PHYSICAL REVIEW B VOLUME 13, NUMBER 2 15 JANUARY 1976

Electronic structure of the *F* center in a lithium-fluoride crystal by the method of linear combinations of atomic orbitals*

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(Received 9 June 1975)

The method of linear combinations of atomic orbitals has been applied to perform a first-principles calculation of the electronic structure of the *F* center in a lithium-fluoride crystal. The one-electron Hamiltonian includes the Coulomb and exchange interaction due to all atoms (or ions) in the crystal and the trapped electron. Slater's approximation for exchange is used. Relaxation displacement of the surrounding lattice sites resulting from the presence of the *F* center is neglected. The *F*-center wave functions are expanded as linear combinations of localized orbitals centered at atomic sites up to the sixth (the seventh in one case) nearest neighbors to the vacancy. The computational work is greatly facilitated by the Gaussian technique which enables us to evaluate all the multicenter integrals associated with the Hamiltonian matrix elements analytically or in terms of the error function. An initial crystal potential is constructed by assuming the charge distribution of the Li^+ and F^- ions in the *F*-center crystal to be the same as those in the perfect crystal. The solution of this initial Hamiltonian is then used for an iterative calculation to take into account the effect of electronic polarization. The energies of the ground state and the Γ_4^- excited state have been calculated and the energy difference agrees well with the experimental absorption frequency. The theoretical values of the hyperfine contact-interaction constants are also in good agreement with experiments.

I. INTRODUCTION

The success of the application of the method of linear combinations of atomic orbitals (LCAO), or the method of tight binding, to band-structure calculations for a variety of crystals, including the alkali metals, transition metals, group-IV element crystals, alkali halides, and polyethylene in recent years has established the usefulness and versatility of this method for studying the electronic structure of solids.[1-10] Another class of problems for which the LCAO method should be well suited is the electronic structure of localized point defects in crystals such as *F* centers and impurity atoms. In fact the concept of LCAO has been used quite extensively to describe localized point defects on a qualitative level. However, the difficulty of evaluating the multicenter integrals, which had been the bottleneck of *ab initio* LCAO calculations of the energy-band structure of perfect crystals, has greatly impeded the progress toward quantitative first-principles calculations.

In the case of perfect crystals, the introduction of Gaussian-type orbitals (GTO) has been mainly responsible for the success of the quantitative application of the method of LCAO.[2] When the atomic orbitals are expressed in the Gaussian form, all the multicenter integrals resulting from the Hamiltonian matrix elements can be reduced to analytic expressions. The same Gaussian technique can be carried over to point-defect crystals; in fact, the general scheme of calculation can be summarized in a straightforward way. The one-electron Hamiltonian for the *F*-center crystal (H_{Fc}) is written as the difference between the one-electron Hamiltonian of the perfect crystal (H_{pc}) and a term corresponding to the point defect, i.e.,

$$H_{Fc} = H_{pc} - H' . \tag{1}$$

The wave functions of the *F*-center electron are expanded as linear combinations of atomiclike orbitals centered at lattice sites on different shells of atoms around the vacancy and their relative weightings are determined by the usual variational procedure. Because of the localized nature of the *F*-center electron, only a few shells need be included in this expansion to reach convergence. All the basic integrals associated with H_{pc} have been evaluated in our previous work on the band structure of LiF.[4] The multicenter integrals connected with H' can be evaluated by the Gaussian method.

Calculation of electronic wave functions for *F* centers has been a subject of active interest for many years.[11] In particular, application of the LCAO method for this purpose has been made by Inui and Uemura[12] and Kojima[13] in the 1950's. More recently Wood and Korringa[14] and also Wood[15] have used the LCAO method to calculate the electronic structure of the *F*-center electron in LiCl. Because of the complexity of the numerical work, a number of approximations, such as neglecting a great deal of the exchange of the *F* electrons with the neighboring ions and neglecting the finite size of the Cl^- ions, etc., were made in Ref. 15. Wood and co-workers[16-18] have subsequently developed methods for calculation of electronic structure of *F* centers which are based on a Hartree-Fock-type formalism but do not involve an LCAO expansion of the *F*-center wave functions.

As in the case of the LCAO calculations of band structure for perfect crystals cited above, the Slater approximation for electron exchange is employed in this work. Furthermore we neglect relaxation (displacement) of the lattice resulting from the presence of the *F* center. Under these assumptions the *F*-center problem is formulated in a Hartree-Fock-Slater scheme. An initial approximation to the Hamiltonian of the *F*-center electron is constructed by assuming the charge distributions of the Li^+ and F^- ions in the *F*-center crystals to be the same as those in a perfect crystal. The distortion of the ionic charge distribution due to the presence of the *F* center is then taken into account by means of an iterative approach. The LCAO expansions of the *F*-center wave functions include up to orbitals of atoms in the sixth shells (and in one case seven shells) from the vacant site. The amplitude of the ground-state *F*-center wave functions at the atomic sites of the first two neighboring shells have been calculated and are compared with the experimental results of the hyperfine structure of electron spin resonance.

II. PRELIMINARY WORK

An *F* center in an ionic crystal is pictured as an anion vacancy with a trapped electron. Although the LiF crystal is generally regarded as ionic, the crystal charge density computed by a superposition of the individual charge density of the free Li^+ and F^- ions at the appropriate sites does not differ much from that generated by a superposition of the neutral free Li and F atoms.[4] The reason for the similarity in charge density between the ionic and the neutral-atom pictures is that the 2*s* wave function of the Li atom is so diffuse that it overlaps strongly with the neighboring F atoms resembling a transfer of charge from the Li to the F sites. If we adopt the neutral-atom picture for the LiF crystal, an *F* center would then be equivalent to a neutral fluorine-atom vacancy. While the model of representing an F center in LiF as a neutral fluorine-atom vacancy cannot be expected to be quantitatively valid, it does offer considerable simplification for the LCAO calculation. For this reason we shall adopt this simplified model for a preliminary calculation to set forth the general computational scheme, to develop numerical procedures, and to obtain a zeroth order *F*-center wave function for the calculation with a more realistic model in Sec. III.

