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Electronic Structure of the *F* Center in LiCl†

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The electronic structure of the *F*-center lattice defect in LiCl is investigated with calculations based on the usual model of the *F* center proposed by de Boer. The ground- and excited-state wave functions and energies of the trapped electron are determined by two different methods. First, the method of linear combination of atomic orbitals (LCAO) is used. This method is capable of yielding good results but the complexity of the necessary calculations is great. In an effort to avoid this complexity the method of vacancy-centered wave functions is investigated. Very simple wave functions are used in this method with satisfactory results. The coefficient of the hyperfine interaction of the *F*-center electron with the nearest-neighbor lithium ion and the oscillator strength of the optical transition are calculated. The distortions of the lattice in the vicinity of the *F* center are calculated. A very small outward movement of the first and second nearest neighbors occurs in the ground state. The situation in the excited state is complicated by the "*p*-type" symmetry of the *F*-electron wave function. In this case, the two nearest-neighbor lithium ions located on the symmetry axis of the wave function are found to undergo a large displacement outward from the vacancy. The other four nearest neighbors displace inward toward the center of the vacancy. The results of the calculations are discussed and detailed comparisons with other work of a similar nature are given.

1. INTRODUCTION

Since the time that de Boer[1] suggested the now familiar model for the *F*-center lattice defect in alkali halides, numerous theoretical calculations of its properties have been published. Two methods of approximation for obtaining the wave functions of the *F* electron have been employed, viz. the linear combination of atomic orbitals (LCAO) method and the "vacancy-centered" (VC) method. The VC method is a variational treatment in which the wave functions are approximated by simple functions, centered with respect to the missing ion site. Tibbs,[2] Simpson,[3] and Krumhansl and Schwartz[4] used the VC method for a calculation of the main *F*-electron transition energy in NaCl. Others who have employed the VC method are Kubo,[5] Nagamiya,[6] Pincherle,[7] Inui and Uemura,[8] Kojima[9] and Gourary and Adrian.[10,11] The calculations reported in the last three references are particularly interesting because of their great similarity. Kojima obtained very accurate results for the transition energy in LiF. Gourary and Adrian have performed calculations on a number of different alkali halide crystals. Blumberg and Das[12] gave a detailed calculation of the hyperfine interaction in KCl. Inui and Uemura and Kojima have also used the LCAO method, obtaining results which are generally not as accurate as those derived by the vacancy-centered method. Muto[13] and Wood[14] have also used the LCAO method.

In this paper we present some calculations on *F* centers in LiCl. The merits of the LCAO and the VC method are compared by evaluating the energies and wave functions of the ground state and the excited state, the oscillator strength of the optical transition and the isotropic hyperfine coupling constant with the nearest Li nuclei. Finally, the VC method is used to obtain the distortions of the lattice for both electronic states.

2. LCAO METHOD

The orbitals that were used in the LCAO method are analytical approximations to the free atom Hartree-Fock $2s$ and $2p$ Li functions[15] centered on the six nearest-neighbor ions, oriented and enumerated as shown in Fig. 1. The ground-state wave function has full octahedral symmetry and is therefore of the form

$$\phi = c_1 \sum_{i=1}^{6} \phi_i + c_2 \sum_{i=7}^{12} \phi_i. \tag{1}$$

The excited state transforms like a vector and has the form

$$\phi' = c_1'(\phi_1 - \phi_2) + c_2'(\phi_7 - \phi_8) + c_3'(\phi_{15} + \phi_{16} - \phi_{23} + \phi_{24}), \tag{2}$$

together with similar expressions for the y and z direction.

The c_k were evaluated for an undistorted lattice. The three center integrals appearing in the calculation were evaluated numerically with the ions replaced by point sources of charge $\pm e$. Details of this calculation are given in reference 14.

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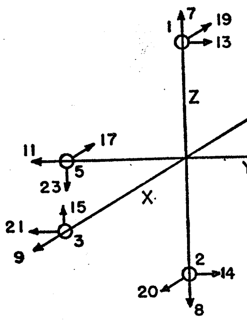

FIG. 1. The six nearest-neighbor ions of the F center. The circles represent s functions and the arrows represent p functions.

