

Theory of F -Center g Values in Divalent Compounds*

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Positive g shifts in the ESR spectra of F centers in some alkaline-earth compounds have been reported by Wertz, Orton, and Auzins, contrary to the theory of Adrian. A model for the F center in divalent compounds is proposed which involves an admixture of a charge-transfer configuration consisting of a hole trapped on an anion adjacent to an F' center. It is shown that the charge-transfer configuration makes a positive contribution to the g shift. Values of a configuration-mixing parameter C^2 inferred from the ESR data are compared with values calculated from a simplified model. Qualitative agreement tends to support the proposed explanation for positive g shifts, but detailed quantitative agreement would require a more elaborate calculation.

I. INTRODUCTION

ALKALI halides with F centers have been studied by a variety of experimental techniques, including electron-spin resonance (ESR).^{1,2,3} These investigations have served to establish the de Boer model⁴ of the F center: an electron trapped at an anion vacancy. The ESR absorption spectrum consists of a single broad line, in some cases with partially resolved structure, with a g value slightly different from the free-electron value. For all of the alkali halides which have been studied by ESR, the g shift is found to be negative (we will accept the value of Holton and Blum⁵ for LiF); for a summary of the experimental values, see Markham.⁶ These results are consistent with the theory of Adrian,⁷ which attributes the g shift to spin-orbit interaction in the vicinity of nearby nuclei, and which predicts only negative g shifts. Theory and experiment are in fair quantitative agreement as well.

More recently, Wertz, Orton, and Auzins⁸ have studied the ESR spectra of F centers in alkaline-earth oxides, sulfides, and selenides. The g values they reported are listed in Table I.⁹ These data are anomalous in that the g shift is positive or zero in seven of the 12 compounds, in contrast to the results for alkali halides and contrary to theory.⁷ In order to account for these results, Wertz *et al.*⁸ have adapted a theory of Kahn and Kittel¹⁰ in which the F -center electron is thought to

reside in excited orbitals on neighboring ions; they attribute the positive g shift to the effect of d orbitals on next-nearest-neighbor anions. However, the predicted positive g shift is much too small to account for the data.

In the present paper an alternative theory is developed to account for the positive g shifts. The mechanism involves admixture of a charge-transfer configuration, and is essentially identical with that proposed qualitatively by Kemp and Neeley.¹¹ States of O^{1-} , S^{1-} , and Se^{1-} are involved, rather than those of O^{3-} , S^{3-} , and Se^{3-} as in Wertz's theory.

In Sec. II an expression is derived for the g shift which includes configuration mixing. This expression is used to infer values of the mixing parameter from the data in Sec. III, which also includes a calculation of F -center wave functions and energy levels. In Sec. IV an idealized model with an effective one-electron Hamiltonian provides the basis for an *a priori* determination of the configuration-mixing parameter; the calculated values are then compared with those inferred from data. Section IV includes a calculation of ground-state energies and wave functions for F' centers. Slater atomic units are used throughout; i.e., energies are in rydbergs and lengths are in Bohr radii.

II. CONFIGURATION MIXING

We propose to explain the positive g shifts for F centers in divalent compounds by postulating that the F -center ground state is a superposition of two configurations, as indicated in Fig. 1. Configuration A just corresponds to the de Boer model, with one electron trapped at an anion vacancy. In the charge-transfer configuration B, one electron is transferred to the vacancy from a next-nearest-neighbor anion; this configuration can be described alternatively as a hole trapped at an anion

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¹ F. Seitz, *Rev. Mod. Phys.* **26**, 7 (1954).

² H. Pick, *Nuovo Cimento Suppl.* **7**, 498 (1958).

³ J. J. Markham, *F Centers in Alkali Halides* (Academic Press Inc., New York, 1966).

⁴ J. H. de Boer, *Rec. Trav. Chim.* **56**, 301 (1937).

⁵ W. C. Holton and H. Blum, *Phys. Rev.* **125**, 89 (1962).

⁶ Reference 3, p. 261.

⁷ F. J. Adrian, *Phys. Rev.* **107**, 488 (1957).

⁸ J. E. Wertz, J. W. Orton, and P. Auzins, *Discussions Faraday Soc.* **31**, 140 (1961).

⁹ J. W. Carson, D. F. Holcomb, and H. Ruchardt, *J. Phys. Chem. Solids* **12**, 66 (1959).

¹⁰ A. H. Kahn and C. Kittel, *Phys. Rev.* **89**, 315 (1953).

¹¹ J. C. Kemp and V. I. Neeley, *Phys. Rev.* **132**, 215 (1963).

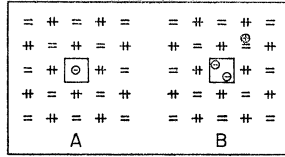


FIG. 1. Configurations for the F center in divalent compounds. Configuration A corresponds to the de Boer model. The charge-transfer configuration B makes a positive contribution to the g shift.

adjacent to an F' center. It can be seen that the two configurations are electrostatically equivalent in that they involve the same distribution of charges among lattice points; thus it is reasonable to expect them to be of comparable stability. The foregoing conclusion applies only to divalent compounds, since the analog of configuration B would be energetically unfavorable in alkali halides. It follows that the present theory is specific to divalent compounds, as it should be. The relative stability of the two configurations and the mechanism for their mixing is treated in more detail in Sec. IV. Interaction with charge-transfer configurations has been employed by Knox¹² in connection with excited states of Tl^+ activators in alkali-halide phosphors. Slater¹³ gives a general discussion of configuration mixing in the Heitler-London scheme.

