

also predicted for 2D and 3D disordered crystal models. However, the intensity of the peaks should be smaller in higher dimensions.

Extension of this work should be useful in several directions. Clearly, numerical work should be performed in three dimensions, and in any dimension with more realistic models. Most importantly, the dependence on mass ratio of our criteria for localization and persistence should be established. (Our own simple force model—forces independent of the atoms involved—applies best to so-called isotopically disordered lattices, but not so well to lattices with mass ratios of 2:1 or higher.) Also, solids with more than two constituents could be studied.

We should finally note that when each atom has an electric charge (ionic crystals), the dipole moment of each of the modes can be readily found from the atomic displacements we have already calculated. The dipole

moment of local modes that are odd is, of course, zero, but that of other local modes is likely to be considerable, and to provide a prominent feature in the absorption spectra of crystals, as most “lattice” modes themselves lack a dipole moment. The present work can be applied rather directly to mixed crystals AX_cY_{1-c} , in which the concentration C can be varied. The absorption spectra of these crystals thus provide a simple tool for observation and the semiquantitative comparison of present results with experiment.²⁴

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Thanks for many useful discussions are due to Dr. Marvin Hass.

²⁴ M. Hass, H. B. Rosenstock, and R. E. McGill, *Solid State Commun.* (to be published).

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Ion-Size Effects in Color Centers

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A modification of the point-ion model is proposed which provides an approximate correction for ion-size effects. The difference between the optimum pseudopotential for the smoothest pseudo-wave-function and the point-ion potential is treated as an ion-size correction to the Hamiltonian, appropriate to a smooth variational trial function. By neglecting the variation of the trial function over the ion cores in the evaluation of matrix elements, one obtains a simple, approximate form for the pseudopotential: $V_p = V_{PI} + \sum_\gamma [A_\gamma + (\bar{V} - U_\gamma)B_\gamma] \delta(\mathbf{r} - \mathbf{r}_\gamma)$, where V_{PI} is the point-ion potential, U_γ is the potential at ion γ due to the other ions, and $\bar{V}$ is the average potential. The coefficients A_γ and B_γ are properties of the ions alone, and have been computed for a large set of ions. The approximate pseudopotential is applied to the calculation of ionization potentials of alkali atoms, where it works well, and of F -band energies in alkali halides and alkaline-earth fluorides, where it is found that all of the coefficients A_γ must be reduced by a factor of 0.53 in order to obtain agreement with experiment. With the adjusted pseudopotential coefficients, the theory accounts well not only for the Ivey law in alkali halides, but also for deviations from the Ivey law. In addition, the seemingly anomalous F -band energy in BaF_2 is accounted for. The empirically adjusted constants may be useful in other color-center problems as well.

I. INTRODUCTION

A RIGOROUS formulation of the electron-excess color-center problem requires that all of the electrons be treated equivalently. However, a vast simplification results from the recognition that the occupied ion-core states are much more tightly bound than the states associated with the color center, and the consequent assumption that the ion-core electrons

simply contribute to the potential seen by the excess electrons. Models based on this assumption include the point-ion model of Gourary and Adrian (GA),¹ with which we shall be primarily concerned, as well as continuum and semicontinuum models.² In the point-ion model, the ions are replaced by point charges, and the resulting potential is used with a smooth variational trial function which is subsequently orthogonalized to

¹ B. S. Gourary and F. J. Adrian, *Phys. Rev.* **105**, 1180 (1957).

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² 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.

the ion-core orbitals for calculation of magnetic properties. The point-ion model has been employed successfully in the study of electron-excess color centers, and accounts well for many of their properties, but it neglects extended-ion effects. More recently, Wood and co-workers³ have treated extended-ion effects in color centers by carrying out Hartree-Fock calculations which explicitly involve the electrons and core states of neighboring ions. While their approach is more exact, it involves an enormous increase in complexity.

In the present work, a modification of the point-ion model is proposed which provides an approximate correction for ion-size effects, but retains much of the simplicity and tractability of the original model. The proposed modification is based on the pseudopotential method of Phillips and Kleinman,⁴ as elaborated by Cohen and Heine⁵ and by Austin, Heine, and Sham.⁶ The difference between the optimum pseudopotential for the smoothest pseudo-wave-function and the point-ion potential constitutes an ion-size correction to the Hamiltonian. A simple, approximate form of this correction is derived in Sec. II by neglecting the variation of the pseudo-wave-function over the ion cores. In Sec. III it is expressed in terms of constants which are evaluated for a number of ions. In Sec. IV, the method is applied to the calculation of ionization potentials of alkali atoms, and to a study of ion-size effects on the F band of alkali halides and alkaline-earth fluorides.

II. APPROXIMATE PSEUDOPOTENTIAL

The pseudopotential method⁴⁻⁶ has been applied extensively in band-structure calculations, particularly for metals.⁷ Its applicability to color centers was recognized at the outset,⁴ but appears to have been exploited only by Gourary and Fein⁸ and by Kübler and Friauf.⁹ The relation of these investigations to the present work will be discussed subsequently.

In order to define terms for future reference, we begin with a concise derivation of the pseudopotential theorem, as formulated by Austin, Heine, and Sham.⁶ For simplicity, it is assumed that all ions have closed-shell configurations and that there is a single excess electron. Slater atomic units are used throughout, i.e., energies are in Rydbergs and lengths in Bohr radii. One seeks the eigenvalues and eigenfunctions of the equation

$$H\Psi = E\Psi, \quad (2.1)$$

³ R. F. Wood and J. Korrington, *Phys. Rev.* **123**, 1138 (1961); A. Meyer and R. F. Wood, *ibid.* **133**, A1436 (1964); R. F. Wood and H. W. Joy, *ibid.* **136**, A451 (1964); R. F. Wood, *J. Phys. Chem. Solids* **26**, 615 (1965).

⁴ J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959).

⁵ M. H. Cohen and V. Heine, *Phys. Rev.* **122**, 1821 (1961).

⁶ B. J. Austin, V. Heine, and L. J. Sham, *Phys. Rev.* **127**, 276 (1962).

⁷ W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

⁸ B. S. Gourary and A. E. Fein, *J. Appl. Phys. Suppl.* **33**, 331 (1962).

⁹ J. K. Kübler and R. J. Friauf, *Phys. Rev.* **140**, A1742 (1965).

