Ab Initio Calculation of the Heisenberg Exchange Interaction between O_2 Molecules

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The exchange interaction between $^3\Sigma_g^-$ O_2 molecules, as obtained from *ab initio* calculations for a singlet, triplet, and quintet dimer, can be well represented by the Heisenberg Hamiltonian. The coupling parameter J depends exponentially on the O_2-O_2 distance, with exponents ranging from 3.6 to 4.2 Å^{-1} for different O_2 orientations. For most orientations the coupling is antiferromagnetic, but for a few J is positive. The different neighbor interactions in α and β O_2 solids, which determine their magnetic order and properties, have been evaluated.

The open-shell (triplet) character of the ground state of the O_2 molecule makes solid O_2 one of the most interesting molecular crystals. Three different phases occur at zero pressure: the α phase which is orientationally as well as magnetically ordered, the β phase which is also orientationally ordered and, possibly, has short-range antiferromagnetic order, and the γ phase which is orientationally disordered and paramagnetic (just as liquid O_2). The (monoclinic) α phase of solid O_2 is the only homogeneous system known which is antiferromagnetically coupled; the molecules are arranged in layers with their axes parallel to each other and perpendicular to the layer (a-b) planes (see Fig. 2 of Ref. 1). The magnetic structure of the (rhombohedral) β phase is still not well established, despite a continuing experimental and theoretical interest over the last twenty years. Recently, some evidence has been obtained for a three-sublattice 120° spin configuration.[2,3] A number of other interesting questions regarding the role of magnetic coupling on the stability of different phases and the interaction between magnons and lattice vibrations (phonons, librons) have not yet been answered either (see recent reviews[1,3,4]).

The main difficulty in interpreting the various experimental data (magnetic, optical) is the lack of knowledge about the exchange interaction between O_2 molecules, which is actually the leading magnetic coupling term. This interaction is usually represented by the Heisenberg Hamiltonian,

$$\hat{H} = -2\sum_{i<j} J_{ij}\hat{S}_i \cdot \hat{S}_j , \qquad (1)$$

but, in spite of semiempirical calculations,[1,5,6]

the dependence of the coupling parameter J_{ij} on the distance between the molecules and their orientations is not known.[1,3,4] The experimental nearest-neighbor values of J_{ij} in α-O_2 range from 3 to 38 K.[1,7]

Several authors[6,8] recognize that the desired information on the exchange interaction between O_2 molecules can, in principle, be obtained from *ab initio* calculations, but they expect these to be very difficult. Here, we report the results of such calculations, however. First, we have calculated the all-electron wave function for an O_2 molecule in its ground state $^3\Sigma_g^-$ by means of the molecular orbital–linear combination of atomic orbitals restricted Hartree-Fock method,[9] using the ATMOL program.[10] In order to evaluate accurately the exchange interaction between O_2 molecules at Van der Waals distances, where only the tails of the monomer molecular orbitals overlap, one needs a rather extensive basis with relatively many diffuse orbitals. Hence, we have used the $11s,6p,2d$ Gaussian-type atomic-orbital basis (contracted to $6s,3p,2d$) which has been designed for calculations on the O_2-He interaction[11] and tested by evaluating several molecular properties.[12] The ground-state energy of O_2 is $-149.$-644691 hartrees at $r_e = 1.208$ Å (estimated[13] Hartree-Fock limit, -149.6659 hartrees) and the quadrupole moment is -0.264 a.u. (experimental, -0.29,[14] ± 0.25[15]).

The (weak) exchange interaction between two O_2 molecules cannot be obtained from a so-called supermolecule (in this case O_4) Hartree-Fock calculation,[16] because of the incorrect asymptotic behavior of the supermolecule wave functions for large O_2-O_2 distance (except for the quintet, $S=2$,

