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THE MOLECULAR CHARACTER OF THE $O^-_2$-CENTER IN ALKALI HALIDES

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Laboratory of Solid State Physics,
Swiss Federal Institute of Technology, Zürich, Switzerland

Abstract. — Like other color centers ($V_K, H$) the $O^-_2$-center in alkali halides has a strong molecular character. It is shown that methods similar to those used in the theory of transition metal salts lead to an understanding of the electronic ground state and $g$-factor of the $O^-_2$-center. It is necessary to invoke a weak covalent bonding with the neighbouring ions. This bonding manifests itself in the crystal field splitting, E. P. R. linewidth and the reduction of orbital angular momentum matrix elements.

The H. F. S. of the $(16O-17O)^-$ center has been measured. The experimental results can be understood by means of a symmetry analysis of molecular hyperfine coupling. Instead of the single parameter $<1/r^3>$ of the Hartree-Fock approximation, four parameters are needed for a complete description of the H. F. S. of a molecule in a $II$ state.

Résumé. — Le centre $O^-_2$ possède un caractère typiquement moléculaire, comme c'est le cas pour certains autres centres colorés dans les halogénures alcalins ($V_K, H$). On montre que des méthodes semblables à celles développées dans la théorie des sels des métaux de transition sont applicables au traitement de l'état électronique fondamental et le facteur $g$ du centre $O^-_2$. Il est nécessaire de considérer une faible liaison covalente avec les ions du voisinage. En tenant compte de cette liaison, l'explication du paramètre du champ cristallin, de la largeur de ligne E. P. R. et de la réduction des éléments de matrice du moment orbital est possible.

On a mesuré la structure hyperfine du centre $(16O-17O)^-$. Les résultats expérimentaux sont interprétés par l'analyse de symétrie du couplage hyperfin moléculaire. Quatre paramètres sont nécessaires pour la description complète de la structure hyperfine d'une molécule dans l'état $II$, au contraire de l'approximation Hartree-Fock qui ne contient que $<1/r^3>$ comme paramètre.

1. Introduction. — We know from optical, paramagnetic resonance and ENDOR experiments that many color centers have, at least in their ground state, a strong molecular character. For instance a hole in the valence band of an alkali halide is localised and forms the self trapped hole or $V_K$-center. Electron spin resonance and ENDOR experiments in KCl show that the hole spends essentially all the time on two chlorine ions forming a $Cl^-_2$ molecule. If we compare the hyperfine splitting of the $V_K$-center in different crystals of different symmetry, we see that it is not much affected by the host crystal (Tab. 1).

The optical absorption bands of the $V_K$-center are also about the same in all host crystals. These facts offer strong support for the assumption that such center can be considered as a molecule in a crystal field.

There is a considerable amount of experimental and theoretical work on transition metal ions in crystals [5]. The question is now, if it is possible to apply this theory with some modification to molecular color centers in alkali halides. Unfortunately the $V_K$-center and most of the other molecular centers are unsuitable examples to discuss this question. The reason is that the ground state of the $V_K$-center is a $\Sigma$ state and hence has no orbital degeneracy.

(*) USAFOSR Postdoctoral Research Fellow.

<table>
<thead>
<tr>
<th>$\text{KCl}$</th>
<th>$\text{NaCl}$</th>
<th>$\text{NH}_4\text{Cl}$</th>
<th>$\text{SrCl}_2$</th>
<th>$\text{NH}_3\text{OHCl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_\parallel$</td>
<td>101</td>
<td>98</td>
<td>98,6</td>
<td>104</td>
</tr>
<tr>
<td>$A_\perp$</td>
<td>9</td>
<td>9</td>
<td>10</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 1: Principal components of the HFS — Tensor for the $V_K$ center (Gauss)
Thus there is little possibility to check angular momentum matrix elements, which are much more sensitive to distortions of the outer part of the wavefunction than are hyperfine matrix elements. We would prefer a center whose corresponding free molecule has an orbitally degenerate ground state. This requirement is met by the $O_2^-$ center.

![Energy diagram for $O_2^-$.](image)

Figure 1 shows that a free $O_2^-$ has an unpaired electron in a $\pi_g$ orbital. The ground state of the molecule is $^2\Pi_g$. In the crystal the molecule is on a halide site [16], with its internuclear axis parallel to [110]. The crystalline surroundings reduce the molecular symmetry from cylindrical to orthorhombic, and thus lift the orbital degeneracy (Fig. 2).

