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Point Defects in Ionic Crystals. I. Methods of Calculating the Electronic Structure*

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Methods which have been developed and employed for the calculation of point defects in ionic crystals are described. These methods involve a detailed Hartree-Fock-like treatment by way of angular-momentum–dependent exchange potentials of the ions within an inner region τ_1 centered about the defect. In the outer region τ_2, composed of the rest of the crystal, the ions are treated in two different approximations, the most successful of which involves an effective-mass formalism. Polarization effects are included by expressions of the form resulting from the work of Toyozawa, Haken, and Schottky. Although the main purpose of the paper is to describe the methods, applications are made to the calculation of the electronic energy levels in the optical absorption of the F center in KCl and NaCl. Good agreement with experiment is found only if polarization effects, which are important even in the ground state, are included. Additional applications will be given in subsequent papers.

I. INTRODUCTION

THIS is the first in a series of papers dealing with the calculation of the electronic structure of point defects in ionic crystals. In it we shall present some of the methods which we have used in extensive calculations on the electronic structure of the F and U^1 centers in alkali halides and the F and F' centers in MgO and CaO. The methods have also been used in calculations on excitons in alkali halide crystals.

In this first paper, in addition to developing our general methods, we shall give the results of calculations of the absorption energy of the F center in KCl and NaCl. These results will serve both to illustrate the methods and to indicate the validity of certain approximations which might be used in subsequent calculations. For example, we shall explore the extent to which a fairly rigorous solution of the Hartree-Fock problem, in which no dielectric polarization effects are included, gives agreement with the experimental absorption energies of the F center in KCl and NaCl. We shall see that if all polarization effects are neglected the agreement is evidently rather poor, whereas if they are included the separations of the energy levels in absorption are much improved.

In order to carry out the calculations associated with the Hartree-Fock part of the model, we found it necessary to develop what we believe is essentially a new approximate method for the evaluation of two-center, one- and two-electron integrals. In previous calculations[1,2] these were done by a conventional method[3] of quantum chemistry (elliptic coordinate transformation), but this method is both more accurate than we need and for our purposes much too time consuming even for a large computer. Basically, the approach we have employed here consists in first determining an angular-momentum–dependent (l-dependent) effective potential including exchange for each type of ion in the crystal and then expanding defect-centered trial functions about the sites of the neighboring ions. Of course, such expansions are not particularly new, but some of the numerical methods employed we believe to be, and these will be described in more detail in the Appendix.

Even with these new methods, the computing time can become quite lengthy, and it is necessary to reduce as far as possible the number of ions whose electronic structure is considered explicitly. This leads us to a consideration of two approximations for taking into account the structure of ions beyond the third neighbors. In fact, however, we shall see that the employment of the effective-mass approximation just beyond the first neighbors seems to work quite well. This fact was utilized in many of the calculations reported in the next paper of this series. We could go a step further by eliminating the details of the first neighbors and extending the effective-mass treatment inward to a radius somewhat less than the first-nearest-neighbor (1nn) distance. We would then have a purely semicontinuum model which has often been used in calculations of the electronic structure of the F center in alkali halide crystals. We shall not report on our calculations with the semicontinuum model here, but the models we do use have a number of features in common with it.

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[1] R. F. Wood and U. Öpik, Phys. Rev. **162**, 736 (1967).

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

[3] See, for example, M. Kotani, A. Ameniya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen Co. Ltd., Tokyo, 1955); or James Miller and J. C. Browne, Technical Report of the Molecular Physics Group, University of Texas (Austin) 1962 (unpublished).

II. THEORY OF A METHOD FOR SOLVING THE PROBLEM IN THE HARTREE-FOCK APPROXIMATION

The physical system in which we are interested consists of a crystal, whose constituent ions (or atoms) have electrons entirely in closed shells, and one additional electron. For the present we shall neglect the overlaps between the core orbitals, i.e., the orbitals describing the electrons in the closed shells, on different ions; this defect will be partly removed at a later stage in the calculation. For the sake of definiteness we shall take our system to be the F center in an alkali halide; the theory will require only minor modifications to make it applicable to other systems and, in part, to conduction-band states. The extension to two-electron defects is also straightforward.

The precise formulation of the Hartree-Fock problem that we wish to solve is as follows: Let $\phi_{\nu i}$ denote the ith core orbital on the νth ion; we assume this orbital to be doubly occupied. Let ψ be the orbital of the additional electron. We wish to determine the orbital ψ so as to make the expectation value of the effective one-electron Hartree-Fock Hamiltonian $\mathcal{H}_{\mathrm{HF}}$, namely,

$$\langle E\rangle = \langle\psi|\mathcal{H}_{\mathrm{HF}}|\psi\rangle/\langle\psi|\psi\rangle, \tag{1}$$

stationary with respect to small variations in ψ, subject to the constraint that ψ be orthogonal to the core orbitals much as in an orthogonalized-plane-wave (OPW) band calculation. Here the effective Hamiltonian is given by

$$\mathcal{H}_{\mathrm{HF}} = -\tfrac{1}{2}\nabla^2 - \sum_\nu \frac{Z_\nu - N_\nu}{|\mathbf{r}-\mathbf{R}_\nu|} + \sum_\nu \mathcal{V}_\nu \tag{2}$$

and the operator $\mathcal{V}_\nu$ is defined by

$$\mathcal{V}_\nu u(\mathbf{r}) = \left(-\frac{N_\nu}{|\mathbf{r}-\mathbf{R}_\nu|} + 2\sum_i \int \frac{[\phi_{\nu i}(\mathbf{r}')]^2}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}'\right) u(\mathbf{r}) - \sum_i \phi_{\nu i}(\mathbf{r}) \int \frac{\phi_{\nu i}(\mathbf{r}')u(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}', \tag{3}$$

where we use atomic units. $u(\mathbf{r})$ is an arbitrary one-electron wave function, Z_ν is the charge number and $\mathbf{R}_\nu$ the position vector of the nucleus of ion ν, N_ν is the number of electrons on ion ν, and we use real wave functions.

In our definition of $\mathcal{H}_{\mathrm{HF}}$, we take the core orbitals $\phi_{\nu i}$ to be the free-ion orbitals, neglecting the distortion caused by the electrostatic field of the effective charge of the vacancy. This can be partly justified in cases where the orbital ψ of the additional electron is compact, as follows.

