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(Heisenberg) exchange and electrostatic interactions between O₂ molecules: An *ab initio* study

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The electrostatic and exchange interactions between two ground state ${}^3\Sigma_g^-$ O₂ 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 O₂-O₂ 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 $\overline{\Delta E}$ 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 O₂ are likely to be strong. A simple four-electron model containing the O₂ 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 O₂ 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 O₂-O₂, 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 O₂-O₂ 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 α phase, stable between 0 and 23.8 K, is the only homogeneous antiferromagnet known to date. Orientationally it is ordered also; the O₂ 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 β phase, stable between 23.8 and 43.8 K, is structurally similar to the α 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 β phase has short range antiferromagnetic order with the three-sublattice 120° spin arrangement proposed earlier.¹³⁻¹⁵ The cubic γ 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 O₂ molecules, which is commonly represented in the form of a Heisenberg Hamiltonian:

$$\hat{H}_{\text{ex}} = -2 \sum_{A < B} J_{AB} \hat{S}_A \cdot \hat{S}_B. \quad (1)$$

It is this coupling which is believed,^{8,18,22,25} for instance, to drive the so-called magnetoelastic β - α 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 -3.0 to -19.8 K for the nearest neighbors in α -O₂. 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 α -O₂^{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 O₂ 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,^{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 (O₂)₂ dimers in molecular beams,^{27,28} in the gas phase,^{29,30} and diluted in solid rare-gas³¹ or nitrogen^{3,32} matrices. For the interpretation of these data, too, it is very useful to have knowledge of the O₂-O₂ 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.³³ In the field of *ab initio* calculations, one has only looked until now at the "chemical bonding" region of O₄,³⁴ 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 O₂-O₂ potential, by means of extensive *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.

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:

$$\hat{H}_{\text{ex}} = \sum_k J_{AB}^{(k)} (\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B)^k, \quad (2)$$

where $\hat{\mathbf{S}}_A$ and $\hat{\mathbf{S}}_B$ are the monomer spin operators. This expression has been formally derived^{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) ($J_{AB}^{(1)} \equiv -2J_{AB}$).

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.³⁷ If one still wishes to account for antiferromagnetic coupling, as found between the H atoms and also between O₂ molecules, one has to invoke artificial charge transfer contributions.^{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, anti-

ferromagnetic coupling can arise naturally, if the nuclear attraction terms dominate over the two-electron exchange, as in H₂. We shall see in the results of Secs. III and IV that in O₂-O₂ both ferro- and antiferromagnetic coupling can occur, depending on the orientations of the O₂ axes which determine the overlap between the open-shell antibonding π_g orbitals.

We have chosen to calculate the rather weak exchange interactions between O₂ molecules in the van der Waals region by perturbation theory. An alternative would be a supermolecule O₄ 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,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-Schrödinger 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 O₂-O₂ 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,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,³⁹ and since it is the O₂-O₂ exchange interaction that we wish to calculate primarily, we confine ourselves, in this paper, to the first order energy, defined as

$$\Delta E^{(1)} = \frac{\langle P_S A \Psi_A^{(0)} \Psi_B^{(0)} | \hat{H} | P_S A \Psi_A^{(0)} \Psi_B^{(0)} \rangle}{\langle P_S A \Psi_A^{(0)} \Psi_B^{(0)} | P_S A \Psi_A^{(0)} \Psi_B^{(0)} \rangle} - \langle \Psi_A^{(0)} | \hat{H}_A | \Psi_A^{(0)} \rangle - \langle \Psi_B^{(0)} | \hat{H}_B | \Psi_B^{(0)} \rangle. \quad (3)$$

The (normalized) monomer $^3\Sigma_g^-$ ground state wave functions $\psi_A^{(0)}$ and $\psi_B^{(0)}$ are taken as restricted Hartree-Fock LCAO-MO functions.⁴⁰ It must be understood, of course, that for a calculation of the complete O₂-O₂ interaction potential, at least the second order (attractive) dispersion interactions have to be added (compare, for instance, the *ab initio* N₂-N₂ potential⁴¹).

For closed-shell molecules, such as N₂, the evaluation of the first order energy (3) is relatively simple, because the monomer MO's φ_μ^A and φ_ν^B occurring in $\Psi_A^{(0)}$ and $\Psi_B^{(0)}$ can be

orthogonalized, without affecting the dimer wave function $P_S A \Psi_A^{(0)} \Psi_B^{(0)}$ (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 O₂-O₂, however, the wave functions $P_S A \Psi_A^{(0)} \Psi_B^{(0)}$, except for the quintet $S = 2$ state, are not invariant under general transformations of the occupied orbitals. Let us divide the O₂ monomer orbitals into two sets: the closed-shell MO's φ_μ^A and φ_ν^B with $\mu, \nu = 1-7$, running over the occupied σ orbitals and the bonding π_u orbitals, and the open-shell MO's φ_i^A and φ_j^B with $i, j = 1-2$ running over the degenerate antibonding π_g orbitals. The electron pairs occupying the latter orbitals in each monomer are coupled to a ${}^3\Sigma_g^-$ state. Now, it is allowed to orthogonalize the closed-shell orbitals φ_μ^A and φ_ν^B among each other and to Schmidt orthogonalize the open shells φ_i^A and φ_j^B onto the closed shells, without altering the total dimer wave functions $P_S A \Psi_A^{(0)} \Psi_B^{(0)}$. The open shells φ_i^A and φ_j^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 problem⁴² in calculating the expectation value over the many-electron wave function $P_S A \Psi_A^{(0)} \Psi_B^{(0)}$. There are several ways to handle this problem, as described by Löwdin,⁴² Prosser, and Hagstrom⁴³ and by ourselves,⁴⁴ 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 $\{\varphi_i^A, \varphi_j^B; i, j = 1-2\}$ and the closed-shell or hole space $\{\varphi_\mu^A, \varphi_\nu^B; \mu, \nu = 1-7\}$. The corresponding spin orbitals, spanning the hole and particle spaces, respectively, will be denoted by $\{\psi_\alpha; \alpha = 1-28\}$ and $\{\psi_a; a = 1-8\}$. 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.^{45,46}

