(Heisenberg) exchange and electrostatic interactions between $O_2$ molecules: An ab initio study

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The electrostatic and exchange interactions between two ground state $^3\Sigma_g^-$ $O_2$ molecules have been calculated ab initio by means of first order exchange perturbation theory. The nonorthogonality problem has been handled in a second-quantized hole-particle formalism by a generalization of Wick's theorem. The splitting between the spin states, $S = 0$, 1, and 2, of the $O_2$-$O_2$ dimer is accurately represented by the Heisenberg Hamiltonian. By means of a spherical expansion for the orientational dependence and exponential functions for the distance dependence of the expansion coefficients, complete analytic potential surfaces have been evaluated, both for the spin-independent term in the Heisenberg Hamiltonian $\Delta E$ and for the exchange coupling parameter $J$. The strong anisotropy and distance dependence of $J$ indicate that magnon-libron and magnon-phonon coupling in solid $O_2$ are likely to be strong. A simple four-electron model containing the $O_2$ open shells only reproduces the structure dependence of $J$ qualitatively, but not quantitatively.

I. INTRODUCTION

The (bulk) properties of molecular matter are essentially determined by the intermolecular potential, which, for normal closed-shell molecules, depends on the distance between the molecules and their orientations. For $O_2$ molecules, however, which have an open-shell $^3\Sigma_g^-$ ground state, the intermolecular potential depends on the orientations of the molecular ($S = 1$) spins also. That is, for $O_2$-$O_2$, three distinct potential surfaces exist, corresponding with the singlet ($S = 0$), triplet ($S = 1$), and quintet ($S = 2$) states of the dimers arising from the coupling of the monomer ground states. The splitting between those surfaces is caused by $O_2$-$O_2$ exchange interactions and there is a further splitting of the nonsinglet surfaces due to smaller magnetic coupling terms.1-3

This extra (spin) degree of freedom leads to many interesting bulk properties. Solid oxygen under its own vapor pressure can exist in three phases which differ not only in structure, but also in their magnetic ordering.1-25 The monoclinic $\alpha$ phase, stable between 0 and 23.8 K, is the only homogeneous antiferromagnet known to date. Orientationally it is ordered also; the $O_2$ molecules are arranged in layers with their axes parallel to each other and perpendicular to the layer (ab) planes (see Fig. 2 of Ref. 1). The rhombohedral $\beta$ phase, stable between 23.8 and 43.8 K, is structurally similar to the $\alpha$ phase; the molecules are just slightly displaced in the layer planes so that they make a hexagonal arrangement. Magnetically it is quite different, however. It has been established recently21-23 that the $\beta$ phase has short range antiferromagnetic order with the three-sublattice 120$^\circ$ spin arrangement proposed earlier.13-15 The cubic $\gamma$ phase, stable from 43.8 K to the melting point at 54.4 K is orientationally disordered and paramagnetic, just as liquid oxygen.

The dominant magnetic coupling term in these condensed phases of oxygen is the exchange interaction between the $O_2$ molecules, which is commonly represented in the form of a Heisenberg Hamiltonian:}

$$\hat{H}_{ex} = -2 \sum_{\alpha \neq \beta} J_{AB} \hat{S}_A \cdot \hat{S}_B.$$  

It is this coupling which is believed,8,18,22,25 for instance, to drive the so-called magnetoelastic $\beta-\alpha$ phase transition. For some time, not much more was known about this interaction than that the coupling was antiferromagnetic ($J_{AB} < 0$). In the usual models for the magnetic structure and excitations (magnons) in solids the coupling parameter $J_{AB}$ is taken as a constant for nearest neighbors and, sometimes, next nearest neighbors in the lattice. In DeFotis' 1981 review,1 one can find values of $J$ obtained from experiments and semiempirical calculations which range from about 3.0 to 19.8 K for the nearest neighbors in $\alpha$-$O_2$. More recent experiments seem to converge towards higher values for this parameter, but there are still substantial differences between, for instance, the values of Stephens et al.21 and Slyusarev et al.,16,17 25 K, and that of Meier et al.,19,24 38 K. It is noteworthy that the differences seem to be related to the type of measurements (magnetic susceptibilities, heat capacities, magnon frequencies) from which the $J$ values have been derived. The recent experimental data on the distance dependence of $J$ and on the relative magnitudes of $J$ for nearest and next nearest neighbors in $\alpha$-$O_2$16,17,19,21 are in reasonable agreement.

In principle, however, the coupling parameter $J_{AB}$ in Eq. 1 depends not only on the distance between the $O_2$ molecules A and B, but also on their orientations, just as the other (spin-independent) terms in the intermolecular potential. In a recent letter by van Hemert and the present authors,26 it is demonstrated that the distance and orientational dependence of $J_{AB}$ can be obtained from ab initio calculations. This preliminary study has shown that indeed $J$ depends strongly on the distance and the orientations of the monomers. In order to obtain the effective $J$ value probed by the measurements, one has to average (thermally) over the lattice vibrations and this might well explain some of the experimental differences. Moreover, the geometry dependence of $J$ indicates that strong coupling can occur between...
the magnons and the lattice vibrations (translational and librational phonons). The possibility of this coupling has been mentioned before \textsuperscript{10,18,22,24} in order to explain some experimentally observed effects and discrepancies, but it could not be introduced quantitatively into the models because the structure dependence of $J$ was not known.

Besides the extensive work on solid oxygen, there are experimental data available on $\text{O}_2$ dimers in molecular beams,\textsuperscript{37,38} in the gas phase,\textsuperscript{39,40} and diluted in solid rare-gas\textsuperscript{31} or nitrogen\textsuperscript{3,32} matrices. For the interpretation of these data, too, it is very useful to have knowledge of the $\text{O}_2$-$\text{O}_2$ potential and, in particular, of the Heisenberg exchange term (1). From scattering data only the isotropic, spin-independent part of this potential has been derived.\textsuperscript{33} In the field of \textit{ab initio} calculations, one has only looked until now at the “chemical bonding” region of $\text{O}_2$,\textsuperscript{34} using small basis sets.