The derivation of the g shift proceeds in close analogy with that of Adrian⁷; however, the introduction of configuration mixing necessitates the employment of many-electron wave functions. The wave function for configuration A with positive spin projection is approximated by

$$\psi_{A\uparrow} = \alpha \phi_{F\uparrow}(0) \prod_i \phi_i(i), \quad (1)$$

where α is the antisymmetrizer, the product extends over all occupied ion orbitals in the crystal, and $\phi_{F\uparrow}$ is a vacancy-centered spin orbital with positive spin projection. The occupied ion orbitals on the same and different centers are assumed to be orthogonal; however, the more diffuse vacancy-centered orbital must be explicitly orthogonalized to the occupied ion orbitals. Thus we will later introduce a spherically symmetrical trial function χ_F to approximate the vacancy-centered orbital; ϕ_F will then be given by

$$\phi_F = N(\chi_F - \sum_i \langle F|i\rangle \phi_i), \quad (2a)$$

$$N = (1 - \sum_i \langle F|i\rangle^2)^{-1/2}, \quad (2b)$$

where $\langle F|i\rangle$ denotes the overlap integral between χ_F and ϕ_i . The wave function for a charge-transfer configuration is of the form

$$\psi_{j\uparrow} = \alpha \phi_{F\uparrow}(0) \phi_{F\downarrow}(j) \prod_{i \neq j} \phi_i(i). \quad (3)$$

When spin-orbit interaction is neglected, the ground-state wave function transforms like Γ_1 of O_h . Thus the appropriate wave function for configuration B is the fully symmetrical combination

$$\psi_{B\uparrow} = (12)^{-1/2} \sum_{j=1}^{12} \psi_{j\uparrow}, \quad (4)$$

where we have assumed that the ion orbitals are numbered such that $\phi_1 - \phi_{12}$ are the $p\sigma$ valence orbitals with negative spin projection on each of the 12 next-nearest-neighbor anions. With configuration mixing, the F -center ground-state wave function is

$$\psi_{\uparrow} = (1 - C^2)^{1/2} \psi_{A\uparrow} + C \psi_{B\uparrow}. \quad (5)$$

The determination of the mixing parameter C will be considered in subsequent sections.

The g shift arises from the combined effect of the orbital Zeeman interaction and spin-orbit interaction at nearby ions in second-order perturbation theory. The problem of calculating g shifts arising from several force centers has been considered by Adrian,⁷ and more formally by Slichter,¹⁴ by Stone,¹⁵ and by Casselman and Markham.¹⁶ The development of Stone¹⁵ is especially useful in the present context. One begins with a gauge-invariant form of the perturbing Hamiltonian derived from the Dirac equation

$$H' = H_1 + H_2, \quad (6a)$$

$$H_1 = \sum_i (g_e \alpha^2 \mathbf{H} \cdot \mathbf{S}_i + \alpha^2 \mathbf{H} \cdot \mathbf{L}_i + \sum_{\gamma} \xi_{\gamma i} \mathbf{L}_{\gamma i} \cdot \mathbf{S}_i), \quad (6b)$$

$$H_2 = \frac{1}{2} \alpha^2 \sum_{\gamma} \sum_i \xi_{\gamma i} (\mathbf{S}_i \times \mathbf{r}_{\gamma i}) \cdot (\mathbf{H} \times \mathbf{d}_i) + \frac{1}{4} \alpha^4 \sum_i (\mathbf{H} \times \mathbf{d}_i), \quad (6c)$$

$$\xi_{\gamma i} = (\alpha^2 / 2r_{\gamma i}) \partial U_{\gamma i} / \partial r_{\gamma i}. \quad (6d)$$

In Eqs. (6), which are expressed in Slater atomic units, \mathbf{L}_i and \mathbf{d}_i are, respectively, the orbital angular momentum and the position of the i th electron with respect to an arbitrary origin, while $\mathbf{L}_{\gamma i}$ and $\mathbf{r}_{\gamma i}$ are the same quantities with respect to the nucleus of ion γ . The function $U_{\gamma i} [= U_{\gamma}(r_{\gamma i})]$ is an effective electrostatic potential due to ion γ , and g_e is the free-electron g value, 2.0023. The term H_1 is of order α^2 , where α is the fine-structure constant, and includes the usual Zeeman interaction and spin-orbit interactions. The term H_2 is of order α^4 and is required for gauge invariance.

The ground state is orbitally nondegenerate, but has a $(2S+1)$ -fold spin degeneracy ($S = \frac{1}{2}$ in the case of the F center). One can proceed by employing the modified second-order degenerate perturbation theory of Pryce¹⁷; then, to second order, the perturbed energy levels are the eigenvalues of the following operator, which operates only within the degenerate ground manifold:

$$\tilde{H} = E_0 + P_0 H_1 P_0 + P_0 H_2 P_0 - \sum_n' \frac{P_0 H_1 P_n H_1 P_0}{E_n - E_0}, \quad (7a)$$

$$P_n = \sum_m |n, m\rangle \langle n, m|, \quad (7b)$$

where P_n is a projection operator for the n th degenerate

¹³ J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I, Chap. 4.

¹⁴ C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, New York, 1963), p. 203.

¹⁵ A. J. Stone, Proc. Roy. Soc. (London) A271, 424 (1963).

¹⁶ T. N. Casselman and J. J. Markham, J. Chem. Phys. 42, 4178 (1965).

¹⁷ M. H. L. Pryce, Proc. Phys. Soc. (London) A63, 25 (1950).