In the fully self-consistent solution of the Hartree-Fock problem, both the core orbitals $\phi_{\nu i}$ and the orbital ψ of the additional electron would be calculated from Hartree-Fock equations in which the one-electron Hamiltonian is

$$\mathcal{H}_{\mathrm{HF}}' = \mathcal{H}_{\mathrm{HF}} + \mathcal{V}', \tag{4}$$

$\mathcal{H}_{\mathrm{HF}}$ being defined as above and $\mathcal{V}'$ being defined, for an arbitrary one-electron wave function $u(\mathbf{r})$, by

$$\mathcal{V}' u(\mathbf{r}) = u(\mathbf{r}) \int \frac{[\psi(\mathbf{r}')]^2}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}' - \epsilon_s \psi(\mathbf{r}) \int \frac{\psi(\mathbf{r}')u(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}', \tag{5}$$

where ϵ_s is 1 or 0 according to whether the spins of the electrons in orbitals ψ and u are parallel or antiparallel. Now, if the orbital $\psi(\mathbf{r})$ is strongly concentrated in the vacancy, then the Hamiltonian $\mathcal{H}_{\mathrm{HF}}'$ represents the effective charge of the vacancy as having been largely neutralized by the additional electron, and consequently the resulting core orbitals $\phi_{\nu i}$, which should be used in defining $\mathcal{H}_{\mathrm{HF}}$, are not greatly distorted by the electrostatic field of the vacancy. And since it is easily seen that

$$\mathcal{V}'\psi = 0, \tag{6}$$

we may still use $\mathcal{H}_{\mathrm{HF}}$ instead of $\mathcal{H}_{\mathrm{HF}}'$ in calculating the orbital ψ of the additional electron.

Of course, this argument does not apply if the orbital ψ is diffuse, nor, for instance, to the single-electron F center in magnesium oxide. In such cases one should, strictly speaking, use distorted (polarized) core orbitals. This is a very complicated problem, and the effect of using polarized core orbitals has not been investigated.

We need a simplified expression for the exchange term involved in the definition of $\mathcal{V}_\nu$, Eq. (3), because in the variational calculation in which the trial function is expanded in some basis set the two-center exchange integrals must be evaluated a very large number of times, and this is too time consuming by the conventional methods. Let us, therefore, consider the purely atomic problem of one electron moving in the field of one single ion. Placing the nucleus of the ion at the origin and dropping the label ν, we may write the Hartree-Fock equation for the orbital ϕ_0 of the outer electron as

$$[-\tfrac{1}{2}\nabla^2 - (Z-N)/r + \mathcal{V} - E_0]\phi_0(\mathbf{r}) = 0. \tag{7}$$

The function ϕ_0 is of the form

$$\phi_0(\mathbf{r}) = r^{-1}P(r)Y(\hat{r}), \tag{8}$$

where $\hat{r} = \mathbf{r}/r$ and $Y(\hat{r})$ is a spherical harmonic. Equation (7) is now by standard methods rewritten as an equation for the radial function $P(r)$; and having solved that radial equation, we can calculate $\mathcal{V}\phi_0(\mathbf{r})$. [More precisely, the calculation of this expression is an essential part of the iterative procedure of solving the radial equation for $P(r)$.]

Our calculations would be greatly simplified if it were possible to replace the operator $\mathcal{V}$ by a numerical function $U(r)$ such that $\mathcal{V}\phi_0(\mathbf{r})$ is equal to $U(r)$ multiplied by $\phi_0(\mathbf{r})$. If it is attempted to define such a function by

$$U(r) = [\phi_0(\mathbf{r})]^{-1}\mathcal{V}\phi_0(\mathbf{r}), \tag{9}$$

TABLE I. An illustration of the insensitivity of the effective exchange potential to the energy E_0 at which it is determined. $2E_0$ is the energy in rydbergs (so that E_0 is in atomic units, 27.21 eV), r is the distance from the nucleus in atomic units, and the tabulated quantity is $\delta(2Z_p)$, where $-r^{-1}\delta(2Z_p)$ is the exchange correction, in rydbergs, to the effective potential energy for an s electron moving in the field of a Ca^{2+} ion.

$2E_0=$	-0.83	-0.4	-0.05
r			
0.02	0.5066	0.5052	0.5042
0.06	1.104	1.101	1.098
0.18	1.298	1.284	1.274
0.80	1.064	1.015	0.979
2.8	0.0729	0.0786	0.0856
4.0	0.0109	0.0314	-0.0576

then it is found that the resulting function $U(r)$ depends fairly strongly on the azimuthal quantum number l, but only slightly on the energy E_0 used in Eq. (7), as long as that energy is well above the core energies. Such a behavior of a numerical potential representing exchange has also been found by other authors; see, e.g., Biermann and Lübeck.[4] An illustration of the dependence of the function $U(r)$ on the energy is given in Table I, and the l dependence is illustrated in Table II.

We see, then, that while we cannot without significant loss of accuracy replace the operator $\mathcal{V}$ by a numerical effective potential energy $U(r)$, we may, nevertheless, define by Eq. (9) a separate numerical function $U_l(r)$ for each angular-momentum quantum number l, and replace the operator $\mathcal{V}$ by a simpler operator $\mathcal{U}$, defined by

$$\mathcal{U}\phi_{0l}(\mathbf{r})=U_l(r)\phi_{0l}(\mathbf{r}), \qquad (10)$$

where $\phi_{0l}(\mathbf{r})$ is a solution of Eq. (7) belonging to the value l of the azimuthal quantum number. In practice, we calculate $U_l(r)$ for $l=0, 1, \cdots, 5$, and use $U_5(r)$ in place of $U_l(r)$ for $l>5$.

If the core orbitals used in defining the operator $\mathcal{V}$ in Eq. (7) are the Hartree-Fock orbitals, obtained by solving the Hartree-Fock problem for the core in the absence of the additional electron, and if Eq. (7) is treated as an eigenvalue equation, then it can be shown that those solutions ϕ_0 that are not core orbitals are orthogonal to core orbitals, even though we have not introduced the nondiagonal parameters. These parameters would be needed only if the solution were to be made fully self-consistent in the sense that the effects of the additional electron in the orbital ϕ_0 on the core orbitals were to be included.[5]

In defining the operator $\mathcal{U}$, it is not necessary to treat Eq. (7) as an eigenvalue equation. The determination of the operator $\mathcal{U}$ can be perfectly meaningfully carried out for an arbitrary value of E_0; the functions ϕ_0 would then be made to satisfy the usual boundary conditions of finiteness at the origin, while ϕ_0 would in general tend to infinity as $r\rightarrow\infty$.

We now define a new Hamiltonian $\mathcal{H}_U$, to be obtained from $\mathcal{H}_{\mathrm{HF}}$ by replacing $\mathcal{V}_\nu$ by $\mathcal{U}_\nu$ in Eq. (2), $\mathcal{U}_\nu$ being the operator $\mathcal{U}$ defined for the νth ion. The operators $\mathcal{H}_{\mathrm{HF}}$ and $\mathcal{H}_U$, when operating on the orbital ψ of the additional electron, are then expected to give very nearly the same result, provided that the value of E_0 used in Eq. (7) is suitably chosen for each ion.