We divide the potential of the perfect crystal $V_{pc}(\vec{r})$ into the Coulomb and exchange parts,

$$V_{pc}(\vec{r}) = V_{pc}^{C}(\vec{r}) + V_{pc}^{X}(\vec{r}) \ . \tag{2}$$

For this preliminary calculation, the overlapping-atomic-potential (OAP) model is used as explained in Ref. 4, i.e., the Coulomb term is approximated by the sum of the electrostatic potential of each constituent atom in its neutral and undistorted form and the resulting function is designated as $[V_{pc}^{C}(\vec{r})]_{\mathrm{OAP}}$. The same superposition of free-atomic charge distribution provides an approximate charge density of the perfect crystal $(\rho_{pc})_{\mathrm{OAP}}$ which in turn gives $[V_{pc}^{X}(\vec{r})]_{\mathrm{OAP}}$, through Slater's approximation, as $-3[3(\rho_{pc})_{\mathrm{OAP}}/8\pi]^{1/3}$. For band-structure calculations we have found it convenient to cast the exchange potential in the form of a superposition of localized functions centered at each lattice site.[4] The potential for the *F*-center crystal likewise can be decomposed into its Coulomb and exchange components as

$$V_{Fc}(\vec{r}) = V_{Fc}^{C}(\vec{r}) + V_{Fc}^{X}(\vec{r}) \ . \tag{3}$$

If the *F* center is to be pictured as a neutral fluorine vacancy, the two Coulomb terms in Eqs. (2) and (3) differ only by the Coulomb potential of the missing fluorine atom (V_F^C), i.e.,

$$[V_{Fc}^{C}(\vec{r})]_p = [V_{pc}^{C}(\vec{r})]_{\mathrm{OAP}} - V_F^{C}(\vec{r}) \ . \tag{4}$$

The subscript *p* under the square brackets indicate that the above expression is intended for this "preliminary work" only. Since the exchange potential is not linear in the crystal charge density, a simple additivity relation similar to Eq. (4) does not apply to the exchange term. Instead we compute the values of the charge density of the *F*-center crystal $(\rho_{Fc})_p$ near the vacancy by superimposing the individual atomic charges at all lattice sites except the vacant one. Since $[\rho_{pc}(\vec{r})]_{\mathrm{OAP}}^{1/3}$ and $[\rho_{Fc}(\vec{r})]_p^{1/3}$ are similar except in the proximity of the vacancy, their difference can be fitted by a function localized at the vacant fluorine site so that

$$[V_{pc}^{X}(\vec{r})]_{\mathrm{OAP}} - [V_{Fc}^{X}(\vec{r})]_p = \eta_F(\vec{r}) \ . \tag{5}$$

Accurate curve fitting can be accomplished by choosing $\eta_F(\vec{r})$ to be spherically symmetrical about the vacancy with the form

$$\eta_F(\vec{r}) = \sum_i q_i \, e^{-\gamma_i |\vec{r}-\vec{R}_v|^2} \ , \tag{6}$$

where $\vec{R}_v$ is the radius vector of the vacant site, and q_i and γ_i are adjustable parameters. Combining Eqs. (2)-(5), we have

$$(H_{Fc})_p = (H_{pc})_{\mathrm{OAP}} - [V_F^{C}(\vec{r}) + \eta_F(\vec{r})] \ . \tag{7}$$

The quantity inside the square bracket can be identified with H' in Eq. (1).

The basis functions are generated by taking LCAO's around the vacancy. Let us place the origin at the vacant site. We form linear combinations of the 1*s*, 2*s*, and 2*p* orbitals of the six Li atoms at $\frac{1}{2}00$, $0\frac{1}{2}0$, etc. (the $\frac{1}{2}00$ shell), in accordance with the irreducible representations of the O_h group, and similarly symmetrized LCAO's of the F atoms in the $\frac{1}{2}\frac{1}{2}0$ shell, of the Li atoms in the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ shell, etc. A typical energy matrix element referred to this set of basis functions may be decomposed into integrals containing the Hamiltonian with two atomic orbitals at different sites. Such integrals for H_{pc} have been evaluated previously for band-structure calculations of LiF.[4] Both $V_F^C(\vec{r})$ and $\eta_F(\vec{r})$ are centered at the vacant site, thus they give rise to a series of three-center integrals. Since the atomic orbitals are written in Gaussian forms, on account of Eq. (6), matrix elements of $\eta_F(\vec{r})$ reduces to integrals of triple products of Gaussians which can be evaluated analytically. The function $V_F^C(\vec{r})$ itself is an integral involving $|\vec{r}-\vec{r}\,'|^{-1}$. The double integrals evolved from the matrix elements of $V_F^C(\vec{r})$ are readily reduced to the error functions.[19]