In the present paper, we have undertaken the task of computing the full distance and orientational dependence of the coupling parameter $J_{AB}$, as well as the other exchange and electrostatic contributions to the $\text{O}_2$-$\text{O}_2$ potential, by means of extensive \textit{ab initio} calculations using sizable bases. As calculations of such interactions between open-shell molecules have not been done before, we have developed a new formalism, which may have other applications as well. The final results have been given in analytic form, so that they can be used in lattice dynamics or scattering calculations, for instance.

\section{II. Theory}

The exchange interactions between two open-shell atoms or molecules can be represented in an exact manner in the form of an effective operator in spin space:

\[ \hat{H}_A = \sum_k J_{AB}^{(k)} \hat{S}_A \hat{S}_B^{(k)}, \]

where $\hat{S}_A$ and $\hat{S}_B$ are the monomer spin operators. This expression has been formally derived\textsuperscript{35,36} via the Dirac identity for the electron permutation operators. If multiple exchange interactions between the atoms or molecules are negligible, then one can truncate the expansion (2) after the bilinear term and obtain the well-known Heisenberg Hamiltonian (1) ($J_{AB}^{(0)} = -2J_{AB}$).

We wish to emphasize that, in order to calculate $J_{AB}$, the overlap between the orbitals on the monomers A and B should not be neglected. Already in the simple Heitler-London model for the exchange between two H atoms, one finds that only the two-electron exchange integral survives, if the overlap is zero. This integral being positive, the exchange coupling constant $J_{AB}$ becomes necessarily positive as well.\textsuperscript{37} If one still wishes to account for antiferromagnetic coupling, as found between the H atoms and also between $\text{O}_2$ molecules, one has to invoke artificial charge transfer contributions.\textsuperscript{1,2} This can be understood by realizing that the neglect of overlap implies that the monomer orbitals are effectively orthogonalized. Orthogonalization of the orbitals leads to the implicit inclusion of charge transfer configurations into the neutral dimer state. Explicit admixture of such configurations is required then, in order to remove these components. If the overlap is not neglected, however, antiferromagnetic coupling can arise naturally, if the nuclear attraction terms dominate over the two-electron exchange, as in $\text{H}_2$. We shall see in the results of Secs. III and IV that in $\text{O}_2$-$\text{O}_2$ both ferro- and antiferromagnetic coupling can occur, depending on the orientations of the $\text{O}_2$ axes which determine the overlap between the open-shell antibonding $\pi^*$ orbitals.

We have chosen to calculate the rather weak exchange interactions between $\text{O}_2$ molecules in the van der Waals region by perturbation theory. An alternative would be a supermolecule $\text{O}_2$ treatment, but then the incorrect asymptotic behavior of the Hartree-Fock wave functions necessitates the inclusion of correlation, for instance via the CI (configuration interaction) method. In such a supermolecule treatment one gets so-called basis set superposition errors,\textsuperscript{38} both at the Hartree-Fock and the CI level. Especially the latter are practically impossible to correct for, and that while they can be even larger than the physical interactions we are interested in.

In the usual Rayleigh–Schroedinger perturbation theory one would employ products of the free monomer wave functions. In order to include explicitly the exchange interactions between the molecules, which for closed-shell systems lead to the repulsive part of the van der Waals potential, it is necessary to fully antisymmetrize these products. In the case of $\text{O}_2$-$\text{O}_2$ we are especially interested in these exchange interactions, as they cause both the exchange repulsion and the splitting between the dimer spin states $S = 0, 1,$ and 2, that can be obtained from coupling the two monomer $S_A = S_B = 1$ states. This spin coupling has to be done explicitly in the zeroth order wave functions, in addition to the antisymmetrization. We denote the spin-projected (by $P_S$) antisymmetrized (by $A$) products by $P_S A \psi_A \psi_B$. If such wave functions are used in some form of exchange perturbation theory,\textsuperscript{39} the first order energy yields the electrostatic and exchange interactions between the unperturbed monomer charge distributions and the second order energy yields the induction and dispersion attractions, plus some exchange contributions as well. The second (and higher) order exchange terms are usually very much smaller than the first order exchange energy,\textsuperscript{39} and since it is the $\text{O}_2$-$\text{O}_2$ exchange interaction that we wish to calculate primarily, we confine ourselves, in this paper, to the first order energy, defined as

\[ \Delta E^{(1)} = \left( \langle P_S A \psi_A \psi_B | \hat{H}| P_S A \psi_A \psi_B \rangle \right) - \left( \langle P_S A \psi_A \psi_B | \hat{H}| P_S A \psi_A \psi_B \rangle \right) \]

The (normalized) monomer $\Sigma^-$ ground state wave functions $\psi_A$ and $\psi_B$ are taken as restricted Hartree–Fock LCAO-MO functions.\textsuperscript{40} It must be understood, of course, that for a calculation of the complete $\text{O}_2$-$\text{O}_2$ interaction potential, at least the second order (attractive) dispersion interactions have to be added (compare, for instance, the \textit{ab initio} $\text{N}_2$-$\text{N}_2$ interaction\textsuperscript{41}).

