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Pseudopotential calculation of *F*-center spin densities in KCl, NaCl, and NaF

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In this paper we give the details of a simple calculational model used recently to interpret the experimental pressure shifts of the *F*-center hyperfine interaction constants in KCl, and report further results on the *F*-center ground-state energies and wave functions for KCl, NaCl, and NaF. The model is based on the pseudopotential approach of Bartram, Stoneham, and Gash, but is modified for consistency with a variational solution and expanded to include contributions from ionic *p* states. Polarization is included by means of an *r*-dependent polarization potential suggested by Fowler and used in the extensive calculations of Öpik and Wood. Ground-state energies calculated from the model are shown to be comparable in accuracy with those resulting from a more rigorous calculation. Spin densities are reported for the first six shells of KCl, NaCl, and NaF, and good agreement with experiment is obtained in nearly all cases.

I. INTRODUCTION

There now exists a wealth of experimental data from which the properties of the F center in alkali halides can be deduced. In particular, electron-nuclear double-resonance (ENDOR) experiments have made it possible to map the F-electron ground-state spin density at surrounding lattice points for a number of materials. Comparison of the ENDOR data with the results of theoretical calculations[1-7] provides a sensitive test of the accuracy of the various models used to describe the F center. In the present work we give the details of a calculational model used recently[8] to interpret the experimental pressure shifts of the hyperfine-interaction constants in KCl, and report further results for the F-center ground-state energies and wave functions for KCl, NaCl, and NaF. The model used is based on the approximate pseudopotential approach of Bartram, Stoneham, and Gash[3] (BSG) which incorporates much of the physics of the actual situation. In this work, the BSG pseudopotential is modified for consistency with a variational method of solution and expanded to include interactions of the F center with ionic p states. Polarization effects, neglected in Ref. 8, are here included by means of an r-dependent polarization potential suggested by Fowler[9] and used with slight modifications in the extensive calculations of Öpik and Wood[5] (ÖW).

It is shown that ground-state energies obtainable from this relatively simple model compare well with the much more rigorous results of ÖW. F-electron spin densities for the first six shells of KCl, NaCl, and NaF calculated from a spherically symmetric pseudo wave function also compare well with more rigorous theoretical results[6] and generally give reasonable agreement with the ENDOR data.

II. CALCULATIONAL MODEL

The derivation of the pseudopotential equation used in these calculations parallels closely that of BSG.[3] We begin with the Schrödinger equation for an F electron with ground-state energy E:

$$(T+V)\psi = E\psi \ ,$$

where V is the usual single-electron Hartree-Fock potential. The F-electron wave function ψ is expected to have much the same oscillatory behavior in the regions of the surrounding ions as do the ion core functions ψ_c, and the pseudopotential method[10-13] attempts to take advantage of this fact by defining a pseudo wave function ϕ as

$$\phi = \psi + \sum_c a_c \psi_c \ ,$$

where the arbitrary parameters $a_c = (\psi_c, \phi)$ are to be selected in accordance with some simplifying criterion. This leads to the Phillips-Kleinman equation

$$T\phi + V_p\phi = E\phi \ , \tag{1}$$

where V_p is the pseudopotential operator defined by

$$V_p\phi = V\phi + \sum_c (E - E_c)(\psi_c, \phi)\psi_c \ . \tag{2}$$

For a suitable choice of the parameters a_c considerable cancellation is expected between the two terms on the right-hand side of Eq. (2). A frequently adopted procedure at this point in a pseudopotential calculation is to remove the arbitrariness in the definition of ϕ by imposing a smoothness condition[12-14] such as that suggested by Cohen and Heine.[12] However, it has been shown[15] that such an approach can in principle lead to some difficulties if a variational technique is to be used to solve Eq. (1). Specifically, it appears that a pseudo wave equation restricted by such a smoothness criterion is fully consistent with a variational solution only if the trial function ϕ_t is required to satisfy the same criterion applied to the true pseudo wave function. The problems which arise from this can be avoided if instead of confining our attention to the smoothest possible pseudo wave function we specify ϕ in Eq. (1) as that unique pseudo wave function which most closely approximates the trial function ϕ_t according to the criterion[15]

