and the AVTZ basis they find a value of -16.5 meV to be compared with -21.2, -19.5 and -22.3 meV for UCCSD(T) and the hybrid MRCI/CASPT2 approaches, respectively. This is in line with the explanation given in the Introduction and in our previous restricted hybrid approach¹⁶: it is well known that MRCI+Q cannot describe accurately the important dispersion interactions and for this reason we adopted a hybrid approach which conveniently combines CCSD(T) calculations for the $S = 2$ state with those at the MRCI and CASPT2 levels to estimate the multiplet splittings, which are mainly due to exchange interactions (note that, despite not being explicitly indicated, MRCI calculations of Ref. 24 also include Davidson's correction).

Table 2 a): Intermolecular well depths (meV) and equilibrium distances ($\text{\AA}$) for H, T, X and L conformations, in $S = 0$ and $S = 1$ spin multiplicities. Comparison between our best results UCCSD(T)-CBS with hybrid-CASPT2²⁴ and hybrid-MRCI methods.²⁴

V(meV) / R($\text{\AA}$)		UCCSD(T)	Hybrid-MRCI	Hybrid-CASPT2
$S = 0$	H	-29.43 / 2.97	-25.19 / 3.06	-32.76 / 2.91
	T	-16.69 / 3.69	-15.94 / 3.72	-17.20 / 3.67
	X	-16.98 / 3.28	-16.17 / 3.27	-17.24 / 3.27
	L	-13.84 / 4.21	-13.96 / 4.23	-14.55 / 4.23
$S = 1$	H	-21.22 / 3.18	-19.53 / 3.21	-22.33 / 3.11
	T	-15.25 / 3.73	-14.81 / 3.78	-15.53 / 3.72
	X	-16.84 / 3.28	-16.11 / 3.32	-16.83 / 3.32
	L	-13.03 / 4.26	-13.32 / 4.29	-13.67 / 4.23

Table 2 b): Intermolecular well depths (meV) and equilibrium distances ($\text{\AA}$) for H, T, X and L conformations, in $S = 2$ spin multiplicity. Comparison between our best results UCCSD(T)-CBS with RCCSD(T).²⁹

V(meV) / R($\text{\AA}$)		UCCSD(T)	RCCSD(T)
$S = 2$	H	-13.98 / 3.43	-13.56 / 3.42
	T	-13.00 / 3.84	-13.04 / 3.83
	X	-16.53 / 3.28	-16.29 / 3.27
	L	-11.69 / 4.31	-12.29 / 4.34

II. Radial terms

We have computed the isotropic terms of the interaction potential for each multiplicity using Eq. 14 and, after averaging them over the spin multiplets, a spin and orientationally averaged potential term V_{sa}^{000} was obtained. It is shown in Fig.3 in comparison with the corresponding hybrid^{24-25, 29} and experimentally derived¹⁸ terms.

It is necessary to clarify that the experimentally-based potential of Ref. 18 only includes four terms in the spherical harmonic expansion (eq.[13]), where the main radial coefficients were mostly obtained by reproducing experimental collision cross sections as a function of collision energy and alignment. In this study two types of experiments were performed: one, with molecules in high rotational states and the other, with molecules rotationally cooled and aligned. In the theoretical analysis for the first case,

the molecules are treated as pseudo-atoms and from the analysis of the effective cross sections it is possible to obtain a reliable estimate of the isotropic coefficient (V^{000}). In the second case the collision event is approximated by that of a pseudo-atom with the oxygen molecule and it is possible to assess the dominant anisotropic component (V^{202}). The last two terms (V^{220} and V^{222}) were obtained by adjusting values of the second virial coefficient as a function of temperature. An analogous expansion was considered for the exchange coupling coefficient J and its components were obtained by exploiting an older *ab initio* determination³⁸ and then scaling its isotropic component (J^{000}) in order to better reproduce the quenching of the glory oscillations of the measured cross sections. In this way they were able to obtain an experimentally derived PES but care has to be taken when making comparisons with theoretical predictions given the main approximations made in their derivations: a reduced number of terms in their expansion and assuming pseudo-atoms to obtain the first anisotropic component, both reasonable approximations but, probably, introducing uncertainties in the PES determination.

