PHYSICAL REVIEW B VOLUME 26, NUMBER 6 15 SEPTEMBER 1982

Unrestricted-Hartree-Fock cluster analysis of F and F_A centers in some alkali halides

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(Received 26 February 1982)

Unrestricted-Hartree-Fock cluster calculations are reported, which include the nearest-neighbor ions of F centers in the lithium and potassium halides, and of F_A(Li) centers in the potassium halides. The Coulomb potential of a surrounding lattice of point ions is included. Optical-absorption energies, including F_A splitting, are found to be in satisfactory agreement with experiment, but ground-state hyperfine-structure constants generally are not. Spin-polarization and impurity-ion-displacement effects are also examined.

I. INTRODUCTION

The F center in an alkali halide poses a theoretical problem of interest in relation to other defects as well, in that its electronic structure may not be neglected. Furthermore, it appears to have some simplifying features, since it is an electrically neutral defect, and the alkali halide lattice has been described with some success by a point-ion model. Indeed the model of an F center as one electron trapped at an anion vacancy in a point-ion lattice was shown to give qualitative agreement with optical-absorption data (the Mollevo-Ivey relation) 25 years ago, by Gourary and Adrian.[1] This point-ion model has since been solved exactly by Laughlin.[2]

It was realized, of course, that more accurate theoretical results required that the electronic structure of ions near the F center be taken into account. This is done intrinsically in one-electron linear combination of atomic-orbital—molecular-orbital (LCAO-MO) calculations, early examples of which are described in Sec. VII of the review by Gourary and Adrian.[3] These early LCAO-MO calculations were rudimentary, due to computational limitations.

Another approach, which has been carried through in considerable detail, is orthogonalization of a simple variational one-electron F-center wave function to the cores of surrounding ions, based on the Hartree-Fock approximation. Kojima[4] applied this method to LiF, including first- and second-nearest neighbors described by free-ion orbitals. Wood and Joy[5] did the same for nine alkali halides, including only nearest neighbors and treating inner electrons of K^+ and Na^+ ions approximately. Wood and Öpik[6] extended some of the work of Wood and Joy, including consideration of second- and third-nearest neighbors. In Refs. 4, 5, and 6, empirical polarization corrections were also introduced, and the exchange energy was only evaluated approximately. Recently, Leung and Song[7] have analyzed the F-center electron in LiF in Hartree-Fock approximation, including up to fifth-nearest neighbors, and evaluated the exchange energy exactly.

Introducing a pseudopotential into the one-electron Hartree-Fock Hamiltonian is in principle equivalent to orthogonalizing to ionic cores. A widely used approximation of the pseudopotential method was introduced for color centers by Bartram, Stoneham, and Gash.[8] It permitted several shells of neighbors to be included, but limited the ion-size correction to spherically symmetric contributions, and in most applications included an empirical parameter. The method was computationally simple enough that it could be applied to a wide variety of color centers, including, in the alkali halides of the NaCl structure, F centers,[8–12] F_A centers,[13–16] and F_B centers,[17,18] and of the CsCl structure, F, F_A, and F_H centers.[19,20] Although acceptable agreement with experimental optical absorption was obtained for F centers, it was found[13–20] that the empirical parameter did not carry over straightforwardly to optical absorption in F_A, F_B, and F_H centers.

In addition to optical-absorption data, ground-state electron nuclear double resonance (ENDOR) data are available for F centers[21–23] and for F_A centers.[24,25] Wood,[26] in obtaining satisfactory agreement with experimental F-center spin densities for several shells of neighbors in KCl, has demonstrated the need to deal with ion-ion overlap and to include sufficient wave-function flexibility and enough neighbors, when using a one-electron wave function orthogonalized to neighboring ions. Harker[9] has analyzed both isotropic and axially symmetric hyperfine constants for the first two shells of neighbors for F centers in all the alkali halides, including ion-ion orthogonalization, with both the pseudopotential ion-size correction of Ref. 8 and point-ion calculations. He found that in the potassium halides the point-ion results for nearest neighbors are somewhat better than those with the ion-size correction, and that results for LiF are particularly bad. In the same way, Harker and Vail[18] analyzed the hyperfine constants for the three inequivalent nearest neighbors of the F_A center in KBr:Li, but found that qualitatively correct results were only obtained in the point-ion approximation.