where

$$H = T + V, \quad (2.2a)$$

$$T = -\nabla^2, \quad (2.2b)$$

and V is a one-electron potential which is the same for all states (V must be Hermitian, but not necessarily local). We proceed by distinguishing a finite subset of eigenfunctions Ψ_c as core orbitals. The remaining eigenfunctions Ψ_v are called valence orbitals. (In the present application, the Ψ_c are identified with the occupied ion-core orbitals which are assumed mutually orthogonal, and the Ψ_v are states of the excess electron.) We introduce a projection operator P for the core states,

$$P = \sum_c |\Psi_c\rangle\langle\Psi_c|, \quad (2.3)$$

which is readily shown to commute with H . Consider the related eigenvalue problem

$$(H + V_R)\phi = \bar{E}\phi, \quad (2.4)$$

where V_R is a nonlocal potential defined by

$$V_R = PO_P, \quad (2.5)$$

and O_P is an arbitrary operator. It follows from the commutativity of H and P and the idempotence of P ($P^2 = P$) that

$$(1 - P)(H + V_R - \bar{E})\phi = (H - \bar{E})(1 - P)\phi = 0, \quad (2.6)$$

with the consequence that

$$(1 - P)\phi = \Psi_v, \quad (2.7)$$

$$\bar{E} = E_v. \quad (2.8)$$

Thus a valence eigenvalue E_v of Eq. (2.1) can be determined by solving the related eigenvalue problem

$$(T + V_p)\phi = E_v\phi, \quad (2.9)$$

where V_p is a pseudopotential defined by

$$V_p = V + V_R \quad (2.10)$$

and ϕ is a pseudo-wave-function. The valence eigenfunction Ψ_v can then be recovered by orthogonalizing ϕ to the core orbitals, as indicated in Eq. (2.7). The foregoing constitutes the pseudopotential theorem; its utility lies in the possibility of specifying V_p in a form which effects a substantial cancellation of potential and kinetic energy within the ion cores, and thus leads to a pseudo-wave-function ϕ which is much smoother than Ψ_v . This procedure greatly enhances the convergence of a plane-wave expansion in band-structure calculations and a one-center expansion in color-center calculations.

Gourary and Fein,⁸ following Cohen and Heine,⁵ have justified the point-ion potential as a model potential which approximates a valid pseudopotential,

$$V_p = V + P(V_{PI} - V), \quad (2.11)$$

where V_{PI} is the point-ion potential. However, the pseudopotential is not unique, and a more appropriate

specification for use with a smooth variational trial function is the pseudopotential which yields the smoothest pseudo-wave-function. The difference between this optimum pseudopotential and the point-ion potential can then be regarded as an ion-size correction to the point-ion Hamiltonian.

Cohen and Heine⁵ have derived the optimum pseudopotential from the criterion that it minimizes the expectation value of the kinetic energy. By virtue of the pseudopotential theorem, this is equivalent to maximizing the expectation value of the pseudopotential,

$$\delta\bar{V}=0, \quad (2.12a)$$

$$\bar{V}=(\phi, V_p \phi)/(\phi, \phi). \quad (2.12b)$$

The variation in Eq. (2.12a) is with respect to V_R . It is facilitated by deriving the alternative expression⁴

$$V_p \phi = [V + (E - H)P]\phi \quad (2.13)$$

from Eqs. (2.1) and (2.7), valid for any choice of V_R . The optimum pseudopotential, which satisfies Eq. (2.12), is given by

$$V_p = V + P(\bar{V} - V). \quad (2.14)$$

It is convenient to separate out the point-ion potential in Eq. (2.14), and rewrite it in the form

$$V_p = V_{PI} + (V - V_{PI}) + P(\bar{V} - V). \quad (2.15)$$

The last two terms on the right-hand side of Eq. (2.15) then constitute the ion-size correction to the Hamiltonian. The first approximation we make is to assume a tight-binding model for the core states, and to neglect the overlaps of ion-core orbitals on different centers. Then the projection operator P can be expressed as

$$P = \sum_{\gamma} P_{\gamma}, \quad (2.16)$$

where P_{γ} projects on the core orbitals of ion γ . In this approximation both V and V_{PI} can be expressed similarly as a sum of contributions from individual ions,

$$V = \sum_{\gamma} V_{\gamma}, \quad (2.17)$$

$$V_{PI} = \sum_{\gamma} V_{PI\gamma}, \quad (2.18)$$

and V_p becomes

$$V_p = V_{PI} + \sum_{\gamma} [(1 - P_{\gamma})(V_{\gamma} - V_{PI\gamma}) - P_{\gamma}V_{PI\gamma} + P_{\gamma}(\bar{V} - U_{\gamma})], \quad (2.19)$$

where

$$U_{\gamma} \equiv \sum_{\gamma' \neq \gamma} V_{\gamma'} \approx \sum_{\gamma' \neq \gamma} V_{PI\gamma'}. \quad (2.20)$$

Each term in the sum over γ in Eq. (2.19) is highly localized within ion core γ .

It is feasible to evaluate the expectation value of the nonlocal operator V_p in this approximation, but the large number of two-center integrals involved would tend to inhibit the use of a flexible trial function ϕ . Accordingly, we take advantage of the smoothness of ϕ and the localization of $V_p - V_{PI}$ to introduce a further approximation: The variation of ϕ over each ion core is

neglected in calculating the expectation value of $V_p - V_{PI}$, with the result

$$(\phi, V_p \phi) = (\phi, V_{PI} \phi) + \sum_{\gamma} C_{\gamma} |\phi(\mathbf{r}_{\gamma})|^2, \quad (2.21)$$

$$C_{\gamma} = A_{\gamma} + (\bar{V} - U_{\gamma})B_{\gamma}, \quad (2.22)$$

$$A_{\gamma} = \int (1 - P_{\gamma})(V_{\gamma} - V_{PI\gamma})d\tau - \int P_{\gamma}V_{PI\gamma}d\tau, \quad (2.23)$$

$$B_{\gamma} = \int P_{\gamma}d\tau. \quad (2.24)$$

For ions with closed-shell configurations, only the s orbitals in P_{γ} make a nonvanishing contribution to C_{γ} , and in particular P_{γ} projects out only the spherically symmetrical part of U_{γ} , which has been treated as constant in Eq. (2.22). Consequently, the angular-momentum dependence of V_p is suppressed by neglecting the variation of ϕ over ion cores. In this approximation, the expectation value of V_p is identical with that of the simple model potential V_p^{δ} , defined by

$$V_p^{\delta} \equiv V_{PI} + \sum_{\gamma} C_{\gamma} \delta(\mathbf{r} - \mathbf{r}_{\gamma}). \quad (2.25)$$

The coefficients C_{γ} incorporate the ion-size effects. A_{γ} and B_{γ} are characteristic only of the ions, but U_{γ} depends on the crystal structure (including defects), while $\bar{V}$ must be determined self-consistently for each state, which makes V_p energy-dependent.

The pseudopotential V_p of Eq. (2.19) is subject to an interesting qualitative interpretation.⁵ To the extent that the set of occupied ion-core orbitals approximates a complete set within the ion, the projection operator P_{γ} approximates a δ function by the closure theorem. On the other hand, P_{γ} tends to zero rapidly outside the ion core. One has the approximate relations

$$P_{\gamma} = \sum_c |\Psi_{\gamma c}(\mathbf{r})\rangle \langle \Psi_{\gamma c}(\mathbf{r}')| \approx \delta(\mathbf{r} - \mathbf{r}'), \quad r < r_{ion\gamma} \\ \approx 0, \quad r > r_{ion\gamma} \quad (2.26)$$

where $r_{ion\gamma}$ is the ionic radius. Thus one may think of P_{γ} as projecting on the *interior* of ion γ , and $1 - P_{\gamma}$ on the *exterior*. It follows that the first term on the right-hand side of Eq. (2.23) is very small, since V_{γ} and $V_{PI\gamma}$ are nearly equal outside the ion core. Further, A_{γ} and B_{γ} are given approximately by

$$A_{\gamma} = 4\pi Q_{\gamma} r_{ion\gamma}^2, \quad (2.27a)$$

$$B_{\gamma} = (4\pi/3) r_{ion\gamma}^3, \quad (2.27b)$$

where Q_{γ} is the net charge of ion γ . In this approximation, the effect of the ion-size correction is to remove the point-ion potential from the interior of the ions and replace it by the average potential.

