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Two-Electron F' Centers in the Alkaline-Earth Oxides and in the Alkali Halides

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The Hartree-Fock-Slater equations for the two-electron orbitals localized about an anion vacancy in MgO, CaO, NaCl, and KCl have been solved numerically in the point-ion-lattice potential. The ionic polarization of the nearest-neighbor ions is treated in a self-consistent manner. It is found that the low-lying F'-center states for MgO and CaO have the following order for increasing values of the energy: ${}^1S(1s,1s)$, ${}^3P(1s,2p)$, ${}^1P(1s,2p)$, and either ${}^3S(1s,2s)$ or ${}^1S(1s,2s)$. The states ${}^3S(1s,2s)$ and ${}^1S(1s,2s)$ both lie above the other three states, but whether the ${}^3S(1s,2s)$ state lies above or below the ${}^1S(1s,2s)$ state depends upon the ionic polarization of the crystal potential. The above ordering, the optical absorption and emission energies between the states ${}^1S(1s,1s)$ and ${}^1P(1s,2p)$, and the spin-forbidden emission energy from the state ${}^3P(1s,2p)$ to the state ${}^1S(1s,1s)$ agree reasonably with the experimental ordering of the states and with the experimental transition energy values for CaO, respectively. The same physical model gives very different results for the F' center in NaCl and in KCl. It is found that only the ground state ${}^1S(1s,1s)$ contains spatially compact (bound) electronic orbitals. The ground-state energies of the F' center in NaCl and in KCl agree to within 20% of the experimental values. The existence of bound excited states for the F' center in these monovalent crystals has been investigated. However, definitive statements on such states are not available at present.

I. INTRODUCTION

THE F' center in ionic crystals consists of two electrons (the defect electrons) localized about a vacant anion site, regardless of the missing anion valence.[1] This center has been known for some time. It plays an important role in those processes which include the creation, destruction, and transformation of F centers (one defect electron).[2] It has been studied much more extensively in the alkali halides than in the alkaline-earth oxides. The reasons for the emphasis on the alkali halides are partly historical. In addition, the impetus for research on the alkali halides has been aided by the relative ease with which pure large single crystals may be obtained. Only recently have experiments on the F' center in the alkaline-earth oxides (CaO) been successfully interpreted.[3] Present experiments on the intrinsic optical properties of the F' center are preliminary and are not definitive. This lack of extensive study on the intrinsic optical properties of the F' center applies to both the alkali halides and the alkaline-earth oxides.

Practical difficulties account for this. There exist in the alkali halides and perhaps even in MgO other centers, particularly the F center, whose absorption bands are in the same region as the absorption band for the F' center. The F' band in the alkali halides (NaCl and KCl) is usually very wide compared to the F band, and it peaks at a somewhat lower energy than the energy at which the F band peaks. This breadth of the F' band may be interpreted as suggesting that one of the F' electrons is excited directly from the ground state into one of the conduction bands. The F' band resembles to some extent the continuum absorption band of the H^- ion. The stability of such ions as the H^- ion occurs because the two electrons are on the average nearer to the nucleus than they are to each other. Such ions have very few bound states. Hence, it is reasonable for us to expect that F' centers in monovalent crystals have substantially fewer bound states than F' centers in divalent crystals and that monovalent F' centers may have only one bound state, the ground state. But, there is neither definitive experimental nor theoretical work on the number of bound states which monovalent F' centers may have.

The F band and the F' band in some alkaline-earth oxides (CaO, for example) have widths which are comparable to one another and their respective band peaks are well-resolved.[3] The F'-band peak is on the low-energy side of the F-band peak. Different difficulties arise in research on the alkaline-earth oxides. Many of the alkaline-earth oxides (e.g., CaO and MgO) are the divalent structural analogs of the halides (NaCl and KCl). But large and pure single crystals of the alkaline-earth oxides are not readily available. Large dislocation densities and impurity concentrations occur in the single crystals because these oxides have high melting points and are prepared usually by the arc-fusion method. Such imperfections hinder the study of the alkaline-earth oxides. Only recently have researchers understood the optical properties of the transition-metal ion impurities well enough to improve their knowledge about the F center and the F' center in the alkaline-earth oxides.[3]

There exist relatively few theoretical calculations on the F' center in contrast to the many calculations on

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[1] B. Henderson and J. E. Wertz have introduced recently [Advan. Phys. **17**, 749 (1968)] a notation which differs from the notation used in the present paper. These authors denote one electron localized about an anion vacancy in the alkaline-earth oxides by the F^+ center and in the alkali halides by the F center. They also denote two electrons localized about an anion vacancy in the alkaline-earth oxides by the F center and in the alkali halides by the F' center. The author uses in this paper the more traditional notation; namely, an F center contains one electron and an F' center contains two electrons, independent of the valence associated with the missing anion.

[2] W. B. Fowler, *Physics of Color Centers* (Academic Press Inc., New York, 1968), pp. 119–121.

[3] B. Henderson *et al.*, Phys. Rev. **183**, 826 (1969); private communication.

the F center. Most of the F' center investigations consider only the alkali halides. The early work of Pekar[4] treats the F' center by a continuum model. He uses a linear combination of hydrogenic "1*s*" and "2*s*" wave functions for the F' electron orbitals in the ground state. Cheban[5] extends Pekar's treatment to include the thermal ionization and photoionization of F' centers. He concludes that the experimentally observed F' bands in NaCl, KCl, and KBr are connected with the transition of an F' electron into one of the conduction bands. Pekar's treatment also forms the basis for the calculations by Kachlishvili[6] on the interaction of a nonlocalized exciton with an F' center. Using a simple variational wave function (a product of two hydrogenic "2*s*" wave functions), Pincherle[7] applies a semicontinuum model to the F' center and estimates the binding energy for NaCl, KCl, PbS, and BaO. Raveche[8] estimates the binding energy for the F' center in NaCl and KCl. He employs a point-ion model in which the polarization effects are neglected. He computes the electron-electron interaction by a perturbation theory in which the F'-center wave function is a product of Gourary's and Adrian's[9] F-center wave functions for the ground state. His approach yields a binding energy of -1.16 eV (-0.0426 a.u.) for KCl and this compares favorably with the experimental value of -1.2 eV (-0.0441 a.u.). Neeley and Kemp[10] use the point-ion lattice model with a Gaussian variational wave function to investigate the F' centers in the alkaline-earth oxides. Their estimated energies for the transition from the ^1S-like ground state to the ^1P-like excited state for MgO and CaO are 5.4 eV (0.199 a.u.) and 4.4 eV (0.161 a.u.), respectively, without lattice distortion and polarization corrections.

La and Bartram[11] proceed in a manner somewhat similar to Raveche's approach. They employ the point-ion lattice model with some features of a semicontinuum model included as well. They obtain solutions for the electrons in a square-well potential, compute the difference between the point-ion potential and the square-well potential by a perturbation theory, and consider the effects of polarization by use of a semicontinuum model. Their results for F' centers in the alkali halides agree fairly well with the experimental results. Strozier and Dick[12] carry out a more detailed calculation on the F' center in KCl. They include polarization effects through the semicontinuum approach and estimate correlation effects for the ground-state wave function. In addition, their vacancy-centered wave functions are orthogonal to the core orbitals of the nearest- and next-nearest-neighbor ions. Their computation of the absorption band shape contains the continuum wave functions for a square-well potential. The results for the F' absorption edge in KCl of 1 eV (0.0368 a.u.) and for the half-width of the band of about 1 eV (0.0368 a.u.) agree reasonably with experiment. They also find that the ground state is the only bound state of their model. Lynch and Robinson[13] use correlated Hylleraas wave functions in a semicontinuum variational calculation. Their resulting binding energies of the F' center in several alkali halides are in fair agreement with the observed optical-absorption edges. In addition, their absorption cross-section calculations, in which the final state consists of one *s*-like bound-electron wave function and one free plane-wave electron wave function, reproduce the gross features of the experimental absorption curves.

All theoretical treatments of the F' center consider models with mathematical descriptions which are by necessity much simpler than those of the real F' center. Most past treatments of the F and F' centers use trial or variational wave functions. Thus, we usually have approximate solutions to a model problem. Consequently, two questions arise in such treatments, namely, how well do the approximate solutions give the exact properties of the model and how well does the model represent the properties of the real system? Solving the model exactly answers best the first question. Comparing the predictions made by such solutions to the model with the experimental properties answers the second question.

In this paper, the author reports his calculations on several states of the F' center in MgO, CaO, NaCl, and KCl. He uses a point-ion-lattice model which incorporates the Hartree-Fock-Slater (HFS) procedure to compute the defect electron orbitals. In addition, the model contains estimates for the correlation energy of the defect electrons[14] and includes the ionic polarization of the nearest-neighbor ions. These approximations constitute the model and make it solvable on a computer. The formalism which leads to an estimate for the correlation energy is analogous to the formalism by which Slater estimates the exchange energy for the free-electron gas.[14,15] The model also obeys completely the Franck-Condon principle that the ionic polarization does not respond to rapid changes in the electronic state of the F' center when the F' center undergoes an optical transition. This means that all low-lying F'-center states should have spatially compact electron orbitals if the model's predictions are to be internally consistent with its assumptions.

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[4] S. I. Pekar, *Electron Theory of Crystals* (GITTA, Moscow, 1951).

[5] A. G. Cheban, Opt. Spectrosc. **14**, 269 (1963).

[6] E. S. Kachlishvili, Fiz. Tverd. Tela **4**, 736 (1962) [English transl.: Soviet Phys.—Solid State **4**, 538 (1962)].

[7] L. Pincherle, Proc. Phys. Soc. (London) **A64**, 648 (1951).

[8] H. J. Raveche, J. Phys. Chem. Solids **26**, 2088 (1965).