As can be seen in Fig. 3, after spin and orientation averaging, the present interaction potential becomes almost identical to the previous hybrid estimations. Comparison with the experimentally derived potential is fairly good although the (three) calculations predict a less attractive interaction (by about 1 meV at the minimum). The differences between theory and experiment might indicate that a saturation of the basis is not yet reached or that the level of correlation, although very high, is still incomplete, being necessary to use even more precise methods such as UCCSDT or UCCSDTQ⁶¹. Note also that an uncertainty of ± 0.6 meV has been assigned to the well depth of the experimentally derived potential.¹⁸

Table 3 gathers the equilibrium properties of these spin-averaged isotropic potential terms together with those of the isotropic terms for each of the spin multiplicities. Comparison between the theoretical and the empirical terms is somewhat worse for the singlet and triplet states than for the quintet and the spin-averaged ones. This is due to a larger experimentally derived J^{000} splitting component, whose absolute value has been indeed increased to reproduce the molecular beam results, as mentioned above.

Fig. 3: Spin averaged isotropic coefficient V_{sa}^{000} , obtained through KK procedure at UCCSD(T)-CBS, Hybrid-CASPT2, and Hybrid-MRCI levels.^{24-25, 29} A comparison with the experimentally derived estimation¹⁸ is also provided.

Table 3: Intermolecular equilibrium distances and well depths of the isotropic coefficient V^{000} for the three spin multiplicities and its spin averaged value V_{sa}^{000} . Comparison between our best results UCCSD(T)-CBS with RCCSD(T),²⁹ hybrid-CASPT2,²⁴⁻²⁵ hybrid-MRCI²⁴⁻²⁵ and experiment.¹⁸

$V(\text{meV}) / R(\text{\AA})$	Hybrid-MRCI	Hybrid-CASPT2	UCCSD(T)	Experiment
$V^{000} S = 0$	-11.03 / 3.88	-11.50 / 3.86	-11.05 / 3.86	-13.27 / 3.80
$V^{000} S = 1$	-10.71 / 3.88	-11.09 / 3.88	-10.72 / 3.88	-12.42 / 3.85
$V^{000} S = 2$	RCCSD(T) -10.37 / 3.91		-10.12 / 3.91	-11.07 / 3.93
V_{sa}^{000}	-10.59/3.91	-10.72/3.91	-10.41/3.91	-11.69/3.91

In Fig. 4 we present an analogous comparison in the case of the spin-averaged largest anisotropic component V_{sa}^{202} . There is an excellent agreement between the unrestricted and restricted methodologies the first ones being slightly deeper. Larger differences are seen in comparison with the experimental determination. As has been discussed before¹⁸ and mentioned above, although this term is the most reliable among the different anisotropic terms reported in experiment, its determination hinges on reasonable assumptions, such as treating a molecule in higher rotational states as a pseudo-atom, but quantitatively ignoring the rotational degrees of freedom may introduce inaccuracies in the estimation. Analogous behavior is observed for each of the multiplicities. A detailed comparison can be found in Table 4.

Fig. 4: Spin averaged first anisotropic coefficient V_{sa}^{202} , obtained through KK procedure at UCCSD(T)-CBS level. Comparison with Hybrid-CASPT2^{23,24}, Hybrid-MRCI²⁴⁻²⁵ and experimentally derived¹⁸ results is also provided.