$$\delta \int |\phi - \phi_t|^2 d\tau = 0 \; . \tag{3}$$

This uniquely determines the parameters a_c in terms of the chosen trial function as $a_c = (\psi_c, \phi_t)$, which leads back to the Phillips-Kleinman equation with the arbitrary terms (ψ_c, ϕ) in the pseudopotential (2) replaced by (ψ_c, ϕ_t). Thus, if a variational approach is to be used to approximate a solution to the pseudo wave equation, then the appropriate procedure is to deal directly with the Phillips-Kleinman pseudopotential which already incorporates the condition (3) on the pseudo wave function. We can still take advantage of the expected smoothness of ϕ by simply choosing a smooth trial function.

With this in mind we now rewrite the Phillips-Kleinman pseudopotential as

$$V_p \phi = V_{\mathrm{PI}} \phi + (V - V_{\mathrm{PI}})\phi + \sum_c (E - E_c)(\psi_c, \phi)\psi_c \; ,$$

where V_{PI} is the point-ion potential, and the remaining terms constitute the ion-size correction. This is expected to be small relative to V_{PI}.

The energy is obtained by minimizing the functional

$$E = \Big((\phi, T\phi) + (\phi, V_{\mathrm{PI}}\phi) + (\phi, (V - V_{\mathrm{PI}})\phi) - \sum_c E_c \, |(\psi_c, \phi)|^2\Big) \Big/ \Big((\phi, \phi) - \sum_c |(\psi_c, \phi)|^2\Big) \; ,$$

with respect to some suitable trial function. Following BSG we now note that the function $V - V_{\mathrm{PI}}$ and the sums over core states can be expressed as sums of terms each of which is large only in the region of some ion site γ. Thus we write

$$(\phi, (V - V_{\mathrm{PI}})\phi) - \sum_c E_c \, |(\psi_c, \phi)|^2 = \sum_\gamma \Big((\phi, (V - V_{\mathrm{PI}})_\gamma \phi) - \sum_i E_{i\gamma} |(\psi_{i\gamma}, \phi)|^2 \Big)$$

and

$$\sum_c |(\psi_c, \phi)|^2 = \sum_\gamma \sum_i |(\psi_{i\gamma}, \phi)|^2 \; ,$$

where the core energy $E_{i\gamma}$ and wave function $\psi_{i\gamma}$ refer to the ith core state on the γth ion site. We further express $E_{i\gamma}$ as the sum of a free-ion core energy $E_{i0\gamma}$ and an approximate crystal potential contribution:

$$E_{i\gamma} = E_{i0\gamma} + W_\gamma - 2/r_\gamma \; ,$$

where W_γ is the Madelung potential energy $\pm 2\alpha_M/a$ of an electron at ion site γ due to all the other ions (in a perfect crystal), a is the lattice spacing, and r_γ is the radial distance from the F center to the γth site (this term corrects for the presence of the F center).

At this point we take advantage of the anticipated smoothness of ϕ and greatly simplify the evaluation of the ion size correction by approximating ϕ in the region of the γth ion site by

$$\phi(r) = \phi(r_\gamma) + \phi'(r_\gamma)\, \rho \cos\theta \; , \tag{4}$$

where ρ and θ are the radial and azimuthal coordinates measured from the γth site along a line joining this site with the center, and ϕ' is the radial derivative of ϕ. We assume here that ϕ is spherically symmetric.