state of O_4). Instead, we have applied a second-quantized hole-particle formalism which starts from the antisymmetrized product of the two monomer $^3\Sigma_g^-$ wave functions, which is then spin projected, so as to represent the three possible spin states, $S=0$, 1 and 2, of the O_2-O_2 dimer. The interaction energy for each of these states is obtained by taking the expectation values of the full dimer Hamiltonian over these wave functions and subtracting the O_2 monomer energies. For this purpose, we have employed a generalization of Wick's theorem to nonorthogonal orbitals.[17] Taking into account the full nonorthogonality between the monomer molecular orbitals is essential for describing correctly the antiferro or ferromagnetic coupling (see below). The interaction energy thus obtained comprises the electrostatic interactions between the (unpolarized) O_2 charge distributions, as well as the exchange interactions between all O_2 electrons, i.e., the closed shell σ and bonding π electrons and the open-shell antibonding $2p\,\pi_g$ electrons. It is the exchange between the open shells (with the electron pair on each O_2 monomer coupled to a $^3\Sigma_g^-$ state) that leads to the splitting of the dimer spin states, while the remaining exchange terms are always repulsive. The calculations have been performed for various distances R between the O_2 monomers and various orientations of their axes, see Table I. For each dimer geometry they took 7 min of central processor time on a CRAY-1S computer.

For all dimer geometries considered the exchange coupling between the monomer triplets can be very well fitted to the form of the Heisenberg Hamiltonian (1), i.e., the quintet-triplet splitting is exactly twice the triplet-singlet splitting (see Table I). This implies that multiple-exchange interactions between O_2 monomers are negligible.[18] Thus, we have obtained the value of the exchange-coupling constant J for various orientations of the O_2 axes as a function of the O_2-O_2 distance R. The R dependence is nearly exponential, $J=J_0\exp[-\alpha(R-R_0)]$, with the exponent α varying from 4.2 Å^{-1} for the linear (L) geometry to 3.6 Å^{-1} for the crossed (X) structure (see Table I). It is remarkable that this R dependence for different orientations is very similar to the R dependence of the total repulsion.

The most striking result is, however, that the sign of the coupling-constant J changes with the orientations. This sign change invalidates the semiempirical models of Refs. 1, 5, and 6. For most orientations, including the parallel (H) geometry that occurs in the layers of α and β solid

O_2, we find antiferromagnetic coupling, but for some orientations the coupling changes to ferromagnetic. So, we conclude that antiferromagnetism can arise quite naturally, without invoking charge transfer,[1,19] from direct exchange between magnetic units, provided that the overlap is not neglected even though it is small. This is obvious already from the simple Heitler-London expression for the exchange between two hydrogen atoms, where the coupling is antiferromagnetic because it is dominated by the electron-nuclear attraction integrals, multiplied by the overlap.[8,20] If the open-shell orbitals are (nearly) orthogonal, as they are by symmetry in the X structure, for example, then the two-electron exchange dominates and the coupling is ferromagnetic.

Now we can draw some conclusions pertinent to the magnetic order in solid O_2. Especially our O_2-O_2 results for the parallel (H), shifted-parallel (S), and nearly parallel (A) geometries are relevant in this respect. First of all we find, in agreement with all measurements, that the coupling between the parallel O_2 molecules in the layers of α and β solids, and also in O_2 layers adsorbed on graphite,[4] is antiferromagnetic. The strongest, intersublattice, coupling J_2 occurs between the nearest neighbors ($R=3.200$ Å) in α-O_2. The intrasublattice coupling J_1 between parallel molecules at $R=3.429$ Å is considerably weaker: $J_1/J_2=0.42$. Still weaker is the coupling between the layers. For the two nearest molecules ($R=4.186$ Å) in adjacent layers of α-O_2 the ratio is $J_3/J_2=-0.044$, according to our calculations for the S geometry. We predict the latter coupling to be ferromagnetic, in contrast to neutron diffraction data[21-23] which indicate antiferromagnetic coupling. This coupling is very weak, however, and the S geometry must be close to a point where the sign of J changes (note also the anomalous R dependence), so that this discrepancy could be due to the inaccuracy in our calculations or to the effect of vibrational averaging in the solid (see below). In any case, it is clear that a molecule in α-O_2 does not possess eight neighbors with the same value of the coupling constant J_2, as has been assumed in several of the magnetic models[1,8,19]; this value should be restricted to the four neighbors within the layers only. The corresponding coupling parameters in the β phase are: $J_1(\beta)=J_2(\beta)\simeq0.76J_2(\alpha)$ for the six parallel neighbors within the layers ($R=3.272$ Å) and $J_3(\beta)\simeq0.96\,J_3(\alpha)$ for shifted-parallel neighbor pairs in different layers ($R=4.207$ Å).