Table 4: Intermolecular distances and potential wells for anisotropic coefficient V^{202} in their three spin multiplicities and its spin averaged value V_{sa}^{202} . Comparison between our best results with restricted methodology^{24-25, 29} and experimentally derived estimations.¹⁸

$V(\text{meV}) / R(\text{\AA})$	Hybrid-MRCI	Hybrid-CASPT2	UCCSD(T)	Experiment
$V^{202} S = 0$	-1.06 / 4.32	-1.08 / 4.32	-1.09 / 4.29	-0.40 / 4.57
$V^{202} S = 1$	-1.04 / 4.32	-1.06 / 4.32	-1.07 / 4.29	-0.38 / 4.62
$V^{202} S = 2$	RCCSD(T) -1.01 / 4.34		-1.03 / 4.31	-0.36 / 4.67
V_{sa}^{202}	-1.02/4.34	-1.03/4.34	-1.05/4.31	-0.37/4.67

III. Coupling constant

The absolute values of J plotted in logarithmic scale are depicted in Fig. 5 for the four limiting geometries. Recall that for all conformations the value of J is negative (antiferromagnetic) except for the X geometry where it is positive (ferromagnetic) in accordance with previous theoretical work^{20, 24, 29, 38} and experimental determinations.^{18, 62} This is consistent with the deeper potential wells for the singlet states with the exception of the X geometry where the ferromagnetic state is slightly favored. As mentioned before both the angular and radial dependence (decaying exponential) can be understood in terms of the overlap of the valence π_g^* orbitals. The exponential behavior is clearly seen for all conformations except for the X structure where the overlap effects are orders of magnitude smaller and the ferromagnetism is slightly favored.²⁰

In general, there is a very good agreement in the predicted values of all theoretical methods. We know from the previous theoretical study²⁴ using restricted methodology

that inclusion of higher order correlation is important to accurately represent the exchange interactions. As expected by now the unrestricted values lie between those of the restricted hybrid approaches. Previous experimental determinations¹⁸ based on collision cross-sections agree well with theory with the sole exception of the X structure where, as mentioned before, the J values are very small. However, note that differences that may seem small due to the use of the log scale in Fig.5, can become more important when comparing detailed properties, as those reported in Tables 3 and 4.

We would like to make reference to the recent determination of J for this same system using symmetry adapted perturbation theory (SAPT)⁶³⁻⁶⁴. In principle SAPT can yield very accurate results for intermolecular forces and therefore a comparison could be most beneficial, however so far, the studies have neglected second-order effects. The recent values reported at SAPT level look similar to those obtained by Wormer and van der Avoird in a pioneering work^{20, 38} using first-order perturbation theory. From our previous restricted studies^{24, 29} we know that neglecting dynamic electron correlation leads to smaller values of the exchange-coupling constant and this is what we observe in the recent SAPT estimates. It would be highly desirable to proceed with the inclusion of second-order effects in SAPT studies to make a more stringent comparison.

In Appendix B) we show comparisons for the coupling constant J obtained at the UHF and UCCSD(T) levels. In agreement with the previous restricted study we find that the UHF values are smaller than those at the correlated level. For example, at the equilibrium geometry of the H configuration there is a $\approx 10\%$ difference (between J_{UHF} and $J_{\text{UCCSD(T)}}$) but for the linear case it is $\approx 25\%$ and in all cases the error increase monotonously with decreasing intermolecular distance.

Fig. 5: Coupling constant J , at UCCSD(T)-CBS level, for H,T,X,L conformations and its comparison with collision experiment estimations¹⁸ and theoretical^{24, 29} reported results. Y axis in logarithmic scale, except for X conformation