This approach maintains the spirit of the BSG approximation, but the increase in complexity which results from the inclusion of a first-order term in the expansion (4) allows us to include the ionic p-state contributions to the pseudopotential which can be of the same order as the s-state contributions. Approximating ϕ by the first-order expansion in the ion-size correction terms eliminates all two-center integrals from these terms and leaves us with the energy functional

$$E = \Big((\phi, T\phi) + (\phi, V_{\mathrm{PI}}\phi) + \sum_\gamma \Big\{\phi^2(r_\gamma)\Big[A_\gamma - \Big(W_\gamma - \frac{2}{r_\gamma}\Big)B_\gamma\Big] + \phi'^2(r_\gamma)\Big[J_\gamma - \Big(W_\gamma - \frac{2}{r_\gamma}\Big)K_\gamma\Big]\Big\}\Big) \Big/ \Big((\phi, \phi) - \sum_\gamma \big[\phi^2(r_\gamma)B_\gamma + \phi'^2(r_\gamma)K_\gamma\big]\Big) \; . \tag{5}$$

The parameters A_γ, B_γ, J_γ, and K_γ are characteristic of the ion type occupying the γth site and are given by

$$A_\gamma = \int (V - V_{\mathrm{PI}})_\gamma \, d\tau - \sum_i E_{i0\gamma} \left(\int \psi_{n\gamma} \, d\tau \right)^2, \quad B_\gamma = \sum_i \left(\int \psi_{i\gamma} \, d\tau \right)^2 ,$$

$$J_\gamma = \int \rho \cos\theta (V - V_{\mathrm{PI}})_\gamma \rho \cos\theta \, d\tau - \sum_i E_{i0\gamma} \left(\int \rho \cos\theta \, \psi_{i\gamma} \, d\tau \right)^2, \quad K_\gamma = \sum_i \left(\int \rho \cos\theta \, \psi_{i\gamma} \, d\tau \right)^2 .$$

It is seen that the parameter B_γ is identical with that of BSG. Our A_γ is simpler in form and somewhat easier to calculate than the equivalent BSG parameter, but in fact the two differ only to the extent that the core wave functions are not true solutions to the appropriate Hartree-Fock equations. Numerically, there is very little difference for the core functions used here. The new parameters J_γ and K_γ clearly result from the inclusion of the first-order term in Eq. (4) the symmetry of which is such that these parameters mainly reflect interactions with the p-type core electrons.

Numerical values for the pseudopotential parameters obtained using the ionic core functions of Paschalis and Weiss[16] (PW) are listed in Table I (atomic units are used throughout; energies in rydbergs). Included are values calculated from free-ion functions and also from crystal anion functions appropriate to NaF, NaCl, and KCl. To obtain these functions PW approximate the crystal potential by a spherical shell of charge, the radius of which is selected such that the potential due to the shell equals the Madelung potential at an ion site in the crystal. For radii appropriate to alkali halides the crystal potential does not significantly alter the cation core functions, hence for cations we use in our calculations the values of A, B, J, and K obtained from the PW free-ion core function (which are essentially the same as those of Clementi[17]). The main effect of the crystal potential on the anion functions is to contract the outerlying p states, as is clearly reflected in Table I by the significant decrease in the p-state overlap parameter K from the free-ion values for F^- and Cl^-. Calculations by PW have shown that the contracted anion functions yield improved agreement with the experimental diamagnetic susceptibility and dipole polarizability for crystal ions. Hence in our calculations of the F-electron hyperfine-interaction constants and ground-state energies we have used values of the anion parameters A, B, J, and K appropriate to the crystal in question. We should note that crystal ion energies listed by PW already contain a contribution from the crystal environment and must therefore be corrected by the Madelung energy for the calculation of the pseudopotential parameters to be used in Eq. (5). This problem does not arise with the free-ion states.