The ground state wave function was subsequently orthogonalized to the Li ion cores by means of the Schmidt procedure.[16] The importance of this, in particular for the calculation of the hyperfine interaction, was pointed out by Gourary and Adrian.[10] For the core function of the Li ion at the site $\mathbf{R}_i$, we used

$$\phi_i^{1s}\sim\exp(-\zeta|\mathbf{r}-\mathbf{R}_i|),\tag{3}$$

with $\zeta=2.69$ a.u. (atomic units).

In an alternative calculation, the wave function of the ground state was written as

$$\psi=c_1\sum_{i=1}^{6}\phi_i+c_2\sum_{i=7}^{12}\phi_i+c_3\sum_{i=1}^{6}\phi_i^{1s},\tag{4}$$

to which the orthogonality condition was applied before the evaluation of the energy. The result was almost the same.

The hyperfine interaction[17,18] was calculated from (4) in terms of $|\psi(R_i)|^2$. Its value was indeed strongly dependent on the orthogonalization, without which it came out an order of magnitude too small.

Finally, the oscillator strength was calculated from

$$f=\frac{m}{\pi\hbar^2}(E'-E)\left|\int\psi' z\psi d^3r\right|^2;\tag{5}$$

ψ' and ψ were taken from Eq. (2) and Eq. (4), respectively. E' and E are the corresponding energies.

Notwithstanding the fact that the functions (2) and (4) were the simplest that could reasonably be selected, the calculations were very tedious, and the prospect of having to treat the lattice distortions with this method was most unappealing. We therefore investigated the merits of the VC method by calculating the same properties.

3. VC METHOD

In a variational calculation with vacancy-centered trial functions, the potential was again replaced by that of a lattice of point charges. The functions were chosen in the form of simple analytic hydrogenlike expressions in the polar coordinates r and ϑ in analogy with the early calculations of Tibbs.[2] This leads inevitably to a violation of the boundary condition at $r=0$ and a corresponding error in the energy. In order to avoid this, Kojima,[9] Gourary and Adrian,[10,11] and others have resorted to matching Bessel functions to hydrogenlike functions. This leads to somewhat more involved calculations without a great gain in accuracy.

The Coulomb potential $\pm|\mathbf{r}-\mathbf{R}_i|^{-1}$ of each ion was expanded in spherical harmonics about the center of the vacancy. For any normalized function $\phi(r,\vartheta)$ which goes to zero exponentially when $r\rightarrow\infty$, we thereby have

$$\int_0^\infty\frac{|\phi|^2}{|\mathbf{r}-\mathbf{R}_i|}d^3r=\frac{1}{R_i}+R_i^2\sum_{n=1}^{\infty}\int_0^\infty|\phi(\rho R_i,\vartheta)|^2\times\rho^nP_n(\cos(\vartheta-\vartheta_i))d^3\rho-R_i^2\sum_{n=0}^{\infty}\int_{\rho>1}|\phi(\rho R_i,\vartheta)|^2(\rho^n-\rho^{-n-1})\times P_n(\cos(\vartheta-\vartheta_i))d^3\rho.\tag{6}$$

For the ground state we used three different trial functions, viz. $\phi_{1s}\sim\exp(-\alpha r)$, $\phi_{2s}\sim r\exp(-\beta r)$, and $\phi_{\mathrm{L.C.}}=a_1\phi_{1s}+a_2\phi_{2s}$. In our first calculations, orthogonalization to the nearest Li-ion cores was performed subsequent to the variational calculation. The parameters α and β in $\phi_{\mathrm{L.C.}}$ were those obtained from the best ϕ_{1s} and ϕ_{2s}, respectively. With the Hamiltonian

$$\mathcal{H}=-\frac{\nabla^2}{2m}+\sum_{i\neq0}^{N}(\pm)_i|\mathbf{r}-\mathbf{R}_i|^{-1},\tag{7}$$

we find

$$\langle\phi_{1s}|\mathcal{H}|\phi_{1s}\rangle=\frac{\alpha^2}{2}-\frac{a_M}{R_1}+4\alpha^3\sum_{i\neq0}^{N}(\pm)_iR_i^2[A_2^i(\alpha)-A_1^i(\alpha)],\tag{8}$$

$$\langle\phi_{2s}|\mathcal{H}|\phi_{2s}\rangle=\frac{\beta^2}{6}-\frac{a_M}{R_1}+\frac{4\beta^5}{3}\sum_{i\neq0}^{N}(\pm)_iR_i^4[A_4^i(\beta)-A_3^i(\beta)],\tag{9}$$

where

$$A_k^i(\alpha)=\int_1^\infty\rho^k\exp(-2\alpha R_i\rho)d\rho.\tag{10}$$

Here a_M is the Madelung constant and R_1 is the lattice constant.