In the theory outlined below we base ourselves on a review by Paldus and Čížek⁴⁵ and lecture notes by Paldus.⁴⁶ 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:

$$S = \begin{pmatrix} S_h & 0 \\ 0 & S_p \end{pmatrix}, \quad (4)$$

where, in our case, the 28-dimensional hole matrix $(S_h)_{\alpha\beta} = \langle \psi_\alpha | \psi_\beta \rangle$ has the form of a unit matrix and the eight-dimensional particle matrix $(S_p)_{ab} = \langle \psi_a | \psi_b \rangle$ 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}:

$$|\psi^\alpha\rangle = \sum_\beta |\psi_\beta\rangle S^{\beta\alpha}, \quad (5a)$$

$$|\psi^a\rangle = \sum_b |\psi_b\rangle S^{ba}$$

with the overlap matrices

$$S^{\alpha\beta} = (S^{-1})_{\alpha\beta} \equiv (S_h^{-1})_{\alpha\beta}, \quad (5b)$$

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

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

$$\eta_\alpha^\dagger |0\rangle = |\psi_\alpha\rangle, \quad \eta^{\alpha\dagger} |0\rangle = |\psi^\alpha\rangle, \quad (6)$$

$$\eta_a^\dagger |0\rangle = |\psi_a\rangle, \quad \eta^{a\dagger} |0\rangle = |\psi^a\rangle.$$

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

$$[\eta_\alpha^\dagger, \eta_\beta]_+ = [\eta_\alpha, \eta_\beta^\dagger]_+ = \delta_{\alpha\beta}, \quad (7)$$

$$[\eta_a^\dagger, \eta_b]_+ = [\eta_a, \eta_b^\dagger]_+ = \delta_{ab}$$

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

$$|\Phi_0\rangle = \left(\prod_\alpha \eta_\alpha^\dagger \right) |0\rangle = (\det S_h) \left(\prod_a \eta^{a\dagger} \right) |0\rangle$$

with

$$\langle \Phi_0 | \Phi_0 \rangle = \det S_h. \quad (8)$$

Now, we invoke the normal ordering operator with respect to the Fermi vacuum.^{45,46} 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

$$\overline{\eta_\alpha^\dagger \eta^\beta} = \eta_\alpha^\dagger \eta^\beta - N(\eta_\alpha^\dagger \eta^\beta). \quad (9)$$

From similar definitions we obtain the following nonzero contractions:

$$\begin{aligned} \overline{\eta_\alpha^\dagger \eta^\beta} &= \overline{\eta^{\alpha\dagger} \eta_\beta} = \delta_{\alpha\beta}, \\ \overline{\eta_\alpha^\dagger \eta_b^\dagger} &= \overline{\eta^a \eta_b^\dagger} = \delta_{ab}, \end{aligned} \quad (10)$$

$$\begin{aligned} \overline{\eta_\alpha^\dagger \eta_\beta} &= S_{\alpha\beta}, \quad \overline{\eta^{\alpha\dagger} \eta^\beta} = S^{\alpha\beta}, \\ \overline{\eta_a^\dagger \eta_b^\dagger} &= S_{ab}, \quad \overline{\eta^a \eta^{b\dagger}} = S^{ab}. \end{aligned}$$

A general n -particle state (for the O₂-O₂ dimer $n = 4$) is given by

$$\eta_{a_1}^\dagger \eta_{a_2}^\dagger \dots \eta_{a_n}^\dagger |\Phi_0\rangle \quad (11)$$

and the dimer Hamiltonian, with one-electron terms $\hat{h}(1)$ and electron repulsion terms $\hat{v}(1,2) = r_{12}^{-1}$, reads^{47,48}

$$\hat{H} = \sum_{p,q} \langle \psi^p | \hat{h} | \psi_q \rangle \eta_p^\dagger \eta_q + \frac{1}{2} \sum_{\substack{p,q \\ r,s}} \langle \psi^p \psi^q | \hat{v} | \psi_r \psi_s \rangle \eta_p^\dagger \eta_q^\dagger \eta_s \eta_r, \quad (12)$$

where the indices p, q, r, s run over hole labels α as well as particle labels a . 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

$$\begin{aligned} E_0 &= \sum_{\alpha} \langle \psi^{\alpha} | \hat{h} | \psi_{\alpha} \rangle + \frac{1}{2} \sum_{\alpha, \beta} \langle \psi^{\alpha} \psi^{\beta} | \hat{v} (1 - \hat{P}_{12}) | \psi_{\alpha} \psi_{\beta} \rangle, \\ \hat{H}_1 &= \sum_{p,q} \langle \psi^p | \hat{f} | \psi_q \rangle N(\eta_p^\dagger \eta_q), \\ \hat{H}_2 &= \frac{1}{2} \sum_{\substack{p,q \\ r,s}} \langle \psi^p \psi^q | \hat{v} | \psi_r \psi_s \rangle N(\eta_p^\dagger \eta_q^\dagger \eta_s \eta_r), \end{aligned} \quad (13)$$

and where the closed-shell Fock operator is given by

$$\hat{f}(1) = \hat{h}(1) + \sum_{\alpha} \langle \psi^{\alpha} | \hat{v} (1 - \hat{P}_{12}) | \psi_{\alpha} \rangle_2. \quad (14)$$

Then, we write the matrix elements over the states (11), employ the generalized Wick theorem again, and note that, as always,^{45,46} only the fully contracted terms survive in the Fermi vacuum expectation value. This yields the following results:

$$\langle \Phi_0 | \eta_{b_n} \dots \eta_{b_1} \eta_{a_1}^\dagger \dots \eta_{a_n}^\dagger | \Phi_0 \rangle = (\det \mathbf{S}_h) (\det \mathbf{\Delta}), \quad (15a)$$

$$\begin{aligned} \langle \Phi_0 | \eta_{b_n} \dots \eta_{b_1} \hat{H}_1 \eta_{a_1}^\dagger \dots \eta_{a_n}^\dagger | \Phi_0 \rangle \\ = (\det \mathbf{S}_h) \sum_{i,j} \langle \psi_{b_j} | \hat{f} | \psi_{a_i} \rangle (\text{cofac} \mathbf{\Delta})_{b_j a_i}, \end{aligned} \quad (15b)$$

$$\begin{aligned} \langle \Phi_0 | \eta_{b_n} \dots \eta_{b_1} \hat{H}_2 \eta_{a_1}^\dagger \dots \eta_{a_n}^\dagger | \Phi_0 \rangle \\ = (\det \mathbf{S}_h) \sum_{i < j} \sum_{k < l} \langle \psi_{b_i} \psi_{b_j} | \hat{v} (1 - \hat{P}_{12}) | \psi_{a_k} \psi_{a_l} \rangle (\text{cofac} \mathbf{\Delta})_{b_i a_k b_j a_l}. \end{aligned} \quad (15c)$$