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

[10] V. I. Neeley and J. C. Kemp, Bull. Am. Phys. Soc. **8**, 484 (1963).

[11] S. Y. La and R. H. Bartram, Phys. Rev. **144**, 670 (1966).

[12] J. A. Strozier, Ph.D. thesis, University of Utah, 1966 (unpublished); J. A. Strozier and G. B. Dick, Phys. Status Solidi **31**, 203 (1969).

[13] D. W. Lynch and D. A. Robinson, Phys. Rev. **174**, 1050 (1968).

[14] H. Mitler, Phys. Rev. **99**, 1835 (1955).

[15] J. C. Slater, Phys. Rev. **81**, 385 (1951).

In this paper, one removes the necessity for asking the first question. The procedure is to solve numerically the HFS equations for the F' center given by the model outlined in the preceding paragraph. Since one does not employ trial or variational wave functions, the first question does not arise. The second question does remain, namely, how well does the model represent the properties of the real system? The numerically computed solutions give the exact properties of the above model. If one has confidence that the above approximations contained in the model are physically reasonable, then comparing the predictions made by such solutions to the model with the experimental properties answers the second question.

The model for the present calculations also includes in a classical treatment the ionic polarization of the nearest-neighbor ions. The researcher first specifies the electronic configuration for the two defect electrons of the initial and final states of an optical transition. The computer finds the minimum value of the total energy for the F' center in its initial state as a function of the distance by which the nearest-neighbor ions move (ionic polarization). It then determines the total energy for the F' center in its final state of the optical transition from the same crystal potential (ionic polarization) as that for the initial state. This is in accordance with the Franck-Condon principle for a lattice which behaves classically.

We shall study here within the framework of the above model the five lowest-lying F'-center states for MgO and CaO. This model predicts the following order for the F'-center energy levels: ${}^1S(1s,1s)$, ${}^3P(1s,2p)$, ${}^1P(1s,2p)$, and either ${}^3S(1s,2s)$ or ${}^1S(1s,2s)$. The states ${}^3S(1s,1s)$ and ${}^1S(1s,2s)$ both lie above the other three states but whether the ${}^3S(1s,2s)$ state lies below or above the ${}^1S(1s,2s)$ state depends upon the ionic polarization of the crystal potential from which these states are computed. This ordering of the states for increasing values of the total F'-center energy agrees with the ordering determined from the experiments of B. Henderson *et al.*[3] The F' center in the alkaline-earth oxides is in some respects similar to the helium atom. However, the order of the energy levels is not the same for the F' center and the helium atom. The helium atom energy levels have the following order: ${}^1S(1s,1s)$, ${}^3S(1s,2s)$, ${}^1S(1s,2s)$, ${}^3P(1s,2p)$, and ${}^1P(1s,2p)$. We shall find that the model is successful for CaO with some qualifications. It predicts the correct ordering of the five lowest-lying states and it predicts optical-absorption and emission energies between the ${}^1S(1s,1s)$ state and the ${}^1P(1s,2p)$ state which agree to within 2 and 20% of the respective experimental values. It also predicts the spin-forbidden emission energy from the ${}^3P(1s,2p)$ state to the ${}^1S(1s,1s)$ state to within 6% of the experimental value.

We shall study also with the same model the F' center in NaCl and KCl. Drastically different results obtain for the F' center in these two alkali halides. The model has for the ground state ${}^1S(1s,1s)$ spatially compact (bound) electronic orbitals. Using the same model to compute the ground-state energy of the F center (one electron) in the alkali halides, the author estimates binding energies of the F' center in NaCl and KCl. The theoretical binding energy for KCl agrees to within 12% of the experimental value.[7] The binding energy predicted by the model for the F' center in NaCl is comparable to that in KCl. The existence of bound excited states for the F' center in monovalent crystals remains uncertain. Definite statements are not available. The attempts to solve for the singlet excited state ${}^1P(1s,2p)$ of the model suggest that the $1s$-like orbital is spatially compact but that the $2p$-like orbital is either spatially very diffuse (but bound) or band like (not bound). The uncertainty of the spatial extent of the second electron orbital arises from two related and practical considerations. The numerical integration procedure converges more slowly the more diffuse the orbital becomes (or equivalently, the smaller the magnitude of its energy eigenvalue becomes). Checking the convergence for such diffuse and perhaps unbound states requires excessive computer times.[16]

II. PRELIMINARIES

The present model for the F' center contains the same treatment of the lattice energy as that given in paper I.[17] The author has given in Secs. II and III of paper I a discussion of the total crystal Hamiltonian and of the classical ionic lattice. Because we shall apply here the results contained in Secs. II and III of Paper I, we summarize below the contents of those two sections in terms of the F' center. We shall view the entire lattice classically.

Using the Born-Oppenheimer approximation, we write the two-electron Hamiltonian for the F' center as the sum of two terms,

$$\mathcal{H}_T(\mathbf{x},\mathbf{y};\mathbf{R})=\mathcal{H}_{F'}(\mathbf{x},\mathbf{y};\mathbf{R})+\mathcal{H}_L(\mathbf{R}). \qquad (1)$$

The expectation value of the operator $\mathcal{H}_{F'}$ gives us the electronic energy of the two defect electrons while the expectation value of $\mathcal{H}_L$, which contains no operators for the two F' electrons (defect electrons), gives us the lattice energy of the crystal. The vectors $\mathbf{x}$ and $\mathbf{y}$ are position vectors for the defect electrons and the vector $\mathbf{R}$ is a generic vector which represents the lattice configuration.

We shall study the optical absorption and emission which the defect electrons may undergo. We denote the state (defect electrons and lattice) of the F' center by

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[16] Whenever the computer requires more than 10 min to compute one state for one value of the nearest-neighbor ionic polarization, then the author considers this as an excessive amount of time. He estimates that the computer would require at least an order of magnitude increase in time to locate the minimum of the total energy as a function of the nearest-neighbor ionic polarization.

[17] H. S. Bennett, Phys. Rev. **169**, 729 (1968). Hereafter, we shall refer to this paper as Paper I. We shall use, whenever possible, the notation of this reference.

$|\eta;\sigma\rangle$. The quantity σ, which plays the role of a quantum number, parametrizes the breathing mode in the lattice vibration. The distance which the nearest-neighbor ions move in a breathing mode from their sites in a perfect lattice is σr_1, where r_1 is the nearest-neighbor distance. The symbol η represents the electronic configuration. We shall consider here the five lowest-lying states. Hence, the symbol η denotes an electronic configuration of the two defect electrons which transforms as one of the following states, ${}^1S(1s,1s)$, ${}^3P(1s,2p)$, ${}^1P(1s,2p)$, ${}^3S(1s,2s)$, and ${}^1S(1s,2s)$, transforms. We shall refer to a state as being relaxed whenever the electronic configuration exists for such a long time that the nearest neighbors move to accommodate the charge density associated with the defect electrons. We also shall refer to a state as being unrelaxed whenever the electronic configuration exists for such a short time that the nearest-neighbor ions cannot move to accommodate the new charge density associated with the defect electrons. The final state of an optical transition which obeys completely the Franck-Condon principle is an unrelaxed state. We illustrate the above by the following process. The F' center which is initially in its relaxed ground state $|{}^1S(1s,1s);\sigma_0\rangle$ becomes excited (absorption) in accordance with the Franck-Condon principle into the excited unrelaxed state $|{}^1P(1s,2p);\sigma_0\rangle$. The excited unrelaxed state $|{}^1P(1s,2p);\sigma_0\rangle$ is assumed to be a quasistationary state with an electronic wave function calculated from the same crystal potential (ionic polarization) as that for the initial-relaxed state $|{}^1S(1s,1s);\sigma_0\rangle$. The lattice then relaxes and thereby the crystal potential, which the defect electrons experience, changes. The excited-relaxed state $|{}^1P(1s,2p)\ \sigma_1\rangle$ calculated from the relaxed crystal potential may differ from the excited-unrelaxed state in both radial and angular properties, even though our notation does not explicitly indicate a change in the angular properties. That is, the spatial extent of the defect electron orbitals may change substantially and higher and lower angular momentum states may be admixed into the excited-relaxed state. The F' center may undergo a transition (emission) to a lower-lying unrelaxed state $|{}^1S(1s,1s);\sigma_1\rangle$ with an electronic wave function calculated from the same crystal potential (ionic polarization) as that for the excited relaxed state $|{}^1P(1s,2p);\sigma_1\rangle$. We present in Fig. 1 a simple-schematic configuration diagram which illustrates some of the F'-center states discussed above.

We want to compute the change in the lattice energy due to replacing an anion with the two defect electrons of the F' center. We first create a vacancy at the anion site $\mathbf{r}_0=\mathbf{0}$ of charge Z_0 by adding an effective vacancy charge $Z_v=-Z_0$ at $\mathbf{r}_0=\mathbf{0}$ and permit no lattice relaxation. This fictitious lattice state will serve as the reference energy for the lattice part of the total F'-center Hamiltonian. We compute the change in the lattice energy ΔE_L (vacancy, distortion) due to replacing an anion with two F'-center electrons by classical ionic-lattice theory. We allow the nearest neighbors to move radially from r_1 to $r_1'=r_1(1-\sigma)$ in order to accommodate the F'-center charge density.