It is clear from the foregoing that, even to obtain agreement with experimental ground-state properties of F-type centers requires fairly thorough treatment of the electronic structure of surrounding ions. The long-range objective of work in this field is to be able to predict color-center properties, for optically excited and thermally activated states as well as for ground states. This requires that electron-phonon interaction and lattice distortion also be included accurately in the theoretical analysis. The immediate objective of the present work is to begin to come to grips with the ion-size problem for ground-state properties by dealing rigorously with a relatively simple model, resisting any temptation to improve agreement with experiment by including *ad hoc* empirical corrections for the model's physical deficiencies. Thus our unrestricted-Hartree-Fock cluster calculations on F and F_A centers, including only nearest neighbors, omit potentially important electronic correlation, and ion-size effects of second and further neighbors, as well as lattice distortion and electron-phonon effects. On the other hand, our calculations include, in a rigorous and self-consistent manner, electronic features which in previous works were treated approximately, or inconsistently, or were neglected. We find that the results include the first satisfactory derivation of F_A-center optical-absorption splitting, as well as a number of other correct properties.

In Sec. II we describe our theoretical method and refer to previous comparable analyses of F centers. In Sec. III our calculations and results are summarized, and in Sec. IV our results are discussed and conclusions presented. The work is based on the Ph.D. thesis of Kung at the University of Manitoba, 1981 (unpublished).

II. METHOD

We shall deal with F-type centers in alkali halides, with and without substitutional alkali impurities. Thus we consider an electron trapped in an anion vacancy. Since we wish to examine the ion-size effect, we take as our model system a molecular cluster of six bare alkali nuclei at nearest-neighbor sites to the vacancy, with n electrons, consisting of the excess (vacancy-trapped) electron, plus those associated with the nearest-neighbor ions. This molecular cluster is embedded in a lattice of point ions of charges $\pm e$ for alkali and halide ions, respectively. We consider this n-electron problem in Hartree-Fock approximation, i.e., we assume that the wave function Ψ is a single Slater determinant. The energy is then a minimum if the orthonormal set of functions $\phi_j(\vec{x})$, $j=1, 2, \ldots, n$, from which Ψ is constructed satisfy the Hartree-Fock equation,

$$F\phi_j(\vec{x})=\epsilon_j\phi_j(\vec{x}) \ , \tag{1}$$

where $(\vec{x})=(\vec{r},s)$ represents electron space $(\vec{r})$ and spin (s) coordinates, and where the Fock operator F in SI units is

$$F=\left[\frac{-\hbar^2\nabla^2}{2m}+V(r)\right]+\frac{e^2}{4\pi\epsilon_0}\times\int\frac{d\tau'}{|\vec{r}-\vec{r}\,'|}[\rho(\vec{x}\,',\vec{x}\,')-\rho(\vec{x},\vec{x}\,')P(\vec{x},\vec{x}\,')] \ , \tag{2}$$

where

$$\rho(\vec{x},\vec{x}\,')=\sum_{j=1}^{n}\phi_j(\vec{x})\phi_j^\dagger(\vec{x}\,') \ . \tag{3}$$

$\int d\tau'$ includes space and spin integration, and $P(\vec{x},\vec{x}\,')$ is an operator which interchanges $\vec{x}$ and $\vec{x}\,'$. In our problem

$$V(\vec{r})=\frac{-e^2}{4\pi\epsilon_0}\left[\sum_{l=1}^{6}\frac{Z_l}{|\vec{r}-\vec{R}_l|}+\sum_{l=7}^{\infty}\frac{I_l}{|\vec{r}-\vec{R}_l|}\right], \tag{4}$$

where $\vec{R}_l$ are ion positions, with $l=1,2,\ldots,6$ corresponding to nearest neighbors of the F-center vacancy, (eZ_l) is nuclear charge, and (eI_l) is ionic charge. The validity of such a cluster-Hartree-Fock model is discussed in detail by Kunz and Klein.[27] In the present case it is the localization of the ions and of the excess electron's charge that is relied upon.