We might now attempt to impose the orthogonality constraint by taking ψ to be of the form

$$\psi(\mathbf{r})=f(\mathbf{r})-\sum_\nu\sum_i \phi_{\nu i}\langle\phi_{\nu i}|f\rangle, \qquad (11)$$

where $\phi_{\nu i}$ are, as above, the Hartree-Fock core orbitals of the free ions. Such an attempt would, however, immediately lead us into a difficulty, because there is no simple way of expressing the result of operating with $\mathcal{H}_U$ on $\phi_{\nu i}$. The operators $\mathcal{U}_\nu$ and $\mathcal{V}_\nu$ give practically the same results only when they operate on a function (such as ψ) which is orthogonal to the core orbitals $\phi_{\nu i}$ on the νth ion; but they give appreciably different results when they operate on the core orbital $\phi_{\nu i}$ itself. We know that the functions $\phi_{\nu i}$ satisfy the equation

$$\left[-\tfrac{1}{2}\nabla^2-\frac{Z_\nu-N_\nu}{|\mathbf{r}-\mathbf{R}_\nu|}+\mathcal{V}_\nu-E_{\nu i}\right]\phi_{\nu i}(\mathbf{r})=0, \qquad (12)$$

but they do not satisfy the equation obtained from this by replacing $\mathcal{V}_\nu$ by $\mathcal{U}_\nu$. Consequently, the calculation of the contributions from the double summation in Eq. (11) to the expectation value of $\mathcal{H}_U$ would be complicated, and the advantage of using $\mathcal{U}_\nu$ in place of $\mathcal{V}_\nu$ would be lost.

We avoid this difficulty by noting that, within the region of the νth ion, $\psi(\mathbf{r})$ is supposed to be, to a good approximation, expressible as a linear combination of solutions of the equation

$$\left(-\tfrac{1}{2}\nabla^2-\frac{Z_\nu-N_\nu}{|\mathbf{r}-\mathbf{R}_\nu|}+\mathcal{U}_\nu-E_0\right)\phi_0=0 \qquad (13)$$

for various energies E_0, all well above the core energies, so that the dependence of $\mathcal{U}_\nu$ on E_0 may be neglected. Each of these solutions of Eq. (13) must, then, be orthogonal to those solutions of Eq. (13), say $\phi_{\nu i}'$, that correspond to the core orbitals. Therefore, instead of Eq. (11), we may write

$$\psi(\mathbf{r})=f(\mathbf{r})-\sum_\nu\sum_i \phi_{\nu i}'\langle\phi_{\nu i}'|f\rangle. \qquad (14)$$

In order to be able to evaluate the expectation value of

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[4] L. Biermann and K. Lübeck, Z. Astrophys. **25**, 325 (1948).

[5] This fact does not seem to be generally known. For example, Hartree and Hartree [Proc. Roy. Soc. (London) **A193**, 299 (1948)] in their work on the sodium atom state that a small but significant nondiagonal parameter had to be introduced to ensure the orthogonality of the $3s$ orbital to the $2s$ orbital. Actually this nondiagonal parameter is merely a measure of the numerical inaccuracies in the calculation. That parameter could be made arbitrarily small by making the numerical errors in the calculation small enough.

$\mathcal{H}_U$ with this form of the wave function, we write

$$\mathcal{H}_U=(\mathcal{H}_U+q/r)-q/r=\mathcal{H}_U'-q/r\,, \tag{15}$$

where q is the valency of the ions in the crystal ($q=1$ for KCl, $q=2$ for MgO, etc.). Since $\mathcal{H}_U'$ represents the effective positive charge of the vacancy as having been neutralized by a negative point charge q, we may regard the functions $\phi_{\nu i}'$ as eigenfunctions of $\mathcal{H}_U'$, i.e., we assume that

$$\mathcal{H}_U'\phi_{\nu i}'=E_{\nu i}''\phi_{\nu i}'\,, \tag{16}$$

where

$$E_{\nu i}''=E_{\nu i}'\pm a_M/a\,. \tag{17}$$

Here $E_{\nu i}'$ is the eigenvalue of Eq. (13) corresponding to the solution $\phi_{\nu i}'$, a_M is the Madelung constant, and a is the nearest-neighbor separation in the lattice.

With these approximations we could write down the expectation value of $\mathcal{H}_U$ in a fairly simple form; however, it is more useful to write down the matrix elements of $\mathcal{H}_U$ and unity between *two* functions of the form (14), say, ψ_κ and ψ_λ, given by (14) with f replaced by f_κ and f_λ, respectively:

$$\begin{aligned}\langle\psi_\kappa|\mathcal{H}_U|\psi_\lambda\rangle\equiv H_{\kappa\lambda}=&\langle f_\kappa|\mathcal{H}_U|f_\lambda\rangle\\&-\sum_\nu\sum_i E_{\nu i}''\langle f_\kappa|\phi_{\nu i}'\rangle\langle\phi_{\nu i}'|f_\lambda\rangle\\&+q\sum_\nu\sum_i(\langle f_\kappa|r^{-1}|\phi_{\nu i}'\rangle\langle\phi_{\nu i}'|f_\lambda\rangle\\&+\langle f_\kappa|\phi_{\nu i}'\rangle\langle\phi_{\nu i}'|r^{-1}|f_\lambda\rangle)\\&-q\sum_\mu\sum_\nu\sum_i\sum_j\langle f_\kappa|\phi_{\mu i}'\rangle\\&\times\langle\phi_{\mu i}'|r^{-1}|\phi_{\nu j}'\rangle\langle\phi_{\nu j}'|f_\lambda\rangle\,,\end{aligned} \tag{18}$$

$$\begin{aligned}\langle\psi_\kappa|\psi_\lambda\rangle\equiv S_{\kappa\lambda}=&\langle f_\kappa|f_\lambda\rangle\\&-\sum_\nu\sum_i\langle f_\kappa|\phi_{\nu i}'\rangle\langle\phi_{\nu i}'|f_\lambda\rangle.\end{aligned} \tag{19}$$

We express ψ as a linear combination, with unknown coefficients, of a number of functions of the type ψ_κ, ψ_λ; and then the energies and the wave functions are obtained by solving the secular equation

$$\det(\mathbf{H}-E\mathbf{S})=0\,, \tag{20}$$

where $\mathbf{H}$ and $\mathbf{S}$ are the matrices whose elements are $H_{\kappa\lambda}$ and $S_{\kappa\lambda}$, given by Eqs. (18) and (19). In practice, we replace the last term of Eq. (18) by the simpler expression

$$+q\sum_\nu\sum_i\langle f_\kappa|\phi_{\nu i}'\rangle\langle\phi_{\nu i}'|r^{-1}|\phi_{\nu i}'\rangle\langle\phi_{\nu i}'|f_\lambda\rangle;$$

this can scarcely be more objectionable than our neglect of the overlaps between the core orbitals on different ions that is reflected in the form of Eq. (19). A further simplification would be to replace Eq. (18) by

$$\begin{aligned}H_{\kappa\lambda}=&\langle f_\kappa|\mathcal{H}_U|f_\lambda\rangle\\&-\sum_\nu\sum_i(E_{\nu i}''-R_\nu^{-1})\langle f_\kappa|\phi_{\nu i}'\rangle\langle\phi_{\nu i}'|f_\lambda\rangle\,,\end{aligned} \tag{21}$$

which would imply that the functions $\phi_{\nu i}'$ are treated as eigenfunctions of $\mathcal{H}_U$. It would appear that the form (18) is probably more accurate.