For closed-shell molecules, such as $\text{N}_2$, the evaluation of the first order energy (3) is relatively simple, because the monomer MO’s $\phi_A$ and $\phi_B$ occurring in $\psi_A$ and $\psi_B$ can be
orthogonalized, without affecting the dimer wave function $P_P A \Psi^{(0)}_P \Psi^{(0)}_B$ (which is a single closed-shell Slater determinant in this case, with $S = 0$). Next, one can simply apply the standard Slater rules for matrix elements over determinants with orthogonal orbitals. In the case of O$_2$–O$_2$, however, the wave functions $P_P A \Psi^{(0)}_P \Psi^{(0)}_B$, except for the quintet $S = 2$ state, are not invariant under general transformations of the occupied orbitals. Let us divide the O$_2$ monomer orbitals into two sets: the closed-shell MO's $\varphi^a$ and $\varphi^b$ with $\mu, \nu = 1$–7, running over the occupied $\sigma$ orbitals and the bonding $\pi_u$ orbitals, and the open-shell MO's $\varphi^a$ and $\varphi^b$ with $i, j = 1$–2 running over the degenerate antibonding $\pi_d$ orbitals. The electron pairs occupying the latter orbitals in each monomer are coupled to a $3\Sigma^-$ state. Now, it is allowed to orthogonalize the closed-shell orbitals $\varphi^a$ and $\varphi^b$ among each other and to Schmidt orthogonalize the open shells $\varphi^a$ and $\varphi^b$ onto the closed shells, without altering the total dimer wave functions $P_P A \Psi^{(0)}_P \Psi^{(0)}_B$. The open shells $\varphi^a$ and $\varphi^b$ have to remain nonorthogonal, however. As we have argued at the start of this section, the explicit consideration of their overlap is essential for obtaining the correct exchange coupling constant $J_{AB}$.

Thus, we are left with the well-known nonorthogonality problem in calculating the expectation value over the many-electron wave function $P_P A \Psi^{(0)}_P \Psi^{(0)}_B$. There are several ways to handle this problem, as described by Löwdin, Prosser, and Hagstrom and by ourselves, but here we outline a new method, based on a second-quantized hole–particle formalism and the generalization of Wick's theorem to nonorthogonal bases. This method allows us to take maximum advantage of the orthogonality between the open-shell or particle space $\{\varphi^a, \varphi^b; i, j = 1$–2$\}$ and the closed-shell or hole space $\{\varphi^a, \varphi^b; \mu, \nu = 1$–7$\}$. The corresponding spin orbitals, spanning the hole and particle spaces, respectively, will be denoted by $\{\varphi^a, \alpha = 1$–28$\}$ and $\{\varphi^a, \alpha = 1$–8$\}$. This identification of holes and particles is equivalent to defining the occupied closed-shell wave function—a single 28-electron Slater determinant—as the Fermi vacuum state. The hole-particle method reduces the problem of 32 electrons effectively to a four-electron problem; the 28 electrons in the Fermi sea enter the Hamiltonian in the form of an effective potential, exactly as in the case of orthogonal orbitals.

In the theory outlined below we base ourselves on a review by Paldus and Čiček and lecture notes by Paldus. These works can be consulted for more details and references to the original literature.

Assume that the one-particle overlap matrix has the following blocked form:

$$S = \begin{pmatrix} S_a & 0 \\ 0 & S_b \end{pmatrix},$$

where, in our case, the 28-dimensional hole matrix $(S_a)_{\alpha \beta} = \langle \varphi^a_\alpha | \varphi^b_\beta \rangle$ has the form of a unit matrix and the eight-dimensional particle matrix $(S_p)_{\alpha \beta} = \langle \varphi^a_\alpha | \varphi^b_\beta \rangle$ contains the overlaps between the open-shell spin orbitals which have been first orthogonalized onto the closed-shell space. The orthogonality between the hole and particle states is essential for the present formalism, but the hole states do not have to be orthogonal. We define the dual or biorthogonal basis $47, 48$:

$$\langle \psi^a | = \sum_b | \psi^b_\alpha \rangle S^*_{ba},$$

$$\langle \psi^a | = \sum_b | \psi^b_\alpha \rangle S^*_{ba}$$

with the overlap matrices

$$S_{\alpha \beta} = (S^{-1})_{\alpha \beta} \equiv (S^{-1})_{\alpha \beta},$$

$$S_{ab} = (S^{-1})_{ab} \equiv (S^{-1})_{ab}.$$

Next we define the creation operators by their action on the physical vacuum state $|0\rangle$:

$$\eta^a_\alpha |0\rangle = |\psi^a_\alpha \rangle, \quad \eta^{* \alpha} |0\rangle = |\psi^{* \alpha} \rangle,$$

$$\eta^a_\alpha |0\rangle = |\psi^a_\alpha \rangle, \quad \eta^{* \alpha} |0\rangle = |\psi^{* \alpha} \rangle.$$  

The Hermitian conjugates of these operators acting on $|0\rangle$ yield the zero vector, as usual. We impose the following anticommutation relations:

$$\{\eta^a_\alpha, \eta^b_\beta \} = \{\eta^a_\alpha, \eta^{* \beta} \} = \delta_{\alpha \beta},$$

$$\{\eta^a_\alpha, \eta^{* \beta} \} = \{\eta^a_\alpha, \eta^{* \beta} \} = \delta_{ab},$$

with all other commutators containing one upper and one lower index vanishing. These relations show that $\eta^a_\alpha$ annihilates a particle created by $\eta^{* \alpha}_\alpha$. Similarly $\eta^a_\alpha / \eta^{* \alpha}_\alpha$ and also $\eta^a / \eta^{* \alpha}$ and $\eta^a / \eta^{* \alpha}$, are annihilation/creation pairs. The Fermi vacuum is given by

$$\langle 0 | \Phi_0 = \left( \prod_{\alpha} \eta^{* \alpha} \right) |0\rangle = \det S_h \left( \prod_{\alpha} \eta^{* \alpha} \right) |0\rangle$$

with

$$\langle \Phi_0 | \Phi_0 \rangle = \det S_h.$$  

Now, we invoke the normal ordering operator with respect to the Fermi vacuum. This operator $N$ orders any product of creation and annihilation operators in such a way that all particle/hole creation operators precede the particle/hole annihilation operators; the sign of the reordered product is the parity of the reordering permutation. Furthermore, we define the contraction of any pair of operators with respect to the Fermi vacuum by

$$\overline{\langle \eta^{* \alpha}_\alpha \eta^a_\beta \rangle} = \langle \eta^{* \alpha}_\alpha \eta^a_\beta \rangle - N \langle \eta^a_\alpha \eta^{* \beta} \rangle.$$  

From similar definitions we obtain the following nonzero contractions:

$$\overline{\langle \eta^{* \alpha}_\alpha \eta^a_\beta \rangle} = \delta_{ab},$$

$$\overline{\langle \eta^a_\alpha \eta^{* \beta} \rangle} = \delta_{ab},$$

$$\overline{\langle \eta^a_\alpha \eta^b_\beta \rangle} = \delta_{ab},$$

$$\overline{\langle \eta^{* \alpha}_\alpha \eta^b_\beta \rangle} = \delta_{ab},$$

$$\overline{\langle \eta^a_\alpha \eta^{* \beta} \rangle} = \delta_{ab},$$

$$\overline{\langle \eta^a_\alpha \eta^b_\beta \rangle} = \delta_{ab}.  