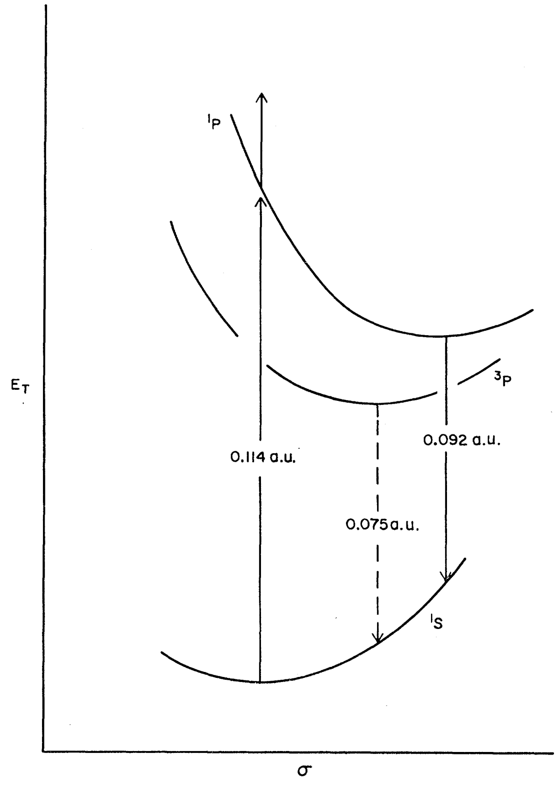

FIG. 1. Schematic configuration-coordinate diagram. The quantity E_T is the total energy of the F' center and σ gives the nearest-neighbor-radial motion (ionic polarization) $r_1'=r_1(1-\sigma)$, where r_1 is the nearest-neighbor distance of the perfect lattice. The F' center has the configuration ${}^1S(1s\uparrow,1s\downarrow)$ for the bottom solid curve, the configuration ${}^3P(1s\uparrow,2p\uparrow)$ for the middle solid curve, and the configuration ${}^1P(1s\uparrow,2p\downarrow)$ for the upper solid curve. The experimental values of the F' center in CaO are given for the optical absorption (0.114 a.u.), the emission (0.092 a.u.), and the spin-forbidden transition (0.075 a.u.).

Before presenting an expression for the total F'-center charge density, we introduce some notation and definitions. The F'-center electronic wave function $\psi_\eta(x,y)$ has the representation,

$$\psi_\eta(x,y)=\langle x,y|\eta;\sigma\rangle. \tag{2}$$

The spatial charge density due to the two defect electrons in the configuration η is

$$\rho_{F'}(\mathbf{r};\eta)=-e\int d^3y\psi_\eta{}^*(r,y)\psi_\eta(r,y), \tag{3}$$

where d^3y means an integration over only the spatial coordinate part $\mathbf{r}$ of the generic coordinate r throughout the entire crystal volume. The generic coordinate r also includes the spin coordinate. We also specify in Eq. (3) that the wave function is normalized to unity. That is, we have the condition

$$\int dy \int dx \psi_\eta^*(x,y)\psi_\eta(x,y)=1\,, \qquad (4)$$

where the integrations over the dx and dy are interpreted to include integration over the entire crystal volume and summation over the spin coordinate. The effective vacancy charge is Z_v. We treat the effective vacancy charge as a point charge and write the charge density $\rho_v(\mathbf{r})$ due to the vacancy in terms of a three dimensional delta function $\delta^3(x)$;

$$\rho_v(\mathbf{r})=Z_v\delta^3(\mathbf{r})\,. \qquad (5)$$

We define for future use $Z_F=-e$, where the magnitude of the electronic charge is e. The total F'-center charge density becomes the sum of the above charge densities,

$$\rho_d(\mathbf{r})=\rho_{F'}(\mathbf{r};\eta)+\rho_v(\mathbf{r})\,. \qquad (6)$$

The change in the lattice energy is written as the sum of many terms. Each researcher has his own way to carry out the summation. We have chosen the method given by Eqs. (17) and (18) of Paper I. The lattice energy for a classical lattice $\langle H_L\rangle -\text{constant}=\Delta E_L$ (vacancy, distortion) $=\Delta E_e+\Delta E_r$, where ΔE_e is the change in electrostatic energy and ΔE_r is the change in the effective repulsive energy which takes into account the Pauli exclusion principle between the ith and jth cores. Because the van der Waals terms increase the formation energy by 5% and decrease the distortion by about 4% and because we do not expect the F'-center electronic part of the Hamiltonian to be accurate to within 5% of the experimental results, we do not include the van der Waals terms in our expression for the cohesive energy from which we compute the lattice energy.[18] In addition, we have found previously that unless we include next-nearest-neighbor repulsions for the F-center core electrons in the alkaline-earth oxides and for the F'-center core electrons in the alkali halides, the distortions for compact electronic states will be excessive. We include, therefore, both first- and second-nearest-neighbor repulsive terms in the cohesive energy. We express the repulsive energy contribution to the cohesive energy by means of the empirically determined Born-Mayer exponential form. Again, we refer the reader to Sec. III of Paper I for the details and to Table I of the present paper for a list of the input data.

TABLE I. Input data for the point-ion model of the F' center with ionic polarization, exchange energy, and Coulomb-correlation energy. The Pauling factor of the ith and the jth ions is β_{ij}. The ionic radius of the cation is ρ_+ and of the anion is ρ_-. The quantity ρ is the stiffness factor in the empirical Born-Mayer exponential form which characterizes the repulsive energy between the ith and the jth ions. The Madelung potential constant at the anion site is α_M. The quantity $\bar{r}_1$ is the nearest-neighbor distance (anion-cation) for the NaCl structure. The series coefficients C_4, C_6, and C_8 appear in the expansion in powers of the lattice distortion σ for the change in electrostatic energy E_1 which occurs when a cation moves in the background of a perfect point-ion-lattice potential; namely, $E_1=-(6/\bar{r}_1)(C_4\sigma^4+C_6\sigma^6+C_8\sigma^8+\cdots)$. The quantities β_{++}, β_{+-}, β_{--}, and α_M are dimensionless. All other quantities are expressed in terms of atomic units (1 a.u. = 27.2 eV for energy and 0.529×10^{-8} cm for length). The crystals NaCl, KCl, MgO, and CaO have the same lattice structure.

	NACl	KCl	MgO	CaO
β_{++}	1.25	1.25	1.50	1.50
β_{+-}	1.00	1.00	1.00	1.00
β_{--}	0.75	0.75	0.50	0.50
ρ	0.599^{a}	0.637^{a}	0.629^{b}	0.629^{b}
ρ_+	2.21^{a}	2.77^{a}	1.76^{b}	2.21^{b}
ρ_-	3.00^{a}	3.00^{a}	2.55^{b}	2.55^{b}
α_M	1.748	1.748	1.748	1.748
$\bar{r}_1$	5.31^{a}	5.93^{a}	3.97^{b}	4.54^{b}
C_4	3.579^{c}	3.579^{c}	3.579^{c}	3.579^{c}
C_6	0.9895^{c}	0.9895^{c}	0.9895^{c}	0.9895^{c}
C_8	2.942^{c}	2.942^{c}	2.942^{c}	2.942^{c}

[a] M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. XVI, p. 52.
[b] M. L. Huggins and Y. Sakamoto, J. Phys. Soc. Japan **12**, 241 (1957).
[c] A. Scholz, Phys. Status Solidi **7**, 973 (1964).

III. POINT-ION MODEL WITH IONIC POLARIZATION

Neglecting lattice vibrations and magnetic interactions, we shall discuss the point-ion Hamiltonian with nearest-neighbor-ionic polarization for the F' center in a relaxed state $|\eta_i;\sigma_i\rangle$ and then in an unrelaxed state $|\eta_f;\sigma_i\rangle$. We denote the total relaxed state by $|\eta_i;\sigma_i\rangle$ and the total unrelaxed state by $|\eta_f;\sigma_i\rangle$. That is, when the subscripts for η and σ are the same, then the state is relaxed, and when the subscripts differ, the state is not relaxed. The notation $|\eta;\sigma_i\rangle$ means that the nearest neighbors are at $r_1'=r_1(1-\sigma_i)$. We limit the motion of the nearest neighbors to a breathing mode and r_1' is their radial distance from the anion vacancy.

We now list the terms of the model Hamiltonian. The kinetic energy operators for the two defect electrons contribute a term

$$\mathcal{H}_1(\mathbf{x},\mathbf{y})=-(\hbar^2/2m)(\nabla_{\mathbf{x}}^2+\nabla_{\mathbf{y}}^2)\,, \qquad (7)$$

where ∇_x^2 operates on the coordinates of one defect electron and ∇_y^2 operates on the coordinates of the other defect electron. The mass of the electron is m.

We consider the ions as point charges Z_ν and we write the defect-electron–point-ion interaction operator in the form

$$\mathcal{H}_2(\mathbf{r};\sigma)=Z_F\sum_{\nu\neq0}{}'\,\{Z_\nu/|\mathbf{r}-\mathbf{r}_\nu|\}\,, \qquad (8)$$

where the prime means that the $\nu=0$ site is not included in the summation, $\mathbf{r}$ is the position vector for one of the defect electrons, and $\mathbf{r}_\nu$ is the location of the νth ion. The Madelung constant is defined by

$$\alpha_M=\bar{r}_1\{\mathcal{H}_2(0;0)/Z_F\}\,, \qquad (9)$$

where $\bar{r}_1$ is the nearest-neighbor distance (anion-cation) for the NaCl structure. The potential energy is invariant under the full cubic group and we may expand it in

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[18] I. M. Boswarva and A. B. Lidiard, Phil. Mag. **16**, 805 (1967).

terms of the Kubic harmonics[19] $Q(\Gamma_i,l,0)$; e.g.,

$$\begin{aligned}\mathcal{H}_2(\mathbf{r};\sigma)=V_{00}(r)Q(\Gamma_1{}^e,0,0;\theta,\varphi)\\ +V_{40}(r)Q(\Gamma_1{}^e,4,0;\theta,\varphi)+\cdots\\ +V_{n0}(r)Q(\Gamma_1{}^e,n,0;\theta,\varphi)+\cdots,\end{aligned}\tag{10}$$

where n is an even integer. Because we shall limit the wave functions to functions which belong to the irreducible representations $\Gamma_1{}^e$("1s") and $\Gamma_4{}^e$("2p") of the cubic group O_h and because the following matrix elements vanish:

$$\langle\Gamma_1{}^e,|Q(\Gamma_1{}^e,n,0;\theta,\varphi|\Gamma_1{}^e\rangle=0$$

and

$$\langle\Gamma_4{}^e|Q(\Gamma_1{}^e,n,0;\theta,\varphi)|\Gamma_4{}^e\rangle=0\tag{11}$$

for all $n\geqslant 4$, we have that

$$\langle\eta;\sigma|\mathcal{H}_2(r;\sigma)|\eta;\sigma\rangle=\langle\eta;\sigma|V_{sph}(r;\sigma)|\eta;\sigma\rangle,$$

where the spherically symmetric part of the point-ion crystal potential is denoted by $V_{sph}(r;\sigma)\equiv V_{00}(r;\sigma)$.