TABLE II. An illustration of the dependence of the effective exchange potential on the angular-momentum quantum number l. r is the distance from the nucleus and the tabulated quantity is $\delta(2Z_p)$, defined as in Table I but this time for the outer electron of a potassium atom, the energy E_0 for each value of l being approximately that of the lowest free-atom state for that value of l (i.e., 4*s*, 4*p*, 3*d*, etc).

	$l=$	0	1	2	3	4	5
r	$2E_0=$	−0.2915	−0.18	−0.11	−0.0625	−0.04	−0.02778
0.02		0.5016	0.4384	0.3708	0.2621	0.178	0.118
0.06		1.094	0.776	0.666	0.436	0.263	0.146
0.18		1.240	1.182	1.034	0.634	0.377	0.217
0.80		1.015	1.090	0.839	0.871	0.789	0.706
2.8		0.136	−0.006	0.209	0.086	0.058	0.043
4.0		0.026	0.005	0.027	0.007	0.004	0.003

In order to use Eqs. (18) and (19), we have to calculate the core function $\phi_{\nu i}'$ and the corresponding energies $E_{\nu i}'$ as solutions of Eq. (13). Such solutions do not have much of a physical meaning, because the operator $\mathcal{U}_\nu$ is not approximately equivalent to $\mathcal{V}_\nu$ when operating on a *core* orbital; they are only intended to be substituted in Eqs. (18) and (19). In particular, while it is found that the wave functions $\phi_{\nu i}'$ are not very different from the corresponding Hartree-Fock core orbitals $\phi_{\nu i}$, the eigenvalues $E_{\nu i}'$ of Eq. (13) are considerably higher than the corresponding Hartree-Fock orbital energies $E_{\nu i}$, and the use of $E_{\nu i}\pm a_M/a$ in place of $E_{\nu i}''$ [as given by Eq. (17)] in Eq. (18) would be quite incorrect. Of course, it would be perfectly correct to orthogonalize the orbital of the additional electron to the Hartree-Fock orbitals $\phi_{\nu i}$ instead of $\phi_{\nu i}'$, but the formula by which this could be achieved would not be (18); it would be much more complicated.

It seems to be generally true that the interaction of an outer electron with a closed-shell core and the interaction of one of the core electrons with the rest of the core cannot be represented by the same numerical effective potential (even if it is l-dependent)—such an effective potential will give either too high an energy for the core electron or too low an energy for the outer electron. (The reason is that a numerical effective exchange potential designed to give correct results for an outer electron does not completely subtract off the Coulomb self-energy of a core electron as the exchange operator does.) We believe this at least partially explains the fact that band-structure calculations[6] which use the same numerical effective exchange potential for the

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[6] P. D. DeCicco, Phys. Rev. **153**, 931 (1967); S. Oyama and T. Miyakawa, J. Phys. Soc. Japan **21**, 868 (1966); Y. Onodera, M. Okazaki, and T. Inui, J. Phys. Soc. Japan **21**, 2229 (1966).

valence band and for the conduction band give band gaps which are nearly always smaller than one might expect to obtain from a truly self-consistent Hartree-Fock band calculation. Such a calculation should give a band gap several eV higher than the observed one, since polarization effects[7] would not be included. Of course, these effects can be included implicitly by adjusting the potential to give the experimental band gap as Onodera *et al.*[6] did in their calculations on KI, but then this goes beyond the Hartree-Fock scheme.

In order to be able to use Eqs. (18) and (19), we have to expand the function f_κ in spherical harmonics about the nuclei of the various ions; and since this has to be done a large number of times, an economical method is needed. Such a method has been developed and programmed, and is briefly described in the Appendix.

We have carried out extensive tests of our method of treating exchange and of the approximate expansion technique described in the Appendix. We expand our trial function f in a series of Slater-type orbitals of the form

$$f(\mathbf{r})=[(2\beta)^{2n+1}/(2n)!]^{1/2}r^{n-1}e^{-\beta r}Y_{l0}(\theta,\phi)\,, \qquad (22)$$

where Y_{l0} is a spherical harmonic of degree l and zero magnetic quantum number. The tests show that the values of the overlap integrals of the form $\langle f(\mathbf{r})|\phi_{\nu i}(\mathbf{r})\rangle$, calculated by our approximate expansion method, differ from the exact values by about 1% if $\phi_{\nu i}$ is a p-type core orbital, except in those cases where the values are very small, when the percentage errors are larger, although the absolute errors are smaller. If $\phi_{\nu i}$ is an s-type core orbital, the errors are between 0.05 and 0.2%. This is considerably more accuracy than we need. In our effective potential method of treating exchange, it is inconvenient to isolate the purely exchange contribution, and so we have carried out the tests on the matrix elements between functions of the form of Eq. (14) for the entire effective Hamiltonian minus the point-ion potential energy and the kinetic-energy operator. The Hamiltonian we used for these tests was that appropriate to the F center in KCl with only the nearest-neighbor K^+ ions treated as extended as in Ref. 2. The largest discrepancy we found between the values of these matrix elements calculated by our approximate methods and the more exact methods (exchange integrals calculated by the elliptic coordinate method) was 0.11 eV. Generally, they were considerably less. Moreover, the errors in the ground and excited states tended to cancel each other so that differences in transition energies calculated by the two methods were of the order of a few hundredths of an eV. In view of the very great saving in machine time—calculations that took a few hours by the old method take a few minutes by the new method—this must be considered very satisfactory. Indeed, it is probable that the approximations that have to be made at present in the physics of the problem, whatever the method used, give rise to errors that are greater than this, so there is not much to be gained by treating the exchange terms more accurately than we have done.

There is some ambiguity in the choice of the energy E_0 to be used in Eq. (7) in the determination of the effective exchange potential, but fortunately the results are not very sensitive to the choice, as long as the value chosen is not too low. In these tests the value of E_0 chosen for each value of the azimuthal quantum number l was the energy of the lowest stationary state of the valence (i.e., series) electron of the neutral atom for the value of l. Using values of E_0 that are several electron volts higher would not change the results very much. The use of lower values of E_0 seemed to make the matrix elements less accurate.