A general $n$-particle state (for the O$_2$–O$_2$ dimer $n = 4$) is given by

$$\langle \psi | = \sum_{\alpha_1 \cdots \alpha_n} \eta^{\alpha_1} \cdots \eta^{\alpha_n} | \Phi_0 \rangle.$$
and the dimer Hamiltonian, with one-electron terms $\hat{H}(1)$ and electron repulsion terms $\hat{v}(1,2) = r_{12}$, reads

\[
\hat{H} = \sum_{p,q} (\psi|\hat{H}|\psi_p) \eta_p^\dagger \eta_q + \frac{1}{2} \sum_{p,q,r,s} (\psi_p^*\psi_q^* \hat{v}|\psi_r|\psi_s) \eta_p^\dagger \eta_q^\dagger \eta_r \eta_s^\dagger,
\]

where the indices $p, q, r, s$ run over hole labels $\alpha$ as well as particle labels $\alpha$. The calculation of the many-electron matrix elements follows by a straightforward application of Wick’s theorem. This theorem, well known for orthogonal orbitals, can be applied without modification if we use the contractions (10). First, we rewrite the Hamiltonian (12) in normal product form with respect to the Fermi vacuum:

\[
\hat{H} = E_0 + \hat{H}_1 + \hat{H}_2
\]

with

\[
E_0 = \sum_{\alpha} (\psi|\hat{H}|\psi_\alpha) + \frac{1}{2} \sum_{\alpha,\beta} (\psi_\alpha^*\psi_\beta^* \hat{v}|\psi_\alpha|\psi_\beta),
\]

\[
\hat{H}_1 = \sum_{p,q} (\psi|\hat{J}^\dagger|\psi_q) N(\eta_p^\dagger \eta_q^\dagger),
\]

\[
\hat{H}_2 = \frac{1}{2} \sum_{p,q,r,s} (\psi_p^*\psi_q^* \hat{v}|\psi_r|\psi_s) N(\eta_p^\dagger \eta_q^\dagger \eta_r \eta_s^\dagger),
\]

and where the closed-shell Fock operator is given by

\[
\hat{J}^\dagger(1) = \hat{H}(1) + \sum_{\alpha} (\psi|\hat{v}|\psi_\alpha) \frac{1}{2} (1 - \hat{P}_{12})|\psi_\alpha)_2.
\]

Then, we write the matrix elements over the states (11), employ the generalized Wick theorem again, and note that, as always, only the fully contracted terms survive in the Fermi vacuum expectation value. This yields the following results:

\[
\langle \Phi_0|\eta_{b_1}...\eta_{b_n} \eta_{a_1}^\dagger...\eta_{a_n}^\dagger|\Phi_0 \rangle = (\det S_n)(\det \Delta),
\]

\[
= (\det S_n) \sum_{\alpha} (\psi_\alpha|\hat{J}^\dagger|\psi_\alpha)(\text{cofac}\Delta)_{p\alpha j},
\]

\[
= (\det S_n) \sum_{\alpha} (\psi_\alpha|\hat{J}^\dagger|\psi_\alpha)(\text{cofac}\Delta)_{p\alpha j},
\]

The overlap matrix $\Delta$ is an $n \times n$ submatrix of the matrix $S_n$:

\[
\langle \Phi_0|\eta_{i_1}...\eta_{i_n} \eta_{a_1}^\dagger...\eta_{a_n}^\dagger|\Phi_0 \rangle = (\det \Delta)(\det \Delta)\]

\[
= (\det \Delta)(\det \Delta)\]

\[
+ (\det \Delta) \sum_{i,j=1}^n (\psi_{i_1}|\hat{J}^\dagger|\psi_{i_j})(\phi_{a_1}...\phi_{a_n}...|\phi_{a_1}...\phi_{a_n})|(-1)^{i+j} + (\psi_{i_1}|\hat{J}^\dagger|\psi_{i_j})(\phi_{a_1}...\phi_{a_n}...|\phi_{a_1}...\phi_{a_n})|(-1)^{i+j} + (\psi_{i_1}|\hat{J}^\dagger|\psi_{i_j})(\phi_{a_1}...\phi_{a_n}...|\phi_{a_1}...\phi_{a_n})|(-1)^{i+j+k},
\]
with the matrices $\Delta_1$ and $\Delta_2$ given by

\[ (\Delta_1)_{ij} = \langle \varphi_i | \varphi_j \rangle, \]  
\[ (\Delta_2)_{ij} = \langle \varphi_i | \varphi_j \rangle, \]  
and the label combinations $\lambda_1 x^2$,$\lambda_2 y^2$,$\lambda_3 z^2$ and $\mu_1 \mu_2 \mu_3 \nu_1 \nu_2 \nu_3$ running over the six determinants in Eq. (17). The effect of the closed shells is simply incorporated in terms of the closed shell energy

\[ E_0 = 2 \sum_{\alpha = 1}^{14} \langle \varphi_\alpha | \hat{h} | \varphi_\alpha \rangle + \sum_{\alpha, \beta} \langle \varphi_\alpha \varphi_\beta | \hat{V}(2 - \hat{P}_{12}) | \varphi_\alpha \varphi_\beta \rangle \]  
and the closed-shell Fock operator

\[ \hat{f}(1) = \hat{h}(1) + \sum_{\alpha = 1}^{14} \langle \varphi_\alpha (2) | \hat{v}(1,2)(2 - \hat{P}_{12}) | \varphi_\alpha (2) \rangle, \]  
where $\hat{h}(1)$ is the usual kinetic energy and nuclear attraction operator. The matrix elements (18), transformed according to Eq. (17), yield the first order energy (3) for $S = 0, 1$, and 2 if the monomer restricted Hartree–Fock energies are subtracted.