For the calculation of the ground state of the *F* center, we select a basis set consisting of the symmetrized (Γ_1^+ symmetry) Li 1*s*, 2*s*, 2*p* atomic orbitals at the $\frac{1}{2}00$ shell and of F 1*s*, 2*s*, 2*p* at the $\frac{1}{2}\frac{1}{2}0$ shell. The basis functions formed by the Li 1*s* and F 1*s*, 2*s*, 2*p* orbitals are primarily responsible for the occupied states of Li^+ and F^- which span the core and valence bands of the crystal, and the Li 2*s* and 2*p* basis functions serve mainly to reproduce the wave function of the *F*-center electron. The Li 1*s* and F 1*s*, 2*s*, 2*p* wave functions were taken from Table XI of a paper by Huzinaga.[20] The Li 2*s* wave function given in that table is very diffuse and extends beyond the $\frac{1}{2}\frac{1}{2}0$ shell. Because of the compact nature of the ground-state wave function of the *F*-center electron, the very tail ends of the Li 2*s* and 2*p* orbitals should not be important for this calculation. Thus in order to reduce the numerical work, we have shortened the range of the Li 2*s* and 2*p* functions by fitting the former as a linear combination of eight *s*-type Gaussians[21] of exponents 921.271, 138.730, 31.9415, 9.353 29, 3.157 89, 1.156 85, 0.444 62, 0.076 663 and fitting the latter with six *p*-type Gaussians[21] of exponents 31.9415, 9.353 29, 3.157 89, 1.156 85, 0.444 62, 0.076 491 8.

The four lowest roots of the secular equation are identified as the levels of the filled bands (F-1*s*, Li-1*s*, F-2*s* core and the valence bands). Above them is the ground state of the *F* center. The ground-state wave function of the *F*-center electron is plotted along the [100], [110], and [111] directions in Fig. 1. The general shape of the wave function near the origin reflects the flat-well nature of the potential. The sharp spike at the $\frac{1}{2}00$ point is due to the presence of the Li^+ ion or may be looked upon as a consequence of the *F*-center wave function being orthogonal to the Li-1*s* core state. Similarly a spike is found at $\frac{1}{2}\frac{1}{2}0$ because of the orthogonality to the lower states corresponding to F 1*s*, 2*s*, and 2*p*. In general one expects at each lattice point a spike of diminishing amplitude as one moves away from the *F* center. Finally we may point out the isotropy of the wave function up to a distance of $r = 0.35a$, where a is the lattice constant of the LiF crystal (7.594 a.u.).

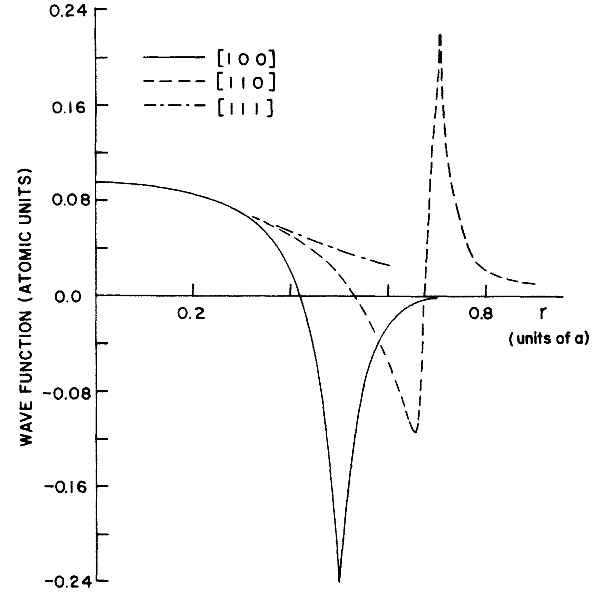

FIG. 1. Wave function (in atomic units) of the *F*-center electron along the [100] direction (solid curve), the [110] direction (uniform dashes), and the [111] direction (long-short dashes) obtained by the procedure of Sec. II. Abscissa is in units of the lattice constant of the crystal.

III. CALCULATION OF ELECTRONIC STRUCTURE

We now come to the main body of the calculation of electronic structure of the *F* center. We still seek to write the Hamiltonian of the *F*-center crystal as the perfect-crystal Hamiltonian minus a certain correction term and to expand the *F*-center wave functions in terms of LCAO basis functions. However, the model of treating the perfect crystal as being composed of undistorted free Li and F atoms introduced in Sec. II will be abolished here. Specifically we will not adopt the OAP model for H_{pc}, and the basis functions will be constructed from functions other than the free-atomic orbitals. Also the *F* center will be represented by the more realistic model of a F^- vacancy with a trapped electron instead of simply a neutral-F-atom vacancy.

A. Initial crystal potential

For a more accurate version of H_{pc}, the potential of the perfect LiF crystal produced by the self-consistent-field (SCF) calculation of Ref. 4 is adopted.

The next step is to curve fit the SCF electron density of the perfect LiF crystal, $\rho_{pc}(\vec{r})$, to a superposition of a localized density function $\rho_{\mathrm{Li}^+}(\vec{r})$ centered at all cation sites and another function $\rho_{F^-}(\vec{r})$ at all anions sites with the constraint that the total charge covered by each $\rho_{\mathrm{Li}^+}(\vec{r})$ and $\rho_{\mathrm{F}^-}(\mathrm{r})$ be two and ten electron units, respectively. (This curve-fitting scheme has been discussed in Ref. 4, although no requirement on the total charge was imposed on the individual charge-density functions there.) To simplify numerical computation, both $\rho_{\mathrm{Li}^+}(\vec{r})$ and $\rho_{\mathrm{F}^-}(\vec{r})$ are taken to be spherically symmetrical with respect to their own origins in the form of linear combinations of Gaussians. Accordingly we can account for an F^- vacancy by simply subtracting from ρ_{pc} the $\rho_{\mathrm{F}^-}(r)$ function associated with the vacant site which is chosen as the origin. To generate the Hamiltonian for an *F* center in the ground state Γ_1^+, we need to have an approximate representation of the charge distribution of the trapped electron. For this purpose we use the results of Sec. II. The spikes in the wave function in Fig. 1 are important to maintain orthogonality to all the lower states but have little effect on the crystal potential, thus we have smoothed them out in order to simplify the charge-density calculation. Furthermore because of the high degree of isotropy of the charge distribution of the trapped electron (Fig. 1), we replace it by its spherical average and express the latter, by curve fitting, as a superposition of Gaussians centered at the origin, designated as $\rho_{te}(\Gamma_1^+|r)$. The charge density of the *F* center crystal then becomes