III. FURTHER DEVELOPMENT OF THE METHODS

A. Orthogonalization of Orbitals on 2nn Negative Ions to the Orbitals on Neighboring Positive Ions

Early in the development of the Hartree-Fock part of the model it became apparent that the transition energies for the main F band were going to be higher than the experimental values. A few rough calculations indicated that the agreement with experiment would be improved somewhat if the overlaps of the core orbitals on the negative ions with those on the positive ions were not neglected as we have assumed up to this point. It can be shown that one should orthogonalize the defect functions to the Wannier orbitals on the neighboring ions instead of to the free-ion orbitals. In any case, if we force the orbitals on the negative ions to be orthogonal to those on their positive neighbors, say by a Schmidt procedure, we should be on firmer ground than to neglect their nonorthogonality altogether. We found that an approximate inclusion of this orthogonality improved the transition energy by almost $\frac{1}{3}$ eV, which is certainly non-negligible. Nevertheless, as we shall see in this and the next paper, even this orthogonalization procedure is probably not entirely adequate.

B. Treatment of Distant Ions as Extended Ions

With the use of the method described in Sec. II, there is no difficulty in including the second- and the third-nearest neighbors of the defect as extended ions in a Hartree-Fock calculation—although the machine time is increased, it still remains within reasonable limits unless the symmetry of the orbital of the defect is very low. Treatment of more distant ions by this method seems impractical. In order to do calculations on more diffuse states of the defect electron, however, it is desirable to treat the electronic structure on even more distant ions than the third neighbors. We have

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[7] W. B. Fowler, Phys. Rev. **151**, 657 (1966).

done this in two different approximations, which we shall describe here and in Sec. III C.

Incidentally, at first sight it might appear that our method described thus far would be very inaccurate when applied to diffuse states, because in our orthogonalization procedure we have neglected the distortions of the core orbitals which arise when the effective charge of the vacancy is not largely neutralized by the charge distribution of the additional electron concentrated in the vacancy. However, this is not necessarily so: If the orbital of the additional electron is rather diffuse, then it may well happen that so little of its charge distribution is in the region of the near neighbors of the defect that the neglect of the distortion of the core orbitals of these neighbors does not matter very much.

Let $f(\mathbf{r})$ be one of the smooth component trial functions to be orthogonalized to the core orbitals of a distant ion. We choose the nucleus of that ion for the origin of a Cartesian system of coordinates, x, y, z, and approximate to $f(\mathbf{r})$ within the volume occupied by that ion by the following quadratic expression:

$$f(\mathbf{r})=a_0+a_xx+a_yy+a_zz+a_2\rho^2+f_d\,, \qquad (23)$$

where f_d stands for terms of d-type symmetry (i.e., $l=2$), and $\rho^2=x^2+y^2+z^2$.

Each of the core orbitals of the ion under consideration is of the form

$$\phi(nl|\mathbf{r})=\rho^{-1}P(nl|\rho)Y_{lm}(\theta,\phi)\,, \qquad (24)$$

where Y_{lm} is a spherical harmonic; only the values $l=0$ and $l=1$ occur in those alkali halides with which we are concerned.

With Eqs. (23) and (24) the overlap integrals $\langle f_\kappa|\phi_{\nu i}\rangle$ and the matrix elements $\langle f_\kappa|\mathcal{U}|f_\lambda\rangle$ of the ionic effective potential energy $\mathcal{U}$ (see Sec. II above) can be written down easily. They involve a few radial integrals which can be calculated and stored once and for all at the beginning of the calculation.

To evaluate the coefficients in Eq. (23) as economically as possible, we use the values of the function $f(\mathbf{r})$ at five points, which are the center and the corners of a regular tetrahedron, namely, the nucleus O of the ion, which is also the origin of the $x-y-z$ system, and points P_1, P_2, P_3, and P_4, whose coordinates in the $x-y-z$ system are, respectively, $(t,-t,-t)$, $(-t,t,-t)$, $(-t,-t,t)$, and (t,t,t). Denoting the values of $f(\mathbf{r})$ at these points by f_0, f_1, f_2, f_3, and f_4, we have

$$a_0=f_0\,, \qquad (25)$$

$$a_2=[\tfrac{1}{4}(f_1+f_2+f_3+f_4)-f_0]/3t^2\,, \qquad (26)$$

$$a_x=(f_1-f_2-f_3+f_4)/4t\,, \qquad (27)$$

with analogous equations for a_y and a_z, and

$$(a_x^2+a_y^2+a_z^2)^{1/2}=[\tfrac{1}{4}(f_1^2+f_2^2+f_3^2+f_4^2)-\tfrac{1}{16}(f_1+f_2+f_3+f_4)^2]^{1/2}/t\,. \qquad (28)$$

There is some doubt as to the best value to use for t; we have chosen it so that the corners of the tetrahedron are in the region of the maximum radial charge density for the outermost p orbital of the ion.

Unfortunately, this method does not completely eliminate the effect of the presence of the d-type terms in Eq. (23). Those d-type terms that belong to the two-dimensional irreducible representation of the cubic group have, indeed, no effect, but those that belong to the three-dimensional representation (i.e., terms of the yz, zx, xy symmetries) affect the values of a_x, a_y, and a_z. The only satisfactory way to remedy this defect would be to evaluate the function $f(\mathbf{r})$ at more than five points, but since the number of ions to be treated in this manner can be very large, this would be liable to increase the machine time very considerably.

The method which we have outlined here estimates the overlap integrals with K^+, Cl^-3p orbitals mostly with an error of a few percent; the errors are larger and may reach 10% if the trial function is rather compact, but in the case of a compact trial function the contributions of the distant ions are less important. The overlaps with ionic $2p$ and $3s$ orbitals are estimated more accurately, and in the case of the $2s$ orbitals the errors are of the order of 0.1%. The matrix elements $\langle f_\kappa|\mathcal{U}|f_\lambda\rangle$ are estimated mostly with an error not exceeding 1%, although errors up to 2% occur occasionally; exceptions to this are matrix elements which are very small because the nucleus of the ion is in a nodal plane of both f_κ and f_λ. The errors in such cases are of the same order of magnitude as these matrix elements themselves, but because of the smallness of these matrix elements, this does not affect the results any more than the other errors do. We shall refer to calculations employing these approximations as "extended ion," although the method to follow also takes into account approximately the extension of the ions.

C. Use of the Effective-Mass Formalism

In the extended-ion method of calculation, described above, we cannot avoid certain sources of error. For example, it might seem that the method for treating the distant ions, described in Sec. III B, is too inaccurate because we use the values of the smooth-component trial functions at only five points within the region of each ion. Actually, this source of error is less serious than would appear at first, because if the wave function of the excess electron is so diffuse that the contributions from distant ions are important, then the relevant smooth-component trial functions are so slowly varying that the approximation of using only five points is quite accurate. This reasoning, however, draws our attention to another, more serious, source of error: the fact that our smooth trial function in regions far away from the defect site is slowly varying, would seem to imply that the trial function is too inflexible for the variational calculation, and a more flexible trial function, perhaps containing a component periodic with the periodicity of the lattice, might possibly lead to an appreciably lower energy. With the view of avoiding this error, as well as certain other errors arising from our imperfect knowledge of the structure of the ions when they are in the crystal, we have developed the following, alternative, method.