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[16] The $2s$ and $1s$ functions on any one ion are already orthogonal to each other.

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For the excited state, two functions were tried, viz. $\phi_{2p}'\sim r\cos\vartheta\exp(-\gamma r)$ and $\phi_{3p}'\sim r^2\cos\vartheta\exp(-\eta r)$. One finds

$$\langle\phi_{2p}'|\mathcal{H}|\phi_{2p}'\rangle=\frac{\gamma^2}{2}-\frac{a_M}{R_1}+\frac{4\gamma^5}{3}\sum_{i\neq0}^{N}(\pm)_i \times R_i^4[A_4{}^i-A_3{}^i+\tfrac{1}{5}(A_6{}^i-A_1{}^i)(3\cos^2\vartheta_i-1)] -\frac{3}{2\gamma^2}\sum_{i\neq0}^{N}(\pm)_i\frac{1}{R_i^3}(3\cos^2\vartheta_i-1), \quad (11)$$

and an analogous expression for $\langle\phi_{3p}'|\mathcal{H}|\phi_{3p}'\rangle$. For the the undistorted lattice, the sum of terms involving $(3\cos^2\vartheta_i-1)$ in (11) vanishes.

The orthogonalization to the nearest-neighbor Li cores was performed by writing for the ground state

$$\psi=b_1\phi+b_2\sum_{i=1}^{6}\phi_i{}^{1s}, \quad (12)$$

and for the excited state

$$\psi'=b_1'\phi'+b_2'(\phi_2{}^{1s}-\phi_1{}^{1s}), \quad (13)$$

and applying the orthogonality condition. The $\phi_i{}^{1s}$ are numbered as in Fig. 1. Owing to symmetry, ϕ' is already orthogonal to the core functions $\phi_3{}^{1s}\cdots\phi_6{}^{1s}$.

The energy can now be written in an obvious notation as

$$E=b_1^2\mathcal{H}_{00}+2b_1b_2\sum_{i=1}^{6}\mathcal{H}_{0i}+b_2^2\sum_{i,j=1}^{6}\mathcal{H}_{ij}, \quad (14)$$

and a similar expression for the excited state energy E'. The terms $\mathcal{H}_{ij}(i\neq j)$ were neglected; $\mathcal{H}_{0i}$ and $\mathcal{H}_{ii}$ were calculated by using the exact potential $V_i(\mathbf{r}-\mathbf{R}_i)$ for the ion in question and inserting the empirical value E^{1s} for the ionization energy of the core electron.

This gives for the ground state

$$\mathcal{H}_{0i}=\left(E^{1s}+\frac{a_M}{R_1}\right)\langle\phi|\phi_i{}^{1s}\rangle-\langle\phi|r^{-1}|\phi_i{}^{1s}\rangle, \quad (15)$$

$$\mathcal{H}_{ii}=E^{1s}+(a_M-1)/R_1, \quad (16)$$

and identical expressions, with ϕ' replacing ϕ, for the excited state.

We found that when we orthogonalized to the ion cores after the variation calculation the energy was raised considerably. With the functions thus obtained, the hyperfine interaction and the oscillator strength were calculated. The hyperfine interaction was too high by a factor of almost 3 and the oscillator strength calculated with Eq. (5) gave $f>1$. We also used[19]

$$f=-\frac{2\hbar^2}{m(E'-E)}\left|\int\psi\frac{\partial}{\partial z}\psi' d^3r\right|^2, \quad (17)$$

which is equivalent with (5) when ψ and ψ' are exact solutions of a Schrödinger equation, but which is more immediately connected with the probability of a radiative transition.

Next, we carried out all of the above calculations for the $2s$ and $3p$ functions by first orthogonalizing them to the ion cores and then varying the parameters. We found that the energy was lowered somewhat and that the calculated values of the hyperfine interaction and the oscillator strength were greatly improved.

4. LATTICE DISTORTIONS

The distortions in the lattice caused by the F-center defect were calculated by minimizing the total energy as a function of the displacements of the ions in the vicinity of the vacancy. We considered separately the case that the electron is in the ground state and the case that it is in the excited state.