We consider the point ions as distributed on shells centered at the anion vacancy. We denote the radius of shell s by r_s; the number of ions on shell s by S_s; and the charge of the νth ion on shell s by $Q_s=Z_\nu$. We then express the spherically symmetric part of the crystal potential $V_{sph}(r;\sigma)$ in terms of the above notation, namely,

$$\begin{aligned}V_{sph}(r;\sigma)&=V_0, &&\text{for}\quad 0<r<r_1'\\ &=V_0-[(S_1Q_1/r_1')-(S_1Q_1/r_1)]Z_vZ_F\\ & &&\text{for}\quad r_1'<r<r_2\\ &=V_n+(D_n/r), &&\text{for}\quad r_n<r<r_{n+1}\end{aligned}\tag{21}$$

where

$$V_0=Z_vZ_F\{(\alpha_M/\bar{r}_1)+[S_1Q_1\sigma/r_1(1-\sigma)]\}$$

where for $n\geqslant 2$, we have

$$V_n=V_0-Z_vZ_F[(S_1Q_1/r_1')+\sum_{i=2}^{n}(S_iQ_i/r_i)],$$

and where

$$D_n=Z_vZ_F\sum_{i=1}^{n}S_iQ_i.$$

The term $[S_1Q_1\sigma/r_1(1-\sigma)]$ represents the total ionic-polarization potential arising from the first shell due to both the point charge Z_v and the F' electrons. The electron-point-ion interaction operator contributes the term

$$\mathcal{H}_2(r;\sigma)=V_{sph}(r;\sigma).\tag{13}$$

Because practical considerations limit the number of shells which we may explicitly treat, we will consider the first 21 shells in our computations and use the Coulomb potential for distances beyond the 21st shell;

$$V_{sph}(r)=(Z_vZ_F/r)\quad\text{for}\quad r>r_{21}.\tag{14}$$

The Coulomb interaction between the two defect electrons contributes the term

$$\mathcal{H}_c(\mathbf{x},\mathbf{y})=(Z_F{}^2/|\mathbf{x}-\mathbf{y}|).\tag{15}$$

Combining the terms (7), (13), and (15), we write the total F'-center Hamiltonian for the point-ion model with ionic polarization as the sum of one-body and two-body operators:

$$\begin{aligned}\mathcal{H}_T(\mathbf{x},\mathbf{y};\sigma)=&\Delta E_L\ \text{(vacancy, distortion)}\\ &-(\hbar^2/2m)\nabla_{\mathbf{x}}{}^2+\nabla_{\mathbf{y}}{}^2)+V_{sph}(\mathbf{x};\sigma)\\ &+V_{sph}(\mathbf{y};\sigma)+(Z_F{}^2/|\mathbf{x}-\mathbf{y}|)\\ =&\Delta E_L+\mathcal{H}_0(\mathbf{x};\sigma)+\mathcal{H}_0(\mathbf{y};\sigma)+\mathcal{H}_c(\mathbf{x},\mathbf{y}),\end{aligned}\tag{16}$$

where

$$\mathcal{H}_0(\mathbf{x};\sigma)=-(\hbar^2/2m)\nabla_{\mathbf{x}}{}^2+V_{sph}(\mathbf{x};\sigma).$$

Because all terms of the model Hamiltonian operator are real, we may choose the electronic wave functions $\psi_\eta(x,y)$ to be real. They also are normalized to the crystal volume:

$$\int dx\int dy\,\psi_\eta{}^*(x,y)\psi_\eta(x,y)=1.\tag{17}$$

The Schrödinger equation for the F'-center wave functions obtains, by performing the variation of the expectation value of the total Hamiltonian,

$$\langle\mathcal{H}_T\rangle=\int dx\int dy\,\psi_\eta{}^*(x,y)\mathcal{H}_T(\mathbf{x},\mathbf{y};\sigma)\psi_\eta(x,y)\Big/\int dx\int dy\,\psi_\eta{}^*(x,y)\psi_\eta(x,y),\tag{18}$$

with respect to the wave functions $\psi_\eta(x,y)$, subject to the normalization constraint. That is, we vary the wave functions $\psi_\eta(x,y)$ for a given electronic configuration to determine the stationary value of the expectation value $\langle\mathcal{H}_T\rangle$. The variation gives the equation

$$\int dx\int dy\,\delta\psi_\eta{}^*(x,y)\{\mathcal{H}_T(\mathbf{x},\mathbf{y};\sigma)-E\}\psi_\eta(x,y)=0.\tag{19}$$

Equation (19) is to be valid for any arbitrary variation of the function $\psi_\eta(x,y)$. Hence, we obtain the Schrödinger equation

$$\mathcal{H}_T(\mathbf{x},\mathbf{y};\sigma)\psi_\eta(x,y)=E\psi_\eta(x,y).\tag{20}$$

Because the Schrödinger equation (20) cannot be solved exactly even by numerical methods, we shall use the self-consistent field method [Hartree-Fock (HF)] to calculate the wave functions of the stationary states of the F' center. Each of the two defect electrons moves in the average field of the other defect electron. Even

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[19] H. A. Bethe and F. C. Van der Lage, Phys. Rev. **71**, 612 (1947); B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

though the model Hamiltonian (16) is spin-independent, we shall include the symmetry effects of the spins of the two defect electrons. The total wave function must be antisymmetric upon interchanging the space and spin coordinates for the two defect electrons in accordance with the Pauli exclusion principle. The wave function is expressed in the self-consistent field approximation as an antisymmetrized sum of products of one electron function $u_1(r)$ and $u_2(r)$. That is, we approximate the wave function $\psi_\eta(x,y)$ by the HF wave functions:

$$\psi_\eta(x,y)\approx\psi_\eta(x,y;HF) = 2^{-1/2}[u_1(x)u_2(y)-u_1(y)u_2(x)]. \quad (21)$$

The functions u_1 and u_2 are normalized to the crystal volume and spin space

$$\int dx\, u^*(x)u(x)=1\,,$$

and may be chosen to be real because the Hamiltonian is real.

We obtain the set of coupled integrodifferential equations for the functions u_1 and u_2 by substituting Eq. (21) into Eq. (19), by carrying out the variation with respect to u_1 and u_2 separately, and by equating to zero the coefficients of δu_1 and δu_2 which appear in the integrand. We introduce the following abbreviations for the coupled equations:

$$I_{12}=I_{21}=\int dx\, u_1(x)u_2(x)\,, \quad (22)$$

$$H_{ij}(\sigma)=H_{ji}(\sigma)=\int dx\, u_i(x)\mathcal{H}_0(\mathbf{x};\sigma)u_j(x)\,, \quad (23)$$

$$\mathcal{G}_{ij}(\mathbf{r})=\int dx\, u_i(x)\mathcal{H}_c(\mathbf{x},\mathbf{r})u_j(x)\,. \quad (24)$$

Using the approximation (21) and Hamiltonian (16), we have the two equations for u_1 and u_2 [20]:

$$[\mathcal{H}_0(\mathbf{r};\sigma)-E+\Delta E_L+H_{22}(\sigma)+\mathcal{G}_{22}(\mathbf{r})]u_1(r) = [I_{12}\{\mathcal{H}_0(\mathbf{r};\sigma)-E+\Delta E_L\}+H_{12}(\sigma)+\mathcal{G}_{12}(\mathbf{r})]u_2(r)\,, \quad (25)$$

and

$$[\mathcal{H}_0(\mathbf{r};\sigma)-E+\Delta E_L+H_{11}(\sigma)+\mathcal{G}_{11}(\mathbf{r})]u_2(r) = [I_{12}\{H_0(\mathbf{r};\sigma)-E+\Delta E_L\}+H_{12}(\sigma)+\mathcal{G}_{12}(\mathbf{r})]u_1(r)\,. \quad (26)$$

Because the bracketed operators in Eqs. (25) and (26) are different functions of r, their solutions $u_1(x)$ and $u_2(x)$ are, in general, orthogonal to one another. However, the structure of the self-consistent field equations (25) and (26), which arises from the antisymmetric properties of the wave function $\psi_\eta(x,y;HF)$, permits us to regard the spin-orbitals u_1 and u_2 as orthogonal functions

$$\int dx\, u_i^*(x)u_j(x)=\delta_{ij}\,. \quad (27)$$

Statement (27) follows from Eqs. (25) and (26) and from the reasoning given below. Replacing u_2 by a new function $u_2'=u_2+cu_1$ in the wave function $\psi_\eta(x,y;\text{HF})$ does not alter the wave function $\psi_\eta(x,y;HF)$. We then choose the constant c so that u_2' and u_1 are orthogonal and then simply call u_2' by the name u_2.