2. $g$-factor and electronic ground state of the $O_2^-$ center.

2.1 Analysis based on a coulombic crystal field approximation. — Let us now discuss the experimental $g$-factor using the model of a molecule showing a Stark effect.

Table II shows that the $g$-factor differs considerably from the free electron value. This means that the orbital moment of the $O_2^-$-center is only partially quenched. The crystal field tends to quench the orbital moment and the spin-orbit-coupling to unquench it again. In our case the two effects are of the same order of magnitude, giving a partially quenched orbital moment.

For a calculation of the ground state and the $g$-factor we take the Coulomb eigenfunctions of the free molecule as basis functions and consider the spin-orbit-interaction and the orthorhombic crystal field splitting as perturbations. We then obtain for the zero-order ground state:

\[
\psi = \cos \alpha \uparrow \pi_g^+ + i \sin \alpha \uparrow \pi_g^-
\]

\[
\psi = \cos \alpha \downarrow \pi_g^- - i \sin \alpha \downarrow \pi_g^+
\]
\( \alpha \) is defined by the ratio of the spin-orbit parameter \( \lambda_{\alpha \parallel} \) to the crystal field parameter \( A_0 \) (See Fig. 3)

\[
\tan 2 \alpha = \frac{\lambda_{\alpha \parallel}}{A_0}.
\]

When contributions from excited states are included to first order, one obtains the following g-factors:

\[
\begin{align*}
g_{xx} &= g_e \cos 2 \alpha + A \cos 2 \alpha - B(1 - \sin 2 \alpha) \\
g_{yy} &= g_e \cos 2 \alpha + A \cos 2 \alpha + B(1 - \sin 2 \alpha) \\
g_{zz} &= g_e + 2 \sin 2 \alpha
\end{align*}
\] (1)

\( A \) and \( B \) are sums of matrix elements between ground and excited Coulomb states divided by the corresponding excitation energies and therefore purely molecular quantities which do not depend upon the crystal field. Within the framework of a pure Coulomb crystal field theory the above expressions are completely general. However, it turns out that the measured quantities \( A \) and \( B \) vary with the host crystal. Thus it is impossible to describe the \( O_2^- \)-center with pure molecular states.

A similar situation was found in transition metal salts by the Oxford group [5].

2.2 General analysis of the g-factor. — We may distinguish two causes for the discrepancy between the experimental g-factor and the g-factor calculated for the molecule in a coulombic crystal field.

1) The wave functions of the ground state are distorted to some extent by the crystalline environment. (For instance by slight covalent bonding.)

2) The excited molecular states entering \( A \) and \( B \) are essentially degenerate with the intrinsic alkali halide excitons and may therefore be severely modified in a manner dependent on host crystal.

To account for the first effect, one must assume only orthorhombic symmetry for the wave functions. We neglect all excited levels except \( ^2\Sigma^+ \), since we expect that this level is most important and least modified by the crystal. The basis states are then the Coulomb states of the center (Fig. 3), and only the magnetic energy is nondiagonal. Using the notation of Koster and Statz [6] we define quantities \( l_i \) and \( \lambda_i \) as follows:

\[
\begin{align*}
\langle \Gamma_2^+ | L_z | \Gamma_4^+ \rangle &= -il_z \\
\langle \Gamma_1^+ | L_y | \Gamma_2^+ \rangle &= -il_y \\
\langle \Gamma_4^+ | L_x | \Gamma_1^+ \rangle &= -il_x \\
\langle \Gamma_2^+ | \mathcal{E}_{\alpha 0} | \Gamma_4^+ \rangle &= i \lambda_{\alpha \parallel} S_z \\
\langle \Gamma_1^+ | \mathcal{E}_{\alpha 0} | \Gamma_2^+ \rangle &= i \lambda_y S_y \\
\langle \Gamma_4^+ | \mathcal{E}_{\alpha 0} | \Gamma_1^+ \rangle &= i \lambda_x S_x
\end{align*}
\] (2)

These expressions predict (for small \( \alpha \)) \( g_{yy} > g_{xx} \). Experimentally such is the case except for \( O_2^- \) in NaCl and NaBr (Tab. II). So far it has been supposed that the axis of the hole orbit is \( x \) (i.e. parallel to [110]). The analysis of the g-factor shows that this is in fact the case in the K- and Rb-halides but that in NaCl, NaBr and possibly also in NaI the axis of the hole orbit is \( y \). Hence for the latter salts the indices \( x \) and \( y \) have to be interchanged in the above expressions.