¹² R. S. Knox, Phys. Rev. 115, 1095 (1959).

manifold, and the sum over m is over the $2S+1$ spin projections. The g values are obtained by retaining only those terms in Eq. (7a) which are bilinear in \mathbf{H} and \mathbf{S} . Only the first term in H_1 contributes in first order, and yields the free-electron g value, g_0 . The terms which contribute to the g shift are

$$\alpha^2 \mathbf{H} \cdot \Delta \mathbf{g} \cdot \mathbf{S} = \sum_{\gamma} \left[(\alpha^2/2) \sum_i P_0 \xi_{\gamma i} (\mathbf{S}_i \times \mathbf{r}_{\gamma i}) \cdot (\mathbf{H} \times \mathbf{d}_i) P_0 - 2\alpha^2 \sum'_n \sum_i \sum_j \frac{P_0 \mathbf{H} \cdot \mathbf{L}_i P_n \xi_{\gamma j} \mathbf{L}_{\gamma j} \cdot \mathbf{S}_j P_0}{E_n - E_0} \right]. \quad (8)$$

Now each term in the sum over γ must be independently gauge-invariant, since it includes all contributions of order α^4 , and the form of ξ_{γ} is arbitrary. Thus, Eq. (8) can be simplified by choosing the nucleus of ion γ as the origin in each term; i.e., \mathbf{L}_i is replaced by $\mathbf{L}_{\gamma i}$ and \mathbf{d}_i by $\mathbf{r}_{\gamma i}$. Up to this point we have followed Stone.¹⁵ In order to achieve a considerable further simplification, we now follow Adrian⁷ in employing the closure approximation: The energy denominator $E_n - E_0$ is replaced by an average value ΔE , which we identify with the F -band energy; then the prime can be dropped from the sum over n in Eq. (8) by virtue of the fact that $P_0 \mathbf{L} P_0$ vanishes, and the sum over intermediate states can be eliminated by means of the identity for projection operators,

$$\sum_n P_n = 1. \quad (9)$$

Finally, we calculate the expectation value of both sides of Eq. (8) in the state of maximum spin projection, $|0, S\rangle$, assuming quantization in the principal axis system of $\Delta \mathbf{g}$, and obtain

$$\Delta g_{zz} = \sum_{\gamma} [(2S)^{-1} \sum_i \langle 0, S | \xi_{\gamma i} (x_{\gamma i}^2 + y_{\gamma i}^2) S_{zi} | 0, S \rangle - 2(S\Delta E)^{-1} \sum_i \sum_j \langle 0, S | \xi_{\gamma j} L_{zi} L_{zj} S_{zj} | 0, S \rangle]. \quad (10)$$

The two terms of Eq. (10) are comparable except for the multiplying factors. However, in the present problem we have $\Delta E \ll 4$ Ry, and consequently the first term may be safely neglected by comparison with the second.

In the case of the F center, we can identify Δg_{zz} with Δg by virtue of cubic symmetry, and we also have $S = \frac{1}{2}$ and $|0, S\rangle = \psi_{\uparrow}$. Thus, after dropping the first term, Eq. (10) becomes

$$\Delta g = -(4/\Delta E) \sum_{\gamma} \sum_i \sum_j \langle \psi_{\uparrow} | \xi_{\gamma j} L_{zi} L_{zj} S_{zj} | \psi_{\uparrow} \rangle. \quad (11)$$

Equation (11) can then be evaluated by using Eqs. (1)–(5) for ψ_{\uparrow} . Since Eq. (11) involves matrix elements of a two-electron operator, antisymmetrization plays an essential role. Note that one can employ the simplifications which have been derived for the evaluation of matrix elements of two-electron operators between Slater determinants. In addition, all multicenter integrals involving the highly localized function ξ_{γ} are neglected. After considerable manipulation, one

obtains for the g shift

$$\Delta g = -(1 - C^2) N^2 \sum_{\gamma} (2|\lambda_{\gamma}|/\Delta E) \langle F | p\sigma_{\gamma} \rangle^2 \times \langle p\sigma_{\gamma} | L_z^2 | p\sigma_{\gamma} \rangle + \frac{1}{2} C^2 \sum_{\beta} (2|\lambda_{\beta}|/\Delta E) \times \langle p\sigma_{\beta} | L_z^2 | p\sigma_{\beta} \rangle. \quad (12)$$

In Eq. (12) we have adopted the approximations of Blumberg and Das¹⁸ in neglecting $\langle F | i \rangle$ for inner shells and in identifying the expectation value of ξ_{γ} with $|\lambda_{\gamma}|$, where λ_{γ} is the spin-orbit coupling constant of the ion less one electron (i.e., of the $1-$ state of the anion and the $3+$ state of the cation). The orbitals $|p\sigma\rangle$ are in the outermost occupied shell, and the sum over γ extends over all ions while the sum over β extends only over the 12 next-nearest-neighbor anions.

The first term on the right-hand side of Eq. (12) is just the g shift predicted by Adrian⁷ and by Blumberg and Das,¹⁸ diminished by the factor $(1 - C^2)$, and is inherently negative; we recognize this term as the contribution of configuration A. The second term is the contribution of configuration B and is inherently positive. The signs of these terms can be understood as follows: In configuration A, the unpaired electron moves outside closed shells in the vicinity of an ion, and thus occupies a less-than-half-filled shell. In configuration B, on the other hand, the unpaired electron occupies the more-than-half-filled valence shell of the anion. Thus configuration mixing can account for the required positive contribution to the g shift.

Equation (12) must apply to the alkali halides as well. However, in that case, one would expect configuration B to be very much higher in energy than configuration A, and consequently the mixing parameter C^2 should be negligibly small. Thus for alkali halides the present theory reduces to the previous theory of Adrian⁷ and of Blumberg and Das,¹⁴ and predicts only negative g shifts, in agreement with experiment.⁶

III. INFERENCE OF MIXING PARAMETER FROM DATA

The theoretical expansion for the g shift, Eq. (12), can be used together with the data of Wertz *et al.*⁸ listed in Table I to infer values of the mixing parameter C^2 . Equation (12) can be expressed alternatively as

$$\Delta g = (1 - C^2) \Delta g_A + C^2 \Delta g_B, \quad (13)$$

where Δg_A is the negative g shift appropriate to configuration A alone and Δg_B is the positive g shift for configuration B alone. It follows from Eq. (13) that C^2 is given by

$$C^2 = (\Delta g - \Delta g_A) / (\Delta g_B - \Delta g_A). \quad (14)$$

Theoretical expressions for Δg_A and Δg_B are obtained by comparison of Eqs. (12) and (13). If the sum over γ is restricted to nearest and next-nearest neighbors,

¹⁸ W. E. Blumberg and T. P. Das, Phys. Rev. **110**, 647 (1958).