The overlap matrix $\mathbf{\Delta}$ is an $n \times n$ submatrix of the matrix \mathbf{S}_p :

$$\langle \Phi_0 | \eta_{v_2} \eta_{v_1} \eta_{u_2} \eta_{u_1} \eta_{x_1}^\dagger \eta_{x_2}^\dagger \eta_{y_1}^\dagger \eta_{y_2}^\dagger | \Phi_0 \rangle = (\det \mathbf{\Delta}_1) (\det \mathbf{\Delta}_2) \quad (18a)$$

and

$$\begin{aligned} \langle \Phi_0 | \eta_{v_2} \eta_{v_1} \eta_{u_2} \eta_{u_1} \hat{H} \eta_{x_1}^\dagger \eta_{x_2}^\dagger \eta_{y_1}^\dagger \eta_{y_2}^\dagger | \Phi_0 \rangle = E_0 (\det \mathbf{\Delta}_1) (\det \mathbf{\Delta}_2) \\ + (\det \mathbf{\Delta}_2) \left[\sum_{i,j=1}^2 \langle \varphi_{u_i} | \hat{f} | \varphi_{x_j} \rangle \langle \varphi_{u_3-i} | \varphi_{x_3-j} \rangle (-1)^{i+j} + \langle \varphi_{u_1} \varphi_{u_2} | \hat{v} (1 - \hat{P}_{12}) | \varphi_{x_1} \varphi_{x_2} \rangle \right] \\ + (\det \mathbf{\Delta}_1) \left[\sum_{i,j=1}^2 \langle \varphi_{v_i} | \hat{f} | \varphi_{y_j} \rangle \langle \varphi_{v_3-i} | \varphi_{y_3-j} \rangle (-1)^{i+j} + \langle \varphi_{v_1} \varphi_{v_2} | \hat{v} (1 - \hat{P}_{12}) | \varphi_{y_1} \varphi_{y_2} \rangle \right] \\ + \sum_{i,j=1}^2 \sum_{k,l=1}^2 \langle \varphi_{u_i} \varphi_{v_k} | \hat{v} | \varphi_{x_j} \varphi_{y_l} \rangle \langle \varphi_{u_3-i} | \varphi_{x_3-j} \rangle \langle \varphi_{v_3-k} | \varphi_{y_3-l} \rangle (-1)^{i+j+k+l}, \end{aligned} \quad (18b)$$

$$\Delta_{ji} = \langle \psi_{b_j} | \psi_{a_i} \rangle \quad i, j = 1, \dots, n, \quad (16)$$

(cofac $\mathbf{\Delta}$) _{$b_j a_i$} is the cofactor of Δ_{ji} in $(\det \mathbf{\Delta})$, and

(cofac $\mathbf{\Delta}$) _{$b_i a_k b_j a_l$} is the cofactor of Δ_{ik} and Δ_{jl} in $(\det \mathbf{\Delta})$.

Although the matrix elements (15) have the same appearance as Löwdin's formulas,⁴² they differ in the important fact that our formulas include the effect of an indefinitely large set of closed shells. In the present case of $n = 4$, the cofactors occurring in these formulas can easily be calculated by the Laplace formula. If the number of particles outside the Fermi sea is large, however, the route via the singular-value decomposition of $\mathbf{\Delta}$ ⁴³ is to be preferred.

For the O₂-O₂ dimer the states (11) with $n = 4$ are Slater determinants $A\psi_A^{(0)}\psi_B^{(0)}$ which are not yet spin projected. In order to get those eigenfunctions of \hat{S}^2 with $S = 0, 1$, and 2 which can be constructed from the monomer triplet ground states $S_A = 1$ and $S_B = 1$, we can take the six determinants with $M_S = 0$ and make linear combinations by the usual vector coupling rules:

$$\begin{pmatrix} |S=2\rangle \\ |S=1\rangle \\ |S=0\rangle \end{pmatrix} = \begin{pmatrix} 1 & -1 & -1 & -1 & -1 & 1 \\ 1 & 0 & 0 & 0 & 0 & -1 \\ 1 & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & 1 \end{pmatrix} \times \begin{pmatrix} \eta_{a_1}^\dagger \eta_{a_2}^\dagger \eta_{b_1}^\dagger \eta_{b_2}^\dagger | \Phi_0 \rangle \\ \eta_{a_1}^\dagger \eta_{b_2}^\dagger \eta_{b_1}^\dagger \eta_{a_2}^\dagger | \Phi_0 \rangle \\ \eta_{b_2}^\dagger \eta_{a_2}^\dagger \eta_{b_1}^\dagger \eta_{a_1}^\dagger | \Phi_0 \rangle \\ \eta_{a_1}^\dagger \eta_{b_1}^\dagger \eta_{a_2}^\dagger \eta_{b_2}^\dagger | \Phi_0 \rangle \\ \eta_{b_1}^\dagger \eta_{a_2}^\dagger \eta_{a_1}^\dagger \eta_{b_2}^\dagger | \Phi_0 \rangle \\ \eta_{b_1}^\dagger \eta_{b_2}^\dagger \eta_{a_1}^\dagger \eta_{a_2}^\dagger | \Phi_0 \rangle \end{pmatrix} \quad (17)$$