$$\rho_{Fc}^{(0)}(\Gamma_1^+|\vec{r}) = \rho_{pc}(\vec{r}) - \rho_{\mathrm{F}^-}(r) + \rho_{te}(\Gamma_1^+|r) \ , \qquad (8)$$

Equation (8) represents only an approximate version of the true charge density of the *F*-center crystal with its trapped electron in the Γ_1^+ ground state because we have assumed, in addition to the approximation introduced to calculate ρ_{te}, no charge redistribution in the neighboring ions brought about by the vacancy and the trapped electron. The superscript (0) in the left-hand side of Eq. (8) signifies that this formula may be regarded as an initial approximation toward an ultimate SCF calculation of the electronic structure of the *F*-center crystal. A similar relation holds for the Coulomb part of the crystal potential if we replace the symbol ρ by V^C. For the exchange part we proceed in the same way as we did in Sec. II, i.e., we curve fit the difference between $-3[3\rho_{pc}(\vec{r})/8\pi]^{1/3}$ and $-3[3\rho_{Fc}^{(0)}(\Gamma_1^+|\vec{r})/8\pi]^{1/3}$ to a function $\xi(r)$ centered at the origin in the form of Gaussians. As an initial approximation to the Hamiltonian for the ground state of the *F*-center electron, we obtain

$$(H_{Fc}^{(0)})_{\Gamma_1^+} = H_{pc} - V^C_{\mathrm{F}^-}(r) + V^C_{te}(\Gamma_1^+|r) - \xi(r) \ . \qquad (9)$$

The computation of multicenter integrals for this Hamiltonian follows the same procedure as outlined in Sec. II.

B. Solution for ground state

Since the solution of H_{Fc} gives, in addition to eigenstates of the *F* center, all the lower states of the full bands of the crystal, a more efficient choice of LCAO basis functions can be made by using, in place of the wave functions of the free atoms, a set of modified Li 1*s* and F 1*s*, 2*s*, and 2*p* orbitals which reflect more accurately the electronic structure of the full bands of the perfect crystal. Such a set of "optimized orbitals"[22] can be generated in the following way. We take the SCF Hamiltonian of the perfect LiF crystal and solve the secular equation at the Γ *point* ($\vec{k}=0$) using a basis set containing seven *s*-type single-Gaussian Bloch sums of the Li atoms, eight *s*-type and five *p*-type single-Gaussian Bloch sums of the F atoms. From the relative weightings of the *s*-type fluorine single-Gaussian Bloch sums in the two eigenvectors corresponding to the F 1*s* and F 2*s* bands, we obtain, respectively, the F 1*s* and F 2*s* optimized orbitals. Likewise the weightings of the Li Bloch sums in the eigenvector of the second lowest root gives the Li 1*s* optimized orbital, and the eigenvector of the Γ-point valence band yields the F 2*p*. Because of the narrowness of all the filled bands, the optimized orbitals determined from the Γ-point solution of the crystal Hamiltonian should provide a good representation of the electron distribution in the crystal. The advantage of using such optimized atomic orbitals for band-structure calculations has been discussed.[22] The optimized orbitals are presented in Table I.

For our initial calculation of the ground state of the *F* center, the basis functions extend up to the sixth shell of atoms. This basis set includes symmetrized LCAO's of the Li 1*s* optimized orbitals at the $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and $1\frac{1}{2}0$ shells, of the F 1*s*, 2*s*, and 2*p* optimized orbitals at the $\frac{1}{2}\frac{1}{2}0$, 100, and $1\frac{1}{2}\frac{1}{2}$ shells, of seven Li *s*-type and six Li *p*-type GTO's (the exponents being the same as those listed in Sec. II with the omission of the shortest-range *s*-type GTO which is already contained in the Li 1*s* optimized orbital) at the $\frac{1}{2}00$ shell, of three *s*-type GTO's (exponents: 0.363 40, 1.207 75, 4.368 85) and three *p*-type GTO's (exponents: 0.273 29, 0.938 26, 2.995 86) at the $\frac{1}{2}\frac{1}{2}0$ shell. In addition we have introduced four *s*-type GTO's of exponents 0.363 40, 1.207 75, 4.368 85, and 12.2164 centered at the origin (the vacant site). Solution of the resulting 36×36 secular equation gives the ground-state energy of the *F*-center electron as −0.1602 a.u. The wave function is displayed in Fig. 2. Aside from the sharp spikes arising from the requirement of being orthogonal to the core states, the envelop of the wave function in Fig. 2 is con-

TABLE I. Optimized orbitals of Li and F expressed as linear combination of normalized GTO's.