TABLE I. g values and g shifts for F centers in divalent compounds [after Wertz *et al.* (Ref. 8)].

Compound	g	$\Delta g (= g - g_0)$
MgO	2.0023	0.0000
CaO	2.0001	-0.0022
SrO	1.9846	-0.0177
BaO	1.936 ^a	-0.0663
MgS	2.0062	+0.0039
CaS	2.0033	+0.0010
SrS	2.0036	+0.0013
BaS	1.9641	-0.0382
MgSe	2.0035	+0.0012
CaSe	2.0030	+0.0007
SrSe	2.0032	+0.0009
BaSe	1.9670	-0.0353

^a Value taken from J. W. Carson *et al.* (Ref. 9).

matrix elements of L_z^2 are readily evaluated and one obtains

$$\Delta g_A = -(8N^2/\Delta E)(|\lambda_c|\langle F|p\sigma\rangle_c^2 + 2|\lambda_a|\langle F|p\sigma\rangle_a^2), \quad (15a)$$

$$\Delta g_B = 4|\lambda_a|/3\Delta E, \quad (15b)$$

where subscripts c and a refer to cation and anion, respectively. The various ingredients required for the evaluation of these formulas will now be taken up in sequence.

A. Vacancy-Centered Orbital and F -Band Energy

A number of investigators have derived one-electron F -center wave functions and F -band energies for alkali halides.^{3,19} Kemp and Neeley¹¹ have treated the F center in MgO, using linear combinations of atomic orbitals (LCAO) as trial functions and the point-ion potential of Gourary and Adrian.²⁰ For the present purpose, it is desirable to employ a simpler trial function in order to facilitate the evaluation of two-center integrals; such simple trial functions were also employed by Wood *et al.*^{21,22} Accordingly, the trial functions for the ground state and first excited state were taken to be, respectively,

$$\chi_F = (\gamma^3/7\pi)^{1/2}(1+\gamma r)\exp(-\gamma r), \quad (16a)$$

$$\chi_{F'} = (\frac{4}{3}\alpha^5)^{1/2}r\exp(-\alpha r)Y_1^m(\theta, \phi). \quad (16b)$$

The energies were calculated from the point-ion potential of Gourary and Adrian²⁰; this potential can be expanded in spherical harmonics, and only the spherically symmetrical part contributes with the chosen trial functions. The parameter γ was varied to minimize the energy of the ground state, and the resulting expression was inverted to obtain the nearest-neighbor distance b as a function of γ in closed form; a similar procedure for

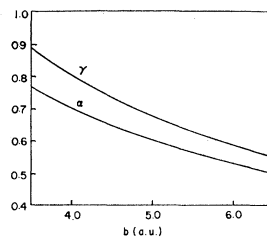


FIG. 2. Exponential parameters for F center wave functions defined by Eq. (16), versus nearest-neighbor distance b .

the excited state yields b as a function of α . The parameters γ and α are plotted as functions of b in Fig. 2, and the energies of the ground and first excited states are plotted versus b in Fig. 3, which also shows the energy difference ΔE , identified with the F -band energy. For MgO, with $b=3.96$ a.u., the ground- and excited-state energies are, respectively, $E_F = -1.339$ and $E_{F'} = -0.926$, with $\Delta E = 0.413$. The corresponding values obtained by Kemp and Neeley¹¹ for MgO are $E_F = -1.408$, $E_{F'} = -1.060$, and $\Delta E = 0.348$. Thus the trial functions of Eqs. (15) are inferior to theirs, as expected, but should be adequate for the present purpose. The experimental²³⁻²⁵ F -band energy is $\Delta E = 0.365$, which lies between these values.

Note that the F -band energy ΔE is calculated here from configuration A alone, and that the vacancy-centered trial function is used without orthogonalization to ion-core orbitals. Although configuration mixing is essential to the determination of g values, it is not expected to have a radical effect on the F -band energy. In any event, since ΔE is employed only as an approximate energy denominator, a more refined calculation is not justified.

B. Ion-Core Orbitals

Both valence p and s orbitals for the divalent anions are required in the evaluation of Eq. (15a); the former appear explicitly in the overlap integral $\langle F|p\sigma\rangle_a$, and both are needed for the evaluation of the normalization constant N^2 . Apparently, the only calculation of divalent anion orbitals available²⁶ is that of Watson²⁶ for O^{2-} . These orbitals are expressed as linear combina-

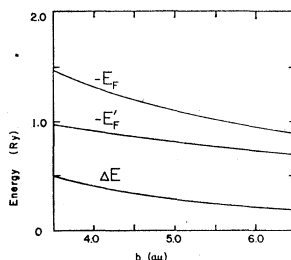


FIG. 3. F center energy levels versus nearest-neighbor distance b , for the two lowest bound states. $\Delta E (= E_{F'} - E_F)$ corresponds to the F band.

¹⁹ B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. X, pp. 127-247.

²⁰ B. S. Gourary and F. J. Adrian, *Phys. Rev.* **105**, 1180 (1957).

²¹ R. F. Wood and J. Koringa, *Phys. Rev.* **123**, 1138 (1961).

²² R. F. Wood and H. W. Joy, *Phys. Rev.* **136**, A451 (1964).

²³ J. E. Wertz, G. S. Saville, L. Hall, and P. Auzins, *Proc. Brit. Ceram. Soc.* **1**, 59 (1964).

²⁴ B. Henderson and R. D. King, *Phil. Mag.* **13**, 1149 (1966).

²⁵ W. A. Sibley and Y. Chen, *Bull. Am. Phys. Soc.* **12**, 411 (1967).

²⁶ R. E. Watson, *Phys. Rev.* **111**, 1108 (1958).

TABLE II. Exponential parameters for anion orbitals (from Watson, Ref. 26).

