

The ground state of two-hole centres in oxides

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Abstract. We discuss the nature of the ground state of the V centre in ionic oxides, where two holes are trapped by a cation vacancy. Experiment appears to indicate an $S = 1$ ground state for BeO and Al_2O_3 and possibly ZnO, with $S = 0$ in MgO and CaO. Simple theoretical arguments suggest $S = 0$. We show that a weak admixture of $[\text{O}^0\text{O}^{2-}]$ configurations into the dominant $[\text{O}^-\text{O}^-]$ configuration can explain the observations. Quantitative calculations are given for MgO, and suggest the singlet state is lowest by about 30 cm^{-1} .

1. Introduction

It has been well known for many years that the ground-state of a two-electron system with an arbitrary real potential, independent of spin and velocity, is a spin singlet (Heisenberg 1928, Herring 1962, Lieb and Mattis 1962). This result allows one to understand why many two-electron colour centres (e.g. the F' and M centres in alkali halides and the F_i centre in alkaline earth oxides) have singlet ground states. It comes as something of a surprise to learn that two-hole centres in oxides—usually the V centre, where two holes are trapped next to a cation vacancy—may have a triplet ground state, since they appear to have nothing in common with known cases of ferromagnetic exchange interactions. The V centres have been studied in MgO (Wertz *et al* 1959, G Rius and R T Cox 1974 private communication), CaO (Henderson and Tomlinson 1969, Abraham *et al* 1975), BeO (Maffeo *et al* 1970), ZnO (Galland and Hervé 1970) and Al_2O_3 (Cox 1966, 1971, 1972). In all cases there is a state with spin 1 which is either the ground state or a very low-lying state. Current data indicate that the singlet ($S = 0$) is definitely lowest in MgO and CaO. For BeO and Al_2O_3 , either the triplet ($S = 1$) is lowest, or it is within 1.5 cm^{-1} of the ground state. The data are inconclusive for ZnO, and are only available at 77 K. But even here the $S = 1$ state must be appreciably populated.

In the present paper we analyse the singlet-triplet splitting in MgO. At the time these calculations were started it was believed that the $S = 1$ state was lowest. Since then, the work of Rius and Cox has shown the singlet state lies lowest, a result in accord with our theory. However, it is clear from our work that systems could occur with the triplet lowest, and we describe the mechanism which makes this possible.

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2. Basic model

In the V centre in MgO, spin-resonance work suggests a ground state in which two holes are trapped on oxygen ions on opposite sides of a cation vacancy. The centre can be described as two ions $[\text{O}^-\text{O}^-]$ in a crystalline environment. If this description as O_2^{2-} is accurate, then a singlet state is expected. The electronic structure of a free O^- ion is $1s^2 2s^2 2p^5$. In the axial crystal field of the defect, the p levels are split into one state (2σ say) directed towards the cation vacancy, and two lower-energy states ($2p_\perp$ say). The 2σ orbitals on each O^- contain one electron, and it is the interaction between these two electrons in the non-degenerate σ orbitals which is of the most importance. It is then hard to think of any interaction which causes the triplet to fall below the singlet. Indeed, as we show in §4, the singlet is lowest in the $[\text{O}^-\text{O}^-]$ model. The peroxide ion, O_2^{2-} , also exhibits a singlet state, although it has a much smaller O^-O^- distance than that in the V centre.

The origin of a triplet state could be understood as follows. If there is weak configuration admixture from states lying at energies δ above the ground state, then the singlet and triplet energies are reduced by different amounts:

$$E_T \rightarrow E_{T0} - \delta_T^2/\epsilon_T, \quad E_S \rightarrow E_{S0} - \delta_S^2/\epsilon_S. \quad (2.1)$$

Here E_{S0} , E_{T0} are the singlet and triplet energies without admixture, and δ_S and δ_T are the matrix elements for the admixture. Whenever δ_T^2/ϵ_T is significantly bigger than δ_S^2/ϵ_S , the triplet will be depressed in energy by a larger amount. This is the origin of a triplet ground state. It should also be noted that, since $(E_{T0} - E_{S0})$ is very small, only very slight admixtures are needed to put the triplet lowest. These admixtures, of less than one percent, are too small to be noticed in spin resonance. We also emphasize that a triplet ground state would *not* violate the theorem cited in §1.