Because the splitting between the $S = 0, 1$, and 2 states in the $O_2$–$O_2$ dimer is primarily due to the exchange interaction between the four open-shell electrons, one can try to calculate this splitting from a simple four-electron model. The orbitals entering this model are just the degenerate $\pi$ orbitals on each monomer, which can be further approximated as simple antibonding combinations of the atomic $2p_\pi$ and $2p_\sigma$ orbitals. The open-shell interactions can be evaluated by using the same formulas (17) and (18), with the closed-shell energy $E_0 = 0$ and the Fock operator (21) replaced by the simple one-electron operator $\hat{h}(1)$ with screened nuclear charges (equal to $+ e$ on each oxygen nucleus). Since the closed shells are omitted completely in this model, it is not necessary to orthogonalize the open-shell orbitals onto the closed-shell space, as before. The calculations by this four-electron model are much cheaper than the all-electron calculations; in Sec. IV, we compare some results. In the literature some other models have been proposed, which are even simpler and, therefore, more approximate.

### III. Computational Aspects and Results

As the weak exchange interactions between $O_2$ molecules are very sensitive to the tails of the monomer orbitals, we have calculated the restricted Hartree–Fock MO wave function for the $1\Sigma_g^-$ ground state of the $O_2$ molecule in a rather extensive basis, (11s,6p,2d) contracted to (6s,3p,2d), of Gaussian-type atomic orbitals (GTO’s) with relatively many diffuse functions. This basis set is similar to one of the larger bases tested by Van Duijneveldt et al., but with still another diffuse function added on each O atom. Moreover, we have repeated the calculations at some points of the potential surface with an even larger (13s,8p,2d) contracted to (8s,4p,2d) basis. The calculated properties of the $O_2$ monomer are listed in Table I, the first order $O_2$–$O_2$ interactions for the two basis sets are compared in Table II. From these data it appears that the results are reasonably converged to the Hartree–Fock limit (to within a few percent) already for the smaller basis, which has been used in our further calculations.

In the four-electron model described at the end of Sec. II, we have used $2p_\pi$ and $2p_\sigma$ orbitals on each oxygen atom, of single-zeta Slater type ($\xi = 2.226a_0^{-1}$), each represented by a contracted set of 6 GTO’s.

The monomer calculations and the computation of the dimer integrals over the partly orthogonalized molecular orbitals, as occurring in expression (18), have been performed with the ATOMOL package. Each point on the potential surface took about 30 min NAS-9040 or 15 min CRAY-1S CPU time. (The more symmetric points in Ref. 26 took only 7 min on the CRAY-1S.) Most of the calculations have been done on the NAS-9040 university computer at Nijmegen.

We have calculated first order $O_2$–$O_2$ interaction energies (3) for the three different spin states $S = 0, 1$, and 2 of the dimer. Since we have found that the splitting between these states is accurately represented by the Heisenberg Hamiltonian (1), see Sec. IV, we present our results in terms of the average first order interaction energy

\[ \overline{\Delta E} = \frac{\Delta E^{(1)}(S = 0) + 3 \Delta E^{(1)}(S = 1) + 5 \Delta E^{(1)}(S = 2)}{9} \]  
and the (average) Heisenberg parameter

\[ J = \frac{\Delta E^{(1)}(S = 0) - \Delta E^{(1)}(S = 1)}{4} \]  
\[ + \frac{\Delta E^{(1)}(S = 1) - \Delta E^{(1)}(S = 2)}{8}. \]  

The internal coordinates describing the $O_2$–$O_2$ potential surface are $R$, the distance between the molecular centers of mass, $\theta_A$, $\theta_B$ and $\varphi = \varphi_B - \varphi_A$, where $(\theta_A, \varphi_A)$ and $(\theta_B, \varphi_B)$ are the polar angles of monomers A and B, respectively, in a body-fixed coordinate frame with the z axis along $R$. In an arbitrary frame the full distance and orientational dependence of the interaction energies is conveniently expressed in the form of a spherical expansion

\[ F(R, \Omega, \omega_A, \omega_B) = (4\pi)^{3/2} \sum_{L,m} F_{L,m,L,m}(R) A_{L,m,L,m}(\Omega, \omega_A, \omega_B) \]  
with angular functions

| TABLE I. | 1\Sigma_g^- | | 1\Sigma_g^- | | 1\Sigma_g^- | | 1\Sigma_g^- | |
|---|---|---|---|---|
| Basis: | (11s, 6p, 2d) | (13s, 7p, 2d) | (13s, 7p, 2d) |
| (hartree) | -149.6447 | -149.6540 | -149.6556 |
| Multipole moments | $Q_2(\omega_B)$ | $Q_2(\omega_B)$ |
| $\Delta e$ | -0.2644 | -0.2636 | -0.2609 |
| $\Delta e$ | -0.2644 | -0.2636 | -0.2609 |
| $\Delta e$ | -0.2644 | -0.2636 | -0.2609 |

* Estimated Hartree–Fock limit (Ref. 51).