	Li 1*s* state
GTO exponents:	921.271, 138.730, 31.9415, 9.353 29, 3.157 89, 1.156 85, 0.444 62
Coefficients[a]:	0.001 413, 0.010 665, 0.052 895, 0.166 427, 0.359 509, 0.390 246, 0.186 976
	F 1*s* and 2*s* states
GTO exponents:	9994.79, 1506.03, 350.269, 104.053, 34.8432, 12.2164, 4.368 85, 1.207 75, 0.363 40
Coefficients (1*s* state)[a]:	0.001 175, 0.008 981, 0.042 848, 0.146 261, 0.357 405, 0.456 990, 0.142 022, −0.001 820, 0.000 793
Coefficients (2*s* state)[a]:	−0.000 268, −0.002 119, −0.009 827, −0.037 661, −0.096 796, −0.202 097, −0.004 208, 0.543 858, 0.560 380
	F 2*p* state
GTO exponents:	44.3555, 10.0820, 2.995 86, 0.938 26, 0.273 29
Coefficients[a]:	0.018 064, 0.108 969, 0.318 552, 0.451 940, 0.374 895

[a] The order of the coefficients corresponds to that of the GTO exponents.

fined to a volume of less than one lattice constant from the vacant site which is well within the $1\frac{1}{2}\frac{1}{2}$ shell. Nevertheless to test the convergence of the LCAO expansion for the wave function of the *F*-center electron, we added to the basis set the F 1*s*, 2*s*, 2*p* optimized orbitals at the seventh shell 110 and repeat the calculation. The ground-state energy of the *F*-center electron is now − 0.1600 a.u., practically the same as the previous value of − 0.1602 a.u.

At this point it is important to mention certain care which must be exercised in choosing the basis functions. The Hamiltonian H_{Fc}, in principle, has an infinite number of eigenstates below the ground-state *F*-center level, because as we augment the LCAO basis set to include the contributions from more and more shells of lattice sites, the number of roots corresponding to the core and valence-band states would increase accordingly. When the basis functions are limited to the first six shells, only three out of each of Li 1*s* and F 1*s*, 2*s*, 2*p* states (of Γ_1^+ symmetry) are anticipated and any core and valence-band states corresponding to the seventh and higher shells should be missing in the solutions of the secular equation. Above the full-band states we have the states of the *F*-center electron whose wave functions are composed of combinations of the single GTO's with some admixture of Li 1*s* and F 1*s*, 2*s*, 2*p* functions. Suppose now we introduce to the basis sets single GTO's of considerable width in all six shells. If these GTO's have significant overlap with the seventh and eighth shells of the lattice sites, the former will try to reproduce some of the full-band states of the seventh and eighth shells resulting in some eigenfunctions which are poor representation of such states. Hence one may find some "extraneous" eigenvalues which are well above the energies of the true full-band states. Since the wave function of the *F*-center electrons are always orthogonal to those of all

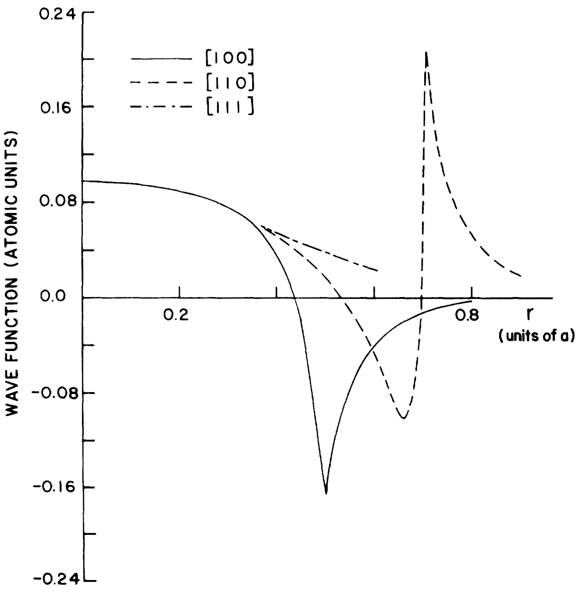

FIG. 2. Wave function (in atomic units) of the *F*-center electron along the [100] direction (solid curve), the [110] direction (uniform dashes), and the [111] direction (long-short dashes) obtained by the procedure of Sec. III B. The abcissa is in units of the lattice constant of the crystal.

the lower states, the presence of some bad full-band-state eigenfunctions may deteriorate the F-center solutions. To safeguard against this complication, the single GTO's should be chosen to have virtually no overlap with the seventh shell of lattice points so that they are orthogonal to all the missing core and valence-band states.

C. Hyperfine contact interaction

Measurements of hyperfine structure of the electron-spin resonance of F centers in LiF have been reported in the literature.[23–26] The hyperfine interaction between the electron spin and the nuclear moments of Li and F in different shells may be separated into two parts, one being isotropic and the other having the form of the dipole-dipole term.[11] The isotropic term is attributed to the contact coupling which is proportional to the absolute square of the wave function of the unpaired electron at the point of the nucleus. If the contributions from any two spin-paired electrons to the contact term are assumed to cancel each other exactly, one can deduce the absolute values of the ground-state F-center wave function at the nearby Li and F sites. Holton and Blum[26] have given a set of "experimental" absolute values of the F-center function at the $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, 100, $1\frac{1}{2}0$, $1\frac{1}{2}\frac{1}{2}$, and 110 sites for LiF.[27] The wave function described in Sec. III B contains orbitals of the first six shells of atoms, thus we can, in principle, obtain its values at $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}0, \ldots, 1\frac{1}{2}\frac{1}{2}$. However, our basis set includes single GTO's only at the first and second shells, and beyond the second shell, no additional variational freedom is provided except the minimal basis functions of Li 1s and F 1s, 2s, 2p orbitals. Since the wave function has spikes at the points of atomic sites and the peak values of these spikes vary more sensitively with respect to addition of basis functions than does the envelope of the function, we can reasonably expect our wave function to give reliable values at $\frac{1}{2}00$ and $\frac{1}{2}\frac{1}{2}0$, but not in general at site points further away. With the six-shell calculation our theoretical values for $|\psi(\frac{1}{2}00, \mathrm{Li})|$ and $|\psi(\frac{1}{2}\frac{1}{2}0, \mathrm{F})|$ are 0.166 and 0.208 a.u., respectively, as compared to the corresponding experimental values of 0.150 and 0.158 a.u. deduced from the results of Holton and Blum.[26] Upon augmenting the basis set to include the F 1s, 2s, 2p orbitals at the seventh shell 110, the new values are $|\psi(\frac{1}{2}00, \mathrm{Li})| = 0.170$ and $|\psi(\frac{1}{2}\frac{1}{2}0, \mathrm{F})| = 0.209$ differing little from the old ones.