III. POLARIZATION

The results obtained by Öpik and Wood[5] indicate that polarization effects can be important even in the case of the compact F-center ground state. In their rigorous calculation of F-center transition energies they treated these effects by means of a polarization potential suggested by Fowler[9] and based on the work of Toyozawa[18] and Haken and Schottky.[19] The electronic contribution to the polarization potential has the form

$$U(r) = (1 - 1/\kappa)\{-\tfrac{1}{2}(\rho_e + \rho_h) + (1/r)[1 - \tfrac{1}{2}(e^{-\rho_e r} + e^{-\rho_h r})]\}, \quad (6)$$

where κ is the high-frequency dielectric constant and ρ_h is determined from the formula

$$U_{\mathrm{ML}}^- = \tfrac{1}{2}(1 - 1/\kappa)\rho_h \ .$$

Here U_{ML}^- is the Mott-Littleton polarization energy[20] associated with the removal of a negative ion from the crystal. Fowler has suggested that the parameter ρ_e should be determined from a similar formula with U_{ML}^- replaced by U_{ML}^+, the polarization energy associated with the removal of a positive ion. However, ÖW found that this prescription does not lead to good agreement with the experimental transition energies unless a cutoff radius is introduced inside which polarization effects are neglected. They found on the other hand that good agreement could be obtained by simply setting $\rho_e = \rho_h$. We have followed this suggestion in our calculations and find that it yields generally reason-

TABLE I. Pseudopotential parameters from PW free- and crystal-ion functions.

	A	B	J	K
Na^+ (free)	55.35	18.91	49.37	22.28
K^+ (free)	109.22	64.60	240.25	178.79
F^- (free)	−50.73	50.83	−120.09	503.28
F^- (NaF)	−36.81	51.75	−120.90	162.75
Cl (free)	−117.69	144.92	−451.84	1897.97
Cl^- (NaCl)	−99.25	145.27	−525.83	1000.29
Cl^- (KCl)	−100.67	146.57	−518.03	1184.54

able values for the hyperfine-interaction constants in the three materials we treat. The polarization parameters used in our work are given in Table II. The value of ρ_h for NaF was obtained from a first-order Mott-Littleton calculation using the ionic polarizabilities of Tessman, Kahn, and Shockley.[21] The values for NaCl and KCl are from Ref. 5.

Previous calculations of lattice distortion in the vicinity of an F center have indicated that in the ground state the distortion is quite small. We have verified this conclusion in our own calculations on KCl in which we allowed the nearest-neighbor K^+ ions to distort and minimized the energy while varying both the distortion and the wave-function parameters. Since the resulting small inward distortion of the K^+ ions had a negligible effect on the wave function, we have omitted lattice distortion in the calculations reported here.

IV. RESULTS AND DISCUSSION

In the calculations described below the evaluation of the various terms in the potential energy was carried out to include contributions from the first 24 shells of ions surrounding the F center. In all cases the pseudo wave function ϕ was approximated by a variational trial function of the form

$$\phi = N(\phi_{m\xi} + C\phi_{n\eta}) , \tag{7}$$

where N is a normalization constant, C an expansion coefficient, and the $\phi_{l\lambda}$ are Slater orbitals given by

$$\phi_{l\lambda} = [(2\lambda/a)^{2l+1}/4\pi(2l)!]^{1/2} r^{l-1} e^{-\lambda r/a} .$$

The exponential parameters ξ and η as well as the coefficient C were varied independently to minimize the energy. In all cases reported here we chose $m=1$, and the integer n was usually allowed to vary over a limited range. Some calculations were also performed with $m=2$ and $n>2$, but this choice invariably yielded a higher energy.

Although the present model is more or less easily extended to treat p-type excited states (with the introduction of a few new pseudopotential parameters), a comparison of calculated F-center transition energies with the experimental values would appear pointless in view of the unsatisfactory excited state results obtained by Öpik and Wood using their extended-ion model, of which our model is an approximation. A more appropriate test of the accuracy of our model is provided, however, by comparing our ground-state energies with the more rigorous results of ÖW. For this purpose we used the free ion pseudopotential parameters A, B, J, and K in Eq. (5) and minimized the energy with respect to a trial function similar to that used by ÖW, choosing $m=1$ and $n=2$ in Eq. (7). The calculations were performed with no polarization effects included, and with the r-dependent polarization potential described above. Our results are given in Table III along with the corresponding energies of Öpik and Wood. It is seen that the pseudopotential calculations reproduce the more rigorous results with an average error of about $2\frac{1}{2}\%$, some of which might be ascribed to the use of somewhat different ion core functions and trial functions. These results would seem to indicate that the errors associated with the approximations we make are not of great consequence as far as their contribution to the ground-state energy is concerned.