The energy was approximated by

$$\mathcal{E}=\mathcal{E}_L+\mathcal{E}_e. \quad (18)$$

Here $\mathcal{E}_L$ is the energy of a fictitious crystal in which a complete halide ion has been removed without permitting any rearrangement of the valence or core electrons other than those connected with the (still arbitrary) displacements of the ions. $\mathcal{E}_e$ is the energy of the F-center electron in this fictitious crystal. $\mathcal{E}_L$ was calculated classically and was written in the form

$$\mathcal{E}_L=\mathcal{E}_1+\mathcal{E}_2-\mathcal{E}_1{}^h-\mathcal{E}_2{}^h. \quad (19)$$

$\mathcal{E}_1$ is the Coulomb energy of the complete, but distorted, lattice; $\mathcal{E}_2$ is the energy of interaction between the ionic cores of that lattice; and $\mathcal{E}_1{}^h$, $\mathcal{E}_2{}^h$ are those terms in $\mathcal{E}_1$ and $\mathcal{E}_2$ involving the removed halide ion. We assumed that only nearest-neighbor ions experience core interaction, and this was represented by a two-body potential of the form

$$V_c(R)=b/R^{\lambda}. \quad (20)$$

The parameter λ was taken from the literature.[20] The quantities $\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_1{}^h$, and $\mathcal{E}_2{}^h$ were expanded in Taylor series in the atomic displacements. All cubic and higher order terms in this expansion were neglected.

TABLE I. Energy of ground state (E) and excited state (E') with LCAO method. R means rigid lattice. P means polarization included. Energy in a.u. ϕ and ψ refer to types of functions used in the text.

	(LiF)[9]		(LiCl)-R only[a]	
	R	P	ϕ	ψ
E	−0.271	−0.094	−0.186	−0.181
E'	−0.118	+0.035	−0.080	
ΔE (calc)	0.153	0.129	0.106	
ΔE (exp)	0.182		0.115	

[a] Present work.

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[19] We thank Dr. E. N. Lassettre for suggesting this.

[20] For LiCl, $\lambda=7$ according to L. Pauling; see F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 80.

TABLE II. Energies corresponding to the VC wave functions in various stages of present calculations. *D* means distortion effects included. Franck-Condon principle applies. Energy in a.u.

	No orthogonalization to ion cores		Orthogonalization after minimization				Orthogonalization before minimization		
	ϕ_{2s}	$\phi_{\text{L.C.}}$	ψ_{2s}	$\psi_{\text{L.C.}}$	$\psi_{2s}{}^D$	$\psi_{\text{L.C.}}{}^D$	ψ_{2s}	$\psi_{2s}{}^D$	Exp
$-E$	0.243	0.247	0.164	0.167	0.155	0.158	0.183	0.174	
$-E'$	0.136[a]	0.144[b]	0.046[a]	0.054[b]	0.040[a]	0.048[b]	0.064[b]	0.059[b]	
ΔE	0.107	0.103	0.118	0.113	0.115	0.110	0.119	0.115	0.115

[a] $2p$ state.
[b] $3p$ state.

Two types of deformations were considered:

(a) An isotropic distortion, applicable when the electron is in the ground state, and characterized by a radial displacement *inward* of the nearest and next-nearest neighbors by the amounts

$$\Delta_1=\delta_1R_1 \quad\text{and}\quad \Delta_2=\delta_2R_1,$$

respectively.

(b) An anisotropic distortion, applicable when the electron is in the excited state and characterized by radial displacements inward of the nearest neighbors by the amounts

$$\Delta_1'=\delta_1'R_1 \quad\text{and}\quad \Delta_2'=\delta_2'R_1.$$

Here Δ_2' applies to the two neighbors in the direction of the excited state wave function and Δ_1' applies to the four other neighbors. Displacements of the next-nearest neighbors were not considered in this case, for reasons of simplicity.