In their F -center calculation, Kübler and Friauf⁹ also employed the optimum pseudopotential for a smooth pseudo-wave-function. However, they adopted the approximation of Austin, Heine, and Sham⁶ in neglect-

ing $\bar{V}$ in Eq. (2.14), and they assumed a superposition of pseudopotentials for isolated ions, thus eliminating U_γ in Eq. (2.19). Their approximation would eliminate the second term on the right-hand side of Eq. (2.22); however, as will become apparent, the coefficient B_γ plays an essential role in the comparison with experiment and the two terms in Eq. (2.22) are in fact comparable. Again following Austin *et al.*,⁶ Kübler and Friauf neglect the variation of ϕ over ion cores in evaluating $V_\pi\phi$ in order to derive a local model pseudopotential. However, they do not continue to neglect the variation over ion cores of the left-hand ϕ in evaluating $(\phi, V_\pi\phi)$. Instead, they expand the local model pseudopotential in Kubic harmonics about the anion vacancy. Equations (2.21)–(2.25) provide a more convenient approximation to the pseudopotential, but do not involve any additional assumptions beyond neglecting the variation of ϕ over ion cores.

III. PSEUDOPOTENTIAL COEFFICIENTS

The coefficients A_γ and B_γ defined by Eqs. (2.23) and (2.24), respectively, are properties of the individual ions. Accordingly, they have been computed for a large set of ions with closed-shell configurations and are tabulated in this section for future reference. (The subscript γ will be dropped in this section, since only properties of single ions are considered.) The potential V is taken to be of the form

$$V = V_H + V_X, \quad (3.1)$$

where V_H is the Hartree potential,

$$V_H(1) = -\frac{2Z}{r_1} + \sum_c \int \frac{|\psi_c(2)|^2}{r_{12}} d\tau_2, \quad (3.2)$$

V_X is the exchange interaction,

$$V_X\chi(1) = - \sum_{c(\text{spins})} \left(\int \frac{\psi_c^*(2)\chi(2)}{r_{12}} d\tau_2 \right) \psi_c(1), \quad (3.3)$$

and the sum is over occupied ion-core spin orbitals. In Eq. (3.3), χ can be either a valence or an ion-core spin orbital. Thus the core orbitals are assumed to be eigenfunctions of a Hamiltonian which does not include the interaction with the valence electron; this approximation is justified by the low valence-electron density within the ion. The potential V is nonlocal by virtue of the exchange interaction, but it satisfies the essential requirements that it be the same for all states and that it be Hermitian, ensuring the orthonormality of the ψ_c 's. The parameter A can also be expressed as a sum of Hartree and exchange contributions $A_H + A_X$, where

$$A_H = \int (1-P)(V_H - V_{PI})d\tau - \int P V_{PI}d\tau, \quad (3.4)$$

$$A_X = \int (1-P)V_Xd\tau. \quad (3.5)$$

With the assumed form of V , the pseudopotential coefficients are given below. The Hartree contribution to A is

$$A_H = 4\pi \left\{ \int_0^\infty [V_H(r) - V_{PI}(r)]r^2dr - \sum_n \int_0^\infty R_{n0}(r)r^2dr \right. \\ \left. \times \int_0^\infty R_{n0}(r)[V_H(r) - V_{PI}(r) - 2Q/r]r^2dr \right\}, \quad (3.6a)$$

where

$$V_H(r) - V_{PI}(r) = 8\pi \int_r^\infty \rho(r')(r'^{-1} - r^{-1})r'^2dr', \quad (3.6b)$$

$$\rho(r) = (4\pi)^{-1} \sum_n \sum_{l=0}^{n-1} 2(2l+1)R_{nl}(r)^2, \quad (3.6c)$$

and $R_{nl}(r)$ is the radial part of an ion-core orbital, with normalization

$$\int_0^\infty R_{nl}(r)^2r^2dr = 1. \quad (3.6d)$$

The exchange contribution to A is

$$A_X = 4\pi \sum_n \left\{ - \sum_{l=0}^{n-1} \int_0^\infty F_{nl}(r)R_{nl}(r)r^2dr \right. \\ \left. + \int_0^\infty R_{n0}(r)r^2dr \sum_n \sum_{l=0}^{n'-1} \int_0^\infty R_{n0}(r) \right. \\ \left. \times F_{n'l}(r)R_{n'l}(r)r^2dr \right\}, \quad (3.7a)$$

$$F_{nl}(r) = 2 \left(r^{-l-1} \int_0^r R_{nl}(r')r'^{l+2}dr' \right. \\ \left. + r^l \int_r^\infty R_{nl}(r')r'^{-l+1}dr' \right). \quad (3.7b)$$

Finally, B is given by

$$B = 4\pi \sum_n \left(\int_0^\infty R_{n0}(r)r^2dr \right)^2. \quad (3.8)$$

Ion-core orbitals were calculated by the Hartree-Fock-Slater method, using the Herman-Skillman program.¹⁰ Divalent anion orbitals were calculated by Montgomery and Bartram,¹¹ who employed a stabilizing potential well of the type introduced by Watson.¹² Pseudopotential coefficients were then computed from Eqs. (3.6)–(3.8) and are listed in Table I. Coefficients for some of the ions were also computed from the

¹⁰ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

¹¹ J. Montgomery and R. H. Bartram (unpublished).

¹² R. E. Watson, *Phys. Rev.* **111**, 1108 (1958).

TABLE I. Pseudopotential coefficients for a number of ions with closed-shell configurations. The units of A_H and A_X are Ry a_0^3 and the units of B are a_0^6 , where a_0 is the Bohr radius.

Ion	Hartree-Fock-Slater			Clementi		
	A_H	A_X	B	A_H	A_X	B
Li ⁺	40.06	6.46	12.71	38.76	6.20	12.14
Na ⁺	50.08	5.96	18.87	50.00	4.99	18.67
K ⁺	98.02	3.46	59.90	105.80	3.03	64.40
Rb ⁺	118.19	0.15	84.54			
Cs ⁺	176.00	2.10	139.05			
F ⁻	-47.94	-9.98	48.88	-43.81	-5.38	50.84
Cl ⁻	-96.19	-26.06	128.01	-94.87	-19.54	144.82
Br ⁻	-116.82	-37.82	154.20	-117.07	-24.02	190.50
I ⁻	-149.75	-37.40	241.49			
Mg ⁺⁺	65.84	5.21	12.64	65.54	4.50	12.48
Ca ⁺⁺	140.18	4.29	43.43	148.89	3.99	46.32
Sr ⁺⁺	179.25	2.22	65.39			
Ba ⁺⁺	254.50	4.22	110.34			
O ²⁻	-157.21	-13.73	80.52			
S ²⁻	-283.25	-31.10	189.30			
Se ²⁻	-307.82	-43.85	210.81			
Te ²⁻	-408.95	-39.67	318.87			
Al ³⁺	7.38	4.35	8.86			

analytic Hartree-Fock wave functions of Clementi.¹³ These are listed in Table I as well. The agreement of the two sets appears satisfactory, and the Hartree-Fock-Slater coefficients are used exclusively in Sec. IV. The computed coefficients are in very rough agreement with Eqs. (2.27) as well.