* Experimental values (Refs. 52 and 53).
The functions $Y_{L_{A},M_{A}}(\Omega)$ are spherical harmonics and the first factor in Eq. (25) is a $3-j$ coefficient.\(^5\) The angular functions $A_{L_{A},L_{B}}(\Omega,\Theta_{A},\Theta_{B})$ depend on the polar angles of $R$ and the molecular axes denoted by $\Omega$, $\Theta_{A}$, and $\Theta_{B}$, respectively. We can always use the special body-fixed frame with $\Omega = (0,0)$, $\Theta_{A} = (\Theta_{A},0)$, and $\Theta_{B} = (\Theta_{B},\Phi_{B})$, because the functions (25) are invariant under overall rotations. Due to this invariance and the orthonormality of the functions, the expansion coefficients can be written as

$$A_{L_{A},L_{B}}(\Omega,\Theta_{A},\Theta_{B}) = \sum_{M_{A},M_{B},M} \left( \begin{array}{ccc} L_{A} & L_{B} & L \\ M_{A} & M_{B} & M \end{array} \right) \times Y_{L_{A},M_{A}}(\omega_{A}) Y_{L_{B},M_{B}}(\omega_{B}) Y_{L,M}(\Omega).$$

The number of quadrature points that have to be included depends on the maximum values of $L_{A}$, $L_{B}$, and $L$.
TABLE IV. Expansion coefficients.

A. Expansion coefficients* of $Δ\bar{E}$, defined by Eqs. (24), (27), and (29); multipole interactions are given by Eq. (28).

<table>
<thead>
<tr>
<th>$L_A$</th>
<th>$L_B$</th>
<th>$L^*$</th>
<th>$g_0$(K)</th>
<th>$α$</th>
<th>$β$</th>
<th>$γ$</th>
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B. Expansion coefficients* of $J$, defined by Eqs. (24) and (29).

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*Terms in the spherical expansion which are less than 1/2000 of the dominant (0, 0, 0) term have been omitted.

\( R > 15a \) the term with $β < 0$ should be put equal to zero.

**The coefficients are symmetric with respect to interchange of \( L_A \) and \( L_B \).

**Terms in the spherical expansion which are less than 1/1000 of the dominant term have been omitted. For \( R > 15a \), the terms with $β < 0$ should be put equal to zero.

**The coefficients are symmetric with respect to interchange of \( L_A \) and \( L_B \).
that must be included in the expansion (24) or, in other words, on the anisotropy of potential $F$. After some experimental with the results of the four-electron model, described in Sec. II, we have found that a $5 \times 5 \times 5$ grid on the interval $0 < \theta_n < \pi/2, 0 < \phi_n < \pi/2, 0 < \rho_n < \pi$ is sufficient to calculate the coefficients $f_{\lambda_n, \mu_n \ell} (R)$ up to $L_A = 8, L_B = 8$, and $L = 14$, inclusive. This interval has been reduced by using the symmetry present in the $O_2-O_2$ dimer; further use of this symmetry leads to 75 "irreducible" points. Truncation of the expansion after the \{$L, L_B, L = (8, 8, 14)$\} term seemed to be allowed, even for the strongly anisotropic $J$ surface. Thus, the complete all-electron calculations have been performed for a grid of 75 angular points and the expansion coefficients (26) have been calculated for $\Delta E$ and $J$ at $R = 5.6$, and $7a_0$. The final results demonstrate that the accuracy of the spherical expansion, up to (8, 8, 14) terms inclusive, is about 0.01% for $\Delta E$ and about 1% for $J$ (root mean square deviation for all grid points). Moreover, we have computed $\Delta E$ and $J$ at 26 other points (see Table III), in order to make an independent check on the accuracy of the expansions.

As the exchange interactions are related to the overlap between the monomer wave functions, they are expected to depend exponentially on the distance $R$. The average first order energy $\Delta E$ contains also the electrostatic multipole–multipole interactions, however, which decrease as $R^{-n}$. These multipole–multipole interactions only contribute to the spherical expansion coefficients with $L = L_A + L_B$. So, the expansion coefficients of $\Delta E$ are finally represented as functions of $R$ by

$$f_{\lambda_A, \mu_A \ell} (R) = \delta_{\lambda_A + \mu_A \ell} C_{\lambda_A, \mu_A} R^{-L_A - L_B - 1} + f_{\lambda_A, \mu_A \ell}^e (R),$$

(27)

where the electrostatic coefficients are given by

$$C_{\lambda_A, \mu_A} = (-1)^{\lambda_A} \left\{ \frac{(2L_A + 2L_B)!}{(2L_A + 1)!(2L_B + 1)!} \right\}^{1/2} Q_{\lambda_A} Q_{\mu_A}$$

(28)

with the multipole moments from Table I (first column).

The exchange contributions $f_{\lambda_A, \mu_A \ell}^e (R)$ are given, as functions of the reduced distance $x = (R - R_0)/R_0$, by

$$f_{\lambda_A, \mu_A \ell}^e (R) = g_{\lambda_A, \mu_A \ell} (x) = g_0 \left( \frac{L_A + \mu_A \ell + 1}{L_A + \mu_A \ell + 1} \right) \times \exp\left( - \alpha^{L_A \mu_A \ell + 1} x - \beta^{L_A \mu_A \ell - 1} x^2 \right),$$

(29)

For $R_0$ we take the nearest neighbor distance in solid $\alpha$-$O_2$ (3.200 Å). The expansion coefficients of $J$ are purely exponential and also given by the form (29). For those coefficients $f_{\lambda_A, \mu_A \ell} (R)$ which change sign, we have assumed that $\beta = 0$; for the positive or negative definite coefficients we have taken $\gamma = 0$. The remaining three parameters, $(g_0, \alpha, \gamma)$ or $(g_0, \alpha, \beta)$, respectively, can be exactly obtained from the calculated values of $f_{\lambda_A, \mu_A \ell}^e (R)$ at $R = 5.6$, and $7a_0$. The final expansion parameters $g_0^{\lambda_A \mu_A \ell}, \alpha^{L_A \mu_A \ell + 1}, \beta^{L_A \mu_A \ell - 1}, \gamma^{L_A \mu_A \ell - 1}$, which completely determine the surfaces $\Delta E (R, \Omega, \omega_A, \omega_B)$ and $J (R, \Omega, \omega_A, \omega_B)$ are collected in Table IV.