	κ_1	κ_2	κ_3
$2s$	1.490	2.803	1.776
$2p$	0.714	3.412	1.384

tions of Slater orbitals²⁷ and are obtained from an analytic Hartree-Fock (HF) solution for O^{2-} stabilized by a potential well produced by a sphere of charge +1 placed at the ionic radius, 2.66 a.u. No such orbitals are available for S^{2-} and Se^{2-} ; however, it can be argued that since the O^{2-} valence orbitals are relatively diffuse and are largely excluded from the ion core by virtue of the Pauli principle, the outer portions of the valence orbitals for S^{2-} and Se^{2-} should be similar to those for O^{2-} . Thus the O^{2-} orbitals of Watson were used for all anions. However, only the outer part of the $2s$ orbital was employed since the inner loop would make a small contribution to the overlap integral and in any case would be appropriate only to O^{2-} . The wave functions employed were

$$|s\rangle_a = 0.0426\eta(2s, \kappa_1) + 0.4090\eta(2s, \kappa_2) + 0.6085\eta(2s, \kappa_3), \quad (17a)$$

$$|p\sigma\rangle_a = 0.2335\eta(2p0, \kappa_1) + 0.3524\eta(2p0, \kappa_2) + 0.5734\eta(2p0, \kappa_3), \quad (17b)$$

where $\eta(nlm, \kappa_i)$ is a normalized Slater orbital of the form

$$\eta(nlm, \kappa_i) = [(2\kappa_i)^{2n+1}/(2n)!]^{1/2} r^{n-1} \times \exp(-\kappa_i r) Y_l^m(\theta, \phi). \quad (18)$$

The parameters κ_i are listed in Table II.

Single, normalized Slater orbitals of the form of Eq. (14) were used for the valence s and p orbitals on the cations, with $n = 2, 3, 4,$ and 5 for $Mg^{2+}, Ca^{2+}, Sr^{2+},$ and Ba^{2+} , respectively. The exponential parameters κ for Mg and Ca were obtained by application of Slater's rules.²⁷ In the case of Sr and Ba, the parameters were obtained from Hartree-Fock-Slater (HFS) orbitals for the neutral atoms calculated numerically by Herman and Skillman.²⁸ The orbitals in question are closed-shell orbitals in the neutral atoms, and the shielding effect of the outer electrons was neglected. The parameters were determined by the requirement that the maximum of the radial part of the Slater orbital coincide with the maximum of the outer lobe of the HFS orbital. The

TABLE III. Exponential parameters κ for cation orbitals. $n = 2, 3, 4,$ and 5 for $Mg^{2+}, Ca^{2+}, Sr^{2+},$ and Ba^{2+} , respectively.

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
ns	3.92	2.92	3.34	3.31
np	3.92	2.92	3.07	3.03

²⁷ J. C. Slater, Phys. Rev. **36**, 57 (1930).

²⁸ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

resulting parameters are listed in Table III. With these parameters, the Slater orbitals were found to agree quite well with the outer portions of the HFS orbitals. Orthogonalization to inner orbitals was neglected, since it was not expected to be important in two-center integrals.

C. Overlap Integrals

The ground-state, vacancy-centered orbital χ_F of Eq. (16a) can be expressed as a sum of two Slater orbitals,

$$\chi_F = [\eta(1s, \gamma) + \sqrt{3}\eta(2s, \gamma)]/\sqrt{7}. \quad (19)$$

Thus the required overlap integrals involve only Slater orbitals, and can be evaluated in closed form in spherical coordinates. The overlap integrals were calculated by the formulas of Lofthus,²⁹ and are listed in Table IV.

TABLE IV. Overlap integrals and normalization constants.

Compound	$\langle F p\sigma\rangle_c$	$\langle F s\rangle_c$	$\langle F p\sigma\rangle_a$	$\langle F s\rangle_a$	N^2
MgO	0.0296	0.0843	0.103	0.0123	1.214
CaO	0.0783	0.152	0.0865	0.0090	1.363
SrO	0.0930	0.148	0.0780	0.0076	1.347
BaO	0.116	0.168	0.0690	0.0064	1.447
MgS	0.0179	0.0587	0.0770	0.0075	1.104
CaS	0.0531	0.114	0.0662	0.0060	1.174
SrS	0.0690	0.119	0.0626	0.0056	1.192
BaS	0.0855	0.134	0.0542	0.0046	1.231
MgSe	0.0160	0.0540	0.0710	0.0067	1.088
CaSe	0.0485	0.107	0.0619	0.0056	1.149
SrSe	0.0580	0.108	0.0562	0.0049	1.146
BaSe	0.0776	0.124	0.0500	0.0042	1.189

Also shown is the normalization constant N^2 , defined by Eq. (2b). It is assumed that only overlap integrals involving valence s and p orbitals on nearest- and next-nearest-neighbor ions make a significant contribution to N^2 ; thus the values of N^2 listed in Table IV were computed by

$$N^2 = (1 - 6\langle F|p\sigma\rangle_c^2 - 6\langle F|s\rangle_c^2 - 12\langle F|p\sigma\rangle_a^2 - 12\langle F|s\rangle_a^2)^{-1}. \quad (20)$$

D. Spin-Orbit Coupling Constants

The only remaining quantities required for the evaluation of Eqs. (15) are $|\lambda_c|$ and $|\lambda_a|$, the spin-orbit coupling constants for the $3+$ charge state of the cation and the $1-$ charge state of the anion, respectively. Values of $|\lambda_c|$ were inferred directly from spectroscopic data,³⁰ and are listed in Table V. Also included in

TABLE V. Spin-orbit-coupling constants, in rydbergs.

Mg^{3+}	Ca^{3+}	Sr^{3+}	Ba^{3+}	O^-	S^-	Se^-
0.01352	0.01892	0.05911	0.10832	0.00123	0.00337	0.01458

²⁹ A. Loftus, Mol. Phys. **5**, 105 (1962).

³⁰ C. E. Moore, Natl. Bur. Std. U. S. Circ. No. **467** (1949).

Table V are values of $|\lambda_a|$ derived by extrapolation from an isoelectronic sequence.