Let V_{per} be the periodic effective Hartree-Fock potential energy of an electron in the perfect crystal, V' any additional potential energy needed to account for the presence of the defect, polarization, etc., and let ϵ_{HF} be the Hartree-Fock approximation to the energy of the bottom of the conduction band. We shall discuss our choice of its value later. Let ψ be the orbital of the excess electron, and g the envelope function for that orbital in the sense of effective-mass theory.

We divide the volume of the crystal into an inner region τ_1, at the center of which is the defect, and an outer region τ_2, consisting of the remainder of the crystal. For the inner region we use the Schrödinger equation (in atomic units)

$$(-\tfrac{1}{2}\nabla^2+V_{\text{per}}+V')\psi=E\psi, \qquad (29)$$

while for the outer region we use the effective-mass equation

$$[-(2m^*)^{-1}\nabla^2+\epsilon_{\text{HF}}+V']g=Eg, \qquad (30)$$

m^* being the effective mass. In Eq. (29), $V_{\text{per}}+V'$ contains the potential energy operator of Eq. (2) plus a polarization contribution to be given below. V', in Eq. (30), we approximate by $-r^{-1}$ in the case of the F center in alkali halides, plus the polarization term.

We define an operator G as follows:

$$G=-\tfrac{1}{2}\nabla^2+V_{\text{per}}+V', \quad \text{in } \tau_1 \qquad (31)$$

$$G=-\tfrac{1}{2}\nabla^2+m^*\epsilon_{\text{HF}}+m^*V', \quad \text{in } \tau_2; \qquad (32)$$

then G can be shown to be Hermitian.

The Hermitian property of the operator G enables us to derive a variational equation for the determination of ψ, g, and E, but only if we make a further approximation whose effects are difficult to ascertain. We may rewrite Eqs. (29) and (30) as

$$G\psi=E\psi, \quad \text{in } \tau_1; \qquad (33)$$

$$Gg=m^*Eg, \quad \text{in } \tau_2. \qquad (34)$$

This suggests that for any functions ψ and g we should define (using real wave functions)

$$\langle E\rangle=\left(\int_{\tau_1}\psi G\psi d\tau+\int_{\tau_2}gGgd\tau\right)\Big/\left(\int_{\tau_1}\psi^2d\tau+m^*\int_{\tau_2}g^2d\tau\right) \qquad (35)$$

and then $\langle E\rangle=E$ if Eqs. (33) and (34) are satisfied. It is also easy to derive the variational equation that, if those equations are satisfied, then

$$\delta\langle E\rangle=0 \qquad (36)$$

for arbitrary variations in ψ and g, *provided* that we impose on the functions the condition that ψ and its normal derivative should be continuous with g and its normal derivative across the boundary between τ_1 and τ_2. These conditions constitute an approximation, and this is a weakness of this effective-mass method. We might attempt to justify them by drawing the boundary surface between the regions τ_1 and τ_2 so that all the points of that surface are as far as possible away from the cores, and by saying that at such points the wave function ψ is close to the smooth (i.e., unorthogonalized) trial function, which in turn is close to the envelope function; but by saying this, we may be committing precisely one of the errors that we are trying to avoid by the use of the effective-mass method, namely, making the smooth trial function, by implication, too inflexible. For example, the envelope function for a Bloch wave in the conduction band is a plane wave; therefore, equating the smooth trial function to the envelope function in such a case would amount to doing an OPW calculation using only one single OPW, instead of a linear combination of a number of them.

However, the same kind of weakness appears to be present also in our extended-ion method—unless a way is found to make the smooth trial function rather more flexible than we have so far done—and while it might seem, on purely theoretical grounds, that in the case of moderately diffuse states the extended-ion method is superior to the effective-mass method, our results seem to indicate that the opposite is actually true. For very diffuse states of the additional electron, the effective-mass method would in any case be expected to be superior to the extended-ion method.

In a practical application of the effective-mass method we simply make the envelope function g equal to the same linear combination of Slater-type functions that represents the smooth trial function in the region τ_1.

D. Inclusion of the Dielectric Polarization of the Crystal

One might expect that at those distances from the vacancy at which effective-mass theory becomes applicable, dielectric polarization effects will also have become important. We have included such effects in our calculations according to the THS (Toyozawa-Haken-Schottky)[8,9] theory and modifications thereof. Let us take the polarization potential $U(r)$ as a sum of an electronic part $U_{\text{el}}(r)$ and an ionic part $U_{\text{ion}}(r)$.

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[8] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **12**, 422 (1954).

[9] H. Haken and W. Schotty, Z. Physik. Chem. (Frankfurt) **16**, 218 (1958).

For U_{el} we write

$$U_{\mathrm{el}}(r)=(1-\kappa_\infty^{-1})\{-\tfrac{1}{2}(\rho_e+\rho_h)+(1/r)[1-\tfrac{1}{2}(e^{-\rho_e r}+e^{-\rho_h r})]\} \tag{37}$$

and for U_{ion},

$$U_{\mathrm{ion}}(r)=(\kappa_\infty^{-1}-\kappa_{\mathrm{st}}^{-1})\{-\tfrac{1}{2}(v_e+v_h)+(1/r)[1-\tfrac{1}{2}(e^{-v_e r}+e^{-v_h r})]\}. \tag{38}$$

In these expressions κ_∞ and κ_{st} are the high-frequency and static dielectric constants, respectively; ρ_e, ρ_h, v_e, and v_h are parameters (*e*—electron, *h*—hole) whose values in the case of Wannier excitons are prescribed by the THS theory. However, we shall follow the prescription only for v_e, i.e., we calculate it by the formula

$$v_e=(2m_e^*\omega_{\mathrm{LO}}/h)^{1/2}, \tag{39}$$

where ω_{LO} is the longitudinal optical phonon frequency. To understand the significance of the parameters more clearly, let us consider the limit of the quantity $-1/r+U(r)$ as r goes to infinity. We have

$$-1/r+U(r)\xrightarrow[r\to\infty]{}-(\kappa_{\mathrm{st}}r)^{-1}-\tfrac{1}{2}(1-\kappa_\infty^{-1})(\rho_e+\rho_h)-\tfrac{1}{2}(\kappa_\infty^{-1}-\kappa_{\mathrm{st}}^{-1})(v_e+v_h). \tag{40}$$

From this relationship, compared to the usual expressions for the energy of a point charge embedded in a dielectric medium, we see that the terms in ρ_e and ρ_h can be interpreted as the self-energy due to the electronic polarization associated with the electron and the hole (in the case of an *F* center, a vacancy). The suggestion then is that the terms in v_e and v_h are the polarization self-energies due to the displacement of the ions. The effective interaction of the electron and the hole is reduced by the static dielectric constant as expected. Note that according to Eqs. (37) and (38) the rates at which the polarization is "turned on" are also determined by the same parameters which determine the magnitude of the polarization effect.