TABLE I. O_2-O_2 (exchange) interaction.

Geometry[a] θ_A, θ_B, ϕ (deg)	R (Å)	Interaction energy (μH)[b] S=2	S=1	S=0	J (K) $\simeq J_0 \exp[-\alpha(R-R_0)]$[c]	
L 0,0,0	3.175	39198	37671	36906	-121	
	3.704	4278	4111	4028	- 13.2	$J_0 = -109$ K $\alpha = 4.184$ Å^{-1}
	4.233	449.3	431.0	421.9	- 1.44	
T 90,0,0	3.175	5220	4919	4769	- 23.7	
	3.704	608.8	572.7	554.7	- 2.85	$J_0 = -21.6$ K $\alpha = 4.044$ Å^{-1}
	4.233	64.8	60.6	58.5	- 0.33	
H 90,90,0	2.117	63030	53201	48334	-772	
	2.646	8328	6975	6300	-107	$J_0 = -12.5$ K
	3.175	1077	898	809	- 14.1	$\alpha = 3.831$ Å^{-1}
	3.704	143.0	120.7	109.5	- 1.76	
X 90,90,90	2.646	5957	6166	6270	+ 16.5	
	3.175	771.6	806.3	823.6	+ 2.73	$J_0 = +2.34$ K $\alpha = 3.586$ Å^{-1}
	3.704	95.3	100.0	102.4	+ 0.37	
S 26.5,26.5,0	3.704	2490	2509	2519	+ 1.52	
	4.233	286.0	292.2	295.3	+ 0.49	
A 80,100,0	3.175	1407	1224	1132	- 14.5	

[a]θ_A, θ_B, and $\phi = \phi_B - \phi_A$ are polar angles of the O_2 axes in a coordinate frame with the z axis along the vector $\vec{R} = \vec{R}_{AB}$ between the O_2 centers of mass.

[b]1 hartree (atomic unit of energy) corresponds to 315 777 K.

[c]R_0 is taken as the nearest-neighbor distance in α-O_2 (3.200 Å).

From the pressure and temperature dependence of the magnetic susceptibility in α-, β-, and γ-oxygen, Meier, Schinkel, and de Visser[7] have deduced that the distance dependence of J, which they assume to be isotropic, can be expressed by the law $J \sim R^{-14}$. In the range of (nearest-neighbor) distances which corresponds with their measurements, 3.1 Å $< R < 3.7$ Å, their data could equally well be fitted[3,7] by an exponential relationship: $J \sim \exp(-\alpha R)$ with $\alpha = 4.3$ Å^{-1}. The agreement with our calculated exponential distance dependence of J with $\alpha = 3.6$ to 4.2 Å^{-1}, depending on the O_2 orientations, is satisfactory.

Finally, we discuss the controversial question regarding the size of the nearest-neighbor coupling parameter J_2 in α-O_2. Different experimental data[1,7] lead to $|J_2|$ values ranging from 3 to 38 K. We predict that this value is $|J_2| = 12.5$ K, if the neighboring molecules are kept parallel at a distance of $R_{nn} = 3.200$ Å. The molecules in the solid are actually vibrating, however, and, as we have found that J depends rather sensitively on the distance between the O_2 molecules and on their orientations, we expect an important effect of the lattice vibrations (phonons) on the strength of the exchange coupling. We have tried to esti-