For further calculations on the F-center ground-state properties of NaF, NaCl, and KCl we used in Eq. (5) the PW crystal anion pseudopotential parameters appropriate to these materials. In the trial function we chose $m=1$ and allowed n to take on integral values from 2–6. We noted little variation of the energy with n for $n>4$. The minimizing values of the wave function parameters are given in Table IV along with the ground state energies obtained. The energies in this case are seen to be significantly lower than those shown in Table III for NaCl and KCl. This is due in part to

TABLE II. Lattice spacing a, high-frequency dielectric constant κ, and polarization parameter ρ_h used in present calculations (ρ_h for NaCl and KCl from Ref. 5).

	a	κ	ρ_h
NaF	4.37	1.74	0.2760
NaCl	5.31	2.25	0.1972
KCl	5.93	2.13	0.1969

TABLE III. Ground-state energies from free-ion parameters for comparison with Ref. 5.

	Present work	Öpik and Wood
NaCl, no pol.	−0.332	−0.345
NaCl, pol. incl.	−0.400	−0.393
KCl, no pol.	−0.292	−0.301
KCl, pol. incl.	−0.360	−0.354

TABLE IV. Pseudo-wave-function parameters and ground-state energies.

	m	n	ξ	η	C	E
NaF	1	6	2.111	11.030	0.422 72	−0.4300
NaCl	1	5	1.898	8.819	0.418 61	−0.4493
KCl	1	6	2.091	11.711	0.411 21	−0.3864

the increased flexibility of the trial function, but the main contribution to the decrease in E must be attributed to the use of crystal anion parameters since calculations using these parameters and a $n=2$ trial function also yield lower energies (-0.447 for NaCl and -0.375 for KCl) than those which result from free-ion parameters.

A zeroth-order approximation to the F-center wave function ψ is obtained by orthogonalizing the pseudo wave function to the PW core states:

$$\psi_0 = N\left[\phi - \sum_{i\gamma} (\psi_{i\gamma}, \phi)\psi_{i\gamma}\right] , \tag{8}$$

where N is the normalization constant

$$N = (\phi, \phi) - \sum_{i\gamma} |(\psi_{i\gamma}, \phi)|^2 .$$

The calculations of Wood[6] and others[7,8] have emphasized the importance of carrying the determination of ψ to a higher order of approximation by orthogonalizing the ion core states on a given site to the core states on neighboring sites. This is accomplished to first order in the ion-ion overlaps by defining a set of core functions $\chi_{i\gamma}$ from the PW functions according to the symmetric orthogonalization procedure[22]:

$$\chi_{i\gamma} = \psi_{i\gamma} - \tfrac{1}{2} \sum_{j\delta} S_{i\gamma, j\delta}\psi_{j\delta} ,$$

where $S_{i\gamma, j\delta}$ are overlap integrals between neighboring ion core states, and the sum is over all the ions neighboring the site γ. Substituting the $\chi_{i\gamma}$ for the PW functions in Eq. (8) gives us the true wave function accurate to first order in the $S_{i\gamma, j\delta}$. Evaluated at the lattice site γ, we can write this

$$\psi_1(r_\gamma) = N\Big(\phi(r_\gamma) - \sum_{i} (\psi_{i\gamma}, \phi)\psi_{i\gamma}(0) + \sum_{i}\sum_{j\delta} S_{i\gamma, j\delta}(\psi_{j\delta}, \phi)\psi_{i\gamma}(0)\Big) , \tag{9}$$

where the $\psi_{i\gamma}(0)$ are evaluated at the symmetry centers of the core functions. Following Wood, we refer to the second term on the right-hand side in Eq. (9) as the direct overlap term and the final term as the indirect overlap term. In our calculations of the indirect overlap terms the j sum was limited to the s and p states of highest energy, and the $S_{i\gamma, j\delta}$ were considered non-zero only for the first-nearest-neighbor (1nn) anion-cation and 2nn anion-anion overlaps. We neglected ion-ion overlap in evaluating the normalization constant N.