In most applications of the Hartree-Fock approximation, the functions $\phi_j(\vec{x})$ are taken to be spin eigenfunctions. In the restricted-Hartree-Fock approximation (RHF) the two spin eigenstates are each associated with $n/2$ spatial functions if n is even, or with $(n\pm1)/2$, respectively, if n is odd. In the unrestricted-Hartree-Fock approximation (UHF) used here, all n functions ϕ_j may have different spatial dependences, but all are required to be spin eigenstates. In the general Hartree-Fock approximation (GHF), the latter restriction is removed. We shall see that UHF has a definite advantage over RHF for the present problem, because one of the eigenstates of F, Eq. (1), is mainly associated with the vacancy. Since in UHF it has definite spin, denoted $+1$, it follows that the remaining even number of states associated with the closed-shell ions interact with this vacancy electron differently through the exchange term P, depending on whether they have spin $+1$ or not.

In our calculations, 18 shells of neighboring ions were included in $V(\vec{r})$, Eq. (4), with fractional values of I_l assigned on faces, edges, and corners of the crystal region thus defined, so that F in Eq. (2) refers to an electrically neutral system, and the Coulomb potential throughout the cluster is highly accurate. The Hartree-Fock eigenfunctions ϕ_j, Eq. (1), are taken as a linear combination of atomic orbitals, $\chi_k(\vec{x})$, localized on ionic and vacancy sites,

$$\phi_j(\vec{x})=\sum_k c_{kj}\chi_k(\vec{x}), \tag{5}$$

where k ranges over atomic orbitals on a given site, and over sites in the molecular cluster (vacancy and six-nearest neighbors, in our case). In Eq. (5), ϕ_j is a spin eigenstate, and the χ_k are Gaussian-type orbitals. For a given set of χ_k, the energy ϵ_j is a minimum with respect to variations of the coefficients c_{kj}, for given j if self-consistency is achieved, and if

$$(\underline{F}-\epsilon_j\underline{S})\cdot\underline{c}_j=0. \tag{6}$$

where $\underline{F}$ and $\underline{S}$ are Fock and overlap matrices, respectively, in the basis of atomic orbitals χ_k, $\underline{c}_j$ is the jth column of the eigenfunction matrix c_{kj}, and

$$S_{kk'}=\int d\tau\,\chi_k\chi_{k'}. \tag{7}$$

If there are more basis functions χ_k than electrons in the cluster, additional (virtual) orbitals are included in the set ϕ_j. The integrals involved in Eqs. (6) and (7) are evaluated using the Caltech version of the POLYATOM integral program. The n lowest solutions for ϕ_j from Eq. (6), for a cluster of n electrons, then enable us to evaluate our approximation to the total energy and wave function. The self-consistent solution of Eq. (6) is carried out iteratively in an orthonormal molecular-orbital basis, using programs based on the UHFONE program of Surratt from the University of Illinois at Urbana-Champaign. For this, an initial guess denoted $\underline{c}^{(I)}$ is made for the eigenfunction matrix $\underline{c}$. This determines an initial Fock matrix $\underline{F}^{(I)}$. Equation (6) is transformed to an orthonormal basis by a unitary transformation $\underline{T}_0$ which diagonalized $\underline{S}$, Eq. (7). At this stage we have

$$(\underline{F}^{(I)'}-\epsilon_j\underline{I})\cdot\underline{c}_j'\approx0, \tag{8}$$

where $\underline{I}$ is the identity matrix, $\underline{F}^{(I)'}=(\underline{T}_0\cdot\underline{F}_{(I)}\cdot\underline{T}_0^{-1})$, and $\underline{c}_j'=\underline{T}_0\cdot\underline{c}_j$, where primes denote the orthonormal basis. In Eq. (8), $\underline{F}^{(I)'}$ is now diagonalized by $\underline{T}$,

$$[(\underline{T}\cdot\underline{F}^{(I)'}\cdot\underline{T}^{-1})-\epsilon_j\underline{I}]\cdot[\underline{T}\cdot\underline{c}_j']=0. \tag{9}$$

This determines the zeroth-order solution $\underline{c}'\approx\underline{c}^{(0)'}$ from $\underline{T}\cdot\underline{c}^{(0)'}=\underline{I}$, $\underline{c}^{(0)'}=\underline{T}^{-1}$. Self-consistency requires that $\underline{T}\approx\underline{I}$ (to within 10^{-5} a.u. in our work). If this is not satisfied, iteration proceeds by using $\underline{c}^{(0)'}$ in place of $\underline{c}^{(I)'}$ to determine $\underline{F}^{(0)'}$ in place of $\underline{F}^{(I)'}$ in Eq. (8), diagonalizing with $\underline{T}_1$, etc., to convergence.