The energy $\mathcal{E}_e$ was calculated with the vacancy-centered functions orthogonalized to the core functions of the nearest ions both before and after minimization of the *F*-electron energy in the undistorted crystal. We found that the change in $\mathcal{E}_e$ was practically the same in both cases as long as the distortions remained small. We took ϕ_{2s} for the ground state and ϕ_{3p}' for the excited state, with screening constants β and η unaltered from the case of no distortions. The value of $\mathcal{E}_e$ for the ground state then follows from an equation of the form (14) in which $\mathcal{H}_{00}$ is given by [see Eq. (9)]:

$$\mathcal{H}_{00}(\delta)=\frac{\beta^2}{6}+\sum_i(\pm)_i\frac{1}{R_i}+\frac{4\beta^5}{3}\sum(\pm)_iR_i^4[A_4^i(\beta)-A_3^i(\beta)]. \qquad (21)$$

The R_i are now the ion positions in the distorted lattice. The normalization constant b_1 [see Eq. (13)] is approximately equal to unity. Consequently, the second term in Eq. (21) cancels against the Coulomb term $\mathcal{E}_1{}^h$. The power series for the remaining terms in $\mathcal{E}_e$ was obtained with graphical methods.

The calculation of the excited state energy $\mathcal{E}_e'$, was entirely analogous, except for the fact that the quadrupole term in $\mathcal{H}_{00}'(\delta')$ [see Eq. (11)] now gives a nonvanishing contribution.

Finally, the influence of distortions on the optical transition energy in absorption was calculated. Owing to the Frank-Condon principle, this is given by $\mathcal{E}_e'-\mathcal{E}_e$, where both terms are taken for the distortion (δ_1,δ_2) belonging to the ground state.

5. RESULTS

The energies obtained in our LCAO calculations are compared to Kojima's results in Table I and our wave functions in this approximation are illustrated in Fig. 2. The energies obtained in various stages of our VC calculations are summarized in Table II. Figure 3 shows the behavior of the energy as a function of variation parameter. A comparison of our best VC results with the calculations of Kojima[9] and Gourary and Adrian[10,11] is presented in Table III.

The coefficients of the LCAO ground-state wave function ψ of Eq. (4) were found to be

$$c_1=0.145,\quad c_2=0.131,\quad c_3=-0.049.$$

The coefficients of ϕ' in Eq. (2) are

$$c_1'=0.307,\quad c_2'=0.142,\quad c_3'=-0.760.$$

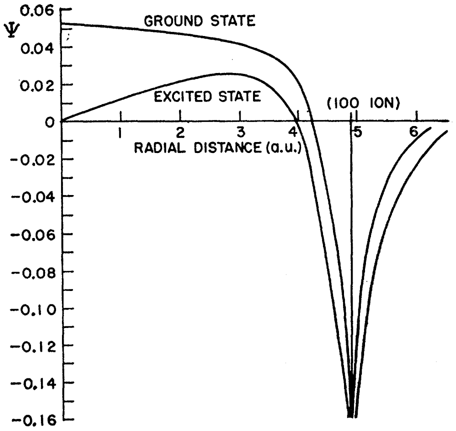

FIG. 2. The radial parts of the ground and excited state wave functions obtained with the LCAO method. The 100 ion is a nearest-neighbor ion. The large negative values of the wave functions at the nearest-neighbor ions are results of the orthogonalization of the wave function to the ion cores.

TABLE III. E and E' with the VC method. Energy in a.u.

	(LiF)[9]		(LiF)[10,11]		(LiCl)[10,11]		(LiCl)[a]	
	R	P	R	P	R	P	R	P
E	-0.205	-0.105	-0.297	-0.299	-0.253	-0.256	-0.183	-0.174
E'	-0.015	$+0.077$	-0.150	-0.147	-0.152	-0.153	-0.064	-0.059
ΔE (calc)	0.193	0.182	0.147	0.152	0.101	0.103	0.119	0.115
ΔE (exp)	0.182		0.182		0.115		0.115	

[a] Present work.

For the VC functions ϕ and ϕ' we found

$$\alpha=0.38,\quad a_1=0.305,\quad \gamma=0.50,$$
$$\beta=0.69,\quad a_2=0.702,\quad \eta=0.69;$$

and for orthogonalization after minimization in Eqs. (12) and (13),

$$b_1=1.02,\quad b_2=-0.08,$$
$$b_1'=1.02,\quad b_2'=\ 0.135;$$

practically the same for ψ_{2s} or $\psi_{\mathrm{L.C.}}$, and ψ_{2p}' or ψ_{3p}'. Figures 4 and 5 illustrate these functions. For orthogonalization to the ion cores before minimization, the results are

$$\beta=0.82,\quad b_1=1.02,\quad b_2=-0.059,$$
$$\eta=0.55,\quad b_1'=1.03,\quad b_2'=\ 0.125.$$

Results for the oscillator strength are summarized in Table IV. The main hyperfine interaction constant, in terms of $|\psi(\mathrm{Li})|^2$, is given in Table V.