The agreement between theory and experiment is very good for $|\psi(\frac{1}{2}00, \mathrm{Li})|$, but a somewhat larger discrepancy is seen in the case of $|\psi(\frac{1}{2}\frac{1}{2}0, \mathrm{F})|$. It should be emphasized that the experimental value of $|\psi|$ were obtained under the assumption that the unpaired F-center electron is solely responsible for the contact coupling. However, the unpaired electron may polarize the atomic core so that the $s\uparrow$ (arrow indicating the spin orientation) and $s\downarrow$ electrons have slightly different wave functions and therefore offer a net contribution to the contact term. Also configuration interaction may provide another source of contribution. Discussion of the core polarization and configuration interaction effects has been given in the literature.[28] However, in the absence of a quantitative estimate of these effects, the agreement between theory and experiment on the hyperfine contact coupling constants should be regarded as quite satisfactory.

It is convenient to view the wave function in Fig. 2 as a smooth varying envelope function plus a number of spikes at the sites of the ions. If one were to allow for a small relaxation of the ions in the F-center crystal, the envelope function at the displaced sites would differ only slightly from the old values. The height of the spikes which may be associated with the requirement of orthogonality to the core ion states, would therefore be expected to undergo only minor change due to lattice relaxation.

D. Γ_4^- excited states

One quantity of immediate interest in the study of F centers is the absorption frequency or the energies of the Γ_4^- states. To calculate their energies, we first symmetrize the orbitals associated with the atoms in the same shell in accordance with the Γ_4^- representation. The basis set consists of the Li 1s optimized atomic orbitals at the $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and $1\frac{1}{2}0$ shells, the F 1s, 2s, 2p functions at the $\frac{1}{2}\frac{1}{2}0$, 100, and $1\frac{1}{2}\frac{1}{2}$ shells, seven s-type and six p-type single GTO's at the $\frac{1}{2}00$ shells, two s-type (exponents: 0.363 40, 1.207 75) and two p-type (exponents: 0.273 29, 0.938 26) at the $\frac{1}{2}\frac{1}{2}0$ shell, amounting to a total of 49 Γ_4^--type symmetrized functions. With the Hamiltonian in Eq. (9), solution of the secular equation gives the lowest unoccupied Γ_4^- level at $E = -0.0058$ a.u. This leads to an energy difference between the Γ_4^- and Γ_1^+ states as 0.154 a.u. (4.20 eV) which is in reasonable agreement with the experimental value 4.82 eV.[29]

IV. IMPROVEMENT BY ITERATION: ELECTRONIC POLARIZATION

In Sec. II the Hamiltonian H_{F_c} was constructed under the assumption that the electronic structure of each ion remains unchanged from the perfect-crystal case. In reality the presence of the point defect causes a distortion of the electron distribution of the ions which is usually referred to as electronic polarization. This is not to be confused with the distortion of the free-ion electronic structure due to the formation of the perfect crystal; the latter has been taken into consideration by the SCF calculation of the band structure.

The effect of electronic polarization can be incorporated into the present LCAO formalism by means of an iterative procedure. Those eigenfunctions of $(H_{Fc}^{(0)})_{\Gamma_1^+}$ which correspond to the occupied states of the ions (or filled-band states) yield directly the degree of polarization of the electron cloud since the presence of the *F* center has been explicitly taken into account in the parent Hamiltonian. Following the procedure described in Sec. III B, we have solved the secular equations of $(H_{Fc}^{(0)})_{\Gamma_1^+}$ for all irreducible representations of the O_h group to determine the "polarized" wave functions for all the electrons of the ions in the first six shells. Examination of the individual charge density shows that the Li^+ ions in the $\frac{1}{2}00$ shell are much less polarized than the F^- ions in the $\frac{1}{2}\frac{1}{2}0$ shell as may be anticipated from the more tightly bound nature of Li^+. Also the degree of polarization of the F^- ions is found to decrease in going from the $\frac{1}{2}\frac{1}{2}0$ to the 100 shell. Assuming the effect of polarization to be negligible beyond the $1\frac{1}{2}\frac{1}{2}$ shell, we use this new charged density for the ions in the first six shells to replace the old one in computing the charge density of the *F*-center crystal. In addition improvement is also made of the charge density of the trapped electron by using the results of the six-shell calculation described in Sec. III B in place of those of Sec. II (see Sec. III A). The above two steps lead to the first-iteration version of charge density of the *F*-center crystal which we shall denote as $\rho_{Fc}^{(1)}(\Gamma_1^+|\vec{r})$. By comparing the numerical values of $\rho_{Fc}^{(1)}(\Gamma_1^+|\vec{r})$ and $\rho_{Fc}^{(0)}(\Gamma_1^+|\vec{r})$, we curve fit $\rho_{Fc}^{(1)}(\Gamma_1^+|\vec{r}) - \rho_{Fc}^{(0)}(\Gamma_1^+|\vec{r})$ and $[\rho_{Fc}^{(1)}(\Gamma_1^+|\vec{r})]^{1/3} - [\rho_{Fc}^{(0)}(\Gamma_1^+|\vec{r})]^{1/3}$ to superpositions of localized functions (e.g., $e^{-\alpha r^2}$ and $r^2 e^{-\alpha r^2}$) around the vacant site and around the lattice sites on the first two shells. The functions centered at the first shell contain also terms like $xe^{-\alpha r^2}$ and those at the second shell contain $(x+y)e^{-\alpha r^2}$, $xye^{-\alpha r^2}$, and $z^2 e^{-\alpha r^2}$. Upon applying these polarization corrections to the Coulomb and exchange potential in Eq. (9), we arrive at the first-iteration Hamiltonian $(H_{Fc}^{(1)})_{\Gamma_1^+}$ which gives the energies of the ground state and the Γ_4^- state of the *F*-center electron as -0.2487 and -0.06725 a.u., respectively.