The HF variational equations (25) and (26) may be solved in principle by numerical iterative techniques. However, we must solve them at many values of the ionic polarization σ in order to find the minimum F'-center energy for a given electronic configuration. Such a procedure requires an excessive amount of computer time. To reduce the computation time, we introduce Slater's[15] simplified version of these HF equations. His simplification is based upon his free-electron exchange approximation for the exchange terms which occur in Eq. (25) and Eq. (26) when the two defect electrons are in a triplet configuration ($S=1$). Slater suggests that the essential features of the HF method are retained by replacing the exchange potentials for the different orbitals u_1 and u_2 with a common exchange potential. A suitable averaging of these individual exchange potentials yields this common exchange potential. Following Slater's suggestion, we assume that the averaged exchange potential for the F' center at the point $\mathbf{r}$ is equal to the exchange potential which a free-electron gas would have if its total electron charge density for both spins were equal to that of the nonuniform system (the two F'-center defect electrons): namely,

$$V_{\text{exch}}(\mathbf{r})=-3e^2[(3/8\pi)e^{-1}|\rho(\mathbf{r})|]^{1/3}. \quad (28)$$

Equation (28) means that the averaged exchange potential for the two F'-center electrons depends only on the local electronic charge density $\rho(\mathbf{r})=\rho_{F'}(\mathbf{r};\eta)$. Thus, the problem of calculating the exchange integrals $\mathcal{G}_{ij}$ when $i\neq j$ for the triplet states is circumvented.

We shall write presently the HFS equations for the F'-center electrons. But first, it is necessary to introduce more notation. When the author listed the five lowest-lying states, he has assumed implicitly that the central-field approximation is reasonable for the low-lying states with angular momentum quantum number $l\leq 2$ in a cubic potential. The most general central field representation for the functions u is

$$u_{nlms}(x)=R_{nlms}(r)Y_{lm}(\theta,\varphi)\alpha_s\,,$$

where $R(r)$ is the radial function, Y_{lm} is a spherical harmonic function, and α_s is the spin function. The principal, orbital, magnetic, and spin quantum numbers are, respectively, n, l, m, and s. We shall use, however, the

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[20] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 140.

more restrictive representation

$$u_{nlm_s}=R_{nl}(r)Y_{lm}(\theta,\varphi)\alpha_s.$$

We define the radial functions $P_{nl}(r)$, $P_{nl}(r)=rR_{nl}(r)$, and normalize them to the crystal volume $\int P_{nl}^2(r)dr=1$.

We express the spherically averaged total electronic charge density for both spins in terms of the radial functions

$$\rho_{\text{av}}(r)=-e[\sigma(r)/4\pi r^2],$$

where the spherical density $\sigma(r)$ is

$$\sigma(r)=\sum_{nl}\omega_{nl}P_{nl}^2(r),$$

and the occupation number of the spatial orbital for both spins is ω_{nl}. The summation $\sum_{nl}\omega_{nl}$ equals 2 for the F' center.

Keeping the above assumptions in mind, we write the HFS variational equations for the F' center when the electrons are in a triplet state:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V_{sph}(r;\sigma)\right.$$
$$\left.+V_c(r)+V_e(r)\right)P_{nl}(r)=E_{nl}P_{nl}(r), \quad (29)$$

where the Coulomb potential $V_c(r)$ has the form

$$V_c(r)=\frac{e^2}{r}\int_0^r\sigma(t)dt+e^2\int_r^\infty\frac{\sigma(t)}{t}dt,$$

and the exchange potential has the form

$$V_e(r)=-3e^2[(3/8\pi)e^{-1}|\rho_{\text{av}}(r)|]^{1/3}.$$

Let us define $V_s(r)=V_c(r)+V_e(r)$ for future use. The HF variational equations for the central field approximation of the F' center in a singlet state become

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V_{sph}(r;\sigma)\right.$$
$$\left.+V_c(r)\right]P_{nl}(r)=E_{nl}P_{nl}(r). \quad (30)$$

Because the change in lattice energy ΔE_L is independent of the defect electron coordinates and occurs only as a constant for fixed σ, we do not include it in these variational equations when computing the radial functions $P_{nl}(r)$ for fixed σ.

The Slater free-electron exchange approximation stresses the similarities between the exchange hole for a free-electron gas and for an atomiclike system such as the F' center. We now mention some difficulties. The above exchange hole in the atomiclike F' center is not, in general, spherically symmetric and does not attain its maximum value at the position of the electron as the exchange hole for the free-electron gas does. As the electrons move away from the vacancy, the exchange hole lags behind. This lag is slight for spatially compact states, but it becomes important for spatially diffuse states. Hence, Eq. (28) becomes suspect at large values of r. The Coulomb potential $V_c(r)$ for the F' center approaches $2e^2/r$ as r becomes sufficiently large. Also, as r becomes large, the exchange potential $V_{\text{exch}}(r)$ approaches zero faster than $1/r$ approaches zero. One electron in the F' center cannot act upon itself. The sum $V_s(r)$ must approach $e^2(\sum_{nl}\omega_{nl}-1)/r$ as r approaches infinity and it should not approach $e^2(\sum_{nl}\omega_{nl}/r)$ as r approaches infinity. Hence, the approximation (28) does not treat the self-energy correctly for large values of r.

The self-Coulomb energy part of the total electronic Coulomb energy cancels exactly in the conventional HF method a corresponding energy in the total exchange energy. This cancellation does not occur in the HFS equations at large r. Following Latter,[21] we alter the sum $V_s(r)$ so that it has the correct asymptotic behavior at large r. We define $V(r)=V_c(r)+V_e(r)$ for $r<r_0$ and $V(r)=e^2|\sum_{nl}\omega_{nl}-1)/r$ for $r\geqslant r_0$. The radius r_0 is that value of r at which

$$V_s(r_0)=e^2(\sum_{nl}\omega_{nl}-1)/r_0.$$

Thus, we use approximation (28) for the region $r<r_0$ in which the exchange hole follows the motion of the electron fairly well and we use the correct asymptotic form $e^2(\sum_{nl}\omega_{nl}-1)/r$ for the region $r\geqslant r_0$. The radial functions $P_{nl}(r)$ and the energy eigenvalues E_{nl} of the innermost orbitals are insensitive to the replacement of $V_s(r)$ with $V(r)$. This replacement alters only slightly the radial functions of the outermost orbitals, while it may alter appreciably the corresponding energy eigenvalues.[22] Because the author computes the F'-center energy from only the HF wave functions and does not sum in the appropriate and usual manner the eigenvalues to obtain the total F' energy, he expects that the above replacement has only a negligible effect on the F'-center energy and on the radial wave functions for the low-lying states. The discontinuity in the slope of the modified HFS potential $V(r)$ does not induce discontinuities in the radial functions. This is important because such discontinuities would give erroneous values for the kinetic energy. Herman and Skillman[22] have examined their HFS radial functions near r_0 and they find that no discontinuities exist out to sixth-order differences.

IV. CORRELATION ENERGY AND TOTAL F'-CENTER ENERGY

The HF method does not include the spatial correlation in the motion of the two defect electrons produced

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[21] R. Latter, Phys. Rev. 99, 510 (1955).

[22] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963), Chap. 1.

by their instantaneous Coulomb repulsion $\mathcal{H}_c(\mathbf{x},\mathbf{y})$. The HF field acting on one electron is obtained by averaging over the motion of the other electron. But even though the Coulomb correlation is neglected, the HF method does introduce a statistical (exchange) correlation in the motion of electron pairs with the same spin through the antisymmetric (determinantal) wave function. This statistical correlation results from the electrons obeying Fermi-Dirac statistics and tends to keep electrons with the same spin apart. Since Coulomb correlation is most important when the electrons are close together and since the statistical correlation tends to keep electrons with the same spin far apart, neglect of the Coulomb correlation in the HF equations for the triplet states of the F' center is tolerable. But, the HF equations for the singlet states of the F' center contain no exchange terms and, hence, no statistical correlations.

Since the Coulomb correlation is much more important for the singlet states of the F' center than it is for the triplet states, we shall follow the procedure of Mitler[14] which estimates the Coulomb correlation energy for atomiclike systems. The approximate HF wave function (21) is the source of the Coulomb correlation problem. It arises from the fact that $\psi_\eta(x,y;HF)$ does not depend upon the distance between the two electrons $|\mathbf{x}-\mathbf{y}|$ and that $\psi_\eta(x,y;\text{HF})$ contains products of one-electron wave functions. We define the correlation energy by the relation

$$E_c=\langle\psi_\eta(x,y)|\mathcal{H}_T|\psi_\eta(x,y)\rangle -\langle\psi_\eta(x,y;HF)|\mathcal{H}_T|\psi_\eta(x,y;HF)\rangle. \quad (31)$$

Let us assume also that a correlation operator $\mathcal{E}_c(|\mathbf{x}-\mathbf{y}|)$ exists such that its expectation value in the approximate representation $\psi_\eta(x,y;HF)$ is the correlation energy

$$E_c=\langle\psi_\eta(x,y;HF)|\mathcal{E}_c(|\mathbf{x}-\mathbf{y}|)|\psi_\eta(x,y;HF)\rangle. \quad (32)$$

We may introduce, then, the correlation potential $W_c(\mathbf{r})$ by the following operation:

$$W_c(\mathbf{r})=\int d^3x\psi_\eta(x,r;HF)\mathcal{E}_c(|\mathbf{x}-\mathbf{r}|)\psi_\eta(x,r;HF). \quad (33)$$

Mitler[14] adapts to atomic helium the free-electron gas approximation given by Wigner[23] for the correlation energy of alkali atoms. This procedure is analogous to Slater's free-electron gas approximation of the exchange energy. These authors introduce in the HF equations an additional central "correlation" potential $W(r)$ to which pairs of electrons with opposite spin are subject. The approximate correlation potential $W(r)$ has the form[23]

$$W(r)=-e^2\frac{0.288}{5.1a_0+r_s(r)}, \quad (34)$$

where a_0 is the Bohr radius and the local density of electrons is

$$e^{-1}|\rho(r)|=[(4\pi/3)r_s^3(r)]^{-1}.$$

We expect that expression (34) is a good estimate for the correlation potential $W_c(r)$; that is, $W(r)\approx W_c(r)$. Mitler[14] applies expression (34) to the ground state for helium and obtains by perturbation theory a ground-state energy which agrees to within $\frac{1}{2}\%$ of the experimental value. Our prescription is, then, to replace $V_c(r)$ in the singlet HF variational equations (30) with $V_c(r)+W(r)$. Because the inequality

$$0\leq W(r_s)/V_{\text{exch}}(r_s)\leq 0.314r_s/(5.1a_0+r_s)\leq 0.314r_s$$

is obtained, we do not include the Coulomb correlation potential in the triplet HF variational equations (29).