We now describe quantitative calculations for the V centre in MgO. Since this work was begun it became clear that the centre did not have an $S = 1$ ground state. However, it is clear that the $S = 0$ and $S = 1$ states lie very close in energy, and it is useful to have estimates of the various contributions to $(E_T - E_S)$. The calculation falls into three main parts. In the first, the wavefunctions of the oxygen ions are calculated for their different charge states and for appropriate environments. In the second, we calculate the amount by which the singlet state lies below the triplet for the $[\text{O}^-\text{O}^-]$ configuration. Finally, we examine the effects of configuration admixture and the question whether weak admixtures of $[\text{O}^0\text{O}^{2-}]$ and $[\text{O}^{2-}\text{O}^0]$ are sufficient to affect the nature of the ground state.

Qualitatively, the model was first analysed by us in 1971. Quantitative calculations using Breene's (1958) O^- wavefunctions were performed soon after (Stoneham, unpublished work and 1975), and gave results similar to those described here.

3. Calculation of oxygen wavefunctions

Three charge-states of oxygen are of interest: O^0 , O^- and O^{2-} . We have calculated energies and wavefunctions for all three ions in several states, both singlets and triplets. Rather than calculate the structure of pairs of ions (e.g. two O^- ions at the appropriate separation, or one O^0 atom and one O^{2-} ion), we have recognized the large interionic distances, calculating the properties of one ion at a time, and incorporating the effects of their interaction later. This is appropriate because we seek corrections of order 10^{-4} eV in energies which are typically several eV.

Table 1. Basis functions used for calculation of eigenvectors.

The exponents of the various types of atomic functions are listed; the weights of the different components were adjusted automatically by the ATMOL program. Exponents are in atomic units.

| Type of orbital | O^0 | O^- | O^{2-} |
|-----------------|---------|---------|----------|
| 1s | 7.6160 | 7.6126 | 7.6126 |
| | 13.3243 | 13.3654 | 13.3654 |
| 2s | 1.7582 | 1.7637 | 0.5000 |
| | 2.5627 | 3.2045 | 1.7637 |
| | 4.2832 | 6.2896 | 3.2045 |
| | 5.9445 | | 6.2896 |
| 3s | | | 0.6986 |
| | | | 0.8358 |
| | | | 0.9142 |
| 2p | 1.1536 | 0.4700 | 0.4700 |
| | 1.7960 | 0.8565 | 0.8565 |
| | 3.4379 | 1.7424 | 1.7424 |
| | 7.9070 | 3.4363 | 3.4363 |
| | | 7.8070 | 7.8070 |

The calculations use the molecular Hartree-Fock program ATMOL (kindly provided by Dr V R Saunders of the Atlas Laboratory), and give wavefunctions for ions in a suitable point-charge environment. The point charges are essential for O^{2-} , which is not stable as a free ion, and the charges are useful for O^0 and O^- because the asymmetry of the crystal field is included. Our choice of point-charge environment is this:

(a) In all cases the five Mg^{2+} nearest-neighbours are included as charges $+2|e|$ at the spacing appropriate to the perfect crystal.

(b) To obtain the correct asymmetry of the crystal field, a point charge at the other oxygen site (across the vacancy) was included. The charge was the difference between the perfect-crystal charge $-2|e|$ and the charge appropriate. Thus, for O^- , another O^- ion replaces O^{2-} , so a charge $+|e|$ is needed. For O^{2-} , an O^0 replaces O^{2-} , and $+2|e|$ is appropriated. No extra point charge is needed for the O^0 wavefunctions calculation. Thus the O^0 , O^- and O^{2-} wavefunctions are calculated in an environment appropriate for the configuration in which they occur.

Reasonably extensive sets of basis orbitals were used for the wavefunctions. The

Table 2. Energy levels for different configurations.

Energy levels are in atomic units. The wavefunctions all have Σ symmetry, and sometimes Π states exist below the states given. To simplify notation, the one-electron states are written $1s, 2s, 2p_{\perp}, 2\sigma, 3\sigma$, where the 2σ state derives mainly from the axial $2p$ state and $2s$, etc; admixtures of s and p states are not written explicitly.

| | | | |
|----------|------------|---|--------------|
| O^0 | $^1\Sigma$ | $ s^2 2s^2 2p^4\rangle$ | -68.0545 572 |
| | $^3\Sigma$ | $ s^2 2s 2p_{\perp}^4 2\sigma\rangle$ | -68.5292 397 |
| O^- | $^2\Sigma$ | $ s^2 2s^2 2p_{\perp}^4 2\sigma\rangle$ | -69.6919 373 |
| O^{2-} | $^1\Sigma$ | $ s^2 2s^2 2p_{\perp}^4 2\sigma^2\rangle$ | -71.0768 518 |
| | $^3\Sigma$ | $ s^2 2s 2p_{\perp}^4 2\sigma^2 3\sigma\rangle$ | -70.9799 171 |

choices, listed in table 1, were guided by those used in the calculations of Clementi (1965), Breene (1958), Watson (1958) and Harker (1974). For each ion we calculated the low-lying singlet and triplet states. The energies of these states are given in table 2. Note that we did not use Koopmans' approximation, and that excitation energies were obtained as the difference between two self-consistent calculations of total energies. No estimates of correlation are included, a point to which we return later.