Strictly speaking the change of the ground-state energy from -0.1602 to -0.2487 a.u. is due to electronic polarization as well as the improvement of the *F*-center electron charge density. The effect of the latter, however, is likely to be small because of the close resemblance of the envelope functions in Figs. 1 and 2. Thus we believe that the suppression of the ground-state energy by 0.0885 a.u. reflects, to a large measure, the change of charge distribution of the ions caused by the point defect. A somewhat analogous situation is found in band-structure calculations of perfect crystals. If one starts with an OAP model for the crystal potential to generate the initial solution and then proceeds to self-consistency by an iterative scheme, the absolute energies change quite significantly from the initial OAP values to the final SCF ones although the changes in energy differences are substantially smaller. For example in the SCF calculation of the pure LiF crystal, this change of energy of the Γ_{15v} state amounts to 0.216 a.u. from the initial to the next-iteration stage,[30] reflecting the effect of charge redistribution in going from the free ions to the crystal.

The energy of the lowest unoccupied Γ_4^- state of the *F*-center electron is likewise suppressed. The shift here is 0.0615 a.u., somewhat smaller than the corresponding value for the Γ_1^+ ground state. The energy difference between the Γ_4^- and Γ_1^+ states now becomes 4.93 eV in closer agreement with the experimental value.

V. DISCUSSION

We have presented a scheme for *ab initio* LCAO calculations of electronic structure of *F* centers based on the Hartree-Fock-Slater method. The Hamiltonian includes the Coulomb and exchange interaction due to all the atoms (or ions) in the crystal and the trapped electron. The *F*-center wave functions are expanded as linear combinations of atomiclike orbitals centered at the atomic sites up to the sixth (or seventh) nearest neighbors to the vacancy. By means of the Gaussian technique all the multicenter integrals necessary for the Hamiltonian matrix elements can be evaluated analytically or expressed in terms of the error function. An initial crystal potential was constructed by assuming the charge distributions of the Li^+ and F^- ions in an *F*-center crystal to be the same as those in the perfect crystal. The solution of this initial Hamiltonian is used to generate an improved crystal potential which in turn provided a set of improved wave functions. In this manner the effect of electronic polarization can be taken into account. This iterative procedure can be carried out to self-consistency, although in the present work we have performed only one iteration. The theoretical values of the absorption frequency and the magnetic hyperfine contact interaction constants are in good agreement with experiments.

While the subject of theoretical calculation of electronic wave functions of *F* centers has been treated extensively in the literature, the general approaches adopted in the majority of these works are very different from ours. Even for the earlier works on the application of the LCAO method to calculate electronic states of the *F* centers in LiF,[12,13] the methods of treatment differ significantly from ours. For instance in the paper by Kojima,[13] the ions were replaced by point charges in calculating the potential-energy integrals, and this modification of the potential was regarded by

Kojima[13] as being not very satisfactory. For these reasons no comprehensive comparison of our results with those of the previous workers will be made. Instead we shall just cite results from a few selected papers as examples of previous calculations. Wood and Joy[16] gave 3.26 eV and (4.59 eV) for the $\Gamma_1^+ - \Gamma_4^-$ absorption energy which may be compared with our value of 4.93 eV. (The value 4.59 eV inside the parenthesis arises from a local minimum in the calculation of the excited state by Wood and Joy, and they believe this to be the appropriate minimum.) The magnetic hyperfine constants have been calculated by Gourary and Adrian. From their results[31] one obtains $|\psi(\mathrm{Li}, \frac{1}{2}00)|$ and $|\psi(\mathrm{F}, \frac{1}{2}\frac{1}{2}0)|$ as 0.170 and 0.120 a.u., respectively (ours being 0.170 and 0.209). While the over-all agreement appears to be reasonable, the vast difference in the method of approach does not allow us to make much quantitative use out of this comparison. Electronic polarization in *F*-center crystals has been examined by several authors[11,32–34] using a semicontinuum model in which the effective-mass approximation is often adopted and a polarization potential expressed in terms of the dielectric constants is introduced. In our method, however, the potential of the finite crystal is treated explicitly as opposed to the effective-mass approximation. Also, instead of using the dielectric constants, we calculate the polarization energy, by means of a Hartree-Fock procedure, directly from the distortion of the electron clouds of the neighboring ions as produced by the vacancy and the trapped electron; thus the questions of validity of the dielectric-constant approximation and of whether or not the polarization can fully respond to the trapped electron, do not arise. The semicontinuum model has been applied to calculate the energies of the *F* centers in NaCl and KCl, but we have found no similar calculations for LiF to make quantitative comparison with our results.