Using the experimental g-factors it is possible to determine the parameters \( \lambda, \lambda_x, \lambda_y, l_z, l_y \) if we put \( \lambda_x = \lambda_y \) and \( l_z = l_y \).

Let us now discuss the parameters listed in Table III. Theoretical estimates [8] give \( \lambda_y l_y/E \approx 0.003 \).

In the free molecule \( l_z \) is unity. However, the distortion of the wavefunction by the crystal reduces \( l_z \) [7]. The \( l_z \) values in table III are smaller than unity in all cases where the parameter \( \lambda_y l_y/E \) is close to the theore-
g-factor parameters computed from experimental g-factors with expressions (3)

<table>
<thead>
<tr>
<th></th>
<th>$\lambda/\Delta$</th>
<th>$l_z$</th>
<th>$\lambda_{l_z}/E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl...</td>
<td>0.249 ± 0.5 %</td>
<td>0.932 ± 0.005</td>
<td>(30 ± 5) x 10^{-4}</td>
</tr>
<tr>
<td>NaBr...</td>
<td>0.193 ± 0.7 %</td>
<td>0.977 ± 0.008</td>
<td>26 ± 5 —</td>
</tr>
<tr>
<td>NaI...</td>
<td>0.052 ± 10 %</td>
<td>1.8 ± 0.2</td>
<td>4 ± 5 —</td>
</tr>
<tr>
<td>KCl...</td>
<td>0.231 ± 0.1 %</td>
<td>0.962 ± 0.001</td>
<td>25 ± 1 —</td>
</tr>
<tr>
<td>KBr...</td>
<td>0.283 ± 0.1 %</td>
<td>0.952 ± 0.001</td>
<td>31 ± 1 —</td>
</tr>
<tr>
<td>KI...</td>
<td>0.263 ± 0.1 %</td>
<td>0.948 ± 0.001</td>
<td>33 ± 1 —</td>
</tr>
<tr>
<td>RbCl...</td>
<td>0.135 ± 3 %</td>
<td>1.090 ± 0.030</td>
<td>5 ± 10 —</td>
</tr>
<tr>
<td>RbBr...</td>
<td>0.169 ± 2 %</td>
<td>1.021 ± 0.020</td>
<td>11 ± 10 —</td>
</tr>
<tr>
<td>RbI...</td>
<td>0.190 ± 0.7 %</td>
<td>1.006 ± 0.007</td>
<td>13 ± 3 —</td>
</tr>
</tbody>
</table>

The conclusion of the g-factor analysis is: The center cannot be described by a pure Coulomb crystal field approximation. The matrix element of $L_z$ in the ground state is sensitive to orthorhombic distortions. However, the fact that $L_z \approx 1$ indicates that the distortion or the covalent bonding to the neighbouring ions is weak. In NaI and the Rb-halides contributions from higher excited states to the g-factor may be comparable to that from the $^2\Sigma^+_g$ state.

2.3 COVALENT BONDING TO THE NEIGHBOURING IONS. — Rather direct information about the spread of the wave function to the neighbouring ions is contained in the superhyperfine structure of $O_2^-$. Therefore we consider first the EPR linewidth (Tab. IV). At solid H$_2$ temperature the linewidth can be attributed to unresolved hyperfine interaction with nuclei of neighbouring ions.

In the K-and-Rb-halides the linewidth decreases with decreasing lattice constant $a$. The width can be written approximately as

$$\Delta H \approx \frac{C}{a^3}$$

where $C$ depends only on the alkali nucleus. This indicates that in the K-and Rb-halides the linewidth is caused essentially by interaction with alkali nuclei.

In certain cases partial resolution of the hyperfine interaction is possible (Fig. 4).

The spectrum consists of 13 lines. From this fact as well as from the intensity ratio one concludes that the EPR line widths if the $O_2^-$-center in different alkali halides. $T = 11$°K (* $T = 2$°K). Peak to peak of first derivative in gauss.