Three other linear combinations of these determinants correspond with the excited ¹ Δ_g states of one or both O₂ monomers. Those will not be considered in the present paper. The indices a_i and b_j label the open-shell π_g orbitals or monomers A and B, respectively; the superscripts \pm correspond with $m_s = \pm \frac{1}{2}$. These labels can be simply substituted into the general formulas (15) for the matrix elements and the integrals over the spinfunctions can be carried out. The four-dimensional overlap matrix $\mathbf{\Delta}$ is always 2×2 block diagonal, due to the orthogonality between the spin functions. Similar simplifications occur in the other integrals because the Hamiltonian \hat{H} is spin independent. The final result, in terms of spatial integrals only, is

with the matrices Δ_1 and Δ_2 given by

$$(\Delta_1)_{ij} = \langle \varphi_{u_i} | \varphi_{x_j} \rangle, \quad (19)$$

$$(\Delta_2)_{ij} = \langle \varphi_{v_i} | \varphi_{y_j} \rangle,$$

and the label combinations x_1, x_2, y_1, y_2 and u_1, u_2, v_1, v_2 running over the six determinants in Eq. (17). The effect of the closed shells is simply incorporated in terms of the closed shell energy

$$E_0 = 2 \sum_{\alpha=1}^{14} \langle \varphi_{\alpha} | \hat{h} | \varphi_{\alpha} \rangle + \sum_{\alpha, \beta}^{14} \langle \varphi_{\alpha} \varphi_{\beta} | \hat{v}(2 - \hat{P}_{12}) | \varphi_{\alpha} \varphi_{\beta} \rangle \quad (20)$$

and the closed-shell Fock operator

$$\hat{f}(1) = \hat{h}(1) + \sum_{\alpha=1}^{14} \langle \varphi_{\alpha}(2) | \hat{v}(1,2)(2 - \hat{P}_{12}) | \varphi_{\alpha}(2) \rangle, \quad (21)$$

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 O₂–O₂ 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 π_g orbitals on each monomer, which can be further approximated as simple antibonding combinations of the atomic $2p_{\pi_x}$ and $2p_{\pi_y}$ 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,^{1,8,20} which are even simpler and, therefore, more approximate.

III. COMPUTATIONAL ASPECTS AND RESULTS

As the weak exchange interactions between O₂ molecules are very sensitive to the tails of the monomer orbitals, we have calculated the restricted Hartree–Fock MO wave function⁴⁰ for the ${}^3\Sigma_g^-$ ground state of the O₂ 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.*,^{49,50} but with still another diffuse *s* 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 O₂ monomer are listed in Table I, the first order O₂–O₂ 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 $2p_x$ and $2p_y$ orbitals on each oxygen atom, of single-zeta Slater type ($\zeta = 2.2266a_0^{-1}$ ⁵⁴), each represented by a contracted set of 6 GTO's.⁵⁵

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 ATMOL package.⁵⁶ 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 O₂–O₂ 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

$$\overline{\Delta E} = [\Delta E^{(1)}(S=0) + 3\Delta E^{(1)}(S=1) + 5\Delta E^{(1)}(S=2)]/9 \quad (22)$$

and the (average) Heisenberg parameter

$$J = [\Delta E^{(1)}(S=0) - \Delta E^{(1)}(S=1)]/4 + [\Delta E^{(1)}(S=1) - \Delta E^{(1)}(S=2)]/8. \quad (23)$$

The internal coordinates describing the O₂–O₂ potential surface are R , the distance between the molecular centers of mass, θ_A , θ_B and $\varphi = \varphi_B - \varphi_A$, where (θ_A, φ_A) and (θ_B, φ_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 expansion³⁸

$$F(R, \Omega, \omega_A, \omega_B) = (4\pi)^{3/2} \sum_{L_A, L_B, L} f_{L_A, L_B, L}(R) A_{L_A, L_B, L}(\Omega, \omega_A, \omega_B) \quad (24)$$

with angular functions

TABLE I. ${}^3\Sigma_g^-$ ground state O₂ properties calculated from restricted Hartree–Fock LCAO wave functions.

Basis:	(11s, 6p, 2d) [6s, 3p, 2d]	(13s, 7p, 2d) [8s, 4p, 2d]	(13s, 7p, 2d) uncontracted	Literature
Energy (hartree)	– 149.6447	– 149.6540	– 149.6556	– 149.6659 ^a
Multipole moments				
$Q_2(ea_0^2)$	– 0.2644	– 0.2636	– 0.2609	$\left\{ \begin{array}{l} -0.29^b \\ \pm 0.25^b \end{array} \right.$
$Q_4(ea_0^4)$	4.095	3.990	4.034	
$Q_6(ea_0^6)$	16.26	18.00	18.12	

^a Estimated Hartree–Fock limit (Ref. 51).

^b Experimental values (Refs. 52 and 53).

TABLE II. O₂-O₂ exchange repulsion $\overline{\Delta E}$ and Heisenberg parameter J with different basis sets at $R = 6a_0$.

Geometry	$\theta_A, \theta_B, \varphi$	$\overline{\Delta E}$ (K)		J (K)	
		[6s, 3p, 2d]	[8s, 4p, 2d]	[6s, 3p, 2d]	[8s, 4p, 2d]
L	0°, 0°, 0°	12 137	12 303	- 121	- 124
T	90°, 0°, 0°	1 601	1 642	- 23.7	- 23.7
H	90°, 90°, 0°	311.8	322.5	- 14.1	- 14.5
X	90°, 90°, 90°	249.1	259.1	+ 2.73	+ 3.42
S	26.5°, 26.5°, 0°	6 460	6 556	- 8.30	- 7.89

$$A_{L_A, L_B, L}(\Omega, \omega_A, \omega_B) = \sum_{M_A, M_B, M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} \times Y_{L_A, M_A}(\omega_A) Y_{L_B, M_B}(\omega_B) Y_{L, M}(\Omega). \quad (25)$$

The functions $Y_{L, M}(\omega)$ are spherical harmonics and the first factor in Eq. (25) is a 3- j coefficient.⁵⁷ The angular functions A and the potential F , for which we can substitute $\overline{\Delta E}$ as well as J , depend on the polar angles of \mathbf{R} and the molecular axes denoted by Ω, ω_A and ω_B , respectively. We can always use the special body-fixed frame with $\Omega = (0, 0)$, $\omega_A = (\theta_A, 0)$, and $\omega_B = (\theta_B, \varphi_B)$, 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

$$f_{L_A, L_B, L}(R) = \pi^{1/2} \int_{\theta_A=0}^{\pi} \int_{\theta_B=0}^{\pi} \int_{\varphi=0}^{2\pi} A_{L_A, L_B, L}(\theta_A, \theta_B, \varphi) \times F(R, \theta_A, \theta_B, \varphi) d(\cos \theta_A) d(\cos \theta_B) d\varphi. \quad (26)$$

Just as in previous work,⁴¹ we have employed the following procedure. The potential F , in this case $\overline{\Delta E}$ and J , has been calculated for a grid of angular points $(\theta_A, \theta_B, \varphi)$ at each distance R . This grid was chosen such that the integration (26) can be carried out numerically. For $\cos \theta_A$ and $\cos \theta_B$ we have chosen the points and weights of Gauss-Legendre quadrature and for φ Gauss-Chebyshev quadrature.⁵⁸ The number of quadrature points that have to be included depends on the maximum values of L_A, L_B , and L .