The contributions of electron correlation to the pseudopotential coefficients are currently being investigated, but have not been included in Table I. However, the short-range correlation effects are expected to be small because of the cancellation of potential and kinetic energy, and the long-range effects are dealt with separately in the applications as polarization corrections.

IV. APPLICATIONS

A. Ionization Potential of Alkali Atoms

The simplest system on which to test the theory of ion-size effects is an isolated alkali atom. The single-valence electron is assumed to occupy a smooth pseudo-wave-function of the form

$$\phi(r) = (\gamma^3/7\pi)^{1/2}(1+\gamma r) \exp(-\gamma r), \quad (4.1)$$

and the corresponding pseudopotential is

$$V_p = -2/r + (A + \bar{V}B)\delta(r). \quad (4.2)$$

The wave-function parameter γ is adjusted to minimize the energy for a fixed value of $\bar{V}$ on the right-hand side of Eq. (4.2),

$$\gamma = [(1+6y)^{1/2} - 1]/y, \quad (4.3a)$$

$$y = 2(A + \bar{V}B)/\pi. \quad (4.3b)$$

The average potential $\bar{V}$ is then recomputed from this

¹³ E. Clementi, IBM J. Res. Develop. **9**, 2 (1965). Tables of atomic functions are available as a supplement to this article.

value of γ ,

$$\bar{V} = -(9/7)\gamma + \gamma^3/14, \quad (4.4)$$

and the procedure iterated to self-consistency (to 0.001 Ry). The ionization potential I is then given by

$$I = -(3/14)\gamma^2 - \bar{V}. \quad (4.5)$$

The computed ionization potentials are compared with experiment¹⁴ in Table II, and the agreement is seen to be quite satisfactory in view of the simplifying assumptions. This calculation is extremely simple, because all of the relevant details of the ion-core orbitals are incorporated in the pseudopotential coefficients A and B .

B. F-Band Energies in Alkali Halides

In this section we consider the application of the ion-size correction to F centers in alkali halides. Buchenauer and Fitchen¹⁵ have recently investigated the effects of ion size on the F band in alkali halides. In particular, they observe that both the departure of F -band energies from the Mollwo-Ivey relation¹⁶ and the shift of F -band energy under hydrostatic pressure depend systematically on the ratio of ionic radii. It is of interest to see how well the present method can account for their experimental data.

In calculating F -band energies, we have followed the procedure of GA rather closely, but with appropriate modification for the ion-size correction to the Hamiltonian. We have adopted their type-III trial wave function for the ground state,

$$R(\Gamma_1^e, 0, 0|r) = A j_0(\xi r/a) k_0(\eta), \quad r < a \quad (4.6a)$$

$$= A j_0(\xi) k_0(\eta r/a), \quad r > a$$

$$\eta = -\xi \cot \xi, \quad (4.6b)$$

and their type-II function for the excited state,

$$R(\Gamma_4^0, 1, 0|r) = A' j_1(\xi' r/a) \exp(-\eta'), \quad r < a \quad (4.7a)$$

$$= A' j_1(\xi') (r/a) \exp(-\eta' r/a), \quad r > a$$

$$\eta' = 3 - \xi'^2 (1 - \xi' \cot \xi')^{-1}, \quad (4.7b)$$

where a is the nearest-neighbor distance. Of the several

TABLE II. Ionization potentials of alkali atoms (Ry). The theoretical values were computed from the pseudopotential coefficients of Table I.

Atom	I_{theor}	I_{expt}^a
Li	-0.364	-0.397
Na	-0.338	-0.378
K	-0.264	-0.319
Rb	-0.249	-0.308
Cs	-0.203	-0.287

^a C. E. Moore (Ref. 14).

¹⁴ C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (1949).

¹⁵ C. J. Buchenauer and D. B. Fitchen, Phys. Rev. **167**, 846 (1968).

¹⁶ H. F. Ivey, Phys. Rev. **72**, 341 (1947).

single-parameter trial functions considered by GA, these proved best in their point-ion calculation. However, it has not been established that they are necessarily best when the ion-size correction is included. With these trial functions, only the spherically symmetrical part of the point-ion potential contributes to the energy, and this may be expressed simply as

$$V_{PI}(r) = -2\alpha_M/a + 2\sum_s n_s Q_s (r_s^{-1} - r^{-1}), \quad r_s < r, \quad (4.8)$$

where α_M is the Madelung constant, $\alpha_M = 1.7476$, and n_s is the number of ions of charge Q_s on a spherical shell of radius r_s . Contributions of the first 30 shells about the vacancy were included in the calculation.

The contribution of the ion-size correction to the energy was evaluated from Eqs. (2.21) and (2.22), and is given by

$$(\phi, (V_p - V_{PI})\phi) = \sum_\gamma [A_\gamma + (\bar{V} - U_\gamma)B_\gamma] |\phi(r_\gamma)|^2, \quad (4.9a)$$

$$\bar{V} = (\phi, V_p \phi). \quad (4.9b)$$

The parameters ξ and ξ' in the trial wave functions were varied to minimize the sum of the point-ion energy and ion-size correction with $\bar{V}$ fixed; $\bar{V}$ was then recomputed from Eq. (3.9b) and the computation iterated to self-consistency (to 0.001 Ry).

The energies were corrected for polarization by the method of GA, which gives

$$E_{pol} = -2\sum_s n_s \alpha_s q_s^2 / r_s^4, \quad (4.10)$$

where q_s is the electronic charge outside a shell of radius r_s ,

$$q_s = \int_{r_s}^{\infty} R(r)^2 r^2 dr, \quad (4.11)$$

and α_s is the polarizability of an ion on that shell. Polarizabilities were obtained from Tessman, Kahn, and Shockley,¹⁷ and the sum was extended over the first 10 shells of ions about the vacancy (the polarization correction converges much more rapidly than the point-ion potential).

A correction was also made for lattice distortion, again following closely the method of GA. Only the six nearest alkali ions were displaced, and these were moved radially into the vacancy by an amount σa . The displacement was determined by expanding the ground-state energy to terms quadratic in σ ,

$$E_{dist}^{(a)} = C\sigma + \frac{1}{2}D\sigma^2, \quad (4.12)$$

and by varying σ to minimize the energy,

$$\sigma_0 = -C/D, \quad (4.13)$$

$$E_{dist}^{(a)} = -\frac{1}{2}D\sigma_0^2. \quad (4.14)$$

However, the coefficients C and D now contain addi-

tional terms arising from the ion-size correction, and are given by

$$C = -2\alpha_M/a + (12/a)(\eta+1)^{-1} \sin^2 \xi + 2(1+\eta)V_+, \quad (4.15)$$

$$D = (2\alpha_M/a)(\lambda-3) + (12/a)(3/\sqrt{2} + \frac{1}{4}) + (24/a) \sin^2 \xi + [8(\eta+1)^2 \Gamma_+ + 2(3+4\eta+2\eta^2)]V_+, \quad (4.16)$$

where the repulsive interaction of two ions is assumed to be $b r_{\alpha\beta}^{-\lambda}$, and where

$$V_+ = \frac{n_1[A_+ + (\bar{V} - U_+)B_+]|\phi(a)|^2}{1 - \sum_\gamma B_\gamma |\phi(r_\gamma)|^2}, \quad (4.17)$$

$$\Gamma_+ = \frac{n_1 B_+ |\phi(a)|^2}{1 - \sum_\gamma B_\gamma |\phi(r_\gamma)|^2}. \quad (4.18)$$

The subscript $+$ denotes nearest-neighbor cations, and $n_1 = 6$ for the rock-salt structure. The change in F -band energy with distortion was determined by computing the change in the expectation value of the point-ion potential and the ion-size correction in both ground and excited states, without expanding in powers of σ . The variation of U_γ with distortion was neglected in making these corrections. The value $\lambda = 9$ was used for all cases.