In the theoretical studies⁶⁵⁻⁶⁶ of the condensed phases of oxygen it is customary to use the Heisenberg Hamiltonian to treat the intermolecular interactions and as such the accurate determination of J is of great relevance for these studies. Furthermore this also motivates the experimental determination of J as was done in the spectroscopic studies by Bini and coworkers⁶² mentioned previously. In Fig. 6 we present values of J

obtained in theoretical and experimental studies. It corresponds to the H geometry which is ubiquitous in the solid phases of oxygen. We notice a very good overall agreement between the unrestricted calculations and the spectroscopic determination, the larger deviations observed at long distances when the coupling is approaching zero. However the values of J that come from a molecular dynamics simulation⁸ of the liquid properties using a non-collinear magnetism density functional approach has differences close to an order of magnitude in the potential well region. It is difficult to pinpoint the precise origin of this large differences but the methodology they use to determine J is indirect and based on the adjustment of a mean-field parameter determined from a comparison with the uniform magnetic susceptibility. They also have approximated the angularly averaged exchange-coupling constant on the basis of selected geometrical configurations. Finally, they are using generalized gradient functionals which cannot properly describe dispersion interactions which represent the main attractive component of the dimer interaction.

Fig. 6: Coupling constant J , at UCCSD(T)-CBS level for H conformation and its comparison with experimental (spectroscopy⁶² and collision experiment¹⁸) and theoretical(molecular dynamic simulation⁸) reported results. Y axis in logarithmic scale.

Summary and Conclusions

We have presented a procedure to calculate the multiplet intermolecular potentials of two monomers with spin equal one that leads to very high accuracy i.e. at the unrestricted coupled cluster level of theory. An analysis of the coupled and uncoupled representations for this type of system shows that the “antiferromagnetic” coupling of the unrestricted approach provides an accurate representation of the triplet state of the complex. Then in combination with a UCCSD(T) calculation of the ferromagnetic ($S = 2$ state) and the assumption of a Heisenberg Hamiltonian one can obtain the desired and technically more difficult singlet state of the complex. The accuracy of the Heisenberg Hamiltonian is tested in an independent way which shows that it is accurate in the well region of the interactions as well as longer distances, with the H configuration showing the largest deviations compared with other orientations. For these cases, it would be

worthwhile to extend the Heisenberg Hamiltonian by including a further biquadratic term.⁶⁷

We make extensive comparisons with accurate restricted potentials as well as experimental determinations of the isotropic radial coefficient and the exchange coupling constant. Regarding comparison with the previous restricted hybrid methodology²⁴ it is encouraging that the new unrestricted approach leads to intermolecular potentials that fall between the lower and upper bounds predicted in that work for a better estimate of the intermolecular potentials. The only exception is the linear configuration which is very close to the upper bound so that the deviation from the expected behavior is very small. The origin of this difference can be traced back to differences already observed for the quintet state when comparing restricted and unrestricted potentials. Apparently, this configuration can be more sensitive to subtle differences in methodology. The two studies taken in conjunction determine with great precision the multiplet intermolecular potentials and certainly represent the most accurate set to date.

Comparison of the radial isotropic coefficient with a reliable experimental determination from collisions in molecular beams¹⁸ shows an overall very good agreement but the differences increase slightly going from the quintet to the singlet state.

A further improvement of this agreement would probably require, on one hand, higher levels of theory in the *ab initio* estimation of the intermolecular potential, capable to take into account higher order correlation effects. The case of higher correlation effects has been studied⁶⁸ for the analogous CO dimer where they found that fifth order effects not properly included at the CCSD(T) level could lead to deviations on the order of those observed here. On the other hand, more accurate models⁶⁹ to interpret the measured molecular beam collision properties would be also needed.

The exchange-coupling parameter is a crucial quantity in the simulation of condensed phases of oxygen through the Heisenberg Hamiltonian. Comparison of the restricted hybrid approach and the present unrestricted procedure shows an excellent overall agreement and highlights the importance of including dynamic electron correlation at a high level. Recent determinations using SAPT and spin-flip³⁰ include only first-order effects and therefore lead to smaller values consistent with our previous observations²⁴ that inclusion of dynamic correlation leads to larger values of J . Agreement with spectroscopic determinations⁶² in the solid phase is also very good. On the other hand, we notice that simulations of the liquid phase based on a non-collinear magnetism DFT approach report an exchange-coupling parameter which is a factor of (roughly) five larger at intermolecular distances close to the equilibrium values found in the dimer and the solid phase.