4. Calculation of $[O^- O^-]$ singlet-triplet splitting

It has been observed by many authors, notably Herring (1962), that one of the worst ways of calculating small singlet-triplet splittings is to evaluate the two energies separately and to take the difference. Specific schemes have been proposed as alternatives. One, particularly suitable here, is that of Berezin (1972), who shows that the singlet-triplet splitting, Δ_0 (without corrections from configuration admixture) can be written as a surface integral over the surface $x = 0$ equidistant from the two oxygen ions. If ψ_L and ψ_R represent the 2σ orbitals on the two oxygen ions, and if subscripts 1 and 2 label the electrons, then:

$$\Delta_0 \simeq \int \dots \int dy_1 dz_1 dx_2 dy_2 dz_2 \left(\phi_1 \frac{\partial \phi_2}{\partial x_1} - \phi_2 \frac{\partial \phi_1}{\partial x_1} \right)_{x_1=0}. \quad (4.1)$$

Here, if $s \equiv \langle \psi_L | \psi_R \rangle$ is the overlap, then

$$\phi_1 \equiv A\psi_{L1}\psi_{R2} + B\psi_{L2}\psi_{R1} \quad (4.2)$$

$$\phi_2 \equiv B\psi_{L1}\psi_{R2} + A\psi_{L2}\psi_{R1} \quad (4.3)$$

where $A \equiv \frac{1}{2}[(1 + s^2)^{-1/2} + (1 - s^2)^{-1/2}]$ and $B \equiv \frac{1}{2}[(1 + s^2)^{-1/2} - (1 - s^2)^{-1/2}]$. The integrand of Δ_0 involves terms from the various basis functions in ψ_L and ψ_R . For the Slater forms adopted, the individual contributions can be evaluated analytically; Berezin gives the simplest case as an example. It is straightforward to evaluate the whole of Δ_0 by summing the contributions with correctly-weighted basis functions. We find:

$$\Delta_0 = 1.276 \times 10^{-5} \text{ au} \quad (4.4)$$

so that the singlet lies below the triplet by about 2.8 cm^{-1} . Even without any effects of configuration admixture, spin-resonance experiments would find it hard to discern that the true ground state was a singlet, not a triplet. Experiments on MgO give a splitting about an order of magnitude larger than Δ_0 .

5. Effects of configuration admixture

The main effect of configuration admixture is to change the singlet-triplet splitting. To discuss this quantitatively, one needs estimates of both the energy levels and the transition matrix element.

5.1. Excited states

The energy levels can be obtained from table 2. There are two states of the pair of oxygens which are of main interest, and, for each of these states, both the $[O^0 O^{2-}]$ and the

$[\text{O}^{2-} \text{O}^0]$ configurations must be included. The states are these:

$|I\rangle$, with both O^0 and O^{2-} in singlet states. This state involves the transfer of an electron from the 2σ state on one site to the 2σ state on the other; there is no corresponding triplet excitation.

$$\text{Excitation energy } E_I \equiv [{}^1E_0 + {}^1E_2 - 2{}^2E_1] = 6.87 \text{ eV}, \quad (5.1)$$

where the energies in table 1 for an ion with charge Q and spin S have been written ${}^{2S+1}E_{-Q}$.

$|II\rangle$, with O^0 in a singlet state and O^{2-} in a triplet state. This state involves the transfer from a 2σ orbital on one site to a 3σ orbital on the other. The corresponding singlet excitation is not bound and has been omitted.

$$\text{Excitation energy } E_{II} \equiv [{}^1E_0 + {}^3E_2 - 2{}^2E_1] = 9.50 \text{ eV}. \quad (5.2)$$

We have also looked at other excited states in which $2s$ electrons are transferred to 2σ and 3σ states. These excitations require over 20 eV and have been ignored.

5.2. Expression for the singlet–triplet splitting

The matrix elements for the singlet and triplet admixtures differ in addition to the different excitation energies. We shall consider the matrix elements δ_S and δ_T in § 5.3; here we want to give a basic expression for the singlet–triplet splitting and to indicate its implications.