Values of the pseudo wave function ϕ and zero- and first-order spin densities $\rho = |\psi|^2$ from Eqs. (8) and (9) are given in Tables V–VII for the first six shells of KCl, and NaCl, and NaF. Shown also are the corresponding experimental spin densities determined from the hyperfine-interaction data of Kersten,[23] Seidel,[24] and Doyle.[25] We consider first the KCl results, which can be compared with the more rigorous values of Wood as well as with experiment. For this purpose we have included also in Table V the isotropic spin densities ρ^s_{d+i} and g-state corrections $\Delta\rho_g = \rho^{s+3g}_{d+i} - \rho^s_{d+i}$ calculated by Wood. We first note that the isotropic spin densities ρ_1 determined from the simplified pseudopotential model are in reasonable agreement with the more rigorously calculated ρ^s_{d+i}. In his work Wood found that the inclusion of a g-like component in the trial function resulted in improved values of the spin density at all shells except shell V. Adding Wood's g-state correction $\Delta\rho_g$ to his ρ^s_{d+i} gives a set of spin densities which deviate from the experimental values by an average error of only 10.3% for shells I to VI. We note that associating the same g-state correction $\Delta\rho_g$ with the values of ρ_1 obtained here yields improved spin densities for all shells (including the fifth), and the resulting values of ρ deviate from experiment by 11.6%. We conclude from this that the isotropic spin densities obtained from the simple model used here are about as accurate as the ρ^s_{d+i} of Wood for shells I to VI.

TABLE V. Values of KCl pseudo wave function ϕ, zero-order spin density ρ_0, first-order spin density ρ_1; isotropic spin density ρ^s_{d+i} and g-state correction $\Delta\rho_g$ from Ref. 6. (ϕ in 10^{-2} a.u.$^{-3/2}$, others in 10^{-2} a.u.$^{-3}$).

Shell	ϕ	ρ_0	ρ_1	ρ^s_{d+i}	$\Delta\rho_g$	ρ_{expt}
I	1.245	11.977	9.102	8.215	+0.971	9.935
II	0.457	2.385	1.800	1.810	−0.106	1.577
III	0.232	0.405	0.265	0.211	−0.066	0.151
IV	0.132	0.195	0.174	0.134	+0.100	0.240
V	0.081	0.050	0.056	0.066	+0.006	0.063
VI	0.052	0.031	0.030	0.033	−0.004	0.023

Calculations on shells VIII and IX indicate that our wave function falls off too quickly to reproduce experimental results in this region. This reflects the inflexibility of our trial function relative to that of Wood and Öpik who included four s-type Slater

TABLE VI. Values of NaCl pseudo wave function ϕ, zero-order spin density ρ_0, and first-order spin density ρ_1 (units as in Table V).

Shell	ϕ	ρ_0	ρ_1	ρ_{expt}
I	1.698	7.121	5.047	5.284
II	0.637	4.767	3.593	2.858
III	0.332	0.280	0.160	0.029
IV	0.197	0.449	0.319	0.105
V	0.125	0.040	0.040	0.052
VI	0.084	0.082	0.076	0.057

orbitals for two of which the parameters were varied to minimize the energy of the first s-like excited state. The contributions from these terms are presumably important in predicting experimental hfi data at outer-lying shells.