Finally, we would like to emphasize that the approach used here based on unrestricted methodology guided by angular momentum coupling analysis can be applied with advantage for the description of other systems where the interacting monomers are $s = 1$ particles. It could be of great use in a variety of studies related to magnetic exchange-coupling phenomena.

Appendix-A)

In the case of two molecules with electronic spin $s_a = s_b = 1$, the basis elements of the coupled representation $|SM\rangle$ are related to those of the uncoupled representation $|s_a m_a, s_b m_b\rangle$ through the well-known Clebsch-Gordan coefficients⁴⁰ as

$$\begin{aligned}
 |2,2\rangle &= |1,1; 1,1\rangle \\
 |2,1\rangle &= \frac{1}{\sqrt{2}} |1,1; 1,0\rangle + \frac{1}{\sqrt{2}} |1,0; 1,1\rangle \\
 |2,0\rangle &= \frac{1}{\sqrt{6}} |1,1; 1, -1\rangle + \sqrt{\frac{2}{3}} |1,0; 1,0\rangle + \frac{1}{\sqrt{6}} |1, -1; 1,1\rangle \\
 |2, -1\rangle &= \frac{1}{\sqrt{2}} |1, -1; 1,0\rangle + \frac{1}{\sqrt{2}} |1,0; 1, -1\rangle \\
 |2, -2\rangle &= |1, -1; 1, -1\rangle \\
 |1,1\rangle &= \frac{1}{\sqrt{2}} |1,1; 1,0\rangle - \frac{1}{\sqrt{2}} |1,0; 1,1\rangle \\
 |1,0\rangle &= \frac{1}{\sqrt{2}} |1,1; 1, -1\rangle - \frac{1}{\sqrt{2}} |1, -1; 1,1\rangle \\
 |1, -1\rangle &= -\frac{1}{\sqrt{2}} |1, -1; 1,0\rangle + \frac{1}{\sqrt{2}} |1,0; 1, -1\rangle \\
 |0,0\rangle &= \frac{1}{\sqrt{3}} |1,1; 1, -1\rangle - \frac{1}{\sqrt{3}} |1,0; 1,0\rangle + \frac{1}{\sqrt{3}} |1, -1; 1,1\rangle.
 \end{aligned} \tag{1}$$

Assuming that the electronic Hamiltonian commutes with the total spin operator, the Hamiltonian matrix in the coupled representation above is diagonal with elements $V_{|S,M\rangle}$ (potential energy matrix). Using the transformation above between the coupled and the uncoupled basis, the original diagonal matrix becomes a block diagonal matrix in the uncoupled representation, as

$$A^T V A = \begin{pmatrix} \left(\frac{1}{3}V_{0,0} + \frac{1}{2}V_{1,0} + \frac{1}{6}V_{2,0}\right) & \left(-\frac{1}{3}V_{0,0} + \frac{1}{3}V_{2,0}\right) & \left(\frac{1}{3}V_{0,0} - \frac{1}{2}V_{1,0} + \frac{1}{6}V_{2,0}\right) & 0 & 0 & 0 & 0 & 0 & 0 \\ \left(-\frac{1}{3}V_{0,0} + \frac{1}{3}V_{2,0}\right) & \left(\frac{1}{3}V_{0,0} + \frac{2}{3}V_{2,0}\right) & \left(-\frac{1}{3}V_{0,0} + \frac{1}{3}V_{2,0}\right) & 0 & 0 & 0 & 0 & 0 & 0 \\ \left(\frac{1}{3}V_{0,0} - \frac{1}{2}V_{1,0} + \frac{1}{6}V_{2,0}\right) & \left(-\frac{1}{3}V_{0,0} + \frac{1}{3}V_{2,0}\right) & \left(\frac{1}{3}V_{0,0} + \frac{1}{2}V_{1,0} + \frac{1}{6}V_{2,0}\right) & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \left(\frac{1}{2}V_{1,1} + \frac{1}{2}V_{2,1}\right) & \left(-\frac{1}{2}V_{1,1} + \frac{1}{2}V_{2,1}\right) & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \left(-\frac{1}{2}V_{1,1} + \frac{1}{2}V_{2,1}\right) & \left(\frac{1}{2}V_{1,1} + \frac{1}{2}V_{2,1}\right) & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \left(\frac{1}{2}V_{1,-1} + \frac{1}{2}V_{2,-1}\right) & \left(-\frac{1}{2}V_{1,-1} + \frac{1}{2}V_{2,-1}\right) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \left(-\frac{1}{2}V_{1,-1} + \frac{1}{2}V_{2,-1}\right) & \left(\frac{1}{2}V_{1,-1} + \frac{1}{2}V_{2,-1}\right) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{2,2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{2,-2} \end{pmatrix} \tag{2}$$