The deformations are presented in Table VI. Our results were obtained from the following expressions for the distortion energy:

$$\Delta\mathcal{E}_1=\frac{3}{R_1}\left[\left(\frac{3\sqrt{2}}{2}+\frac{1}{4}\right)\delta_1^2 - \left(4\sqrt{2}+\frac{8\sqrt{6}}{9}+\frac{52\sqrt{10}}{125}\right)\delta_1\delta_2 + \left(\frac{3}{4}+\frac{21\sqrt{2}}{8}+\frac{7\sqrt{6}}{18}\right)\delta_2^2\right],$$

$$\Delta\mathcal{E}_1'=\frac{3}{R_1}\left[\left(\frac{\sqrt{2}}{2}+\frac{1}{6}\right)\delta_1'^2+\sqrt{2}\delta_1'\delta_2'+\tfrac{1}{12}\delta_2'^2\right],$$

$$\Delta\mathcal{E}_2=\frac{a_M}{R_1}[(\lambda-1)\delta_1^2+2\sqrt{2}\delta_1\delta_2+2(\lambda-1)\delta_2^2],$$

$$\Delta\mathcal{E}_2'=\frac{a_M(\lambda-1)}{3R_1}[2\delta_1'^2+\delta_2'^2],$$

$$\Delta\mathcal{E}_2^h=\frac{a_M}{R_1}[\delta_1+\tfrac{1}{2}(\lambda+1)\delta_1^2],$$

$$\Delta\mathcal{E}_2'^h=\frac{a_M}{3R_1}[2\delta_1'+\delta_2'+\tfrac{1}{2}(\lambda+1)(2\delta_1'^2+\delta_2'^2)],$$

$$\Delta\mathcal{E}_e-\Delta\mathcal{E}_1^h=\frac{1}{R_1}[2.255\delta_1+10.789\delta_1^2-0.146\delta_2],$$

$$\Delta\mathcal{E}_e'-\Delta\mathcal{E}_1'^h=\frac{1}{R_1}[-1.68\delta_1'+5.43\delta_2'-5.05\delta_1'^2+10.39\delta_2'^2] + \frac{72}{R_1^3}[\delta_1'-\delta_2'+2\delta_1'^2-2\delta_2'^2],$$

The energy of the excited state when excited-state distortions are taken into account is -0.088 a.u. compared to -0.059 a.u. when the ground-state distortions are used.

6. DISCUSSION

The energy values obtained, for a rigid lattice, with the LCAO method, as listed in Table I, apply to different crystals but are based on equivalent Hamiltonians. There is a difference in computational techniques, in that Kojima evaluated three center integrals by means of an expansion in spherical harmonics, where we used graphical methods, but barring errors one expects comparable results. Table I indicates a difference of 0.085

TABLE IV. The oscillator strength.

	VC[a]	VC[b]	LCAO[c]	VC[c] Eq. (5)	VC[c] Eq. (17)	Exp
LiF	0.85	0.997				0.82[d]
LiCl		0.967	0.68	0.67	0.81	0.81[e]
KCl		0.985				0.85[f]

[a] From reference 9. Wave functions orthogonalized to ion cores.
[b] From reference 10. Wave functions not orthogonalized to ion cores.
[c] Present work with $\beta=0.82$ and $\eta=0.55$ in VC method.
[d] R. T. Bate and C. V. Heer, J. Phys. Chem. Solids **7**, 1, 14 (1958).
[e] F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).
[f] R. H. Silsbee, Phys. Rev. **103**, 1675 (1956).

TABLE V. Isotropic hyperfine interaction in LiCl. Nearest Li ions only.

	LCAO[a]	VC[b]	Exp[18]
$\lvert\psi(\mathrm{Li})\rvert^2$	160×10^{21} cm^{-3}	101×10^{21} cm^{-3}	75×10^{21} cm^{-3}

[a] From present work.
[b] From present work with $\beta=0.82$.