TABLE III. Comparison of the analytic representations of $\overline{\Delta E}$ and J with *ab initio* data calculated independently.

Geometry			R (a_0)	$\overline{\Delta E}_{ab\;initio}$ (K)	$\overline{\Delta E}_{anal}^a$ (K)	Dev. (%)	$J_{ab\;initio}$ (K)	J_{anal}^a (K)	Dev. (%)
θ_A	θ_B	φ (deg)							
0	0	0	4	891 336	867 695	2.6	− 9877	− 9757	1.2
			5	105 857	105 540	0.3	− 1122	− 1079	3.8
			6	12 137	12 123	0.1	− 121	− 118	2.2
			7	1 324.7	1 324.3	0.0	− 13.2	− 13.0	1.6
			8	139.00	139.84	0.6	− 1.44	− 1.57	9.0
90	0	0	4	95 858	89 670	6.5	− 1467	− 1300	11
			5	12 833	12 808	0.2	− 192	− 191	0.8
			6	1 600.8	1 599.9	0.1	− 23.7	− 23.6	0.4
			7	186.54	186.42	0.1	− 2.85	− 2.84	0.4
			8	19.80	20.53	3.7	− 0.33	− 0.43	30
90	90	0	4	18 353	16 826	8.3	− 772	− 762	1.3
			5	2 416.1	2 393.2	0.9	− 107	− 104	3.0
			6	311.82	311.63	0.1	− 14.1	− 14.0	1.1
			7	41.62	41.69	0.2	− 1.76	− 1.75	0.6
			8	7.02	7.29	3.8	− 0.20	− 0.23	11
90	90	90	4	13 717	12 869	6.2	+ 70.7	+ 17.3	75
			5	1 914.0	1 945.7	1.7	+ 16.5	+ 15.1	8.5
			6	249.13	250.75	0.7	+ 2.73	+ 2.60	4.8
			7	30.81	30.78	0.1	+ 0.37	+ 0.36	1.6
			8	3.96	4.13	4.3	+ 0.04	+ 0.01	71
26.5	26.5	0	4	328 975	338 241	2.8	− 3757	− 2926	22
			5	48 813	48 826	0.0	− 230	− 221	4.1
			6	6 459.9	6 460.4	0.0	− 8.30	− 7.70	7.2
			7	789.42	789.20	0.0	+ 1.52	+ 1.58	3.4
			8	91.28	90.27	1.1	+ 0.49	+ 0.47	4.9
100	80	0	6	415.40	414.69	0.2	− 14.5	− 14.1	2.8

^a Analytic representation by Eqs. (24) and (27)–(29), with the coefficients from Table IV.

TABLE IV. Expansion coefficients.

A. Expansion coefficients^a of ΔE , defined by Eqs. (24), (27), and (29); multipole interactions are given by Eq. (28).

L_A	L_B	L^b	$g_0(K)$	α	β	γ
0	0	0	1592.83	12.527	1.083	...
2	0	2	975.55	12.696	1.081	...
2	2	0	164.96	12.170	2.185	...
2	2	2	-252.29	12.497	1.731	...
2	2	4	597.69	13.234	0.793	...
4	0	4	92.42	15.316	4.712	...
4	2	2	17.97	13.466	5.314	...
4	2	4	-27.60	14.482	4.522	...
4	2	6	78.15	15.875	3.580	...
4	4	0	0.844	11.980	6.708	...
4	4	2	-1.193	12.704	6.060	...
4	4	4	1.960	14.126	5.552	...
4	4	6	-4.264	16.157	5.896	...
4	4	8	15.84	17.962	4.934	...
6	0	6	1.363	13.032	...	-28.159
6	2	4	1.005	17.441	18.233	...
6	2	6	-1.349	12.488	...	-7.139
6	2	8	1.880	14.204	...	-20.401
6	4	10	0.918	16.403	...	-8.679
6	6	12	0.173	20.358	-6.999	...
8	0	8	-0.315	13.578	...	13.101
8	2	10	-0.545	14.758	...	10.188

B. Expansion coefficients^c of J , defined by Eqs. (24) and (29).

L_A	L_B	L^d	$g_0(K)$	α	β	γ
0	0	0	-4.429 6	11.876	...	-7.702
2	0	2	-4.425 2	14.908	2.847	...
2	2	0	-1.306 8	12.674	0.669	...
2	2	2	0.629 2	14.487	-0.340	...
2	2	4	-3.245 0	13.884	-0.662	...
4	0	4	0.898 1	6.545	15.248	...
4	2	2	0.376 3	8.494	2.215	...
4	2	4	0.066 2	11.217	...	-32.713
4	2	6	2.379 3	10.644	1.199	...
4	4	0	-0.099 9	6.061	-0.632	...
4	4	2	0.043 6	9.986	...	24.588
4	4	4	-0.180 2	10.009	...	8.199
4	4	6	0.717 7	11.764	...	7.207
4	4	8	-8.689 1	11.161	0.838	...
6	0	6	0.403 5	10.655	2.013	...
6	2	4	0.049 1	9.963	-3.250	...
6	2	6	-0.015 9	11.578	...	23.155
6	2	8	0.771 4	12.356	-1.926	...
6	4	4	-0.008 61	9.443	...	-11.254
6	4	6	0.013 3	10.816	...	-23.285
6	4	8	0.110 8	12.689	...	11.907
6	4	10	-2.800 9	12.198	-0.165	...
6	6	0	0.036 7	14.620	0.405	...
6	6	2	0.065 5	14.701	0.087	...
6	6	4	0.058 3	14.835	0.348	...
6	6	6	0.027 0	15.156	-4.066	...
6	6	8	0.022 7	19.269	21.686	...
6	6	10	0.022 3	13.570	...	19.605
6	6	12	-1.256 9	13.675	-1.800	...
8	0	8	0.047 3	12.057	-2.379	...
8	2	10	0.110 2	13.905	-4.428	...
8	4	10	0.002 36	13.696	...	72.913
8	4	12	-0.439 4	13.321	-1.011	...
8	6	2	0.009 30	15.679	-3.791	...
8	6	4	0.022 9	14.669	1.554	...
8	6	6	0.032 8	15.213	-0.916	...
8	6	8	0.022 4	15.422	-0.911	...
8	6	10	0.012 7	15.834	2.592	...
8	6	12	0.000 84	13.905	...	81.246
8	6	14	-0.260 8	15.120	-3.747	...