E. Analysis of Data

The quantities listed in Tables II-V and Fig. 3 were used to evaluate Δg_A and Δg_B from Eqs. (15). Values of the mixing parameter C^2 were then inferred from Eq. (14) and the g -shift data listed in Table I. The quantities Δg_A , Δg_B , and C^2 are listed in Table VI, which also in-

TABLE VI. g -shift contributions Δg_A and Δg_B and mixing parameter C^2 inferred from data (Ref. 8). Also listed is the neighbor distance b (Ref. 31).

Compound	$b(\text{a.u.})$	Δg_A	Δg_B	C^2
MgO	3.96	-0.0007	0.0029	0.195
CaO	4.52	-0.0043	0.0049	0.219
SrO	4.85	-0.0185	0.0054	0.033
BaO	5.21	-0.0626	0.0060	
MgS	4.88	-0.0019	0.0148	0.347
CaS	5.35	-0.0030	0.0173	0.197
SrS	5.52	-0.0119	0.0182	0.438
BaS	5.98	-0.0370	0.0208	
MgSe	5.13	-0.0047	0.0696	0.079
CaSe	5.56	-0.0059	0.0799	0.077
SrSe	5.86	-0.0119	0.0870	0.129
BaSe	6.24	-0.0345	0.0972	

cludes the nearest-neighbor distance b .³¹ It can be seen by comparison of Table V with Table I that the experimental g shift in the barium compounds is accounted for very well by the large negative contribution of configuration A alone; in the worst case the discrepancy is 5%. The sign of the discrepancy precludes the extraction of a mixing parameter, but in any event, the parameter must be very small. A substantial mixing is implied for some compounds, but configuration A predominates in all cases.

IV. CALCULATION OF MIXING PARAMETER

The *a priori* determination of the mixing parameter C^2 of Eq. (5) is considered in the present section. It will be seen that the rather extreme simplifying assumptions demanded by the complexity of the problem allow only a qualitative comparison with experiment.

The mixing parameter is obtained by diagonalizing the matrix of the Hamiltonian between configurations, and is given by

$$C^2 = \frac{[\frac{1}{2}(H_{BB} - H_{AA}) - E]^2}{[\frac{1}{2}(H_{BB} - H_{AA}) - E]^2 + H_{AB}^2}, \quad (21a)$$

$$E = [H_{AB}^2 + \frac{1}{4}(H_{BB} - H_{AA})^2]^{1/2}. \quad (21b)$$

The eigenvalues of the matrix are given by

$$E^\pm = \frac{1}{2}(H_{AA} + H_{BB}) \pm E; \quad (22)$$

the corrected energy of the F -center ground state is then E^- , while E^+ is the energy of an excited state which primarily involves the charge-transfer configuration.

³¹ R. W. G. Wyckoff, *Crystal Structures* (John Wiley & Sons, Inc., New York, 1964), Vol. I.

The Hamilton H is given by

$$H = \sum_i f_i + \frac{1}{2} \sum_{i \neq j} g_{ij}, \quad (23a)$$

$$f_i = -\nabla_i^2, \quad (23b)$$

$$g_{ij} = 2/r_{ij}, \quad (23c)$$

and the matrix elements are calculated with wave functions $\psi_{A\uparrow}$ of Eq. (1) and $\psi_{B\uparrow}$ of Eq. (4). As in Sec. II, the overlaps of ion orbitals on different centers are assumed to vanish. In addition, three-center exchange integrals of the form $\langle \phi_{F\downarrow}(1)\phi_j(2) | g_{12} | \phi_k(1)\phi_{F\downarrow}(2) \rangle$ are neglected. We proceed by substituting for $\psi_{B\uparrow}$ in terms of $\psi_{j\uparrow}$ from Eq. (4). With the foregoing assumptions, terms of the form $\langle \psi_{j\uparrow} | H | \psi_{k\uparrow} \rangle$ vanish for $j \neq k$. Furthermore, all terms in the sum over next nearest neighbors are identical by symmetry; thus the required combinations of matrix elements are

$$H_{BB} - H_{AA} = \langle \psi_{j\uparrow} | H | \psi_{j\uparrow} \rangle - \langle \psi_{A\uparrow} | H | \psi_{A\uparrow} \rangle, \quad (24a)$$

$$H_{AB} = (12)^{1/2} \langle \psi_{A\uparrow} | H | \psi_{j\uparrow} \rangle, \quad (24b)$$

where the choice of anion j is arbitrary. Substitution for H from Eq. (18a), for $\psi_{A\uparrow}$ from Eq. (1), and for $\psi_{j\uparrow}$ from Eq. (3), yields

$$H_{BB} - H_{AA} = \langle \phi_{F\downarrow}(1) | h | \phi_{F\downarrow}(1) \rangle - \langle \phi_j(1) | h | \phi_j(1) \rangle, \quad (25a)$$

$$H_{AB} = (12)^{1/2} \langle \phi_j(1) | h | \phi_{F\downarrow}(1) \rangle, \quad (25b)$$

$$h = f_1 + \langle \phi_{F\uparrow}(2) | g_{12}(1 - P_{12}) | \phi_{F\uparrow}(2) \rangle + \sum_{i \neq j} \langle \phi_i(2) | g_{12}(1 - P_{12}) | \phi_i(2) \rangle, \quad (25c)$$

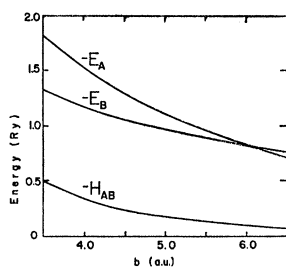
where P_{12} is the transposition operator, which appears as a consequence of antisymmetrization. The operator h of Eq. (25c) can be regarded as an effective one-electron Hamiltonian for the electron involved in the charge transfer. The first term of Eq. (25a), $\langle \phi_{F\downarrow}(1) | h | \phi_{F\downarrow}(1) \rangle$, is then the energy E_B of one electron in an F' center adjacent to a hole trapped at anion j (configuration B), while the second term, $\langle \phi_j(1) | h | \phi_j(1) \rangle$, is the energy E_A of one electron on an anion adjacent to an F center (configuration A). The degree of mixing is determined by the relative magnitudes of the difference of these two energies and the off-diagonal element H_{AB} .