Two previous sets of work have applied the above approach to the F center of LiF. Chaney and Lin[28] and Chaney[29] included the electronic structure of ions out to sixth-nearest neighbors in their calculations, but used Slater's statistical-exchange approximation and performed only one iteration, not achieving self-consistency. Murrell and Tennyson[30,31] have treated exchange rigorously and carried the LCAO-MO calculations to self-consistency, including up to third-nearest neighbors in the cluster. In order to do this, they required more extensive contractions than we have used (see Sec. III), they used the RHF approximation, and included only up to eighth-nearest neighbors in the surrounding point-ion lattice. The particular importance of their work is the analysis of second- and third-neighbor effects, and of nearest-neighbor displacements.

In addition to the works cited above, Yu, de Siqueira, and Connolly[32] have analyzed the F center (and others) in KCl in a self-consistent calculation, using the multiple-scattering $X\alpha$ method, which incorporates statistical exchange and other approximations not included in the present work. Their results exhibit the spin-polarization effect.

III. CALCULATION AND RESULTS

A. F Centers

In principle, a basis function $\chi_k(\vec{x})$ in Eq. (5) is taken to be a spherical harmonic with Gaussian localization centered on an ionic site $\vec{R}_l$,

$$\chi_k \sim \exp[-\alpha_k(\vec{r}-\vec{R}_l)^2] \; , \tag{10}$$

where α_k is referred to as the exponent. In practice, χ_k may have a specified linear combination of such Gaussians, in which case we say that χ_k is a contraction of its constituent Gaussians. The exponents and the linear coefficients in a contraction are usually based on subsidiary calculations, or on experience.

Initially, we have investigated the sensitivity to choice of basis set of F-center ground-state properties in LiF. The results from four basis sets are given in Table I. For the six Li^+ ions: (a) $(11s/4s)$, meaning 11 s-type orbitals contracted to four, from the atomic orbital compilation of Huzinaga[33]; (b) same as (a), plus p-type functions (p_x,p_y,p_z) having $\alpha=0.95$; (c) same as (b), plus p-type functions with $\alpha=0.20$; (d) seven uncontracted s-type orbitals from Chaney and Lin,[27] plus two additional s type with α's equal to 2.50 and 0.05. For the vacancy-centered basis functions, cases (a), (b), and (c) had four uncontracted s type, with α's given in Table II along with the $(11s/4s)$ set, and case (d) had four s types from Ref. 27, plus two others, with α's of 2.50 and 0.05. The spin density of Table I is defined by

$$S(\vec{R}_l)=\left\langle \Psi \left| \sum_{j=1}^{n} \sigma_{zj}\delta(\vec{r}_j-\vec{R}_l) \right| \Psi \right\rangle = \left[\sum_{j=1}^{n^+} |\phi_j(\vec{R}_l)|^2 - \sum_{j'=n^+ +1}^{n} |\phi_{j'}(\vec{R}_l)|^2 \right] , \tag{11}$$

where σ_{zj} is the Pauli spin operator σ_z for the jth electron, and n^+ is the number of orbitals ϕ_j having σ_z eigenvalues equal to $+1$. From Table I we see that inclusion of p-type Li orbitals lowers the cluster's ground-state energy by 0.08–0.11 eV, with a corresponding small effect on spin density, and that the Chaney and Lin basis (d) is highest in energy. Since basis sets (b) and (c) have 46 and 64 basis functions, respectively, compared to 28 for set (a), the very large increase in computation does not seem justified. Accordingly, in what follows, basis set (a), Table II, is used exclusively for the lithium halides.

F-center optical-absorption energies and nearest-neighbor ground-state hyperfine-structure constants were evaluated for the lithium and potassium halides. The basis set used for K^+ was taken from Huzinaga's contractions[33] of $(14s/4s)$ and $(10p/3p)$ for argon, with vacancy-centered basis functions the same as for the lithium halides, Table II. For optical absorption the excited state

TABLE I. Ground-state energy and spin density S, Eq. (11), at nearest-neighbor Li^+ site, both in a.u. for the F center in LiF, calculated from four basis sets described in the text.

Basis set	Energy	S
(a)	−52.6600	0.039
(b)	−52.6629	0.036
(c)	−52.6642	0.035
(d)	−52.6428	0.041

TABLE II. Exponents and contraction coefficients of basis set (a), described in text, for s-type basis functions used for F-center calculations in the lithium halides.

