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**Ab Initio Calculation of the Heisenberg Exchange Interaction between O\textsubscript{2} Molecules**

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The exchange interaction between O\textsubscript{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\textsubscript{2}-O\textsubscript{2} distance, with exponents ranging from 3.6 to 4.2 \( \text{Å}^{-1} \) for different O\textsubscript{2} orientations. For most orientations the coupling is antiferromagnetic, but for a few \( J \) is positive. The different neighbor interactions in \( \alpha \) and \( \beta \) O\textsubscript{2} solids, which determine their magnetic order and properties, have been evaluated.

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The open-shell (triplet) character of the ground state of the O\textsubscript{2} molecule makes solid O\textsubscript{2} one of the most interesting molecular crystals. Three different phases occur at zero pressure: the \( \alpha \) phase which is orientationally as well as magnetically ordered, the \( \beta \) phase which is also orientationally ordered and, possibly, has short-range antiferromagnetic order, and the \( \gamma \) phase which is orientationally disordered and paramagnetic (just as liquid O\textsubscript{2}). The (monoclinic) \( \alpha \) phase of solid O\textsubscript{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) \( \beta \) 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, librions) 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\textsubscript{2} molecules, which is actually the leading magnetic coupling term. This interaction is usually represented by the Heisenberg Hamiltonian:

\[
\hat{H} = -2 \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j ,
\]

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 \( \alpha-\text{O}_2 \) range from 3 to 38 K.\(^{1,7}\)

Several authors\(^{5,8}\) recognize that the desired information on the exchange interaction between O\textsubscript{2} molecules can, in principle, be obtained from \( \text{ab initio} \) 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\textsubscript{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 \textsc{Atmol} program.\(^{10}\) In order to evaluate accurately the exchange interaction between O\textsubscript{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\textsubscript{2}-He interaction\(^{11}\) and tested by evaluating several molecular properties.\(^{12}\) The ground-state energy of O\textsubscript{2} is \(-149.644691 \text{ hartrees} \) at \( r_e = 1.208 \text{ Å} \) (estimated\(^{13}\) Hartree-Fock limit, \(-149.6659 \text{ hartrees} \)) and the quadrupole moment is \(-0.284 \text{ a.u.} \) (experimental, \(-0.29,^{14} \pm 0.25 \text{ a.u.} \)).

The (weak) exchange interaction between two O\textsubscript{2} molecules cannot be obtained from a so-called supermolecule (in this case O\textsubscript{4}) Hartree-Fock calculation,\(^{16}\) because of the incorrect asymptotic behavior of the supermolecule wave functions for large O\textsubscript{2}-O\textsubscript{2} distance (except for the quintet, \( S=2 \),
state of $\text{O}_2$. Instead, we have applied a second-
quantized hole-particle formalism which starts from
the antisymmetrized product of the two мо-
nomer $^3\Sigma_g^-$ wave functions, which is then spin
projected, so as to represent the three possible
spin states, $S=0$, 1 and 2, of the $\text{O}_2-\text{O}_2$ 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 $\text{O}_2$ monomer energies. For
this purpose, we have employed a generalization
of Wick's theorem to nonorthogonal orbitals.\textsuperscript{17}
Taking into account the full nonorthogonality be-
tween the monomer molecular orbitals is essential
for describing correctly the antiferro or fer-
romagnetic coupling (see below). The interaction
energy thus obtained comprises the electrostatic
interactions between the (unpolarized) $\text{O}_2$ charge
distributions, as well as the exchange interac-
tions between all $\text{O}_2$ electrons, i.e., the closed
shell $\sigma$ and bonding $\pi$ electrons and the open-
shell antibonding $2p\pi_g$ electrons. It is the ex-
change between the open shells (with the electron
pair on each $\text{O}_2$ 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 $\text{O}_2$ 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 ex-
change coupling between the monomer triplets
can be very well fitted to the form of the Heisen-
berg Hamiltonian (1), i.e., the quintet-triplet
splitting is exactly twice the triplet-singlet split-
ing (see Table I). This implies that multiple-
exchange interactions between $\text{O}_2$ monomers are
negligible.\textsuperscript{18} Thus, we have obtained the value of
the exchange-coupling constant $J$ for various
orientations of the $\text{O}_2$ axes as a function of the $\text{O}_2-
$ $\text{O}_2$ distance $R$. The $R$ dependence is nearly expo-
nential, $J=J_0 \exp\{-\alpha(R-R_0)\}$, with the exponent
$\alpha$ varying from 4.2 $\text{Å}^{-1}$ for the linear (L) geometry
to 3.6 $\text{Å}^{-1}$ for the crossed (X) structure (see Ta-
ble 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) ge-
ometry that occurs in the layers of $\alpha$ and $\beta$ solid
$\text{O}_2$, we find antiferromagnetic coupling, but for
some orientations the coupling changes to ferro-
magnetic. So, we conclude that antiferromagnet-
isim can arise quite naturally, without invoking
charge transfer,\textsuperscript{1,19} from direct exchange be-
tween 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 hydro-
gen atoms, where the coupling is antiferromag-
netic because it is dominated by the electron-nu-
clear attraction integrals, multiplied by the over-
lap.\textsuperscript{5,20} 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 ferromag-
netic.