mate this effect, both for translational and libra-
tional molecular motions. A rather arbitrary
tilt of the molecular axes by $10°$ (angular fluctua-
tions in the α solid are about $16°$[3]), which leads
from the H geometry to the A structure, increases
the total repulsion between two neighboring O_2
molecules by 36%, but the value of J changes only
by 3%. One cannot exclude that different angular
motions might cause a larger change in J, but, be-
cause of the very steep distance dependence of J,
we expect a more pronounced effect of the trans-
lational vibrations. Adopting the mean value for
the molecular displacements, $\langle u^2 \rangle^{1/2} = 0.078 R_{nn}$
$= 0.25$ Å, which Etters, Helmy, and Kobashi[3]
have obtained from lattice-dynamics calculations,
we estimate from a simple model with independ-
ently vibrating molecules that the effective vi-
brationally averaged exchange-coupling constant
$\langle |J_2(R)| \rangle$ may be as large as $2.5 |J_2(R_{nn})|$, which
amounts to about 30 K. The final solution to the
controversy about the size of J_2, which is actually
caused by the interpretation of the different ex-
perimental data by means of too simple models
(where J is assumed to be a constant), will have
to be given via lattice-dynamics calculations in
which the full distance and orientation dependence
of J is taken into account. By extending our *ab
initio* calculations on O_2-O_2 dimers to a finer
grid of O_2 orientations, we plan to obtain this
orientational (and distance) dependence of J in
analytic form,[17] in the same way as, for example,
the potential surface of N_2-N_2 dimers has been
calculated.[24] However, the results in this Letter
demonstrate already that the knowledge of the
distance dependence of the exchange-coupling
parameter J for the nearest-neighbor orienta-
tions in α and β O_2 crystals provides useful in-
sight into the magnetic coupling in solid O_2.

[1]G. C. de Fotis, Phys. Rev. B 23, 4714 (1981).

[2]P. W. Stephens, R. J. Birgeneau, C. F. Majkrzak,
and G. Shirane, Phys. Rev. B 28, 452 (1983).

[3]R. D. Etters, A. A. Helmy, and K. Kobashi, Phys.
Rev. B 28, 2166 (1983).

[4]K. Kobashi, M. L. Klein, and V. Chandrasekharan,
J. Chem. Phys. 71, 843 (1979).

[5]C. A. English, J. A. Venables, and D. R. Salahub,
Proc. Roy. Soc. London, Ser. A 340, 81 (1974).

[6]R. J. Meier, Phys. Lett. 95A, 115 (1983).

[7]R. J. Meier, C. J. Schinkel, and A. de Visser, J.
Phys. C 15, 1015 (1982).

[8]E. J. Wachtel and R. G. Wheeler, J. Appl. Phys. 42,
1581 (1971).

[9]M. F. Guest and V. R. Saunders, Mol. Phys. 28, 819
(1974).

[10]V. R. Saunders and M. F. Guest, Daresbury Labor-
atory, Warrington, United Kingdom.

[11]J. van Lenthe and F. B. van Duijneveldt, to be pub-
lished.

[12]J. G. C. M. van Duijneveldt-van de Rijdt and F. B.
van Duijneveldt, J. Mol. Struc. 89, 185 (1982).

[13]P. Cade and A. C. Wahl, At. Data Nucl. Data Tables
13, 4 (1974).

[14]D. E. Stogryn and A. P. Stogryn, Mol. Phys. 11, 371
(1966).

[15]E. R. Cohen and G. Birnbaum, J. Chem. Phys. 66,
2443 (1977).

[16]V. Adamantides, D. Neisius, and G. Verhaegen,
Chem. Phys. 48, 215 (1980).

[17]P. E. S. Wormer and A. van der Avoird, to be pub-
lished.

[18]F. A. Matsen, D. J. Klein, and D. C. Foyt, J. Phys.
Chem. 75, 1866 (1971).

[19]Yu. B. Gaididei, V. M. Loktev, A. F. Prikhot'ko, and
L. I. Shanskii, Fiz. Nizk. Temp. 1, 1365 (1975) [Sov. J.
Low Temp. Phys. 1, 653 (1975)].

[20]W. Heitler, *Elementary Wave Mechanics* (Oxford
Univ. Press, London, 1956), 2nd ed.

[21]M. F. Collins, Proc. Phys. Soc. London 89, 415
(1966).

[22]R. A. Alikhanov, Pis'ma Zh. Eksp. Teor. Fiz. 5, 430
(1967) [JETP Lett. 5, 349 (1967)].

[23]R. J. Meier and R. B. Helmholdt, to be published.

[24]R. M. Berns and A. van der Avoird, J. Chem. Phys.
72, 6107 (1980).