where V is the diagonal matrix in the coupled representation, A is the matrix that connects the two representations and the uncoupled basis has been ordered as:

$$\begin{bmatrix} |1,1; 1, -1\rangle \\ |1,0; 1,0\rangle \\ |1, -1; 1,1\rangle \\ |1,1; 1,0\rangle \\ |1,0; 1,1\rangle \\ |1,0; 1, -1\rangle \\ |1, -1; 1,0\rangle \\ |1,1; 1,1\rangle \\ |1, -1; 1, -1\rangle \end{bmatrix} \quad [3]$$

Now, using the Heisenberg Hamiltonian [Eq. 3 of Methodology section] to approximate the energies of the coupled spin states [Eq. 4 of Methodology section], the potential energy matrix in the uncoupled representation becomes:

$$A^T V A = \begin{bmatrix} V_{sa} + 2J & -2J & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -2J & V_{sa} & -2J & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -2J & V_{sa} + 2J & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & V_{sa} & -2J & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2J & V_{sa} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & V_{sa} & -2J & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2J & V_{sa} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{sa} - 2J & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{sa} - 2J \end{bmatrix}. \quad [4]$$

Now, it can be seen that the triplet state energy, $V_{sa} + 2J$ (Eq. 4 of Methodology section), can be reproduced by the pre-diagonalization expectation value from $|1,1; 1, -1\rangle$ or $|1, -1; 1,1\rangle$ (diagonal elements (1,1) or (3,3) of the matrix above), as specified in Eq. 5 of the Methodology section.

Adding now a further bilinear-biquadratic term to the Heisenberg Hamiltonian,^{41, 70}

$$\mathcal{H}_{int} = V_{sa} - 2J \mathbf{s}_a \cdot \mathbf{s}_b + \gamma (\mathbf{s}_a \cdot \mathbf{s}_b)^2 \quad [5]$$

the singlet, triplet and quintet energies become

$$\begin{aligned} V_{|S=0\rangle} &= V_{sa} + 4J + 4\gamma \\ V_{|S=1\rangle} &= V_{sa} + 2J + \gamma \\ V_{|S=2\rangle} &= V_{sa} - 2J + \gamma \end{aligned} \quad [6]$$

so the expected value of the Hamiltonian for the antiparallel spin states are

$$\langle 1, \pm 1, 1, \mp 1 | \mathcal{H}_{int} | 1, \pm 1, 1, \mp 1 \rangle = V_{sa} + 2J + \gamma, \quad [7]$$

i.e., identical to the energy of the triplet state $V_{|S=1\rangle}$, as concluded for the simpler (bilinear) Heisenberg Hamiltonian model.

Appendix-B)

Fig. 7: Coupling constant J , at UHF-AQVZ and UCCSD(T)-AVQZ levels, for H,T,X,L conformations. Y axis in logarithmic scale, except for X conformation.

Data availability statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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