^a Terms in the spherical expansion which are less than 1/2000 of the dominant (0, 0, 0) term have been omitted.For $R > 15a_0$ the term with $\beta < 0$ should be put equal to zero.^b The coefficients are symmetric with respect to interchange of L_A and L_B .^c Terms in the spherical expansion which are less than 1/1000 of the dominant term have been omitted. For $R > 15a_0$ the terms with $\beta < 0$ should be put equal to zero.^d 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 experimentation 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 $0 \leq \theta_A \leq \pi/2$, $0 \leq \theta_B \leq \pi/2$, $0 \leq \varphi \leq \pi$ is sufficient to calculate the coefficients $f_{L_A, L_B, L}(R)$ up to $L_A = 8$, $L_B = 8$, and $L = 14$, inclusive. This interval has been reduced by using the symmetry present in the O₂-O₂ dimer; further use of this symmetry leads to 75 "irreducible" points. Truncation of the expansion after the $(L_A, L_B, L) = (8, 8, 14)$ 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 $\overline{\Delta E}$ 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 $\overline{\Delta E}$ and about 1% for J (root mean square deviation for all grid points). Moreover, we have computed $\overline{\Delta E}$ 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 $\overline{\Delta E}$ contains also the electrostatic multipole-multipole interactions, however, which decrease as R^{-n} . These multipole-multipole interactions only contribute³⁸ to the spherical expansion coefficients with $L = L_A + L_B$. So, the expansion coefficients of $\overline{\Delta E}$ are finally represented as functions of R by

$$f_{L_A, L_B, L}(R) = \delta_{L_A + L_B, L} C_{L_A, L_B} R^{-L_A - L_B - 1} + f_{L_A, L_B, L}^{\text{ex}}(R), \quad (27)$$

where the electrostatic coefficients are given by

$$C_{L_A, L_B} = (-1)^{L_A} \left[\frac{(2L_A + 2L_B)!}{(2L_A + 1)!(2L_B + 1)!} \right]^{1/2} Q_{L_A} Q_{L_B} \quad (28)$$

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

The exchange contributions $f_{L_A, L_B, L}^{\text{ex}}(R)$ are given, as functions of the reduced distance $x = (R - R_0)/R_0$, as

$$\begin{aligned} f_{L_A, L_B, L}^{\text{ex}}(R) &= g_{L_A, L_B, L}(x) \\ &= g_0^{L_A, L_B, L} (1 + \gamma^{L_A, L_B, L} x) \\ &\quad \times \exp(-\alpha^{L_A, L_B, L} x - \beta^{L_A, L_B, L} x^2). \end{aligned} \quad (29)$$

For R_0 we take the nearest neighbor distance in solid α -O₂ (3.200 Å). The expansion coefficients of J are purely exponential and also given by the form (29). For those coefficients $f_{L_A, L_B, L}^{\text{ex}}(R)$ 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, α, γ) or (g_0, α, β) , respectively, can be exactly obtained from the calculated values of $f^{\text{ex}}(R)$ at $R = 5, 6$, and $7a_0$. The final expansion parameters $g_0^{L_A, L_B, L}$, $\alpha^{L_A, L_B, L}$, $\beta^{L_A, L_B, L}$, and $\gamma^{L_A, L_B, L}$, which completely determine the surfaces $\overline{\Delta E}(R, \Omega, \omega_A, \omega_B)$ 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 $\Delta E^{(1)}$ surfaces for the three spin states $S = 0, 1$, and 2 of the O₂-O₂ dimer, can be accurately represented by the Heisenberg Hamiltonian (1). That is, the triplet-quintet splitting ($\cong 4$ J) is twice the singlet-triplet splitting ($\cong 2$ J). This implies that multiple exchange interactions are negligible. Only for distances R which are considerably smaller than the nearest neighbor distance in solid α -O₂ ($R_0 = 3.2$ Å), we observe deviations from this rule, but then the O₂-O₂ exchange repulsion itself is already of the same size as the ${}^1\Delta_g$ - ${}^3\Sigma_g^-$ splitting in the O₂ 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 $\overline{\Delta E}$ and J , but where one should realize that our first order model (3) does not hold anymore.

The structure dependence of $\overline{\Delta E}$ 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 $\overline{\Delta E}$ 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 $\overline{\Delta E}$ 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 $\overline{\Delta E}$ between the O₂ 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" $\overline{\Delta E}$ 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 N₂-N₂ repulsion.⁴¹ 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 O₂ quadrupole moment is about four times smaller than the N₂ 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 $R \geq 5.5a_0$. In Fig. 1 we observe, for instance, that J changes sign four times for a simple parallel rotation of two O₂ molecules from the linear config-