IV. DISCUSSION

As mentioned already in Sec. III, we have found, in the first place, that the splitting between the $\Delta E$ surfaces for the three spin states $S = 0, 1$, and 2 of the $O_2-O_2$ dimer, can be accurately represented by the Heisenberg Hamiltonian (1). That is, the triplet–quintet splitting ($\approx 4J$) is twice the singlet–triplet splitting ($\approx 2J$). This implies that multiple exchange interactions are negligible. Only for distances $R$ which are considerably smaller than the nearest neighbor distance in solid $\alpha$-$O_2$ ($R_0 = 3.2$ Å), we observe deviations from this rule, but then the $O_2-O_2$ exchange repulsion itself is already of the same size as the $\Delta E$ splitting in the $O_2$ monomers, so that the theory which leads to the effective spin Hamiltonian (2) breaks down anyway. This occurs actually for the smallest distance in Table III, $R = 4a_0 = 2.117$ Å, where we have still given $\Delta E$ and $J$, but where one should realize that our first order model (3) does not hold anymore.

The structure dependence of $\Delta E$ and $J$ has been given analytically, in the form of a spherical expansion (24) for the orientational dependence, with coefficients (27)–(29) depending on $R$ (see Table IV). In Table III we observe from the values given at $R = 5.6$, and $7a_0$, that the spherical expansions accurately reproduce the values of $\Delta E$ and $J$, even for various orientations which have not been used in deriving these expansions. Even subtle features, such as the sign change of $J$ for the $S$ geometry between $R = 6$ and $7a_0$ are reproduced. In principle, the expansion has been continued up to $L_A = 8, L_B = 8, L = 14$ terms inclusive. In practice, we could neglect several lower terms, especially for $\Delta E$ which is much less anisotropic than $J$ (see below). From the values given in Table III at $R = 4$ and $8a_0$, we can see that even the extrapolation of our results to smaller and larger distances is reasonable in general. We emphasize, however, that the physically important region lies between 5 and $7a_0$ (2.646 and 3.704 Å). For smaller distances $R$ the exchange repulsion $\Delta E$ between the $O_2$ molecules is so large that such distances cannot be reached in most physical processes. For distances beyond $R = 7a_0$ the exchange interactions especially $J$, have almost completely died out.

The orientational dependence of the "exchange repulsion" $\Delta E$ is strong, but relatively simple (see Fig. 1). Many of the higher terms in the spherical expansion vanish. The behavior of this exchange repulsion can be roughly described as an atom–atom repulsion depending exponentially on the intermolecular atom–atom distances; it is very similar to the $N_2-N_2$ repulsion. The multipole–multipole interactions have not been explicitly plotted in Fig. 1, because they are completely negligible at $R = 6a_0$. Note in this respect that the $O_2$ quadrupole moment is about four times smaller than the $N_2$ quadrupole.

The orientational dependence of $J$ is very interesting. Even the higher terms in the spherical expansion contribute significantly, although at $(L_A, L_B, L) = (8, 8, 14)$ the expansion seems finally converged. Especially marked is the (4,4,8) term, being the largest of all for $R > 5.5a_0$. In Fig. 1 we observe, for instance, that $J$ changes sign four times for a simple parallel rotation of two $O_2$ molecules from the linear config-

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FIG. 1. Orientational dependence of $\Delta E$ and $J$. The full lines represent the results of the all-electron calculations, the dashed line refers to the four-electron model described in the text. The multipole contributions to $\Delta E$ are not drawn explicitly because they are negligible at $R = 6a_0$.

The $J$ values from the simple four-electron model explained at the end of Sec. II show the same slow convergence of the spherical expansion. Qualitatively they follow the orientational dependence of the all-electron $J$ values (see Fig. 1); quantitatively they are quite inaccurate, however. The orientational dependence of the older semiempirical models for $J^{1,8}$ is even qualitatively incorrect.

Next we turn to the experimental data on solid oxygen. In agreement with all measurements, we find that the coupling between O$_2$–O$_2$ pairs in the parallel ($H$) geometry, as they occur in the layers of $\alpha$ and $\beta$ O$_2$ crystals, but also in O$_2$ layers adsorbed on graphite, is antiferromagnetic. The strongest, intersublattice, coupling $J_2$ occurs between the nearest neighbors ($R_0 = 3.200 \, \text{Å}$) in $\alpha$–O$_2$. It is not possible, however, to make a direct comparison between our value of $J_2$ calculated at $R = 3.200 \, \text{Å}$, $J_2 = -12.5 \, \text{K}$, and the experimental values, because the averaging of $J$ over the lattice vibrations can make a substantial difference. Thus we have found from a simple model of independent harmonic oscillators that the averaging of $J_2(R)$ over the translational phonons can effectively increase $J_2$ by a factor of 2.5 ($\langle J_2 \rangle \approx -30 \, \text{K}$), which brings it in the range of recent experimental data: $J_2 = -25, 16, 17, 21 - 38 \, \text{K}$. This increase is due to the steep exponential distance dependence of $J_2(R)$; the strong orientational dependence (see Fig. 1) indicates that averaging over the librations may change the effective $J_2$ as well. In Fig. 2 we have plotted explicitly the variation of $J_2$ along the normal coordinates of some librational modes in $\alpha$-O$_2$.

FIG. 2. Variation of the (intersublattice) exchange coupling parameter $J_2$ between the nearest neighbors in solid $\alpha$-O$_2$ along some normal coordinates of libration. The labels $a$ and $b$ refer to librations around the crystal $a$ and $b$ axes, respectively, (Ref. 1); the + and - signs denote in-phase and out-of-phase librations of the molecules on different sublattices.