Since we must include both $[\text{O}^0 \text{O}^{2-}]$ and $[\text{O}^{2-} \text{O}^0]$ configurations, the singlet and triplet are lowered in energy by terms $-2\delta_S^2/E_I$ and $-2\delta_T^2/E_{II}$ respectively. In all, the singlet lies beneath the triplet by

$$\Delta = \Delta_0 + 2\delta_S^2/E_I - 2\delta_T^2/E_{II}. \quad (5.3)$$

It is important that E_I and E_{II} are comparable, for then modest differences in δ_S and δ_T can invert the order of the levels. In particular, the sign of Δ can easily vary from crystal to crystal.

5.3. Matrix elements

A separate calculation of the matrix elements is needed. There are two possible levels of detail. In the first, which we adopt, we concentrate entirely on the one-electron functions between which an electron is exchanged on going from $[\text{O}^- \text{O}^-]$ to $[\text{O}^0 \text{O}^{2-}]$ or $[\text{O}^{2-} \text{O}^0]$. Thus the matrix elements reduce to a sum of expressions primarily involving the 2σ orbitals for the singlet excitations and 2σ and 3σ in the triplet case. A second level of detail (cf Rimmer 1964, who gives explicit expressions in another context) would include corrections because the other orbitals are slightly modified after the transfer of the electron. It would be inconsistent (as well as laborious) for us to use the fuller approach, because our calculations of Δ_0 , the splitting without configuration admixture, ignored corresponding details.

Suppose we have an approximate eigenstate $|0\rangle$, consisting of a single configuration (i.e. a single Slater determinant). The admixture of a second configuration $|1\rangle$ gives a wavefunction:

$$|\tilde{0}\rangle = N(|0\rangle + A|1\rangle) \quad (5.4)$$

where A is given by

$$A = -\delta/E_{10} \quad (5.5)$$

and the change in energy is

$$\Delta\epsilon = -\delta^2/E_{10}. \quad (5.6)$$

Here N is a normalizing factor, and δ and E_{10} are given by

$$\delta = \langle 0|\mathcal{H}|1\rangle - \langle 0|1\rangle \langle 0|\mathcal{H}|0\rangle, \quad (5.7)$$

$$E_{10} = \langle 1|\mathcal{H}|1\rangle - \langle 0|\mathcal{H}|0\rangle, \quad (5.8)$$

where \mathcal{H} is the total Hamiltonian. The values for E_{10} were given earlier in this section; we are now concerned with δ . Two results are useful. First, if two configurations differ by one orbital only, and if the order of the orbitals in the two determinants correspond, then (e.g. Griffith 1961)

$$\langle 0|\mathcal{H}|1\rangle = \langle k_0|\mathcal{H}_1|k_1\rangle + \sum_{i \neq k} [\langle k_0 i k_1 i\rangle - \langle i k_0 k_1 i\rangle]. \quad (5.9)$$

Here \mathcal{H}_1 is the one-electron part of the total Hamiltonian; the electron-electron interactions are included in the two-electron elements $\langle ab cd\rangle$ where the i are assumed unaffected by the electron transfer from $|k_0\rangle$ to $|k_1\rangle$. The second point is that our basis orbitals have a small but finite overlap. To the desired degree, orthogonality can be ensured by the well-known modification

$$|k_0\rangle \rightarrow |k_0\rangle - \frac{1}{2}\langle k_1|k_0\rangle |k_1\rangle \quad (5.10a)$$

and

$$|k_1\rangle \rightarrow |k_1\rangle - \frac{1}{2}\langle k_0|k_1\rangle |k_0\rangle. \quad (5.10b)$$

The contributions to the matrix element δ divide into two main parts: those involving the two oxygen ions, and those from the rest of the crystal. The dominant terms prove to be those from the rest of the crystal, outside the two oxygen ions. This part is difficult to obtain exactly, for it involves three-centre integrals which cause problems even if we represent the terms in the Hamiltonian (\mathcal{H}'' say) by a sum of point-charge contributions. However, a rough estimate (actually exact for Gaussian functions) can be found in terms of the Madelung potential, corrected by omitting the contributions from the vacancy site and the two oxygen ions already treated. In the $\langle 0|\mathcal{H}''|0\rangle$ term, the potential at an oxygen site is needed, i.e. $(-\alpha + \frac{1}{2})Z e^2/a$, where α is the Madelung constant and $Z = 2$ is the ionic charge. For the $\langle 1|\mathcal{H}''|0\rangle$ element, we assume the point-ion potential varies slowly in the region of the maximum overlap, so that it can be factored out of the matrix element. The potential at the cation vacancy is $(\alpha - 2)Z e^2/a$. In all, we have