Lithium ions		Vacancy	
Exponent	Coefficient	Exponent	Coefficient
3184.467	0.0216	2.000	
480.512	0.1665		
108.863	0.8723		
30.289	0.1001	0.750	
9.641	0.3090		
3.339	0.6666		
1.249	0.7176	0.080	
0.467	0.3183		
0.079	−0.0547	0.015	
0.066	0.6988		
0.025	0.3937		

TABLE III. *F*-center optical-absorption energies (eV) in lithium and potassium halides: GA, Ref. 1; WJ, Ref. 5; BSG, Ref. 8; UHF, present work; experiment, Ref. 34.

	GA	WJ	BSG	UHF	Experiment
LiF	3.99	3.26	5.49	3.54	5.13
LiCl	2.76	3.22	3.34	3.32	3.34
LiBr	2.58	2.93	2.86	3.05	2.7
LiI	2.14		2.48	2.65	3.25
KF	2.60	2.81	2.93	3.02	2.80
KCl	1.99	2.39	2.18	2.35	2.33
KBr	1.83	2.26	1.98	2.22	2.12
KI	1.64		1.80	2.03	1.89

was taken to have the vacancy-centered *s*-type functions of the ground state replaced by *p*-type orbitals with the same set of α's. Thus for a given alkali, only the lattice spacing changes, both in the cluster and in the surrounding point-ion lattice, as the halide changes. The results are shown in Table III, compared with earlier calculations for optical absorption and with experiment.[34] The agreement with experiment is moderately good except at two extermes, LiF and LiI. The experimental value for LiI has been questioned.[35]

We remarked earlier that spin polarization of neighboring ions might be significant, due to the unpaired *F*-center electron, and that the UHF approximation allows for this effect. It is illustrated by the results for LiF in Fig. 1, showing the molecular-orbital energies ϵ_j and their degeneracies for each value of spin. A similar but less marked effect occurs in the potassium halides, for which the energy-level diagram is much more complicated.[36] This effect is discussed further in Sec. IV (see Table VII).

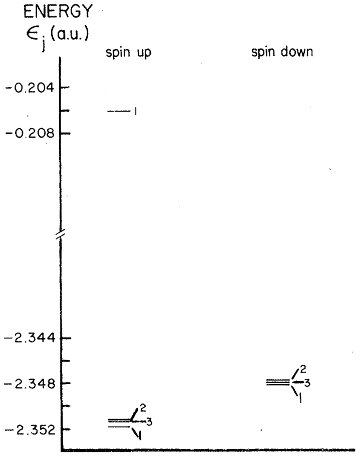

FIG. 1. Orbital-energy spectrum of the nearest-neighbor molecular cluster for the *F* center in LiF, illustrating the spin polarization of Li^+ levels by the *F*-center electron. The number associated with a level is its degeneracy.

The hyperfine interactions between electronic and nuclear magnetic dipole moments are expressible in terms of the hyperfine-interaction tensor $\underline{A}$,[37] which consists of an isotropic (scalar) part denoted a, and an anisotropic part $\underline{B}$, whose axially symmetric part is denoted $b=\frac{1}{2}B_{zz}$. The quantities a and b have been obtained experimentally for nearest neighbors to *F* centers in most alkali halides,[21–23] and relate directly to the electronic density, given by $S(\vec{R}_l)$ in Eq. (11), as follows:

$$a(\vec{R}_l)=\frac{8\pi}{3\hbar}g_e\mu_e g_l\mu_l S(\vec{R}_l)\,, \tag{12}$$

where g_λ,μ_λ are the g factors and Bohr magnetons for electrons ($\lambda=e$) and for nuclear species l ($\lambda=l$), and

$$b(\vec{R}_l)=\frac{g_e\mu_e g_l\mu_l}{2\hbar}\int d^3r_l S(\vec{r}_l)\frac{(3z_l^2-r_l^2)}{r_l^5}\,, \tag{13}$$

where $\vec{r}_l=(\vec{r}-\vec{R}_l)$, and z_l is its z component. In evaluating the integrals in Eq. (13), several approximations are made, as described by Harker,[9] based on the integrand's localization about $\vec{R}_l$ due to its $(r_l)^{-3}$ dependence, and the localization of basis functions χ_k about ionic sites. Thus we consider only contributions to $S(\vec{r}_l)$ from χ_k's localized on ion l and on the vacancy, and for the latter we use

$$\int d^3r_l\chi_k\left[\frac{3z_l^2-r_l^2}{r_l^5}\right]\chi_{k'} \approx\frac{(3z_l^2-R_l^2)}{R_l^5}\int_{r<R_l}d^3r\,\chi_k\chi_{k'}\,. \tag{14}$$