<table>
<thead>
<tr>
<th></th>
<th>$H_{0//x}$</th>
<th>$H_{0//y}$</th>
<th>$H_{0//z}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl...</td>
<td>7.0</td>
<td>7.1</td>
<td>5.3</td>
</tr>
<tr>
<td>NaBr...</td>
<td>8.6</td>
<td>7.7</td>
<td>6.9</td>
</tr>
<tr>
<td>NaI*...</td>
<td>9.6</td>
<td>10.4</td>
<td>6.8</td>
</tr>
<tr>
<td>KCl...</td>
<td>5.4</td>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>KBr...</td>
<td>4.3</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>KI...</td>
<td>3.4</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>RbCl...</td>
<td>31.8</td>
<td>21.3</td>
<td>26.0</td>
</tr>
<tr>
<td>RbBr...</td>
<td>24.5</td>
<td>19.3</td>
<td>26.8</td>
</tr>
<tr>
<td>RbI...</td>
<td>20.5</td>
<td>15.2</td>
<td>18.6</td>
</tr>
</tbody>
</table>

FIG. 4. — Second derivative of the EPR absorption signal of the $O_2^-$ center in KCl.
splitting arises from interaction with four equivalent nuclei with spin 3/2, i.e., with the four K nuclei in the xz plane (Fig. 2). A crude estimate shows that this splitting cannot be explained by the pure dipole-dipole interaction of the K nuclei with an O\textsuperscript{2-} π-function. It is necessary to include a slight covalent bonding to the four alkali neighbors in the xz-plane.

In the Na-halides, on the other hand, the linewidth increases with increasing lattice constant (Tab. III). Since the magnetic moment of the halide nuclei increase in the sequence Cl, Br, I, this indicates that the linewidth arises essentially from interactions with halide nuclei.

The investigation of the linewidth leads to a qualitative understanding of the crystal field splitting \( \Delta_0 \) (Fig. 3). Consider first the case of O\textsuperscript{2-} in K- and Rb-halides. A slight covalent bonding to the four alkali ions in the xz plane splits the \( \Pi_0 \) state of the free molecule as indicated in figure 5.

![Energy diagram of the O\textsuperscript{2-} center](image)

Fig. 5. — Energy diagram of the O\textsuperscript{2-} center (schematically). A slight covalent bonding of O\textsuperscript{2-} with the neighboring four alkalis in the xz-plane is assumed.

The overlap with the nearest neighbors is larger for the \( \pi^* \) wavefunctions of the molecule than for the \( \pi^0 \) wavefunctions. Therefore the upper antibonding level is \( \Gamma^+ \) and the hole which was originally in the \( \Pi_0 \) state is now in the \( \Gamma^+ \) state. This is in contrast with a simple Coulomb repulsion argument according to which the four positively charged alkali ions (Fig. 2) would repel the hole.

In the sodium halides where the interaction with halide ions dominates the covalency argument does not work. Thus it is understandable that in NaCl and NaBr the ground state of the O\textsuperscript{2-} center is \( \Gamma^+ \) (axis of the hole orbit parallel to \( y \)). In the K- and Rb-halides \( \Delta_0 \) can be interpreted as the energy difference between the two antibonding levels (Fig. 5). Therefore one expects that \( \Delta_0 \) increases with increasing covalency or in other words with increasing linewidth per magnetic moment of the alkali nuclei. The comparison between tables III and IV shows that this is in fact the case (with exception of KI).

It is possible to describe the covalency in the K- and Rb-halides by a L. A. C. O. approximation [7]. This theory gives a relation between the E. P. R. linewidth and the orbital moment matrix element \( l_z \) introduced in (2). The analysis of the experimental linewidths predicts a reduction by only 0.5% of \( l_z \) from the free-molecule value of unity. The reduction obtained from the analysis of the g-factor is about an order of magnitude larger (Tab. III). A similar situation is familiar for transition metal ions [9]. The origin of the discrepancy is the following: For the \( l_z \)-reduction the region of the wavefunction away from the interior of either the O\textsuperscript{2-} or the alkali-ions is important, and it is just there where L. C. A. O. approximation is inadequate. Only in one well-known case, namely (NiF\textsubscript{6})\textsuperscript{4-} [10], has it been possible with great effort to obtain agreement between orbital reduction factors determined directly and those calculated from superhyperfine fields by a covalency theory. To sum up, one can say that for the O\textsuperscript{2-}-center just as for the transition metal ions the crystal field splittings, the EPR linewidth (caused by unresolved hyperfine interaction with neighboring ions) and the reduction of matrix elements with respect to those of the free ion are closely related to covalent bonding effects and cannot be explained by a pure Coulomb crystal field theory.