$$\langle 0|\mathcal{H}''|1\rangle - \langle 0|1\rangle \langle 0|\mathcal{H}''|0\rangle \simeq \frac{Z e^2}{a} \langle 0|1\rangle (2\alpha - \frac{5}{2}) \quad (5.11)$$

where α is 1.7476. The overlap $\langle 0^0 2\sigma|O^{2-} 2\sigma\rangle$ is 0.0105, so that this contribution to the singlet matrix element is $\delta_S'' = 0.0715$ eV. By contrast, the overlap $\langle O^0 2\sigma|O^{2-} 3\sigma\rangle$ is much smaller, being only 0.00171. Despite the wider spread of the 3σ orbital, the overlap is less and the contribution to the triplet matrix element is $\delta_T'' = 0.0116$ eV. The part from the oxygen ions alone is straightforward, involving two-centre integrals at most. We denote this part of the Hamiltonian by \mathcal{H}' . These terms have been calculated using the MIDAT program of F R A Hopgood, based on an earlier program of Corbato and Switendick. For simplicity, the integrals in this much smaller part were calculated for a

O^-O^- system rather than $O^{2-}O^0$. Thus for the admixture of $|I\rangle$ we find

$$\langle 0|\mathcal{H}'|1\rangle = 0.0098 \text{ eV} \quad (5.12a)$$

and

$$-\langle 0|1\rangle \langle 0|\mathcal{H}'|0\rangle = 0.0280 \text{ eV}. \quad (5.12b)$$

The total matrix element for the singlet admixture is the sum of contributions (5.11) and (5.12), $\delta_s = 0.109 \text{ eV}$. This admixture leads to a lowering of the singlet state by

$$2\delta_s^2/E_1 = 27.9 \text{ cm}^{-1}. \quad (5.13)$$

By contrast, the triplet is negligibly lowered ($2\delta_T^2/E_{II} < 1 \text{ cm}^{-1}$). This is partly a result of the small overlap and partly because δ_T' and δ_T'' prove to have opposite signs, giving some cancellation. However, the smallness of δ_T is clearly a special feature of MgO, and the detailed results suggest that in other systems δ_s and δ_T could easily be comparable.

5.4. Comparison with experiment

Collecting together the results of (4.4), (5.3) and (5.13), the singlet state should be lowest in MgO by

$$\Delta = 30.7 \text{ cm}^{-1}, \quad (5.14)$$

a singlet-triplet splitting which is dominated by configuration-admixture of higher singlet states.

The splitting has not yet been measured accurately, but R T Cox and G Rius (private communication) have shown that the triplet state lies above the singlet in MgO, and that the population of the triplet state becomes negligible as one lowers the sample temperature from 20 K to 6 K. Both these results agree with our prediction (5.14).

A second point to check concerns D , the zero-field splitting in the triplet state. Experiment gives a value very close to that expected from dipole-dipole interactions within $[O^-O^-]$. If there are admixtures of $[O^0O^{2-}]$, then some changes will result. We find that the admixture leads to a negligible change in D . The change has the form $(\delta_T/E_{II})^2\rho$, where δ_T/E_{II} is a measure of the admixture and ρ is the spin-spin interaction within the triplet O^{2-} . Since δ_T is very small ($\delta_T/E_{II} < 10^{-4}$) and ρ (whilst not accurately known) will be a few cm^{-1} at most, the change in D is less than 10^{-7} cm^{-1} . This should be compared with the experimental value of 0.021 cm^{-1} (Henderson and Wertz 1968).

6. Conclusions

We have examined the effects of a weak configuration admixture of $[O^0O^{2-}]$ and $[O^{2-}O^0]$ into the dominant $[O^-O^-]$ configuration in MgO. Our conclusion is that the configuration admixture dominates in the singlet-triplet splitting, giving a value consistent with experiment both in sign and magnitude. The degree of admixture is also consistent with the spin-resonance data for the triplet.

The results for MgO have an important implication for other crystals, for δ_T is small because of special cancellations associated with the precise form of the 3σ wavefunction for O^{2-} . In other cases, δ_s and δ_T could easily be comparable. Since the excitation energies E_1 and E_{II} are comparable, it is perfectly possible that the triplet should be the

ground state in some crystals. However, the singlet-triplet splitting should be small in any case, allowing an appreciable population of the triplet state, even when the singlet lies lowest.

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