F -band energies were calculated for the 17 alkali halides with rock-salt structure, and were compared with the experimental values of Buchenauer and Fitchen¹⁵ and of Hughes, Pooley, Rahman, and Runciman.¹⁸ The agreement with experiment was very poor, the computed F -band energies being much too large for compounds with large cations and much too small for compounds with large anions (e.g., 0.313 Ry for CsF and 0.058 Ry for LiI). The discrepancy is essentially due to the fact that the A_γ 's are too large in magnitude compared with the B_γ 's; the ion-size correction then adds a strong repulsive potential to the large cations, and a strong attractive potential to the large anions. Since the wave function is more diffuse in the excited state than in the ground state, these added potentials have a greater effect on the energy of the excited state. In order to improve the agreement with experiment, we have diminished all of the A_γ 's by the same factor α , which we have treated as an adjustable parameter. For each value of α , the parameters ξ and ξ' were optimized for all 17 alkali halides. The best agreement (least-squares fit to experimental data) was obtained with $\alpha = 0.53$, and the resulting F -band energies are listed in Table III, where they are compared with experimental values.

The comparison with experiment can be seen more clearly in Figs. 1 and 2. In Fig. 1, the F -band energies are plotted as a function of nearest-neighbor distance, and it can be seen that the values calculated in this work are in better agreement with experiment and with the

¹⁷ J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

¹⁸ A. E. Hughes, D. Pooley, H. U. Rahman, and W. A. Runciman, Atomic Energy Research Establishment Research Report No. AERE-R.5604 (unpublished).

TABLE III. Comparison of calculated F -band energies (Ry) in alkali halides with experimental values measured at 77°K.^{a,b} The pseudopotential coefficients A_H and A_X of Table I have been diminished by the factor 0.53. The compounds are listed in ascending order of the ratio of ionic radii R ($=r_-/r_+$).

Compound	ΔE_{theor}	ΔE_{expt}^a	ΔE_{expt}^b
CsF	0.135	0.139	0.139
RbF	0.169	0.178	0.179
KF	0.202	0.210	0.206
RbCl	0.140	0.150	0.149
RbBr	0.128	0.136	0.136
NaF	0.278	0.276	0.274
KCl	0.161	0.169	0.172
KBr	0.146	0.154	0.153
RbI	0.121	0.125	0.126
KI	0.135	0.136	0.138
NaCl	0.201	0.202	0.204
LiF	0.386	0.377	0.378
NaBr	0.176	0.174	0.173
NaI	0.160	0.153	...
LiCl	0.242	0.241	0.243
LiBr ^c	0.208	...	0.199
LiI	0.184	...	0.240

^a C. J. Buchenauer and D. B. Fitchen (Ref. 15).

^b A. E. Hughes *et al.* (Ref. 18).

^c The value reported for LiBr in Ref. 15 appears to be in error.

Ivey law than are the point-ion calculations of Gourary and Adrian. Figure 2 shows that the present theory is able to account as well for departures from the Ivey law. Following Buchenauer and Fitchen,¹⁵ we have normalized the F -band energies to the Ivey law,

$$\Delta E_{\text{Ivey}} = 4.18a^{-1.84}, \quad (4.19)$$

and have plotted them in Fig. 2 as a function of the ratio of ionic radii R ($\equiv r_-/r_+$). (We have preferred to use the ionic radii of Zachariasen.¹⁹ However, this choice is not critical for the comparison.) The terms A_γ and $(\bar{V} - U_\gamma)B_\gamma$ of the coefficient C_γ in Eq. (2.25) are of opposite sign for both types of ion. Furthermore, it follows from Eq. (2.27) that B_γ increases more rapidly than A_γ with increasing ionic radius. With the reduced values of A_γ , there is substantial cancellation of the two terms in C_γ and the ion-size correction is much smaller. In compounds with relatively large cations (small R), the ion-size correction adds a net attractive potential to the cations with a consequent reduction of the F -band energy from the point-ion value. Compounds with larger R have a moderately repulsive potential added to the cations, with a corresponding increase in F -band energy. In compounds with relatively large anions (large R), the added attractive potential at the anions is now much reduced and no longer significantly depresses the F -band energy. It can be seen from Fig. 2 that the trend of the experimental data is reproduced very well, and there is satisfactory agreement for all compounds except LiI; the experimental F -band energy of LiI is clearly anomalous, and remains unexplained by the present theory.

¹⁹ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., p. 105.

C. Pressure Shift of the F Band

The shift of the F band in alkali halides under hydrostatic pressure has been investigated by Jacobs²⁰ and by Buchenauer and Fitchen.¹⁵ The latter investigators have plotted the quantity $-(\partial \ln E / \partial \ln a)_T$ as a function of the ratio of ionic radii R . If the dependence of the F -band energy on lattice constant were governed by the Ivey law in this experiment, then $-(\partial \ln E / \partial \ln a)_T$ would have the constant value +1.84 for all compounds. There are two notable features of its actual dependence on R . For most compounds, the pressure shift is about twice as large as the Ivey law would predict. This has been attributed by Jacobs²⁰ to an enhanced local compressibility. The second feature, which is of interest here, is that the pressure shift decreases with diminishing R and actually changes sign for CsF.

The present work provides a possible explanation for the second feature in terms of an unequal compression of anions and cations. Equations (2.27) suggest that the pseudopotential coefficients A_γ and B_γ may be regarded as continuous functions of the ionic radii, and are therefore diminished as the ions are compressed. It is reasonable to assume that as the solid is compressed, the sum of the ionic radii is constrained to equal the nearest-neighbor distance,

$$r_+ + r_- = a. \quad (4.20)$$

Then the F -band energies are uniquely functions of R

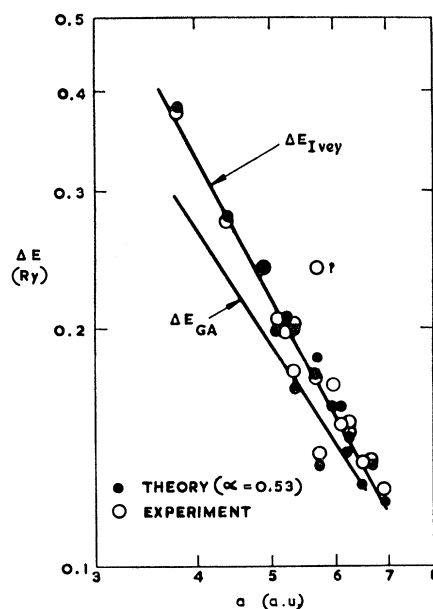


FIG. 1. F -band energies in rydbergs as a function of the nearest-neighbor distance. Open circles denote the average of experimental values, Refs. 15 and 18, and solid circles are theoretical values with $\alpha=0.53$. ΔE_{Ivey} represents the Ivey law, Eq. (4.19), and ΔE_{GA} is from the point-ion calculations of Gourary and Adrian (Ref. 1).