Hence, the HFS equations which include the ionic polarization, exchange energy, and correlation energy and from which we numerically compute the radial wave functions for a given value of distortion σ become

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V_{sph}(r;\sigma)+V(r)\right]P_{nl}(r)=E_{nl}P_{nl}(r) \quad (35)$$

for the triplet F'-center states and

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V_{sph}(r;\sigma)+V_c(r)+W(r)\right]P_{nl}(r)=E_{nl}P_{nl}(r) \quad (36)$$

for the singlet F'-center states.

The author does not compute here the total energy of the F' center by summing the eigenvalues of the HF variational equations and substracting one-half times the expectation values of those two-body operators which are estimated in the self-consistent field method by effective one-body potentials. The numerical results from Chap. I of Ref. 22 suggest that the HF wave functions $P_{nl}(r)$ are less sensitive to modifications in effective potentials than are the eigenvalues E_{nl}. For this reason, the author expects that the more accurate way to compute the total energy of the F' center for a given value of the ionic polarization σ is to compute the total energy directly from the original Hamiltonian (16) by using the HF wave functions which obtain from Eqs. (35) and (36). The triplet state has total a energy

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[23] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938); E. Wigner, Phys. Rev. **46**, 1002 (1934).

given by

$$E_T[\eta(nl\uparrow;n'l'\uparrow);\sigma]$$

$$=\Delta E_L(\sigma)+\int d^3x\,u_{nl}(x)\mathcal{H}_0(\mathbf{x},\sigma)u_{nl}(x)$$

$$+\int d^3x\,u_{n'l'}(x)\mathcal{H}_0(\mathbf{x},\sigma)u_{n'l'}(x)$$

$$+\int d^3x\int d^3y\,u_{nl}(x)u_{n'l'}(y)\mathcal{H}_c(\mathbf{x},\mathbf{y})u_{nl}(x)u_{n'l'}(y)$$

$$-\int d^3x\int dy\,u_{nl}(x)u_{n'l'}(y)\mathcal{H}_c(\mathbf{x},\mathbf{y})u_{nl}(y)u_{n'l'}(x)\,. \tag{37}$$

Similarly, the singlet state has a total energy given by

$$E_T[\eta(nl\uparrow;n'l'\downarrow);\sigma]$$

$$=\Delta E_L(\sigma)+\int d^3x\,u_{nl}(x)\mathcal{H}_0(\mathbf{x},\sigma)u_{nl}(x)$$

$$+\int d^3x\,u_{n'l'}(x)\mathcal{H}_0(\mathbf{x},\sigma)u_{n'l'}(x)$$

$$+\int d^3x\int d^3y\,u_{nl}(x)u_{n'l'}(y)\mathcal{H}_c(\mathbf{x},\mathbf{y})u_{nl}(x)u_{n'l'}(y)$$

$$+\tfrac{1}{2}\bigg[\int d^3x\,u_{nl}(x)W(\mathbf{x})u_{nl}(x)$$

$$+\int d^3x\,u_{n'l'}(x)W(\mathbf{x})u_{n'l'}(x)\bigg]. \tag{38}$$

The terms containing the correlation potential $W(r)$ must be included in order to obtain Eq. (36) by a variation of the functions u_{nl} and $u_{n'l'}$ which appear in the expectation value of the Hamiltonian $\mathcal{H}_T$.

V. ABSORPTION AND EMISSION

Referring the reader to Fig. 1, we shall describe 5 of the low-lying states of the F' center. The initial state of an optical transition is a relaxed state, which we shall denote by $|\eta_i;\sigma_i\rangle$. We minimize $E_T(\eta_i;\sigma)$ with respect to the ionic polarization σ to obtain the energy of the initial state $E_i=E_T(\eta_i;\sigma_i)$. The value σ_i is that value of σ for which $E_T(\eta_i;\sigma)$ attains its minimum value. The F' center then undergoes an optical transition to the state $|\eta_f;\sigma_i\rangle$, which is assumed to be a quasistationary state with an electronic wave function calculated for the same distortion σ_i as that for the initial state $|\eta_i;\sigma_i\rangle$. This is a statement of the Franck-Condon principle. We emphasize that the distortion σ represents the ionic displacement of the nearest-neighbor ions due to both the two defect electrons and the effective vacancy charge Z_v. The total energy of the final state is $E_f=E_T(n_f;\sigma_i)$. The optical absorption energy for a transition from state i to state f is

$$E(i,f)=E_T(\eta_f;\sigma_i)-E_T(\eta_i;\sigma_i)\,, \tag{39}$$

and the optical-emission energy from state i to state f is

$$E(i,f)=E_T(\eta_i;\sigma_i)-E_T(\eta_f;\sigma_i)\,, \tag{40}$$

where each term on the right-hand side of Eqs. (39) and (40) is a negative number.

The expectation value of a given power of the radial coordinate r gives us information on the spatial extent of the two defect electron wave functions. As a measure of the spatial extent, we have chosen to consider the first and third powers of r for each of the orbitals, namely,

$$r_{nl}[s,\eta(nl;n'l');\sigma]=r_1^{-s}\int R_{nl}(r)r^sR_{nl}(r)4\pi r^2dr \tag{41}$$

and

$$r_{n'l'}[s,\eta(nl;n'l');\sigma]=r_1^{-s}\int R_{n'l'}(r)r^sR_{n'l'}(r)4\pi r^2dr\,, \tag{42}$$

where $s=1$ or $s=3$ and r_1 is the nearest-neighbor distance of the perfect lattice. The ratio

$$r_e(nl)=[r_{nl}(s=3)/r_1^2r_{nl}(s=1)]$$

also indicates to what extent the radial functions have extended tails. Values of $r_e<1$ indicate compact states and values of $r_e>1$ indicate diffuse states. The author has chosen to present the wave function data in this manner and not to present many numerical tables of the wave functions as functions of the radial coordinate.

VI. RESULTS AND CONCLUSIONS

We report in this section the results of the preceding point-ion model with ionic polarization and correlation energy. We shall divide the presentation of our results into two groups: the alkaline-earth oxides (MgO and CaO) and the alkali halides (NaCl and KCl). We use the Born-Mayer empirical form [Eq. (15) of Paper I] for the repulsive energy terms. Table I contains the values of the input data which we have used.

The author computed the low-lying state of the helium atom to check his F'-center computer programs. He obtains when the Coulomb correlation energy is included a ground-state energy of -2.881 a.u. and a ${}^1S(1s,1s)$ to ${}^1P(1s,2p)$ transition energy of 0.73 a.u. These numbers compare favorably with the respective experimental values of -2.904 and 0.78 a.u. The numerical procedures selected by the author give the energy eigenvalues to an accuracy of $(|\Delta E|/E)\approx 0.001$. They also give the self-consistent potential which appears in the HF equation to an accuracy of $(|\Delta V|/V)\approx 0.01$. The quantities ΔE and ΔV are, respectively, the changes in the trial eigenvalue and the self-consistent potential which occur between two successive iterations in the numerical integration procedure. Solving the F'-center problem to greater accuracy requires an excessive amount of computer time. The author does not feel that the rather simple model given in this paper warrants greater numerical accuracy in the solution of the HF equations.

Experimental studies of the F' center in MgO have been reported only very recently.[24] We do have more detailed experimental F'-center studies in CaO[3] with which to compare the predictions of the present model. Tables II and III give for MgO and CaO the 5 lowest-lying F'-center states in the perfect point-ion lattice. These calculations include the Coulomb correlation energy for the singlet states and the exchange energy for the triplet states. Tables IV and V contain for MgO and CaO, respectively, the 3 lowest-lying singlet states for absorption from the ground state. These calculations include both the correlation energy and the ionic polarization of the nearest neighbors. The calculated absorption energy for MgO of 0.145 a.u. agrees to within 20% of the recently reported value.[24] Much better agreement obtains for CaO. The calculated absorption energy for CaO of 0.116 a.u. agrees to within 2% of the experimental value of 0.114 a.u. Tables VI and VII present the theoretical results for the low-lying singlet states when the initial state is $^1P(1s,2p)$. Again, the Coulomb correlation energy and the ionic polarization of the nearest neighbors are included. The theoretical emission energy

TABLE II. The five lowest-lying states for MgO of the F' center in the prefect-point-ion lattice ($\sigma=0$) with exchange and Coulomb correlation. Triplet states are computed from Eqs. (35) and (37) and singlet states are computed from Eqs. (36) and (38). The states $^1S(1s,1s)$, $^3P(1s,2p)$, $^1P(1s,2p)$, $^3S(1s,2s)$, and $^1S(1s,2s)$ are labeled, respectively, in this table by A, B, C, D, and E for convenience. The total energy of state X is $E_T(\mathrm{X};\sigma=0)$, where X = A, B, C, D, or E. The transition energy from state X to state Y is $E(\mathrm{X,Y})$. The quantities n and l are the principal and angular-momentum quantum numbers for the symmetry of the one-electron orbitals from which the F'-center configuration is made. The spatial extent quantities $r_{nl}(s)$ and $r_e(nl)$ are dimensionless and the energies are expressed in terms of atomic units (1 a.u. = 27.2 eV).