Since in the case of the *F* center the hole is a vacancy with an infinite effective mass, it would seem that v_h should be much larger than v_e. Fowler[10] has considered modifications of the THS theory for this case. He concludes that it is reasonable to determine v_h from the equation

$$v_h=2/a, \tag{41}$$

in which a is the nearest-neighbor distance. This has the effects of giving a large self-energy due to ionic displacement around the vacancy and of turning on that part of the static dielectric constant associated with the vacancy rather rapidly as the electron-vacancy separation increases. Since we intend to take the lattice relaxation around the vacancy into account by classical ionic-crystal theory, some care must be exercised to avoid double counting of the associated self-energy. We shall discuss this problem in more detail in Paper II.

The value of ρ_h is chosen so that the magnitude given by the classical expression for the electronic polarization self-energy is just equal to the polarization energy associated with the removal of a negative ion as calculated by a Mott and Littleton[11] type of self-consistent calculation. Calling the Mott and Littleton value U_{ML}^-, we have the expression

$$U_{\mathrm{ML}}^-=\tfrac{1}{2}(1-\kappa_\infty^{-1})\rho_h \tag{42}$$

with which to determine ρ_h. It does not matter greatly whether one uses a zero, first, or higher-order Mott and Littleton approximation. Fowler[7] has suggested the same procedure for determining ρ_h and a similar procedure for determining ρ_e but with U_{ML}^+ (polarization energy associated with the removal of a positive ion) replacing U_{ML}^- in Eq. (42). We have found that this suggestion does not give satisfactory results unless we at the same time introduce other modifications, as we shall explain in Paper II. Instead, we have found it convenient to equate ρ_e and ρ_h, and we believe the results we obtain at least partially justify this procedure, although it would certainly be difficult to adduce any arguments *a priori* for it.

Returning now briefly to the incorporation of the effective mass into our model, we make the following assumption. The negative of the experimental electron affinity χ_{expt} will be taken as the bottom of the conduction band, ϵ_{expt}, in the presence of a filled valence band and with both electronic and ionic polarization effects included. This means that we have

$$\epsilon_{\mathrm{expt}}=\epsilon_{\mathrm{HF}}-\tfrac{1}{2}(1-\kappa_\infty^{-1})\rho_e-\tfrac{1}{2}(\kappa_\infty^{-1}-\kappa_{\mathrm{st}}^{-1})v_e \tag{43}$$

as an equation which determines ϵ_{HF}. There is some doubt as to whether or not the last term should be included, since it is not clear to what extent the ions can follow the electron in a process which measures the electron affinity. However, since this term is small, it does not matter greatly whether we include or exclude it.

A somewhat more detailed account of the dielectric polarization effects is given in Ref. 1, and they will be discussed further in the Paper II.

IV. PRELIMINARY APPLICATION OF THE METHODS TO THE *F* CENTER IN KCl AND NaCl

The methods described thus far, are sufficient to enable us to calculate the absorption energy of the *F* center in alkali-halide crystals in a number of different approximations provided we neglect lattice relaxation effects. Here we shall use the results of such calculations on KCl and NaCl to draw a number of conclusions about the various approximations and to indicate a suitable model for the more extensive calcu-

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[10] W. B. Fowler, Phys. Rev. 135, A1725 (1964).

[11] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).

TABLE III. Input data for the calculations. Explanation of the symbols and discussion of the values listed are given in the text.

Crystal	a (a.u.)	m^*	κ_∞	κ_{st}	$\rho_e=\rho_h$ (a.u.$^{-1}$)	$v_e=v_h$ (a.u.$^{-1}$)	χ_{expt} (eV)
KCl	5.936	0.5	2.13	4.68	0.1969	0.0339	0.6
NaCl	5.330	0.6	2.25	5.62	0.1972	0.0299	0.8

lations to be presented in Paper II. We choose KCl and NaCl because some estimate of the necessary input data exists from experimental work and because Hartree-Fock wave functions are available in a convenient form for K^+, Na^+, and Cl^- ions.[12] Table III gives some of the data we have used. a is the nearest-neighbor distance in the perfect crystal, and we have taken the values shown from Table 3 of Tosi and Fumi.[13] The value of the effective mass m^* for KCl we have taken from the work of Hodby *et al.*[14] As far as we know, a comparable value for the effective mass for NaCl has not yet been obtained. Therefore, we have chosen $m^*=0.6$, since this value has been used frequently in the past by other authors. The values of κ_∞ and κ_{st} are taken from the literature.[15] ρ_e and ρ_h are chosen in a manner already described (Sec. III D). For the states involved in absorption we take $v_e=v_h=0$ for the following reason. The ground state of the F center involved in the absorption process has a compact wave function. We therefore expect the F electron to be moving so rapidly that the ions in the crystal cannot follow its motion to any appreciable extent, and so we can assume v_e to be very nearly zero. Also, the compact electronic wave function shields almost completely the effective charge of the vacancy, and so we also expect v_h to be very small or zero for the ground state. In calculating the excited states involved in absorption, even though they may have diffuse wave functions, we invoke the Franck-Condon principle and neglect all polarization effects due to ionic motion, i.e., we take $U_{\text{ion}}\equiv 0$. This can be done by putting $v_e=v_h=0$.

We can now test the following approximations: the effect of including and excluding the dielectric polarization contributions; the question of whether the effective-mass approximation or the approximation outlined in Sec. III B seems to give better agreement with experiment; and the effect of the choice of the radius R_a at which we go over to one or the other of these approximations. Tables IV and V give the results of these tests on KCl and NaCl, respectively. The larger values of R_a were obtained from the equation

$$\tfrac{4}{3}\pi R_a{}^3=(3a)^3.$$

That is, we have chosen a cube such that, when it is centered at the defect site, the faces are midway between the first and fourth neighbors. The volume of the cube is equated to the volume of a sphere in order to determine R_a, which then lies between the third- and fourth-nearest-neighbor distances. The smaller values of R_a are chosen by locating approximately that radius at which a $-r^{-1}$ potential equals the spherically symmetric part of the point-ion potential. This turns out to be approximately $1.137a$. With these two choices of R_a we are, thus, able to test the approximation of treating the structure on the first, second, and third neighbors in detail and accurately and that of treating only the first neighbors in such a manner. Since both of these choices of R_a are somewhat arbitrary, we shall in Paper II investigate further the effects of varying R_a.

In Tables IV and V we show the first two levels of s-like and p-like symmetry. The $1s-2p$ and $1s-3p$ transitions should correspond to the main F band and the low-energy side of the K band, respectively. Experiments on the Stark effect in F centers[16] indicate that the $2s$ and $2p$ levels should lie very close to each other. These then are the criteria we shall use for judging the various approximations. In carrying out these calculations, we have expanded the smooth part of the trial function, i.e., $f(\mathbf{r})$ of Eq. (14), in terms of five Slater-type orbitals of the form indicated in Eq. (22). These orbitals were chosen so that the first three should represent primarily the wave function of the first level of a given symmetry and the next two the wave function of the second level of that symmetry. A g component has been included in the s-like wave functions, but its contribution is quite small. The contribution of an f component to the p-like states was also found to be quite small in the early calculations and was subsequently dropped. More details of the wave functions will be given in Paper II.