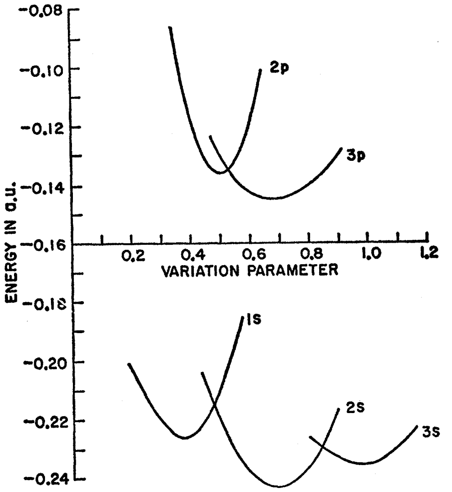

FIG. 3. Energy of the *F*-center electron as a function of the variation parameter for various vacancy centered trial functions. These are the energies before orthogonalization to the ion cores.

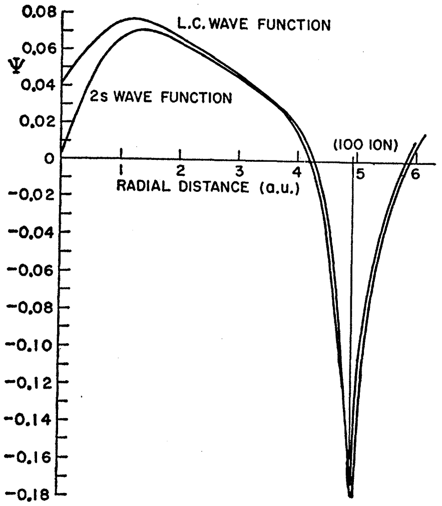

FIG. 4. The vacancy-centered ground state wave functions in LiCl. Orthogonalization to the ion cores was carried out after minimization. The effect of minimization after orthogonalization is to increase the wave function in the vacancy and decrease it at the neighboring ions.

a.u. for the ground state energies in LiF and LiCl, whereas Gourary and Adrian's results with the VC method (Table III, under heading "*R*") indicate only a difference of 0.044 a.u. The LCAO wave functions obtained by Kojima also differ considerably from ours. Kojima finds that the coefficient of the *p*-terms, in the ground state, is about five times as large as the coefficient of the *s*-terms, whereas we find them to be almost equal. It seems to us that this discrepancy must be attributed in part to a numerical error which is perhaps excusable in view of the complexity of the LCAO calculations.

In evaluating the energies for a rigid lattice, obtained with the VC method, as given in Table III under "*R*," Gourary and Adrian's results must first be corrected for effects due to orthogonalization to the ion cores which are not included in their energies. We found that for LiCl orthogonalization raises the ground state energy by 0.060 a.u. and the excited state energy by 0.080 a.u. Applying these corrections to Gourary and Adrian's results for LiCl gives fairly satisfactory agreement, for both states, with our calculations. If the same numerical correction is applied to LiF, their result for the ground-state energy is much closer to Kojima's value, but there exists a large discrepancy for the excited state, for which we have no explanation. Gourary and Adrian have carried out the orthogonalization in the case of the ground state of LiF and the effect on the energy is in accord with our results (see reference 11). A comparison of the calculated oscillator strength (Table IV) gives no further clues.

TABLE VI. Lattice distortions in units of the nearest neighbor distance. Minus sign means displacement outward from center of vacancy.

	(LiF)[9]	(LiF)[11]	(LiCl)[10]	(LiCl)[a]
δ_1	+0.074	−0.020	+0.029	−0.013
δ_2	+0.026			−0.002
δ_1'				+0.045
δ_2'				−0.175

[a] Present work.

The effect of electric polarization on the energy is listed separately in Table III. There are two contributions, due to induced ionic dipole moments and ionic displacements, respectively. Kojima, as well as Gourary and Adrian, found the influence of ionic polarization to be quite small. This is to be expected, especially for the ground state, where the electron is confined almost entirely to the vacancy. We neglected ionic polarization for this reason. Table III indicates large discrepancies

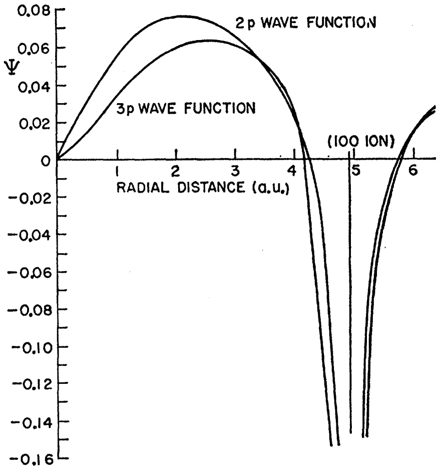

FIG. 5. The vacancy-centered excited state wave functions in LiCl.

between the various calculations. They are closely correlated with the discrepancies in the lattice distortions, as given by the displacements δ_1 and δ_2 for the ground state in Table VI. We attribute these discrepancies to the following.