These approximations amount to neglect of ion-ion contributions to b, and to treating the vacancy-centered orbitals as contributing to a point dipole. Thus,

$$b(\vec{\mathrm{R}}_l) \approx \frac{g_e \mu_e g_l \mu_l}{2\hbar} \left[\sum_{kk'}^{(0)} c_k c_{k'} \left[\frac{3z_l^2 - R_l^2}{R_l^5} \right] \int_{r<R_l} d^3 r\, \chi_k \chi_{k'} + \sum_{kk'}^{(l)} c_k c_{k'} \int d^3 r_l \chi_k \left[\frac{3z_l^2 - r_l^2}{r_l^5} \right] \chi_{k'} \right], \tag{15}$$

where (0),(l) restrict summations to terms involving χ's localized on the vacancy and on ion l, respectively. The values of a and b, calculated from our results using Eqs. (11), (12), and (15) are given in Tables IV and V, compared with earlier calculations and with experiment.

B. F_A centers

The optical absorption of F_A centers is split into two components[38] because the F-center symmetry is lowered by the substitutional alkali impurity (Li^+ in the present work). These components are denoted F_{A1} and F_{A2}, corresponding to excited states that principally overlap nearest-neighbor impurity and host cations, respectively. This absorption splitting has usually been thought to be an ion-size effect, although the role played by asymmetrical lattice distortion (a sort of indirect ion-size effect) has also been considered. Previous theoretical work[13–16] has not been satisfactory in describing this splitting. We have therefore analyzed the F_A(Li) center of KCl and KBr, using the same basis sets for the K^+ ions and the vacancy as in the F-center calculations, Table II, and six uncontracted s-type Gaussians[33] for the Li^+ impurity. The Li^+ impurity is taken to occupy the (0,1,0) position, even though in KCl this is only the center of its tunneling motion amoung four equivalent off-axis sites.[39] For F_{A1} and F_{A2} excited states are therefore taken to correspond to p_y- and p_z-type functions, respectively. Hyperfine structure (hfs) data are available for the F_A(Li) center in both KCl (Ref. 24) and KBr (Ref. 25), and we have evaluated the nearest-neighbor ground-state a and b coefficients, using Eqs. (11), (12), and (15). For the F_A center there are three inequivalent nearest neighbors, and therefore three sets of hfs data: for the Li^+ impurity, for the host K^+ ion on the defect axis, denoted K_α^+, and for the four K^+ ions in a plane perpendicular to the axis, denoted K_β^+. In order to assess the effect of lattice relaxation in the defect. the KCl:Li results were recalculated with the Li^+ ion displaced outward by 0.08 nearest-neighbor distance. This value is thought to be realistic, as it was obtained by Ong and Vail[15] in a self-consistent lattice-statics analysis of the defect with the approximate pseudopotential method of Bartram *et al.*[8] The results of our F_A-center calculations are collected and compared with experiment in Table VI.

IV. DISCUSSION AND CONCLUSION

Apart from the static-lattice approximation, our analysis has two principal deficiencies: neglect of correlation, apart from that inherent in the UHF approximation, amounting to partial neglect of electronic polarization, and restriction of the cluster to nearest-neighbor ions. Another possible deficiency in calculations of this sort is lack of flexibility of the basis set. We shall discuss the discrepancies between our results and experimental data in relation to these deficiencies.

First we single out the F center in LiF, because

TABLE IV. Isotropic hyperfine constant a (MHz) of nearest-neighbor ions for the F-center ground state in lithium and potassium halides: GA, Ref. 1; BSG, Ref. 9; UHF, present work, with ^{7}Li and ^{39}K; experimental data as quoted in Ref. 9.