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The distance dependence of \( J(R) \) which we find from our calculations is roughly exponential, cf. Eq. (29), with the exponents varying between 11 and 15 \( R^{-1} \) \( (3.4 \text{ and } 4.7 \text{ Å}^{-1}) \) for the leading terms. This agrees well with the exponential \((\text{exponent} = 4.3 \text{ Å}^{-1}, \text{Ref. 22})\) and \( R^{-n} \) laws \((n = 10, \text{Ref. 21}, n = 12 \text{ to } 15, 17, 18, n = 14 \text{ Ref.)} \) obtained from pressure and temperature dependent measurements on \( \alpha, \beta, \text{ and } \gamma \text{ O}_2 \). Also the ratio \( J_{/}/J_{/} \) between the intrasublattice \((R = 3.429 \text{ Å})\) and intersublattice \((R = 3.200 \text{ Å})\) coupling in \( \alpha-\text{O}_2 \), which we calculate \((\theta_\alpha = 0^\circ, \varphi = 3^\circ) J_{/}/J_{/} = 0.42, \) is in good agreement with experiment: \( J_{/}/J_{/} = 0.41 \pm 0.012 \). 

From the preliminary calculations we have found that the coupling between the nearest \( \text{O}_2 \) pairs \((R = 4.186 \text{ Å})\) in adjacent layers of \( \alpha-\text{O}_2 \) is very weak, but ferromagnetic \((J_\text{F} > 0)\). The latter result, which was obtained by keeping the \( \text{O}_2 \) molecules in a shifted-parallel \((S)\) geometry \((\theta_\alpha = \theta_\beta = 26.5^\circ, \varphi = 0^\circ)\) at \( R = 4.186 \text{ Å} \), is contrary to experiment. In Fig. 1 we observe, however, that the \( (\theta_\alpha) \text{ positive value of } J_{/} \text{ just occurs in a narrow } (\pm 4^\circ) \text{ range of } \theta_\alpha \text{ and } \theta_\beta \text{ angles around } 20^\circ; \text{ also at smaller distance } (R = 3.175 \text{ Å}) J_{/} \text{ for } \theta_\alpha = \theta_\beta = 26.5^\circ \text{ is negative again (see Table III)}. \text{ It is clear that the angular and distance averaging of } J_{/} \text{ may easily change its sign. It will still remain small, though, as found from recent experiments.}^{16,17,21} \text{ Finally, we like to make some remarks pertinent to } \text{O}_2-\text{O}_2 \text{ dimers. Such dimers have been prepared in supersonic molecular beams both at higher } (T = 50 \text{ to } 100 \text{ K})^{19} \text{ and low } (T = 2 \text{ K})^{20} \text{ temperature. The amount of dimers that could be magnetically defected was practically zero at low temperature and about 70\% at higher temperature. The information which can be inferred from these data is that the } \text{O}_3-\text{O}_2 \text{ dimer has a singlet or antiferromagnetically coupled ground state, with the triplet and quintet states lying somewhat higher. All states are about equally populated at } T = 50 \text{ K}. \text{ In other words, the effective (vibrationally averaged) exchange parameter } J \text{ is negative for the ground state and not larger than about } 10 \text{ K in absolute value. Our calculations show, see Fig. 1, e.g., that many possible dimer geometries could satisfy this requirement, one of them being the parallel } (H) \text{ structure which occurs for the neighbors in solid } \alpha \text{ and } \beta \text{ O}_2 \text{ and which has been proposed also for } \text{O}_3-\text{O}_2 \text{ dimers in the gas phase}^{29} \text{ and in rare gas matrices.}^{31} \text{ More precise measurements, which will be performed soon,}^{28} \text{ in combination with our calculated results, can yield more detailed information.} \text{ V. CONCLUSION} \text{ From } ab \text{ initio calculations which we believe to be fairly accurate in the range of the van der Waals minimum, we have obtained the full anisotropic potential surface for the exchange repulsion, the electrostatic interactions, and the Heisenberg exchange coupling between a pair of ground state } (1\Sigma^+_g) \text{ O}_2 \text{ molecules. The dispersion interactions have still to be added in order to construct a complete O}_2-\text{O}_2 \text{ potential, but these mainly long range interactions will hardly change the magnetic (exchange) coupling in which we are primarily interested. The results are all presented in analytic form (Table IV) so that they can be directly used, for instance, in scattering calculations. calculations of the rovibrotional states of O}_2-\text{O}_2 \text{ dimers, and lattice dynamics calculations on solid O}_2. \text{ In particular for solid O}_2 \text{ which appears to be a system of great interest,}^{1,20} \text{ our results seem to be in agreement with the experimental data available. The strength of our data is, however, that they provide complete information on the structure dependence of the coupling parameter } J_{AB} \text{ in the Heisenberg Hamiltonian (1), which determines the magnetic order in the low-temperature } \alpha \text{ and } \beta \text{ phases, as well as the transition between them. We have found that this coupling depends very sensitively on the orientations of the O}_2 \text{ molecules in the solid even more so than the exchange repulsion; it is also a steep function of the intermolecular separations. This indicates that the differences in } J \text{ values obtained from different type of measurements}^{1} \text{ may be (partly) due to a different averaging sensed by the experiments. It also points to a potentially strong coupling between the magnetic lattice excitations (magnons) and the phonons (both translational and vibrational). Our results for the structure dependence of the } J_{AB} \text{ are in the form needed for inclusion of this couplings in lattice dynamics calculations, via the Heisenberg Hamiltonian. Such calculations are in progress.}^{62} \text{ Furthermore, our data will be helpful for interpreting the existing and forthcoming experimental results}^{27-31} \text{ on } \text{O}_2-\text{O}_2 \text{ dimers.} \text{ ACKNOWLEDGMENTS} \text{ We like to thank Dr. Marc van Hemert for making available his version of the spherical expansion program. We thank the University Computing Center at Nijmegen for supplying us with ample time on their NAS-9040 computer.}
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25B. Kuchta (to be published).
28J. Mettes and J. Reuss (private communication).
44J. Paldus, University of Nijmegen (unpublished lecture notes).
48J. van Lenthe and F. B. van Duijneveldt (to be published).
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60A. J. Jansen, W. Briels, and A. van der Avoird (to be published).