To assess the ultimate utility of the LCAO method for *F*-center calculations, we may mention some possible refinements which can be added to the present work. As indicated in Sec. I, relaxation of the crystal lattice due to the *F* center is neglected in this paper. Allowance for small displacements of the ions near the imperfection can be accomplished by introducing a correction term in the Hamiltonian corresponding to the difference between the relaxed and unrelaxed lattice; the necessary integrals and matrix elements again can be evaluated by the same Gaussian technique. The calculation can then be carried out to self-consistency by the iterative procedure outlined in Sec. IV using the appropriate relaxed lattice structure. Improvement for the calculation of the excited state (Γ_4^-) likewise can be made. In Sec. IV the excited state was taken as the unoccupied orbital of the Hamiltonian $(H_{Fc}^{(1)})_{\Gamma_1^+}$ which was generated by placing the *F*-center electron in the Γ_1^+ state (the ground-state configuration). The use of unoccupied orbitals of the ground-state configuration to approximate the excited states has been a common practice. However, recent calculations of the CO molecule[35] indicate that while this approximation may give satisfactory energy, the oscillator strengths computed by this approximation and by using the wave function derived from the proper excited configuration may differ by almost a factor of two. To deduce the excited-state Hamiltonian $(H_{Fc})_{\Gamma_4^-}$ for the *F*-center problem, one may assign the trapped electron to the unoccupied Γ_4^- orbital reported in this paper and calculate the charge density of the crystal in this excited configuration from which the Coulomb and exchange potentials may be obtained. An iterative scheme similar to the one for the ground state may be employed to achieve self-consistency. This would then enable us to calculate properties pertaining to the excited state such as oscillator strengths. All the refinements outlined in this paragraph can be incorporated into the LCAO formalism, although they would entail more complex computational work. Development of the necessary numerical technique is underway.

The method of LCAO has been employed over many years for qualitative description of *F* centers, but quantitative *ab initio* application in the past had not been entirely successful due to the difficulty of handling the multicenter integrals. In this paper we have shown that with the Gaussian technique the computational work for an *ab initio* calculation is reduced to a very manageable level and demonstrated the utility of the LCAO method for first-principles quantitative studies of electronic energies of *F* centers.

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[*] Work supported in part by the National Science Foundation and in part by the University of Texas at Dallas Organized Research Fund.

[1] E. E. Lafon and C. C. Lin, Phys. Rev. 152, 579 (1966).

[2] R. C. Chaney, T. K. Tung, C. C. Lin, and E. E. Lafon, J. Chem. Phys. 52, 361 (1970).

[3] R. C. Chaney, C. C. Lin, and E. E. Lafon, Phys. Rev. B 3, 459 (1971).

[4] R. C. Chaney, E. E. Lafon, and C. C. Lin, Phys. Rev. B 4, 2734 (1971).

[5] J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973).

[6] R. A. Tawil and J. Callaway, Phys. Rev. B 7, 4242 (1973).

[7] W. Y. Ching and J. Callaway, Phys. Rev. Lett. 30, 441 (1973).

[8] J. Rath and J. Callaway, Phys. Rev. B 8, 5398 (1974).

[9] W. Y. Ching and J. Callaway, Phys. Rev. B 9, 5115

(1974).

[10] J. E. Falk and R. J. Fleming, J. Phys. C 6, 2954 (1973).

[11] B. S. Gourary and F. J. Adrian, Solid State Phys. 10, 127 (1960).

[12] T. Inui and Y. Uemura, Prog. Theor. Phys. 5, 252 (1950).

[13] T. Kojima, J. Phys. Soc. Jpn. 12, 908 (1957).

[14] R. F. Wood and J. Korringa, Phys. Rev. 123, 1138 (1961).

[15] R. F. Wood, Phys. Rev. Lett. 11, 202 (1963).

[16] R. F. Wood and H. W. Joy, Phys. Rev. 136, A451 (1964).

[17] U. Öpik and R. F. Wood, Phys. Rev. 179, 772 (1969).

[18] R. F. Wood and U. Öpik, Phys. Rev. 179, 783 (1969).

[19] I. Shavitt, in *Methods of Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1963), Vol. 2, p. 1.

[20] S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).

[21] The terms s- and p-type GTO's as used in this paper refer to what are called 1s- and 2p-type GTO's in Ref. 20.

[22] J. E. Simmons, C. C. Lin, E. E. Lafon, D. F. Fouquet, and R. C. Chaney, J. Phys. C 8, 1549 (1975).

[23] N. W. Lord, Phys. Rev. 105, 756 (1957); Phys. Rev. Lett. 1, 170 (1958).

[24] R. Kaplan and P. J. Bray, Phys. Rev. 129, 1919 (1963).

[25] W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Lett. 5, 197 (1960).

[26] W. C. Holton and H. Blum, Phys. Rev. 125, 89 (1962).

[27] What we refer to as the $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}0$, ... sites are designated as [100], [110], ..., respectively, in Ref. 26.

[28] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University, London, 1970), pp. 695–706.

[29] H. F. Ivey, Phys. Rev. 72, 341 (1947).

[30] W. P. Menzel (private communication).

[31] See Ref. 11, p. 232.

[32] J. A. Krumhansl and N. Schwartz, Phys. Rev. 89, 1154 (1953).

[33] W. B. Fowler, Phys. Rev. 135, A1725 (1964); 151, 657 (1966).

[34] For additional discussions and references, see W. B. Fowler, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).

[35] S. Chung and C. C. Lin, Phys. Rev. A 9, 1954 (1974).