	GA	BSG	UHF	Experiment
LiF	101.0	93.6	61.29	38.15
LiCl	22.5	38.2	32.76	19.1
LiBr	15.0	32.1	26.83	
LiI	7.0	17.1	21.15	
KF	49.7	51.3	18.56	34.3
KCl	24.7	28.4	8.23	20.7
KBr	19.9	21.8	7.32	18.2
KI	13.6	17.3	5.90	15.1

TABLE V. Axially symmetry anisotropic hyperfine constant b (MHz) of nearest-neighbor ions for the F-center ground state in lithium and potassium halides: GA, Ref. 1; BSG, Ref. 9; UHF, present work, with ^{7}Li and ^{39}K; experimental data as quoted in Ref. 9.

	GA	BSG	UHF	Experiment
LiF	3.45	3.55	2.79	3.2
LiCl	1.90	1.80	1.95	1.72
LiBr	1.50	1.50	1.38	
LiI	1.20	1.20	0.85	
KF	1.55	1.45	1.42	1.6
KCl	0.78	0.75	0.57	0.94
KBr	0.65	0.66	0.43	0.77
KI	0.48	0.47	0.29	0.62

TABLE VI. F_A(Li) centers in KCl and KBr: F_{A1} and F_{A2} optical-absorption energies (eV), isostropic (a) and axially symmetric anisotropic (b) hyperfine constants (MHz) of nearest-neighbor ions for the F_A-center ground state. UHF (displ) and UHF refer to present work, with and without 8% displacement of Li^+ ions. For notation K_α and K_β, see text.

	KC:Li			KBr:Li	
	UHF	UHF (displ)	Experiment	UHF	Experiment
F_{A1}	2.26	2.17	1.98[a]	1.89	1.82[a]
F_{A2}	2.48	2.34	2.25[a]	2.10	2.00[a]
a(Li)	23.74	15.91	7.88[b]	21.90	6.93[c]
$a(K_\alpha)$	7.83	7.93	23.71[b]	5.85	22.41[c]
$a(K_\beta)$	7.83	8.54	23.36[b]	6.66	21.09[c]
b(Li)	0.95	0.78	0.63[b]	0.79	0.58[c]
$b(K_\alpha)$	0.52	0.52	0.99[b]	0.40	0.84[c]

[a] Reference 38.
[b] Reference 24.
[c] Reference 25.

this is the only system for which other comparable theoretical analysis is available.[28–31] With a nearest-neighbor cluster we have obtained the optical-absorption energy 3.54 eV, compared to 5.14 eV experimentally. Tennyson and Murrell[31] and Chaney,[29] including, respectively, three and six shells of neighbors (the latter not fully self-consistent) obtained 4.6 and 4.71 eV, respectively. Furthermore, Leung and Song[7] obtained 5.9 eV, orthogonalizing to five shells of neighbors, including exchange rigorously. On the other hand, when Tennyson and Murrell included only nearest neighbors in their cluster they obtained 3.6 eV, in a calculation that differs only slightly from ours, in basis set, treatment of Coulomb potential, and using RHF. These results, and the fact that discrepancies between our results and experiment for other alkali halides are relatively small, suggest that neighbors beyond the first are particularly important for F-center optical absorption in LiF. Nevertheless, for the nearest-neighbor ground-state spin density we obtain 0.039, compared to Tennyson and Murrell's 0.06 and the experimental 0.023. While our basis set is somewhat more extensive than that of Tennyson and Murrell, and our UHF should be preferable to their RHF treatment, they include up to third neighbors self-consistently. Since the second neighbors are relatively diffuse F^- ions, their accurate inclusion would seem to be important. However, each nearest Li^+ has five nearest F^- neighbors, only four of which are treated self-consistently by Tennyson and Murrell, with the fifth treated as a point charge. This may partly account for the discrepancy in the spin-density results.