²⁰ I. S. Jacobs, Phys. Rev. 93, 993 (1954).

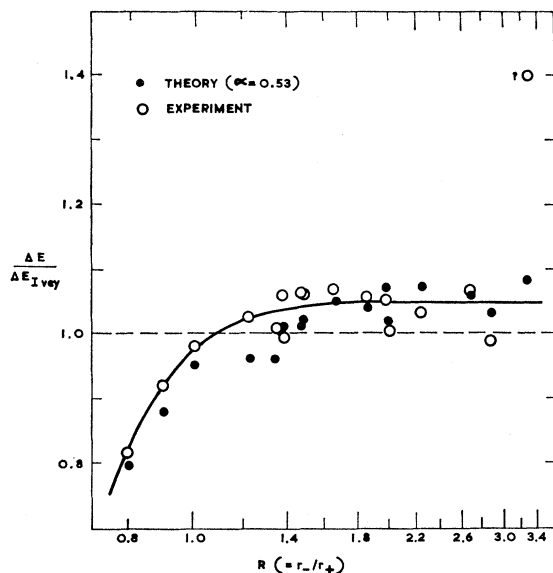


FIG. 2. *F*-band energies normalized to the Ivey law as a function of the ratio of ionic radii. Open circles denote the average of experimental values, Refs. 15 and 18, and solid circles are theoretical values with $\alpha = 0.53$. The curve is a saturating exponential fit to the experimental data, Eq. (4.22).

and a . However, it is not clear how the compression is distributed between anions and cations.

Mansikka and Bystrand,²¹ in a theoretical investigation of the compressibility of LiF, have shown that the fluorine $2p$ orbitals are substantially compressed, and that there is a slight expansion of the remaining orbitals which is smaller by an order of magnitude. Thus, to a first approximation the anions take up the entire compression and the cations are unaffected. For want of any further information, let us assume that this result is applicable to all of the alkali halides. Then R_+ is constant under compression and the pressure shift is given by

$$-\left(\frac{\partial \ln E}{\partial \ln a}\right)_{r_+} = -\frac{a}{E} \left(\frac{\partial E}{\partial a}\right)_R - \frac{(1+R)}{E} \left(\frac{\partial E}{\partial R}\right)_a. \quad (4.21)$$

(Note that if the ions were compressed in proportion to their size, the pressure shift would be given by the first term alone.)

In order to test these suppositions the experimental *F*-band data shown in Fig. 2 were fitted to a saturating exponential,

$$\Delta E(a, R) = \Delta E_{\text{Ivey}}(a) [1.05 - 18.0 \exp(-5.5R)]. \quad (4.22)$$

Substitution of Eq. (4.22) in Eq. (4.21) yields a pressure shift which depends only on R ,

$$-\left(\frac{\partial \ln E}{\partial \ln a}\right)_{r_+} = +1.84 - \frac{99(1+R) \exp(-5.5R)}{[1.05 - 18.0 \exp(-5.5R)]}. \quad (4.23)$$

²¹ K. Mansikka and F. Bystrand, J. Phys. Chem. Solids **27**, 1073 (1966).

This expression is plotted in Fig. 3 and compared with the experimental values. Except for the factor of 2 which has been attributed to enhanced local compressibility, the agreement is quite good, especially the value of R for which the pressure shift changes sign. Thus it appears possible to account in part for the observed pressure shift of *F*-band energies in terms of a rather simple model for ion-size effects.

This interpretation of the pressure shift is by no means certain, however, and other models are possible which involve purely mechanical effects of relative ion sizes.

D. Alkaline-Earth Fluorides

In applying the ion-size correction to *F* centers in alkali halides, it was found necessary to diminish the pseudopotential coefficients A_γ by a factor α ($= 0.53$) in order to obtain good agreement with experiment. This result suggests the definition of a set of semiempirical pseudopotential coefficients obtained from Table I by reducing A_H and A_X by the factor 0.53. The utility of such a definition depends on how well this set of coefficients works for other color centers or other compounds. In order to investigate this point, we have applied the ion-size correction to *F* centers in the alkaline-earth fluorides, CaF_2 , SrF_2 , and BaF_2 , and have carried out the computation for several values of α .

The method of calculation was essentially the same as for the alkali halides, with appropriate modifications for the fluorite structure. The trial functions of GA, Eqs. (4.6) and (4.7), were again employed, and contributions of the first 20 shells of ions were included.

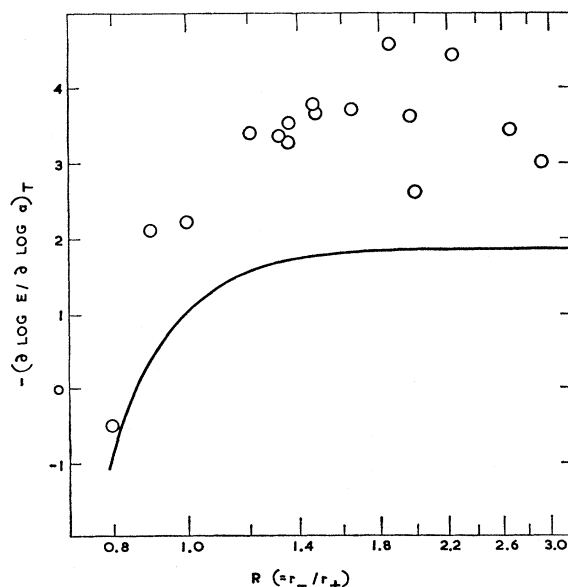


FIG. 3. Pressure shift of *F*-band energies as a function of the ratio of ionic radii. The points are the experimental values of Buchenauer and Fitchen (Ref. 15). The curve is derived from the data of Fig. 2 and the assumption that the cations are incompressible.

TABLE IV. Comparison of calculated F -band energies (Ry) in alkaline-earth fluorides with experiment^a and with the results of a point-ion calculation.^b The pseudopotential coefficients A_H and A_X of Table I have been diminished by the factor 0.53.

Compound	ΔE_{theor}	ΔE_{expt}^a	$\Delta E_{\text{theor}}^b$
CaF ₂	0.264	0.243	0.235
SrF ₂	0.214	0.206	0.214
BaF ₂	0.153	0.147	0.193

^a B. C. Cavenett *et al.* (Ref. 22).

^b H. S. Bennett and A. B. Lidiard (Ref. 23).

There are two Madelung constants in fluorite.²² If we take them to be the absolute value of the electrostatic potential at the ion site in units of e/a , where a is the nearest-neighbor distance, they are given by

$$\alpha_+ = 3.315, \quad (4.24a)$$

$$\alpha_- = 1.762. \quad (4.24b)$$

In Eq. (4.8), α_m is replaced by α_- . The ion-size and polarization corrections are the same as for alkali halides, but the distortion correction is modified as follows: Equations (4.15) and (4.16) are replaced by

$$C = -(\alpha_+ + \alpha_-)/a + (16/a)(\eta + 1)^{-1} \sin^2 \xi + 2(1 + \eta)V_+, \quad (4.25)$$

$$D = (\alpha_+ + \alpha_-)(5\lambda - 11)/3a + 10\sqrt{3}/a\sqrt{2} + (32/a) \sin^2 \xi + [8(\eta + 1)^2\Gamma_+ + 2(3 + 4\eta + 2\eta^2)]V_+, \quad (4.26)$$

and $n_1 = 4$ in Eqs. (4.17) and (4.18).