State	A	B	C	D	E
E_T	−1.110	−1.005	−0.956	−0.805	−0.810
$r_{nl}(1)$	0.826	0.751	0.821	0.694	0.782
$r_{nl}(3)$	0.760	0.597	0.748	0.483	0.663
$r_e(nl)$	0.920	0.795	0.912	0.695	0.854
$r_{n'l'}(1)$	0.826	0.900	0.949	2.065	2.269
$r_{n'l'}(3)$	0.760	0.982	1.168	11.973	15.007
$r_e(n'l')$	0.920	1.092	1.231	5.798	6.615
E(A,C)	0.144				
E(D,B)	0.200				
E(C,E)	0.146				

TABLE III. The five lowest-lying states for CaO of the F' center in the perfect point-ion lattice ($\sigma=0$) with exchange and Coulomb correlation. The notation in this table is the same as the notation given in Table II.

State	A	B	C	D	E
E_T	−0.991	−0.922	−0.879	−0.728	−0.731
$r_{nl}(1)$	0.818	0.714	0.813	0.689	0.775
$r_{nl}(3)$	0.719	0.571	0.710	0.466	0.635
$r_e(nl)$	0.879	0.767	0.873	0.677	0.820
$r_{n'l'}(1)$	0.818	0.873	0.914	1.873	2.176
$r_{n'l'}(3)$	0.719	0.859	0.986	9.421	13.013
$r_e(n'l')$	0.879	0.984	1.079	5.030	5.980
E(A,C)	0.112				
E(D,B)	0.195				
E(C,E)	0.148				

TABLE IV. The three lowest-lying singlet states for the F' center in MgO. These singlet states are computed from Eqs. (36) and (38). The initial state is $^1S(1s,1s)$ and $\sigma=0.005$. The value of σ remains the same for the other two states. The notation is explained in Table II.

State	A	C	E
E_T	−1.100	−0.954	−0.798
$r_{nl}(1)$	0.820	0.814	0.776
$r_{nl}(3)$	0.740	0.729	0.652
$r_e(nl)$	0.902	0.895	0.839
$r_{n'l'}(1)$	0.820	0.936	2.260
$r_{n'l'}(3)$	0.740	1.106	14.836
$r_e(n'l')$	0.902	1.181	6.566
E(A,C)	0.145		
E(A,C; expt.)	0.183[a]		
E(C,E)	0.157		

[a] Y. Chen *et al.*, Bull. Am. Phys. Soc. **14**, 872 (1969).

TABLE V. The three lowest-lying singlet states for the F' center in CaO. These singlet states are computed from Eqs. (36) and (38). The initial state is $^1S(1s,1s)$ and $\sigma=0.017$. The value of σ remains the same for the other two states. The notation is explained in Table II.

State	A	C	E
E_T	−0.996	−0.879	−0.701
$r_{nl}(1)$	0.800	0.796	0.760
$r_{nl}(3)$	0.667	0.659	0.594
$r_e(nl)$	0.834	0.829	0.782
$r_{n'l'}(1)$	0.800	0.887	2.135
$r_{n'l'}(3)$	0.667	0.880	12.428
$r_e(n'l')$	0.837	0.992	5.822
E(A,C)	0.116		
E(A,C; expt.)	0.114[a]		
E(C,E)	0.179		

[a] B. Henderson *et al.*, Phys. Rev. **183**, 826 (1969).

TABLE VI. The two lowest-lying singlet states for the F' center in MgO. These singlet states are computed from Eqs. (36) and (38). The initial state is $^1P(1s,2p)$ and $\sigma=-0.007$. The value of σ remains the same for the other state. The notation is explained in Table II.

State	A	C
E_T	−1.097	−0.956
$r_{nl}(1)$	0.836	0.830
$r_{nl}(3)$	0.792	0.779
$r_e(nl)$	0.948	0.939
$r_{n'l'}(1)$	0.836	0.969
$r_{n'l'}(3)$	0.792	1.274
$r_e(n'l')$	0.948	1.315
E(C,A)	0.141	

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[24] Y. Chen *et al.*, Bull. Am. Phys. Soc. **14**, 872 (1969).

TABLE VII. The two lowest-lying singlet states for the F' center in CaO. These singlet states are computed from Eqs. (36) and (38). The initial state is ${}^1P(1s,2p)$ and $\sigma=0.009$. The value of σ remains the same for the other state. The notation is explained in Table II.

State	A	C
E_T	−0.994	−0.880
$r_{nl}(1)$	0.808	0.804
$r_{nl}(3)$	0.689	0.681
$r_e(nl)$	0.853	0.848
$r_{n'l'}(1)$	0.808	0.898
$r_{n'l'}(3)$	0.689	0.923
$r_e(n'l')$	0.853	1.027
E(C,A)	0.114	
E(C,A; expt.)	0.092[a]	

[a] B. Henderson *et al.*, Phys. Rev. **183**, 826 (1969).

from ${}^1P(1s,2p)$ to ${}^1S(1s,1s)$ for CaO of 0.114 a.u. is within 20% of the experimental value of 0.092 a.u. The correct experimental value of this transition energy in MgO remains in doubt.[24] The present model, however, fails to predict the correct Stokes shift. The theoretical Stokes shift is $E(A,C;\text{absorption})-E(A,C;\text{emission})=0.002$ a.u. for CaO and the experimental CaO Stokes shift is 0.022 a.u. This failure to give the correct Stokes shift by an order of magnitude suggests that the present model should be improved for emission calculations. Such improvements might correspond to those contained in Paper I[18] and Paper II.[25] However, the models in those papers would require a substantial increase in computer time when they are applied to the two defect electron centers.

TABLE VIII. The low-lying states for the F' center in MgO from which the spin-forbidden transition energy may be computed. State A is computed from Eqs. (36) and (38) and states B and D are computed from Eq. (35) and Eq. (37). The initial state is ${}^3P(1s,2p)$ and $\sigma=-0.005$. The value of σ remains the same for the other two states. The notation is explained in Table II.

State	A	B	C
E_T	−1.098	−1.005	−0.816
$r_{nl}(1)$	0.833	0.755	0.698
$r_{nl}(3)$	0.782	0.609	0.491
$r_e(nl)$	0.939	0.807	0.703
$r_{n'l'}(1)$	0.833	0.909	2.089
$r_{n'l'}(3)$	0.782	1.024	12.281
$r_e(n'l')$	0.939	1.127	5.879
E(B,A; spin-forbidden)	0.093		
E(B,D)	0.189		

TABLE IX. The low-lying states for the F' center in CaO from which the spin-forbidden transition energy may be computed. State A is computed from Eqs. (36) and (38) and states B and D are computed from Eq. (35) and Eq. (37). The initial state is ${}^3P(1s,2p)$ and $\sigma=0.013$. The value of σ remains the same for the other two states. The notation is explained in Table II.

State	A	B	D
E_T	−0.995	−0.924	−0.707
$r_{nl}(1)$	0.805	0.734	0.683
$r_{nl}(3)$	0.679	0.545	0.454
$r_e(nl)$	0.844	0.742	0.665
$r_{n'l'}(1)$	0.805	0.856	1.750
$r_{n'l'}(3)$	0.679	0.800	8.231
$r_e(n'l')$	0.844	0.935	4.705
E(B,A; spin-forbidden)		0.071	
E(B,A; spin-forbidden; expt)		0.075[a]	
E(B,D)		0.216	

[a] B. Henderson *et al.*, Phys. Rev. **183**, 826 (1969).

TABLE X. The low-lying excited singlet states of the F' center in MgO. These singlet states are computed from Eqs. (36) and (38). The initial state is ${}^1S(1s,2s)$ and $\sigma=-0.058$. The value of σ remains the same for the other state. The notation is explained in Table II.

State	C	E
E_T	−0.917	−0.870
$r_{nl}(1)$	0.870	0.913
$r_{nl}(3)$	1.002	1.152
$r_e(nl)$	1.153	1.261
$r_{n'l'}(1)$	2.341	1.324
$r_{n'l'}(3)$	16.900	3.889
$r_e(n'l')$	7.217	2.938
E(E,C)	0.048	

TABLE XI. The low-lying excited singlet states of the F' center in CaO. These singlet states are computed from Eqs. (36) and (38). The initial state is ${}^1S(1s,2s)$ and $\sigma=-0.052$. The value of σ remains the same for the other state. The notation is explained in Table II.

State	C	E
E_T	−0.834	−0.771
$r_{nl}(1)$	0.885	0.840
$r_{nl}(3)$	0.983	0.855
$r_e(nl)$	1.111	1.018
$r_{n'l'}(1)$	1.117	2.246
$r_{nl''}(3)$	2.201	14.385
$r_e(n'l')$	1.971	6.405
E(E,C)	0.063	

Tables VIII and IX contain the results for the spin-forbidden transition from the ${}^3P(1s,2p)$ state to the ${}^1S(1s,1s)$ state. The theoretical transition energy for this transition in CaO is 0.071 a.u. It agrees to within 6% of the experimental value of 0.076 a.u.[3] Hence, the present model agrees reasonably well with three of the four known experimental quantities for CaO, namely, the absorption energy, the emission energy, and the spin-forbidden-transition energy. The model does not give, however, the correct Stokes shift.