A. Difference of Diagonal Elements

The difference of diagonal elements was estimated from idealized models for the F' center and the anion. The one-electron energy of the F' center was calculated by the method employed by La and Bartram³² for F' centers in alkali halides. Ground-state energies and wave functions were determined by series solution of the HF equations for two electrons in a square-well potential of depth $-4\alpha_M/b$ and range b , where α_M is the Madelung constant, 1.7476. The difference between the spherically symmetrical part of the point-ion potential

³² S. Y. La and R. H. Bartram, *Phys. Rev.* **144**, 670 (1966).

FIG. 4. Matrix elements of the Hamiltonian between configurations versus nearest-neighbor distance b . E_A is the energy of an outer $p\sigma$ electron on an anion adjacent to an F center and E_B is the energy of an electron in an F' center adjacent to a trapped hole. H_{AB} is the off-diagonal element, and $E_B - E_A$ is the difference of diagonal elements.



and the square-well potential was subsequently treated as a perturbation. In the present application, the interaction of the electrons was included only when they were inside the well, and no correction was made for polarization; these effects are thought to be unimportant in view of the compactness of the wave functions and the local charge neutrality of the F' center. The adjacent trapped hole was treated as a point positive charge; its contribution to the one-electron energy in first order is just $-\sqrt{2}/b$. The one-electron energy E_B is plotted as a function of b in Fig. 4. The F' center calculation also yields wave functions, which are included here for possible future reference. The wave functions are of the form $(4\pi)^{-3/2}r^{-1}P(r)$, where

$$P(r) = A\alpha^{-1} \sum_{n=0}^{\infty} C_{2n+1}(\alpha r)^{2n+1}, \quad r < b \quad (26a)$$

$$P(r) = B\beta^{-1} \exp(-\beta r), \quad r > b \quad (26b)$$

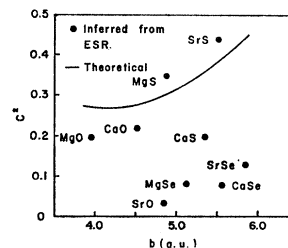
and $C_1=1$. The parameters are listed in Table VII for a selected set of compounds; since they are functions only of b , they may be obtained by interpolation for the remaining compounds.

Watson's²⁶ treatment of the O^{2-} ion yields a one-electron energy for the $2p$ orbital of -0.1602 , including the potential energy of his shouldered well. In order to compare this value with the one-electron energy for the F' center, one must subtract the potential energy at the bottom of the shouldered well, $-2/2.66$ a.u. $= -0.752$ a.u., and add the potential energy at the center of the anion site due to the rest of the lattice, $-4\alpha_M/b$. Finally, the adjacent F center is treated as a point positive charge and its first-order contribution to the energy is $-2\langle p\sigma | r_a^{-1} | p\sigma \rangle$, where r_a is measured from the center

TABLE VII. Parameters of ground-state wave functions for F' centers in divalent compounds. The parameters are defined by Eqs. (26).

	MgO	CaO	BaO	CaSe	BaSe
C_3	$10^{-1} \times -0.3171$	-0.2593	-0.2024	-0.1765	-0.1339
C_5	$10^{-2} \times -0.1383$	-0.1363	-0.1309	-0.1274	-0.1201
C_7	$10^{-4} \times 0.4697$	0.3596	0.2588	0.2161	0.1509
C_9	$10^{-6} \times 0.3586$	0.4666	0.5050	0.5027	0.4749
C_{11}	$10^{-7} \times -0.3015$	-0.2247	-0.1537	-0.1245	-0.0814
C_{13}	$10^{-9} \times 0.1849$	0.0126	-0.0833	-0.1060	-0.1203
C_{15}	$10^{-11} \times 1.2236$	0.9558	0.6532	0.5212	0.3265
A	0.3332	0.2733	0.2209	0.1991	0.1658
B	9.8224	11.5906	14.1141	15.6728	19.1308
α	1.0237	0.9444	0.8680	0.8338	0.7774
β	0.8442	0.8054	0.7656	0.7471	0.7160

FIG. 5. Configuration mixing parameter C^2 versus nearest-neighbor distance b . Points inferred from ESR data are compared with the theoretical curve.



of the anion vacancy, at a distance of $\sqrt{2}b$ from the nucleus of the anion in question. The one-electron energy E_A for the oxygen compounds is then a function only of nearest-neighbor distance b , and is given by

$$E_A = 0.5918 - 4\alpha_M/b - 2\langle p\sigma | r_a^{-1} | p\sigma \rangle. \quad (27)$$

The two-center integral in Eq. (27) is of the form of a one-electron Coulomb integral. Although Loftus³³ provides formulas for this type of integral, it was found expedient to derive a simpler, closed expression in spheroidal coordinates, which is given in the Appendix. The calculated values of E_A are plotted as a function of b in Fig. 4. This curve was applied as well to sulfur and selenium compounds, for which no calculations are available; the justification is the same as that for using O^{2-} wave functions for these compounds, but is more doubtful since we are interested in the small difference of two large energies, $H_{BB} - H_{AA} = E_B - E_A$.