3. The hyperfine structure of (\( ^{16}\text{O} - ^{17}\text{O} \)). — So far we have discussed how some matrix elements change if we put the molecule into a crystal and what the limits are of a purely molecular treatment of the resulting center. Now we shall show, taking the example of the O\textsuperscript{2-}-center, that the study of a molecular center in a crystal can yield similar information as gas spectroscopy of the free molecule.

\(^{16}\text{O} \) has no nuclear spin. To measure the paramagnetic field at the O\textsuperscript{2-} nuclei the crystals were doped with \(^{17}\text{O} \) enriched oxygen. Since \(^{17}\text{O} \) has a nuclear spin \( I = 5/2 \) one observes (instead of one line as for \( ^{16}\text{O} - ^{18}\text{O} \)) 6 lines of equal intensity for

\[ \text{Fig. 5. — Energy diagram of the O}_2^\text{-} \text{center (schematically). A slight covalent bonding of O}_2^\text{-} \text{with the neighboring four alkalis in the xz-plane is assumed.} \]
(16O – 17O)− (Fig. 6) and 11 lines for (17O – 17O)− with intensity ratio 1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1. The (17O – 17O)− lines are just barely visible.

**TABLE V**

Principal components of the HFS-tensor of (16O–17O)−, \( T = 11^\circ \text{K} \)

<table>
<thead>
<tr>
<th></th>
<th>( A_{xx} )</th>
<th>( A_{yy} )</th>
<th>( A_{zz} ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>189.3 ± 0.2</td>
<td>0 ± 10</td>
<td>55.1 ± 0.2</td>
</tr>
<tr>
<td>KBr</td>
<td>181.3 ± 0.2</td>
<td>0 ± 10</td>
<td>71.1 ± 0.2</td>
</tr>
<tr>
<td>KI</td>
<td>184.3 ± 0.2</td>
<td>0 ± 10</td>
<td>64.2 ± 0.2</td>
</tr>
<tr>
<td>RbCl</td>
<td>201.6 ± 1.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RbI</td>
<td>193.7 ± 0.5</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Since the H. F. S. — interaction is proportional to \( 1/r^3 \), only the part of the wavefunction near the nucleus is important. It is just this part which is not much affected by the environment. Thus we can describe the H. F. S. to a good approximation in terms of molecular wave functions. The coefficients, in favorable cases, can be taken from the analysis of the \( g \)-factor. In L. C. A. O-Hartree-Fock approximation one single molecular parameter, namely \( < 1/r^3 > \), determines the H. F. S. of a \( \Pi \) state. For a general correlated many-electron wavefunction the number of independent parameters is larger. It has been shown [7] that for a complete description of the H. F. S. of \( \text{O}_2^- \) four molecular parameters are needed.

They can be defined as follows [7]:

\[
|\psi(0)|^2 \text{ Spin density at the nucleus}
\]

\[
< \frac{1}{r^3} > \text{ averaged over orbital moment density}
\]

\[
< \frac{1}{r^3} > \text{ averaged over two different matrix elements of spin density.}
\]

For atomic functions

\[
< \frac{1}{r^3} > = < \frac{1}{r^3} >
\]

and for atomic Hartree-Fock functions one has

\[
< \frac{1}{r^3} > = < \frac{1}{r^3} > = < \frac{1}{r^3} >^1.
\]
The expressions for the principal components of the H. F. S.-tensor become then [7]:

\[
A_{xx} = 2 \mu_B \frac{\mu_{1}}{I} \left[ \frac{8 \pi}{3} \cos 2 \alpha |\psi(0)|^2 \right. \\
+ \frac{1}{10} \cos 2 \alpha \frac{1}{r_3} \left. >_0 + 3 (1 - \sin 2 \alpha) \frac{1}{r_3} >_2 \right],
\]

\[
A_{yy} = 2 \mu_B \frac{\mu_{1}}{I} \left[ \frac{8 \pi}{3} \cos 2 \alpha |\psi(0)|^2 \right. \\
+ \frac{1}{10} \cos 2 \alpha \frac{1}{r_3} \left. >_0 - 3 (1 - \sin 2 \alpha) \frac{1}{r_3} >_2 \right].
\]

\[
A_{zz} = 2 \mu_B \frac{\mu_{1}}{I} \left[ \frac{8 \pi}{3} |\psi(0)|^2 - \frac{1}{5} \frac{1}{r_3} >_0 + \\
\sin 2 \alpha \frac{1}{r_3} >_1 \right].
\]