The F -band energies computed for $\alpha = 0.53$ are listed in Table IV, where they are compared with the experimental values of Cavenett, Hayes, and Hunter²³ and the point-ion calculations of Bennett and Lidiard.²⁴ The results of the present calculation are seen to provide a considerable improvement over the point-ion results. In particular, the trend of values with increasing cation radius is much better, and the low transition energy for BaF₂, which was previously thought anomalous,²⁴ is now explained in terms of an added attractive potential on the Ba⁺⁺ ion.

The F -band energies in the alkaline-earth fluorides are very sensitive to the factor α , and the value $\alpha = 0.53$ is very nearly optimum (the value $\alpha = 0.51$ yields a somewhat lower mean-square deviation but a less satisfactory trend). Thus the definition of a set of semi-empirical pseudopotential coefficients in which the A_γ incorporate the factor 0.53 appears to be well justified.

E. Detailed Results of F -Center Calculations

In this section, detailed results of the F -center calculations with $\alpha = 0.53$ are presented for both alkali halides and alkaline-earth fluorides. Table V shows the total energy E of the ground state as well as separate

contributions to this energy from the point-ion potential, ion-size correction, polarization, and distortion.

The distortion parameter σ_0 and wave-function parameters ξ and η are shown in Table VI, which also lists pseudopotential coefficients C_+ and C_- for the cations and anions nearest the vacancy, respectively. Corresponding quantities for the first excited state are shown in Tables VII and VIII. The excited state energies were calculated for the same ionic configurations as the ground state, and thus, by the Frank-Condon principle, are appropriate for the interpretation of absorption spectra; energies for the relaxed excited state were not determined.

V. DISCUSSION

An ion-size correction to the point-ion model Hamiltonian has been derived from the pseudopotential theorem. This correction is actually a nonlocal operator, but it has been put into a very simple approximate form [Eqs. (2.22)–(2.25)] by neglecting the variation of the pseudo-wave-function over the ion cores. The simplified form of the ion-size correction works well in the calculation of ionization potentials for alkali atoms. However, in applying the correction to F centers in alkali halides and alkaline-earth fluorides, it has been found necessary to reduce all of the pseudopotential coefficients A_γ by a factor 0.53 in order to obtain agreement with experiment. Since the same reduction factor works for all compounds considered, it is proposed that a set of semi-empirical pseudopotential coefficients for color centers be defined which incorporate this factor. The source of the discrepancy between theory and experiment which necessitates the introduction of an empirical factor is not apparent.

TABLE V. Contributions to the ground-state energies of F centers in alkali halides and alkaline-earth fluorides. E_{PI} includes the kinetic energy and point-ion potential. E_{IS} is the ion-size correction; E_{pol} and E_{dist} are, respectively, the corrections for polarization and distortion; and E is the total energy. All energies are in Rydbergs.

Compound	E_{PI}	E_{IS}	E_{pol}	E_{dist}	E
CsF	-0.442	-0.068	-0.014	-0.022	-0.547
RbF	-0.469	-0.048	-0.010	-0.009	-0.536
KF	-0.490	-0.017	-0.007	-0.003	-0.516
RbCl	-0.422	-0.013	-0.003	-0.003	-0.442
RbBr	-0.407	-0.010	-0.003	-0.002	-0.422
NaF	-0.543	0.036	-0.003	-0.000	-0.510
KCl	-0.437	0.001	-0.002	-0.002	-0.440
KBr	-0.422	0.001	-0.002	-0.001	-0.424
RbI	-0.389	-0.002	-0.002	-0.002	-0.395
KI	-0.392	0.007	-0.001	-0.002	-0.398
NaCl	-0.474	0.023	-0.001	-0.000	-0.453
LiF	-0.593	0.059	-0.001	-0.001	-0.535
NaBr	-0.455	0.017	-0.001	-0.000	-0.439
NaI	-0.429	0.016	-0.000	-0.001	-0.414
LiCl	-0.505	0.031	-0.000	-0.000	-0.475
LiBr	-0.482	0.022	-0.000	-0.000	-0.460
LiI	-0.453	0.020	-0.000	-0.001	-0.434
CaF ₂	-0.535	-0.018	-0.009	-0.002	-0.563
SrF ₂	-0.511	-0.057	-0.011	-0.007	-0.586
BaF ₂	-0.479	-0.115	-0.017	-0.020	-0.631

²² A. D. Franklin, J. Phys. Chem. Solids **29**, 823 (1968).

²³ B. C. Cavenett, W. Hayes, and I. C. Hunter, Solid State Commun. **5**, 653 (1967).

²⁴ H. S. Bennett and A. B. Lidiard, Phys. Letters **18**, 253 (1965).

TABLE VI. Ground-state parameters for F centers in alkali halides and alkaline-earth fluorides. σ_0 is the distortion parameter (the nearest cations are displaced *inward* by $\sigma_0 a$); ξ and η are wave-function parameters defined by Eqs. (4.6) and C_+ and C_- are the pseudopotential coefficients of Eq. (2.25) appropriate to the nearest cations and anions, respectively, in the ground state.

Compound	σ_0	ξ	η	C_+	C_-
CsF	0.080	2.23	1.71	-26.31	-18.30
RbF	0.044	2.25	1.80	-14.25	-16.47
KF	0.021	2.27	1.91	-2.25	-14.43
RbCl	0.025	2.31	2.10	-2.49	-31.08
RbBr	0.021	2.31	2.10	0.71	-42.90
NaF	-0.000	2.30	2.06	10.16	-9.68
KCl	0.017	2.33	2.20	5.56	-29.84
KBr	0.015	2.32	2.18	7.70	-41.81
RbI	0.023	2.36	2.36	4.43	-42.18
KI	0.019	2.38	2.51	11.28	-38.32
NaCl	0.007	2.35	2.32	13.30	-21.92
LiF	-0.007	2.28	1.97	9.83	-5.32
NaBr	0.007	2.34	2.26	14.20	-33.52
NaI	0.013	2.38	2.50	15.24	-31.08
LiCl	0.003	2.33	2.23	12.69	-16.59
LiBr	0.003	2.32	2.14	13.44	-28.11
LiI	0.010	2.37	2.44	14.24	-24.83
CaF ₂	0.015	2.24	1.76	1.27	-7.93
SrF ₂	0.028	2.22	1.67	-12.81	-10.85
BaF ₂	0.055	2.17	1.49	-39.68	-14.37

The neglected variation of the pseudo-wave-function over ion cores appears to be the most serious approximation, and we now consider qualitatively the effect of this variation on the ratio B_γ/A_γ . Comparison of Eqs. (2.21) and (2.22) with Eq. (2.19) suggests the definition of parameters A'_γ and B'_γ by

$$A'_\gamma \equiv [(\phi, (1-P_\gamma)(V_\gamma - V_{PI\gamma})\phi) - (\phi, P_\gamma V_{PI\gamma}\phi)] / |\phi(\mathbf{r}_\gamma)|^2, \quad (5.1)$$

$$B'_\gamma \equiv (\phi, P_\gamma \phi) / |\phi(\mathbf{r}_\gamma)|^2. \quad (5.2)$$

If the first term in the numerator of A'_γ is neglected, the ratio B'_γ/A'_γ is given by

$$B'_\gamma/A'_\gamma = -(\phi, P_\gamma V_{PI\gamma}\phi) / (\phi, P_\gamma \phi). \quad (5.3)$$