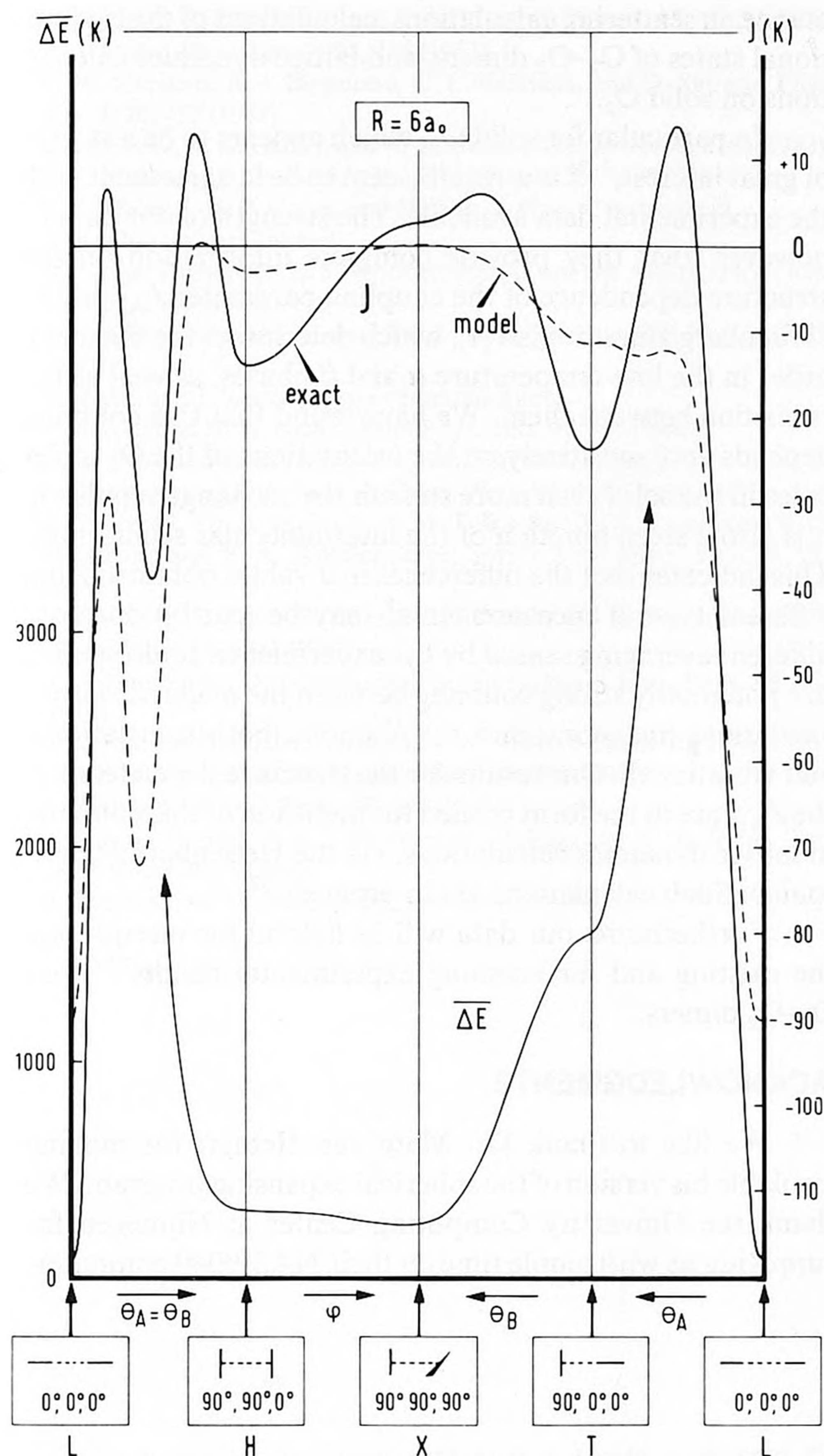


FIG. 1. Orientational dependence of $\overline{\Delta E}$ and J . The full lines represent the results of the all-electron calculations, the dashed line refers to the four-electron model described in the text. The multipole contributions to $\overline{\Delta E}$ are not drawn explicitly because they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

uration ($\theta_A = \theta_B = 0^\circ$) to the H structure ($\theta_A = \theta_B = 90^\circ$, $\varphi = 0^\circ$). Most sign changes qualitatively follow the (4,4,8) term. They can be understood by considering the nodal character of the open-shell antibonding π_g orbitals on the O₂ monomers, and remembering that (see Sec. II) for zero overlap between the monomer orbitals, J has to be positive (Hund's rule), while for "normal" overlap (i.e., overlap which is not specifically small because of near cancellation between positive and negative lobes of the wave functions) J is negative. A typical example of almost zero overlap, due to symmetry, is the crossed (X) structure ($\theta_A = \theta_B = \varphi = 90^\circ$).

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,¹ we find that the coupling between O₂-O₂ pairs in the parallel (H) geometry, as they occur in the layers of α and β O₂ crystals, but also in O₂ layers adsorbed on graphite,^{12,59-62} is antiferromagnetic. The strongest, intersublattice, coupling J_2 occurs between the nearest neighbors ($R_0 = 3.200 \text{ \AA}$) in α -O₂. It is not possible, however, to make a direct comparison between our value of J_2 calculated at $R = 3.200 \text{ \AA}$, $J_2 = -12.5 \text{ K}$, 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 oscillators²⁶ that the averaging of $J_2(R)$ over the translational phonons can effectively increase J_2 by a factor of 2.5 ($\langle J_2 \rangle \cong -30 \text{ K}$), which brings it in the range of recent experimental data: $J_2 = -25,^{16,17,21} -38 \text{ K}.$ ¹⁹ 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 α -O₂.