B. Off-Diagonal Element

We now consider the evaluation of the off-diagonal element H_{AB} of Eq. (25b), which can be written in terms of the nonorthogonalized vacancy-centered orbital χ_F by means of Eqs. (2):

$$H_{AB} = (12)^{1/2} N (\langle F | h | p\sigma \rangle - \langle F | p\sigma \rangle \langle p\sigma | h | p\sigma \rangle), \quad (28)$$

where $|F\rangle$ denotes $\chi_{F\downarrow}$ and $|p\sigma\rangle$ denotes ϕ_j . Consistent with the approximations made for the diagonal elements, it is further assumed that $|p\sigma\rangle$ is an eigenfunction of $h + 2/r_a$, i.e., of the one-electron Hamiltonian excluding the potential due to the adjacent F center. Then Eq. (28) becomes

$$H_{AB} = -2(12)^{1/2} N (\langle F | r_a^{-1} | p\sigma \rangle - \langle F | p\sigma \rangle \times \langle p\sigma | r_a^{-1} | p\sigma \rangle). \quad (29)$$

The only new two-center integral in this expression is $\langle F | r_a^{-1} | p\sigma \rangle$, a one-electron resonance integral, which was evaluated by formulas of Loftus.³³ For convenience, the normalization constant N was set equal to unity in evaluating Eq. (29), since, except for this factor, H_{AB} depends only on b . It can be seen from Table IV that this approximation introduces a small error. The calculated values of H_{AB} are plotted in Fig. 4.

The mixing parameter C^2 was then calculated from Eqs. (21), with matrix elements from Fig. 4, and is plotted as a function of b in Fig. 5. The values of C^2

³³ A. Loftus, Mol. Phys. 6, 115 (1963).

inferred from ESR data, listed in Table IV, are also shown in Fig. 5 for comparison.

V. DISCUSSION AND CONCLUSIONS

The positive g shift for F centers in some divalent compounds has been accounted for by admixture of a charge-transfer configuration involving transfer of an electron to the vacancy from an adjacent anion. The contribution of the charge-transfer configuration to the g shift has been shown to be positive, and the theory is specific to divalent compounds, as required. The mixing parameter C^2 , defined by Eq. (5), was inferred from ESR data in Sec. III and calculated *a priori* from a simplified model in Sec. IV; the results are compared in Fig. 5. It can be seen that the model provides a degree of mixing of the order of magnitude required to account for the positive g shifts. However, detailed quantitative agreement is not obtained; in particular, the observed values of C^2 are not simply a function of nearest-neighbor distance b , but appear to depend on the structures of the ions. The observed mixing in the barium and selenium compounds is very much less than predicted, while the quantitative agreement is satisfactory for the remaining compounds with the exception of SrO. Actually, a number of approximations are involved in the calculation of both observed and predicted values of C^2 ; e.g., the use of free-ion values for λ_c and extrapolated values for λ_a . In addition, the neglected contributions of inner shells would tend to depress Δg_A and thereby give nonvanishing observed values of C^2 in the barium compounds. The closure approximation and the identification of the average energy denominator with ΔE , the F -band energy, constitute extreme approximations. However, it is believed that the greatest error arises in the calculation of the relatively small difference of diagonal elements, $H_{BB} - H_{AA}$, from simplified models for the F' center and the anion. Apparently, configuration A is more strongly favored in compounds with the heaviest constituents (Ba and Se) than the model suggests. The discrepancy in Se compounds probably results from the use of the O^{2-} one-electron energy for E_A . The source of the discrepancy in Ba compounds and SrO is less apparent, but may be related to the large ionic radius of the cation relative to the nearest-neighbor distance. It is concluded that the results of the calculation tend to support the theory that configuration mixing is responsible for positive g shifts, but a more elaborate model which takes more account of the structure of the ions would be required for detailed quantitative agreement.

The foregoing analysis implies the existence of low-lying charge-transfer states. These include an admixture of configurations A and B with Γ_1 symmetry lying $2E$ above the ground state, where E is defined by Eq. (21b), to which optical transitions are forbidden. In addition, there are charge-transfer states of other symmetry lying $E + \frac{1}{2}(E_B - E_A)$ above the ground state.

Since $E + \frac{1}{2}(E_B - E_A)$ is comparable with ΔE , it appears that the $2p$ state of the F center may be unstable against decomposition into an F' center and a valence-band hole, even though it is very stable against decomposition into a vacancy and a conduction electron.³⁴

In a recent paper by Blum,³⁵ which appeared after the completion of the present work, the positive g shift of hydrogen atoms in CaF_2 is attributed to essentially the same mechanism as contemplated here, but a substantially different formulation is employed.

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APPENDIX

The two-center integral appearing in Eq. (27) can be expressed as

$$\langle p\sigma | r_a^{-1} | p\sigma \rangle = \sum_{i=1}^3 \sum_{j=1}^3 D_i D_j K \{ 2p\sigma, 2p\sigma; \kappa_i \kappa_j \}, \quad (A1)$$

where the D_i 's are coefficients in the expansion of $|p\sigma\rangle_a$ in Slater orbitals in Eq. (17b), and K is a Coulomb integral of the form

$$K \{ 2p\sigma, 2p\sigma; \kappa_i \kappa_j \} = \int r_a^{-1} \eta_b(2p0, \kappa_i) \eta_b(2p0, \kappa_j) d\tau, \quad (A2)$$

which can be evaluated in spheroidal coordinates with the result

$$K \{ 2p\sigma, 2p\sigma; \kappa_i \kappa_j \} = (b^4/2) (\kappa_i \kappa_j)^{5/2} (A_1 B_0 + A_0 B_1 + 2A_2 B_1 + 2A_1 B_2 + A_3 B_2 + A_2 B_3), \quad (A3)$$

$$A_k = A_k(p) = \int_1^\infty \xi^k \exp(-p\xi) d\xi, \quad (A4)$$

$$B_k = B_k(p) = \int_{-1}^1 \eta^k \exp(-p\eta) d\eta, \quad (A5)$$

$$p = (\kappa_i + \kappa_j) b / \sqrt{2}. \quad (A6)$$

The subsidiary integrals A_k and B_k are readily generated from recursion relations.

³⁴ J. C. Kemp, W. M. Zinniker, and E. B. Hensley, *Phys. Letters* **25A**, 43 (1967). These investigators have observed F to F' conversion in CaO by illumination on the long-wavelength side of the F band. A possible interpretation is that this effect involves a transition from the ground state of the F center to a charge-transfer state, leaving an F' center and a free hole.

³⁵ H. Blum, *J. Chem. Phys.* **46**, 650 (1967).