Now we can draw some conclusions pertinent to
the magnetic order in solid $\text{O}_2$. Especially our
$\text{O}_2-\text{O}_2$ 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 $\text{O}_2$ molecules in the lay-
ers of $\alpha$ and $\beta$ solids, and also in $\text{O}_2$ layers ad-
sorbed on graphite,\textsuperscript{4} is antiferromagnetic. The
strongest, intersublattice, coupling $J_2$ occurs
between the nearest neighbors ($R = 3.200 \text{ Å}$) in $\alpha-
$ $\text{O}_2$. The intrasublattice coupling $J_3$ between parallel
molecules at $R = 3.429 \text{ Å}$ is considerably weaker:
\begin{equation}
J_3/J_2 = 0.42.
\end{equation}
Still weaker is the coupling be-
tween the layers. For the two nearest molecules
($R = 4.186 \text{ Å}$) in adjacent layers of $\alpha-\text{O}_2$ the ratio is
\begin{equation}
J_3/J_2 = -0.044,
\end{equation}
according to our calculations for the S geometry. We predict the latter coupling to be ferromagnetic, in contrast to neutron dif-
fraction data\textsuperscript{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
$\alpha-\text{O}_2$ does not possess eight neighbors with the same value of the coupling constant $J_2$, as has
been assumed in several of the magnetic mod-
els\textsuperscript{1,8,19}; this value should be restricted to the
four neighbors within the layers only. The cor-
responding coupling parameters in the $\beta$ phase
are: $J_3(\beta) = J_4(\beta) \approx 0.76 J_3(\alpha)$ for the six parallel
neighbors within the layers ($R = 3.272 \text{ Å}$) and $J_3(\beta)
\approx 0.96 J_3(\alpha)$ for shifted-parallel neighbor pairs in
different layers ($R = 4.207 \text{ Å}$).
TABLE I. O$_2$-O$_2$ (exchange) interaction.

<table>
<thead>
<tr>
<th>Geometry $^{a)}$</th>
<th>R (Å)</th>
<th>Interaction energy (μH) $^{b)}$</th>
<th>$J$ (K) $^{c)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_A, \theta_B, \phi$ (deg)</td>
<td>S=2</td>
<td>S=1</td>
</tr>
<tr>
<td>L</td>
<td>0,0,0</td>
<td>3.175</td>
<td>39198</td>
</tr>
<tr>
<td></td>
<td>3.704</td>
<td>4278</td>
<td>4111</td>
</tr>
<tr>
<td></td>
<td>4.233</td>
<td>449.3</td>
<td>431.0</td>
</tr>
<tr>
<td>T</td>
<td>90,0,0</td>
<td>3.175</td>
<td>5220</td>
</tr>
<tr>
<td></td>
<td>3.704</td>
<td>608.8</td>
<td>572.7</td>
</tr>
<tr>
<td></td>
<td>4.233</td>
<td>64.8</td>
<td>60.0</td>
</tr>
<tr>
<td>H</td>
<td>90,90,0</td>
<td>2.117</td>
<td>63030</td>
</tr>
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<td></td>
<td>2.646</td>
<td>8328</td>
<td>6975</td>
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<tr>
<td></td>
<td>3.175</td>
<td>1077</td>
<td>898</td>
</tr>
<tr>
<td></td>
<td>3.704</td>
<td>143.0</td>
<td>120.7</td>
</tr>
<tr>
<td>X</td>
<td>90,90,90</td>
<td>2.646</td>
<td>5957</td>
</tr>
<tr>
<td></td>
<td>3.175</td>
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<td>806.3</td>
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</tr>
<tr>
<td></td>
<td>4.233</td>
<td>286.0</td>
<td>292.2</td>
</tr>
<tr>
<td>A</td>
<td>80,100,0</td>
<td>3.175</td>
<td>1407</td>
</tr>
</tbody>
</table>

$^{a)}\theta_A$, $\theta_B$, 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 a-C$^3$ (3.200 Å).

From the pressure and temperature dependence of the magnetic susceptibility in $\alpha$, $\beta$, and $\gamma$-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$^{5,7}$ 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 $\alpha$-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 $R_{min} = 3.200$ 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 librational molecular motions. A rather arbitrary tilt of the molecular axes by 10° (angular fluctuations 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 O₂ 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, because of the very steep distance dependence of J, we expect a more pronounced effect of the translational vibrations. Adopting the mean value for the molecular displacements, \( (\langle u^2 \rangle)^{1/2} = 0.078 R_{\text{m}} = 0.25 \) Å, which Etters, Helmy, and Kobashi3 have obtained from lattice-dynamics calculations, we estimate from a simple model with independently vibrating molecules that the effective vibrationally averaged exchange-coupling constant \( |J_2(R)| \) may be as large as 2.5|J₂(Rm)|, 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 experimental 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 \textit{ab initio} calculations on O₂-O₂ dimers to a finer grid of O₂ 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 N₂-N₂ 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 orientations in α and β O₂ crystals provides useful insight into the magnetic coupling in solid O₂.

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