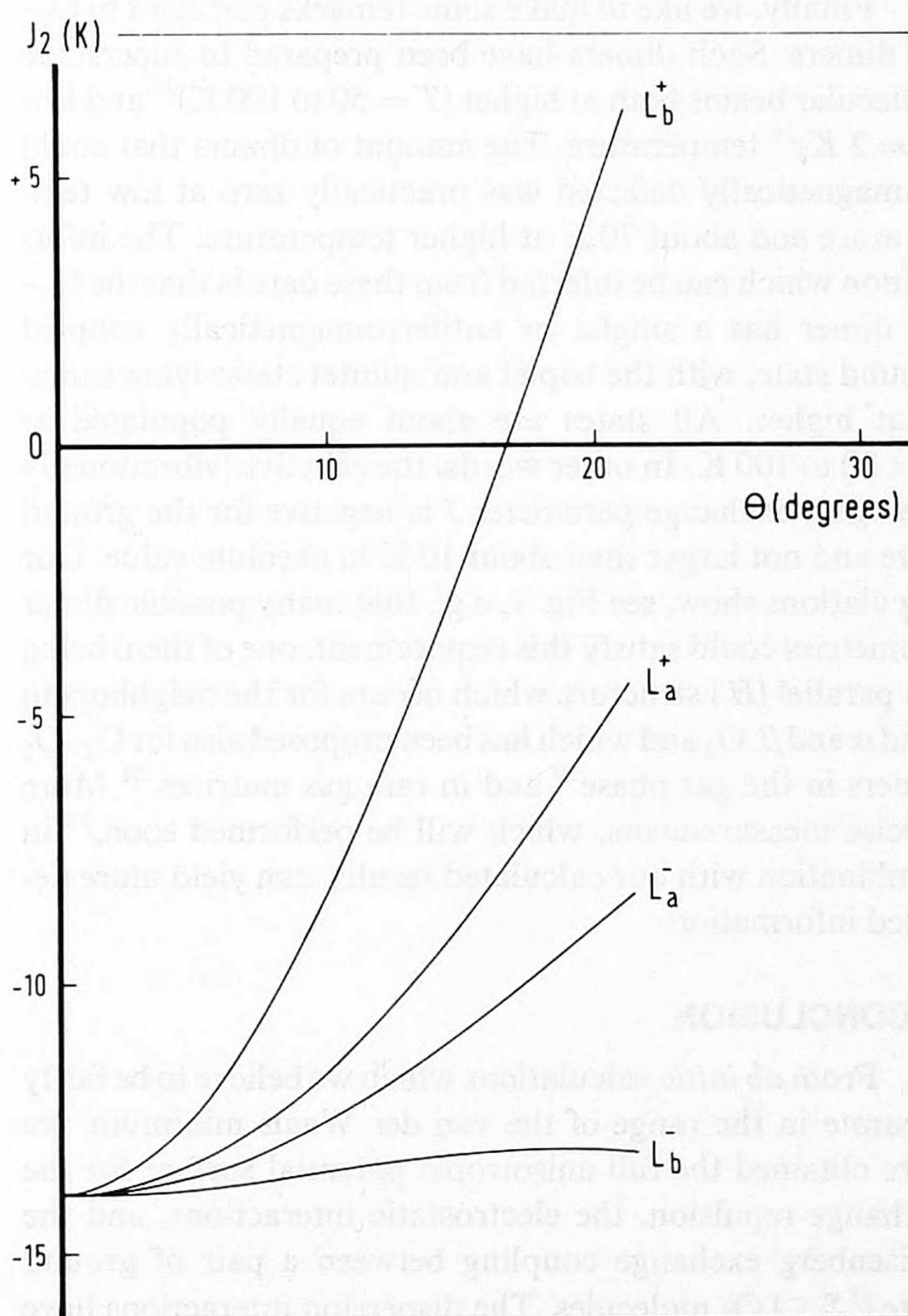


FIG. 2. Variation of the (intersublattice) exchange coupling parameter J_2 between the nearest neighbors in solid α -O₂ along some normal coordinates of libration. The labels a and b refer to librations around the crystal a and b axes, respectively, (Ref. 1); the + and - signs denote in-phase and out-of-phase librations of the molecules on different sublattices.

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 $15 R_0^{-1}$ (3.4 and 4.7 \AA^{-1}) for the leading terms in the spherical expansion. This agrees well with the exponential (exponent $\cong 4.3 \text{ \AA}^{-1}$, Ref. 22) and R^{-n} laws ($n = 10$, Ref. 21, $n = 12$ to 15 ,^{17,18} $n = 14$ ¹⁹) obtained from pressure and temperature dependent measurements on α , β , and γ O₂. Also the ratio J_1/J_2 between the intrasublattice ($R = 3.429 \text{ \AA}$) and intersublattice ($R = 3.200 \text{ \AA}$) coupling in α -O₂, which we calculate ($\theta_A = \theta_B = 90^\circ$, $\varphi = 0^\circ$): $J_1/J_2 = 0.42$, is in good agreement with experiment: $J_1/J_2 = 0.41$ to 0.43 ,^{16,17} 0.5 ± 0.1 .²¹

From the preliminary calculations²⁶ we have found that the coupling between the nearest O₂ pairs ($R = 4.186 \text{ \AA}$) in adjacent layers of α -O₂ is very weak, but ferromagnetic ($J_3 > 0$). The latter result, which was obtained by keeping the O₂ molecules in a shifted-parallel (S) geometry ($\theta_A = \theta_B = 26.5^\circ$, $\varphi = 0$) at $R = 4.186 \text{ \AA}$, is contrary to experiment. In Fig. 1 we observe, however, that the (small) positive value of J_3 just occurs in a narrow ($\pm 4^\circ$) range of θ_A and θ_B angles around 20° ; also at smaller distance ($R = 3.175 \text{ \AA}$) J_3 for $\theta_A = \theta_B = 26.5^\circ$ is negative again (see Table III). So it is clear that the angular and distance averaging of J_3 may easily change its sign. It will still remain small, though, as found from recent experiments.^{16,17,21}

Finally, we like to make some remarks pertinent to O₂-O₂ dimers. Such dimers have been prepared in supersonic molecular beams both at higher ($T = 50$ to 100 K)²⁷ and low ($T = 2 \text{ K}$)²⁸ temperature. The amount of dimers that could be magnetically deflected was practically zero at low temperature and about 70% at higher temperature. The information which can be inferred from these data is that the O₂-O₂ 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 $T = 50$ to 100 K . In other words, the effective (vibrationally averaged) exchange parameter J is negative for the ground state and not larger than about 10 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) structure which occurs for the neighbors in solid α and β O₂ and which has been proposed also for O₂-O₂ dimers in the gas phase²⁹ and in rare gas matrices.³¹ More precise measurements, which will be performed soon,²⁸ in combination with our calculated results, can yield more detailed information.

V. CONCLUSION

From *ab 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 ($^3\Sigma_g^-$) O₂ molecules. The dispersion interactions have still to be added in order to construct a complete O₂-O₂ 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 in-

stance, in scattering calculations, calculations of the rovibrational states of O₂-O₂ dimers, and lattice dynamics calculations on solid O₂.

In particular for solid O₂, which appears to be a system of great interest,¹⁻²⁵ 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} in the Heisenberg Hamiltonian (1), which determines the magnetic order in the low-temperature α and β phases, as well as the transition between them. We have found that this coupling depends very sensitively on the orientations of the O₂ 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 values obtained from different type of measurements¹ 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} are in the form needed for inclusion of this coupling in lattice dynamics calculations, via the Heisenberg Hamiltonian. Such calculations are in progress.⁶²

Furthermore, our data will be helpful for interpreting the existing and forthcoming experimental results²⁷⁻³¹ on O₂-O₂ dimers.

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