The most significant part of the variation of ϕ over ion cores arises from the exponential factors in Eqs. (4.6a) and (4.7a). Accordingly, we assume that $\phi(\mathbf{r})$ has the form

$$\phi(\mathbf{r}) = \phi(\mathbf{r}_\gamma) e^{-\eta(r \cos\theta)/\alpha}, \quad (5.4)$$

where θ is with respect to the line joining ion γ with the anion vacancy. In addition, the approximation of Eq. (2.26) is adopted, with the result

$$\frac{B'_\gamma/A'_\gamma}{B_\gamma/A_\gamma} = \frac{3(1 - \tanh x/x)}{2(1 - 1/\cosh x)}, \quad (5.5)$$

$$x \equiv 2\eta r_{\text{ion}}/\alpha. \quad (5.6)$$

The right-hand side of Eq. (5.5) varies between 1 and 1.5 over the range $0 \leq x < \infty$; however, for the largest ions considered here, it does not exceed 1.2. Thus the variation of the pseudo-wave-function over ion cores leads to a modification of B_γ/A_γ which is in the right

direction, but is not large enough in the present approximation. A more accurate treatment might yield a larger effect. From another point of view, the variation of the pseudo-wave-function introduces a projection on occupied p and d orbitals, and thus the angular-momentum dependence of the pseudopotential is involved.

Another major approximation is the neglect of overlaps of occupied ion-core orbitals on different centers. As a consequence of the nonorthogonality of ion-core orbitals, the operator P of Eq. (2.16) is not idempotent and hence is not a valid projection operator. Since the P_γ are idempotent, P^2 is given, to terms linear in overlap integrals, by

$$P^2 = P + \sum_{\lambda \neq \gamma} \sum_{\gamma} P_\lambda P_\gamma. \quad (5.7)$$

In order to estimate the effect of our approximation, we introduce a modified projection operator P' , defined by

$$P' \equiv P - \sum_{\lambda \neq \gamma} \sum_{\gamma} P_\lambda P_\gamma. \quad (5.8)$$

It follows from Eqs. (5.7) and (5.8) that P' is idempotent to terms linear in overlap integrals. The use of P' leads to modified expressions for the pseudopotential coefficients,

$$A'_\gamma = A_\gamma + \sum_{\lambda \neq \gamma} \int P_\lambda P_\gamma V_\gamma d\tau, \quad (5.9)$$

$$B'_\gamma = B_\gamma - \sum_{\lambda \neq \gamma} \int P_\lambda P_\gamma d\tau. \quad (5.10)$$

To the extent that V_γ in Eq. (5.9) can be replaced by the average value of $V_{PI\gamma}$ over the interior of the ion $\bar{V}_{PI\gamma}$, the changes in the coefficients are related by

$$\delta A_\gamma \approx -\bar{V}_{PI\gamma} \delta B_\gamma. \quad (5.11)$$

TABLE VII. Contributions to the excited-state energies of F centers in alkali halides and alkaline-earth fluorides. The symbols are defined in the caption of Table V.

Compound	E_{PI}	E_{IS}	E_{pol}	E_{dist}	E
CsF	-0.290	-0.084	-0.043	0.005	-0.411
RbF	-0.296	-0.052	-0.036	0.017	-0.367
KF	-0.299	0.003	0.031	0.013	-0.314
RbCl	-0.286	-0.010	-0.015	0.008	-0.302
RbBr	-0.280	-0.009	-0.013	0.007	-0.294
NaF	-0.304	0.092	-0.019	-0.000	-0.232
KCl	-0.291	0.016	-0.011	0.007	-0.279
KBr	-0.285	0.012	-0.010	0.006	-0.278
RbI	-0.276	0.003	-0.007	0.006	-0.274
KI	-0.281	0.018	-0.005	0.006	-0.263
NaCl	-0.300	0.049	-0.006	0.004	-0.252
LiF	-0.298	0.162	-0.004	-0.008	-0.149
NaBr	-0.294	0.034	-0.006	0.004	-0.262
NaI	-0.290	0.034	-0.003	0.005	-0.255
LiCl	-0.304	0.071	-0.002	0.002	-0.233
LiBr	-0.300	0.048	-0.002	0.002	-0.253
LiI	-0.296	0.043	-0.001	0.004	-0.249
CaF ₂	-0.301	0.027	-0.040	0.014	-0.300
SrF ₂	-0.299	-0.049	0.044	0.020	-0.371
BaF ₂	-0.294	-0.149	-0.050	0.015	-0.478

TABLE VIII. Excited-state parameters for F centers in alkali halides and alkaline-earth fluorides. ξ' and η' are wave-function parameters defined by Eqs. (4.7), and C_+' and C_-' are the pseudo-potential coefficients of Eq. (2.25) appropriate to the nearest cations and anions, respectively, in the excited state.

Compound	ξ'	η'	C_+'	C_-'
CsF	3.15	3.04	-19.89	-16.05
RbF	3.14	2.98	- 8.06	-12.89
KF	3.13	2.95	4.44	- 8.97
RbCl	3.22	3.27	2.66	-23.29
RbBr	3.21	3.23	5.71	-33.78
NaF	3.11	2.90	13.54	- 0.92
KCl	3.24	3.32	10.79	-18.65
KBr	3.22	3.27	12.77	-28.78
RBI	3.30	3.57	8.47	-30.64
KI	3.32	3.63	14.56	-25.09
NaCl	3.22	3.27	15.23	- 8.83
LiF	3.10	2.86	12.93	6.61
NaBr	3.19	3.17	15.99	-18.90
NaI	3.31	3.59	16.53	-14.63
LiCl	3.22	3.27	14.26	- 0.84
LiBr	3.18	3.13	14.87	-10.74
LiI	3.30	3.56	15.23	- 6.05
CaF ₂	3.07	2.78	8.39	0.08
SrF ₂	3.06	2.76	- 5.25	- 5.20
BaF ₂	3.06	2.77	-34.14	-11.92

But Eqs. (2.27) imply that $\tilde{V}_{FI\gamma}$ is approximately equal to $-A_\gamma/B_\gamma$, and thus Eq. (5.11) can be written

$$\delta A_\gamma/A_\gamma \approx \delta B_\gamma/B_\gamma. \quad (5.12)$$

Consequently, A_γ and B_γ are reduced in the same proportion when overlaps are included, and again the required adjustment in the ratio B_γ/A_γ is not explained.

We have seen previously that the unadjusted pseudo-potential coefficients work well for isolated alkali atoms. Furthermore, when A_γ is reduced by 0.53, the computed ionization potentials of Li and Na are much too large, and no self-consistent solution is obtained at all for the other alkali atoms. Thus the reduction in A_γ appears to be a property of the ions when they are incorporated in ionic crystals, and one can only infer that the discrepancy arises from the use of free-ion orbitals for the occupied core states²⁵ and the variation of the pseudo-wave-function over the ions.

The required reduction of A_γ clearly demands further investigation. Nevertheless, the fact that just one adjustable parameter provides good results for F -band energies in 17 alkali halides and three alkaline-earth fluorides encourages one to believe that the adjusted coefficients will prove useful in other color-center calculations as well.

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²⁵ J. Hermason and J. C. Phillips, Phys. Rev. **150**, 652 (1966).