The NaCl spin densities shown in Table VI indicate that our wave function falls off at about the correct rate, but the agreement with experiment is not as good as for KCl. It is seen that the largest errors are associated with shells III and IV which, judging by Wood's KCl results, are the shells likely to be most strongly affected by the inclusion of a g-like component in the trial function. We note that the deviation of the calculated NaCl spin densities from the experimental values is in the same direction as in KCl at all shells except the fourth, so that the inclusion of a g-state contribution would be expected to improve the agreement with experiment everywhere except at shell IV. Hence, although a g-state correction could reduce significantly the error at shell III, the symmetry of the g state is such that the factor-of-3 discrepancy at shell IV would be increased considerably. An error of this magnitude would appear difficult to explain without making some disturbing suggestions. The possibility of mistaken experimental data—always a tempting suggestion in a theoretical work—is very unlikely in view of the fact that the original results of Seidel have been verified by Deigen *et al.*,[26] and neither author suggests particular difficulties in analyzing the shell-IV data. A more apparent though less appealing possibility is that the NaCl pseudo wave function is in fact not smooth in the region of shells III and IV. Such a suggestion has no obvious theoretical justification, and the entirely reasonable results we obtain at shells V and VI give strong support to the validity of our smooth function. However, this possibility cannot be completely excluded and in fact would appear to be supported to some extent by the experimental results of Wolbarst[27] on LiCl, for which the spin densities at shells III and IV are also reported to be unexpectedly small. Further studies are clearly required to clarify the theoretical interpretation of the NaCl shell-IV data.

TABLE VII. Values of NaF pseudo wave function ϕ, zero-order spin density ρ_0, and first-order spin density ρ_1 (units as in Table V).

Shell	ϕ	ρ_0	ρ_1	ρ_{expt}
I	2.041	10.150	8.495	9.061
II	0.715	2.064	1.700	2.305
III	0.356	0.311	0.226	0.254
IV	0.201	0.160	0.136	0.155
V	0.122	0.037	0.038	0.059
VI	0.078	0.025	0.022	0.036

The NaF spin densities given in Table VII show fair agreement with experiment but are seen to be consistently lower than the experimental values. Although part of this error can be ascribed to the omission of terms of higher order[28] in the $S_{i\gamma,j\delta}$ in Eq. (9), we are nevertheless led to conclude that the NaF pseudo wave function calculated from this model falls off somewhat too quickly. A number of possible explanations can be proposed for this, among them inflexibility of the trial function, but we believe it may be the case that the simple ÖW prescription of setting $\rho_e = \rho_h$ in the polarization potential is less accurate for NaF than for the chlorides. We have undertaken further calculations on NaF in which ρ_e was determined by Fowler's prescription and a cutoff radius introduced at $R = 0.6a$, and we find that this approach yields significantly improved spin densities at the outer shells.

Our previous calculations[8] on KCl indicate that the omission of polarization effects leads to a pseudo wave function which falls off much too rapidly to predict experimental spin densities beyond the first few shells. Thus it would appear that polarization is important in determining the magnitude of the F-electron wave function outside the immediate vicinity of the center. As the form of polarization potential used here is extremely convenient, further investigations into the conditions of its applicability would be very helpful.

V. CONCLUSIONS

We have demonstrated that the F-center ground state can be described with reasonable accuracy on the basis of a simple calculational model. Ion size effects in this model are incorporated by means of a BSG-type pseudopotential modified for consistency with a variational solution and expanded to include p-state contributions. Comparison of the ground-state energies obtained here with the results of the more rigorous calculations of Öpik and Wood indicates that the errors introduced in the pseudopotential by the first-order expansion of the pseudo wave function are acceptably small, and appear to be considerably smaller than the error which results from the use of free-anion core functions. Some cancellation of error in the pseudopotential is expected since the first-order expansion of ϕ tends to underestimate the direct overlaps (ψ_c, ϕ) while the omission of ion-ion overlap increases the (ψ_c, φ) at most shells.

The isotropic component of the spin density calculated for shells I–VI in KCl agrees well with the corresponding results of Wood and is expected to yield excellent agreement with experiment when corrected with a g-like component. Similar results are found for NaCl except at shell IV, which appears to be anomalous. Calculated spin densities for NaF show reasonable agreement with experiment, but the pseudo wave function falls off somewhat too rapidly, possibly indicating inaccuracies in the simplified polarization potential used.

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