If the H. F. S.-parameters are true molecular quantities and not affected by the crystal, then \(A_{xx}\) versus \(\sin 2 \alpha\) should give a straight line (Fig. 7). The value of \(<1/r^3>^i\) is determined by the slope. Similarly, \(A_{xx}\) plotted versus \(\sin 2 \alpha\) should give a straight line for small values of \(\alpha\) (Fig. 8).

Figures 7 and 8 show that it is indeed possible to fit the measured \(A_{ii}\) with a good accuracy with four H. F. S.-parameters using the \(\alpha\) values derived from the analysis of the \(g\)-factor. The results of the fit are summarized in table VI together with other hyperfine parameters of oxygen. (Note that in this table \(<1/r^3>^i\) is defined as \(1/2(<1/r^3>^0 + <1/r^3>^2)\).

The error in the parameters of \(O_2\) comes mainly from the relatively large error in \(A_{yy}\) (Tab. V).

It is possible to qualitatively understand correlation corrections to Hartree-Fock hyperfine predictions by the unrestricted Hartree-Fock method, in which unpaired electrons are allowed to polarize closed shells. The spin density at the nucleus \(|\psi(0)|^2\) (vanishing in Hartree-Fock approximation) arises from a spin polarization of the 1\(s\) and 2\(s\) shells, or in a diatomic molecule of the \(\sigma\) shells. The large \(\sigma_u - \sigma_g\) splitting allows molecular configurations with \(|\psi(0)|^2 \neq 0\) to have less excitation energy than the corresponding atomic configurations. Therefore, \(|\psi(0)|^2\) is expected to be larger in molecules than in atoms. Furthermore \(|\psi(0)|^2\) should be proportional to the number of unpaired (\(\sigma\) polarizing) electrons. Indeed, \(|\psi(0)|^2\) in \(O_2\) is twice that in \(O_2^+\) (Tab. VI).

The difference between \(<1/r^3>^i\) and the Hartree-Fock value arises from an orbital polarization of the
2p shell (or of the π shells in the molecule) in which electrons of different magnetic quantum number have different radial functions. Since the $\pi_u - \pi_d$ splitting is relatively small the difference between $<1/r^3>^1$ and the Hartree-Fock value should be about the same for the molecule and for the atom. The small difference between molecular and atomic $<1/r^3>^1$ shown in table VI could be attributed to the overlap-renormalization of atomic orbitals in an antibonding LCAO molecular orbital.

The difference between $<1/r^3>^s$ and the Hartree-Fock value for $<1/r^3>$ is mainly due to the following effects:

1) Spin polarization of the 2p shell.

2) Spin-dependent admixture of d orbitals into the s shell. The same reasoning applied above for $|\psi(0)|^2$ holds also for $<1/r^3>^s$ in that the large $\sigma_u - \sigma_d$ splitting causes a larger polarizability in the molecule than in the atom. Table IV indicates furthermore that the many-electron contribution to $<1/r^3>^1$ in $O_2$ is larger than in $O_2^-$, presumably because $O_2$ has two polarizing electrons. The difference between $<1/r^3>^s$ and $<1/r^3>^i$ comes from molecular binding effects.

4. Conclusion. — The principal conclusion of this investigation is the following: The electronic structure of molecular centers in alkali halides can be analyzed by applying methods similar to those used for transition metal salts. The additional complications which arise because of the lower symmetry of the molecules can be overcome.

The present investigation forms a basis for the understanding of a number of interesting phenomena due to $O_2^-:

1) Paraelastic alignment of $O_2^-$ in alkali halides [14].

2) Magnetic and elastic interactions between $O_2^-$ centers in alkali halides.

3) Magnetic and elastic cooperative phenomena in the alkali superoxides [15].

Work along these lines is underway in Zürich and supported by the Swiss National Science Foundation.

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References