Kojima calculated the forces acting on the first and second nearest-neighbor ions in order to determine the displacements. His calculation is quite analogous to the calculations involved in classical ionic crystal theory. The effect of the F-center electron is introduced only through the fact that some of the electronic charge extends outside of the vacancy. The actual repulsive interaction between the F electron and the core electrons is neglected. This interaction is quite large and can not be omitted.

Gourary and Adrian, on the other hand, use an energy method to calculate the displacement of the nearest-neighbor ions. Their results show the displacements to be small and in toward the vacancy. However, these authors, in reference 10, have neglected the repulsive interactions between the F electron and the core electrons. They speculated, correctly, that inclusion of this interaction would cause the ions to move outward. In reference 11, they included this interaction and obtained results for the displacements in fairly good agreement with ours. They find, however, that the energy of the F electron is lowered whereas we find that it is raised. This difference could be due to the fact that they have not allowed for the displacements of next-nearest neighbors or it could be due to the fact that the results refer to different crystals.

Neither Kojima nor Gourary and Adrian calculate the distortions in the excited state, so there is no theoretical basis for comparison with our results. Russell and Klick[21] have constructed configuration coordinate curves for the ground and excited states of the F center derived from experiments on a number of different crystals. The configuration coordinate curves give the displacement of the nearest-neighbor ions in the excited state relative to the displacements in the ground state. Unfortunately, no statement can be made about the absolute displacements. The results of Russell and Klick show that the nearest-neighbor ions in the excited state are displaced outward relative to the same ions in the ground state by about 13% of the nearest-neighbor distance. It is difficult to interpret this figure, however, since Russell and Klick have not allowed for asymmetric distortion in the excited state. Table VI indicates a relative outward displacement between the ground and excited state of about 16% for the nearest-neighbor ions, but, due to the approximation of only nearest-neighbor displacements for the excited state, we must accept our result with some reservation.

The importance throughout these calculations of using wave functions which behave properly near the ion is evident. In this connection, it should be mentioned that the early calculations of the energy performed by Tibbs,[2] Simpson,[3] and by Krumhansl and Schwartz[4] are very similar to the VC calculations reported here. The excitation energies in all of the calculations of this type seem to be too low by approximately 0.01 a.u. if orthogonalization to the ion cores is not considered. This is exactly the amount by which Tibbs was off in his calculation on NaCl back in 1939.

The most sensitive indicator for the behavior near the adjacent ions is, of course, the hyperfine interaction, which is given in Table V. The influence of matching is seen from the fact that Kojima, who matches the two branches of his wave functions in LiF at a point nine-tenths of the distance from the center of the vacancy to the nearest-neighbor lithium ions, obtains a value of the hyperfine interaction which is too large by a factor of 2; Gourary and Adrian, on the other hand, in reference 10, carry out the matching process at the full nearest-neighbor distance and obtain a value which is too large by a factor of 3. In reference 11, they also match the two branches of their wave function at nine-tenths of the nearest-neighbor-ion distance which, along with overlap and distortion effects, improves their value for the hyperfine interaction considerably.

We have seen that the calculated value of the hyperfine interaction depends very strongly on the extent to which the wave function of the F electron overlaps the wave function of the core electrons bound to the surrounding ions. This overlap in turn depends on the distortion of the lattice in the vicinity of the vacancy. The dependence is such that the value of the hyperfine interaction increases with an increase in the overlap. An inward displacement such as Kojima obtains for the nearest-neighbor ions increases the overlap between the F-electron wave function and the ion-core functions and thus should cause an increase in the calculated value of the hyperfine interaction relative to the value for the undistorted lattice. An outward displacement of the nearest-neighbor ions has just the opposite effect. This could account for a considerable part of the discrepancy between Kojima's results for LiF and those of Gourary and Adrian for the same crystal.

We conclude from the results reported here that the properties of the F center can be described quite well with simple hydrogenic wave functions provided that they are orthogonalized to the neighboring ion core functions.

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[21] G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).