Tables X and XI contain the results for emission from the singlet state ${}^1S(1s,2s)$ to the singlet state ${}^1P(1s,2p)$. The author knows of no reported experiments in either MgO or CaO which treats this transition.

The F'-center calculations for the alkali halides are not as straightforward as those for the alkaline-earth oxides. Both theoretical and experimental studies indicate that the alkali halide F' center has very few bound states. They also suggest that it might have only one bound state, the ground state. In fact, there is no firm

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[25] H. S. Bennett, Phys. Rev. **184**, 918 (1969). Hereafter, we shall refer to this paper as Paper II.

evidence that it has at least one bound excited state. The numerical integration of the singlet HFS Eq. (36) for the ground state ${}^1S(1s,1s)$ in the alkali halides converges very slowly.

After 10 min of computation on a digital computer, the self-consistent potential criterion that $|\Delta V|\,V \leq 0.01$ is not met. The numerical integration of the HFS Eq. (35) with the Coulomb correlation potential $W(r)$ added to the potential $V(r)$ converges much faster than that for the HFS Eq. (36). We consider this triplet-state $1s$ orbital, which obtains from the triplet HFS Eq. (35) with the potential $V(r)$ replaced by the potential $V(r)+W(r)$, as a good approximation to the singlet-state $1s$ orbital which would obtain from the singlet HFS equation (36) if computer time were not a limitation. Inserting the triplet-state–$1s$-orbital approximation to the singlet-state–$1s$-orbital into Eq. (38) for the singlet state gives the ground-state ${}^1S(1s,1s)$ energy of the F' center in the alkali halides. Table XII contains the results for a perfect lattice $\sigma=0$. The ground-state energies of the F' center in NaCl and in KCl given in Ref. 11 agree to within 4% of the values given in Table XII. The author does not include the results when the nearest neighbors move to accommodate the two defect electrons. The inward motion of the neighboring ions becomes very large ($\sigma \approx 0.20$) and the classical ionic lattice model from which the change in lattice energy is computed may be incorrect for such large distortions. Table XII also contains for $\sigma=0$ the binding energy of the F' center in the alkali halides. The F'-center binding energy E_B is the difference in energy (for the same value of σ) between the ground-state F'-center energy $E_T\,[F'$ center, ${}^1S(1s,1s)$; $\sigma=0]$ and the ground-state F-center energy $E_T\,[F$ center, $1s$; $\sigma=0]$:

$$E_B=E_T[F',{}^1S(1s,1s)\,;\,\sigma=0]-E_T(F,1s\,;\,\sigma=0)\,. \qquad (43)$$

The F-center energy for the ground state is given by the expression

$$E_T(F,\,1s,\,\sigma=0)=\Delta E_L(\sigma)+\int d^3r\,u_{1s}(r)\mathcal{H}_0(\mathbf{r}\,;\,\sigma=0)u_{1s}(r)\,, \qquad (44)$$

where the "$1s$" F-center wave function is the $u_{1s}(r)$ solution to the HFS equation (36) with $V_c(r)=0$ and $W(r)=0$.

TABLE XII. The ground-state energies of the F' and F centers in NaCl and KCl for the perfect point-ion lattice $\sigma=0.0$. The ground-state energy of the F' center ${}^1S(1s,1s)$ is computed by substituting the orbital, which is obtained from Eq. (35) modified by the addition of the Coulomb correlation potential $W(r)$ to the potential $V(r)$, into Eq. (38). The ground-state energy of the F center is computed by substituting the orbital, which is obtained from Eq. (36) with $W(r)=0$ and with $V_c(r)=0$, into Eq. (44). The binding energy E_B is computed from Eq. (43). The nearest-neighbor ions are at their perfect-lattice positions $\sigma=0.0$. The remaining notation is explained in Table II.

	NaCl	KCl
$E_T(F')$	-0.289	-0.270
$E_T(F'$; Ref. a)	-0.300[a]	-0.276[a]
$r_{1s}(1)$	0.862	0.839
$r_{1s}(3)$	1.089	0.948
$r_e(1s)$	1.262	1.130
$E_T(F)$	-0.239	-0.220
$r_{1s}(1)$	0.723	0.710
$r_{1s}(3)$	0.563	0.527
$r_e(1s)$	0.779	0.742
E_B(theory)	0.051	0.050
E_B(theory; Ref. b)	0.047[b]	0.043[b]
E_B(expt.)		0.044[c]

[a] S. Y. La and R. H. Bartram, Phys. Rev. **144**, 670 (1966).
[b] H. J. Raveche, J. Phys. Chem. Solids **26**, 2088 (1965).
[c] L. Pincherle, Proc. Phys. Soc. (London) **A64**, 648 (1951).

The theoretical binding energy in KCl is 0.0496 a.u. and it agrees to within 12% of the experimental value of 0.0441 a.u. The theoretical binding energy for KCl from Ref. 8 is 0.0426 a.u. Experimental F'-center binding energies in NaCl have not been determined. The author's value is 0.0505 a.u. for the binding energy in NaCl and it agrees to within 6% of the value given in Ref. 8 of 0.0474 a.u.

The author has examined also the possible singlet excited state ${}^1P(1s,2p)$. Again, the numerical integration of the singlet Eq. (36) for $1s$-like and $2p$-like orbitals does not converge in a reasonable time for either the $1s$-like orbital or the $2p$-like orbital. The numerical integration of Eq. (35) modified by replacing the potential $V(r)$ with the potential $V(r)+W(r)$ has also questionable convergence for a bound $2p$-like orbital in an alkali halide F' center. After 10 min of computation, a compact $1s$-like orbital obtains, but the trial eigenvalue for the $2p$-like orbital is very small, about -0.001 a.u. The eigenvalue accuracy condition $(|\Delta E|/E) \leq 0.001$ is not satisfied by the $2p$-like trial eigenvalue. This suggests, perhaps, that the self-consistent potential for the nth iteration of the numerical integration procedure for the two F'-center electrons admits a bound $1s$-like orbital which is compact and either a bound $2p$-like orbital which is very diffuse and which has an eigenvalue very close to zero (0 a.u.$> E > -0.001$ a.u.), or a conduction-band $2p$-like wave function with a positive eigenvalue. The author has modified the numerical integration procedure so that it may accommodate $2p$-like conduction-band wave functions at those iterations having a self-consistent potential for which the integration of the $2p$-like orbital converges very slowly, if at all, and for which the trial $2p$-like eigenvalue is very close to zero. Whenever the trial eigenvalue becomes greater than -0.001 a.u., the Milne method[26] is used to integrate the radial HFS equations for a bound $1s$-like orbital and a conduction-band wave function with positive eigenvalue $E=0.001$ a.u. and with the angular-momentum quantum number $l=1$. This modification enables the author

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[26] The author thanks Professor E. H. Hygh for a copy of his computer program for the solution of a system of N equations by the Milne's method. L. J. Page, *et al.*, Phys. Rev. Letters **21**, 348 (1968).

to consider the possible situation in which the integration procedure has the following features. The iterated self-consistent potential initially admits bound $1s$-like and $2p$-like orbitals. As the number of iterations increases, the self-consistent potential for the nth iteration admits only one bound $1s$-orbital. The second $2p$-like orbital is a conduction-band wave function with positive eigenvalue. The self-consistent potential then changes with succeeding iterations so that it again admits bound $1s$-like and $2p$-like orbitals. The modification also contains estimates of the number of bound states which the self-consistent potential at each iteration admits.[27] The results of this modification for both NaCl and KCl are qualitatively the same. The iteration proceeds until the trial eigenvalue for the $2p$-like bound orbital becomes greater than -0.001 a.u. The trial eigenvalue for the $2p$-like function in the HFS equations is set equal to $+0.001$ a.u. Milne's method then yields a $2p$-like conduction-band wave function. The self-consistent potential does not change sufficiently to admit a bound $2p$-like orbital. The estimate for the number of bound states is between 1 and 2 at the end of the numerical integration.

These results indicate that the point-ion-lattice model given above for the F' center in the alkali halides (NaCl and KCl) has only one state (the ground state) for which the two electron orbitals are both bound. The nature of possible excited states remains uncertain. The possibility of an excited state having a bound $1s$-like orbital and a conduction-band $2p$-like wave function seems to be consistent within the framework of the point-ion-lattice model. But more experimental and theoretical research is required before definitive statements may be made about the excited states of F' centers in the alkali halides. We expect that the effects of electronic and ionic polarization are much more important for F' centers in monovalent crystals than they are for F' centers in divalent crystals.

Finally, the author concludes with a summary of the results of the present paper. The point-ion-lattice model with ionic polarization of the nearest neighbors and with Coulomb correlation energy for singlet states and exchange energy for the triplet states accounts rather well for the experimental observations on the F' center in CaO. It gives the correct ordering of the lowest-lying states as determined by experiment and reasonable values for the absorption, emission, and spin-forbidden transition energies. It fails only in predicting the experimental value for the Stokes shift. Among all of the presently known experimental measurements, the Stokes shift is most sensitive to the electronic polarization. The F'-center model given here neglects the electronic polarization. Models exist which include such effects for F centers.[2,4,18,25] Their application to the F' center is formally straightforward. However, the computation time for them becomes prohibitive within the framework of existing computer programs. The same point-ion-lattice model also agrees well with the ground-state observations on the F' center in the alkali halides NaCl and KCl. Questions about the nature of the low-lying-excited F'-center states in the monovalent crystals remain unanswered. The F' center in the alkali halides also requires a much more sophisticated treatment for the motion and electronic polarization of the neighboring ions than does the F' center in the alkaline-earth oxides. However, before substantial progress can be made in computing the electronic structure of the F center or F' center, more effort should be devoted to the model used to represent the host lattice of these point defects.

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[27] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Mass., 1958), p. 185.