We next consider the whole set of data relating to F centers in the lithium and potassium halides, Tables III, IV, and V. Except for LiF, which we have discussed above, and LiI, for which the experimental value is anomalous,[35] the calculated optical absorptions, Table III, are in good qualitative agreement with experiment. Two criticisms of our analysis are possible. First, our ground and excited states represent energy minimizations with respect to different bases, one with only s-type orbitals at the vacancy, and the other with only p type. Probably more serious is the neglect of other than nearest neighbors, which can be expected to affect the excited-state result particularly, since it tends to be more diffuse than the ground state. Furthermore, one ought to bear in mind the possibility that Gaussian localization may not be appropriate for a diffuse excited state, in which case even a quite ambitious basis set of Gaussians may not be very accurate. On the plus side, the present work allows rigorously for self-consistent core adjustment to the defect, in both ground and excited states, within the UHF approximation. In particular, spin polarization is included, as illustrated for LiF in Fig. 1. For the hfs constants a and b, Tables IV and V, respectively, rough qualitative agreement with experiment occurs, with the potassium halide values all somewhat low. In spite of the fair agreement, we are sensitive to the importance of additional neighbors for these properties. Thus in Tables IV and V we see that in the potassium halides, with increasing anion size, neglected in our calculations, the fractional discrepancy with experiment increases. Spin polarization $P = (S - |\phi^{(0)}|^2)$, the difference between the total spin density S and that for the orbital $\phi^{(0)}$ which is principally vacancy centered, makes a contribution to the isotropic hfs constant a. Complete results for P are given in Table VII, and from comparison with Table IV we see that it accounts for about 20% of the calculated value of a in LIF, but considerably less in the potassium halides, for example, ~3% in KCl.

As with the F center, the calculated optical absorptions for F_A centers, Table VI, are in good qualitative agreement with experiment. The calculations support the view that the absorption splitting is dominated by the ion-size effect *per se*, and not by the associated impurity-ion displacement. Also as with the F center, the isotropic hfs constants a for the host cations are low compared with experiment. However, there is a large discrepancy between calculated and experimental a values at the Li^+ impurity in both KCl and KBr F_A(Li) centers. In fact, the experimental spin densities at the Li^+ ions are very small compared to those at the host K_α ions, because from Eq. (2),

$$\frac{S(\mathrm{Li})}{S(\mathrm{K}_\alpha)}=\frac{g(^{39}\mathrm{K}_\alpha)}{g(^{7}\mathrm{Li})}\frac{a(\mathrm{Li})}{a(\mathrm{K}_\alpha)}=0.12\frac{a(\mathrm{Li})}{a(\mathrm{K}_\alpha)}\;. \tag{16}$$

Thus from Table VI we find $S(\mathrm{Li})/S(\mathrm{K}_\alpha)$ equal to 0.040 and 0.037 for F_A(Li) centers in KCl and KBr, respectively. By contrast, the calculated results are about 10 times higher, 0.36 and 0.45 with the Li^+ ion undisplaced, and 0.24 in KCl:Li with 8% displacement. Thus resonable displacement of the Li^+ ion does not begin to account for the discrepancy, nor does the off-axis tunneling motion deduced for the F_A(Li) in KCl,[39] if one accepts the view of Watanbe *et al.*[25] that such tunneling does not occur in KBr. Hopefully inclusion of further neighbors in the defect cluster will clarify this anomaly.

In this work the physical assumption neglecting correlation, and the practical restriction to a nearest-neighbor cluster, leave us with results which though encouraging, are preliminary. Introduction of a reliable correlation correction, and extension to larger clusters by using core pseudopotentials for larger ions and more limited basis sets, should be feasible. The computations reported here were performed on an Amdahl 470/V7 system, and required up to 2 h of CPU time (for the excited states of the F_A center). While these are certainly major computations, they are within the reach of many researchers, and with the advent of much faster computers, such as the CRAY 1-S, considerably more reliable color-center calculations than have been available in the past should now become common.

TABLE VII. Spin polarization $P=(S-|\phi^{(0)}|^2)$ a.u., at nearest-neighbor sites for the F-center ground state in lithium and potassium halides. For notation, see text.

	S	$\lvert\phi^{(0)}\rvert^2$	P
LiF	0.03530	0.02866	0.00664
LiCl	0.01892	0.01452	0.00467
LiBr	0.01545	0.01181	0.00364
LiI	0.01219	0.00926	0.00293
KF	0.08911	0.08296	0.00615
KCl	0.04126	0.04006	0.00120
KBr	0.03516	0.03425	0.00091
KI	0.02832	0.02838	−0.00006

ACKNOWLEDGMENTS

This research was supported in part by an operating grant to J. M. Vail from the Natural Sciences and Engineering Research Council of Canada, and by a grant to A. B. Kunz from the U. S. National Science Foundation, Grant No. NSF-DMR-80-20250. A. Y. S. Kung acknowledges the award of a University of Manitoba Graduate Scholarship. The authors are indebted to R. S. Weidman for much helpful discussion, and to C. H. Woo and A. H. Harker for helpful communications.

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