Let us examine the results for KCl first. Probably the most striking one is that all of the calculations with polarization correspond much more closely to the experimental results than do those without polarization. Furthermore, even in the ground state there is a polari-

TABLE IV. Some results of the calculations on KCl. R_a is given in atomic units. All energies are given in eV. At -180°C the experimental values of $\Delta E(1s\rightarrow 2p)$ and $\Delta E(1s\rightarrow 3p)$ are approximately 2.3 and 2.7 eV, respectively.

KCl	No polarization		Polarization included		
	Effective mass		Extended ion	Effective mass	
R_a	11.048 a.u.	6.749	11.048	11.048	6.749
E_{1s}	-4.09 eV	-4.09	-4.81	-4.81	-4.84
E_{2s}	-0.74 eV	-0.52	-2.00	-2.46	-2.52
E_{2p}	-1.31 eV	-1.25	-2.37	-2.53	-2.46
E_{3p}	$+0.01$ eV	-0.04	-1.56	-2.14	-2.09
$\Delta E(1s\rightarrow 2p)$	2.78 eV	2.84	2.44	2.28	2.38
$\Delta E(1s\rightarrow 3p)$	4.10 eV	4.05	3.25	2.67	2.75

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[12] P. S. Bagus, Phys. Rev. **139**, A619 (1965).

[13] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25**, 45 (1964).

[14] J. W. Hodby, J. A. Borders, F. C. Brown, and S. Foner, Phys. Rev. Letters **19**, 952 (1967).

[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948).

[16] G. Chiarotti, U. M. Grassano, and R. Rosei, Phys. Rev. Letters **20**, 1043 (1966).

TABLE V. Some results of the calculations on NaCl. R_a is given in atomic units. All energies are given in eV. The experimental value of $\Delta E(1s \rightarrow 2p)$ is 2.77 eV at 0°K. The $1s \rightarrow 3p$ transition, interpreted as giving rise to the low-energy side of the K band, is difficult to discern in the NaCl experimental data.

			Polarization included		
NaCl	No polarization		Extended ion	Effective mass	
R_a	9.920	6.060	9.920	9.920	6.060
E_{1s}	−4.68	−5.06	−5.34	−5.35	−5.85
E_{2s}	−0.88	−0.92	−2.20	−2.77	−2.82
E_{2p}	−1.18	−1.93	−2.26	−2.65	−3.07
E_{3p}	−0.02	−0.04	−1.81	−2.32	−2.46
$\Delta E(1s \rightarrow 2p)$	3.49	3.13	3.09	2.70	2.79
$\Delta E(1s \rightarrow 3p)$	4.66	5.03	3.53	3.04	3.39

zation contribution of roughly 0.7 eV. The extended-ion calculation apparently does not do as well as the effective-mass calculations, which give results remarkably close to the experimental ones for all three of our chosen criteria. Generally speaking, the results for $R_a = 11.048$ a.u. and $R_a = 6.749$ a.u. are close to each other for the calculations both with and without polarization. This suggests that ϵ_{HF} as determined by Eq. (43) is quite effective in duplicating the effects of the detailed electronic structure on the 2nn and 3nn ions as well as more distant ions. This is important, since the elimination of the need to consider the detailed structure on the negative ions will greatly extend the usefulness of the model in addition to cutting down significantly on the computing time.

The results for NaCl are analogous to those for KCl, although the effects of going from an R_a between the third and fourth neighbors to one between the first and second are much more pronounced. We believe this is attributable in part to our inadequate orthogonalization of the outer orbitals on the negative ions to the orbitals on the neighboring ions. In NaCl, the overlap of the outer orbitals on one Cl⁻ ion with those on a neighboring Cl⁻ ion is much larger than in KCl, and we have neglected this effect altogether. Orthogonalization to the orbitals on the neighboring positive ions has been carried out in both crystals, however. This difficulty with the detailed treatment of the negative ions, whose contributions are not negligible, makes it even more important that the model in which the effective-mass treatment cuts in just beyond the first-nearest neighbors apparently works fairly satisfactorily.

We shall not discuss these results further here, since the main purpose of this paper was to present the methods. In Paper II a much more thorough discussion of these and other results for the F center in KCl, KBr, KI, and NaCl will be given.

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APPENDIX

Let $f(\mathbf{r})$ be a given function of the position vector $\mathbf{r}$, and let it be required to expand this function in spherical harmonics about a given point O which is usually not the point from which $\mathbf{r}$ is measured. We choose the point O to be the origin of a Cartesian system of coordinates x, y, z and assume that the mathematical behavior of the function is such that it can be expanded in terms of the functions $x^\mu y^\nu z^\sigma$ in some neighborhood of O, where μ, ν, σ are non-negative integers.

In practice we can only use a finite number of the functions $x^\mu y^\nu z^\sigma$, and it seems reasonable to include *all* such functions with $\mu+\nu+\sigma$ less than or equal to some number L, except only for functions that are disallowed by the symmetry of the function $f(\mathbf{r})$, and to include none of the functions that have $\mu+\nu+\sigma > L$. A suitable value of L can easily be determined by a small amount of trial and error.

It can be shown that the function $x^\mu y^\nu z^\sigma$, where $\mu+\nu+\sigma = l$, is expressible as ρ^l multiplied by a linear combination of spherical harmonics of degrees l, $l-2$, $l-4$, $\cdots$, 1 or 0 (see, for example, Weyl[17]); here

$$\rho = (x^2+y^2+z^2)^{1/2}.$$

Therefore the expansion may be written as

$$f(\mathbf{r}) = \sum_{l=0}^{L} \sum_{m=0}^{l} [g_c(lm|\rho)\mathcal{P}_l^m(\cos\theta)\epsilon_m \pi^{-1/2} \cos m\phi + g_s(lm|\rho)\mathcal{P}_l^m(\cos\theta)\pi^{-1/2} \sin m\phi], \quad \text{(A1)}$$

where ρ, θ, ϕ are defined by $x = \rho \sin\theta \cos\phi$, $y = \rho \sin\theta \sin\phi$, $z = \rho \cos\theta$, $\epsilon_0 = 2^{-1/2}$, $\epsilon_m = 1$ for $m \geq 1$, $\mathcal{P}_l^m$ are the *normalized* associated Legendre functions, so that

$$\int_{-1}^{+1} [\mathcal{P}_l^m(u)]^2 du = 1, \quad \text{(A2)}$$

and, for q denoting either c or s,

$$g_q(lm|\rho) = \rho^l [b_0^{(q)}(lm) + b_2^{(q)}(lm)\rho^2 + \cdots + b_{e(L-l)}^{(q)}(lm)\rho^{e(L-l)}], \quad \text{(A3)}$$

$e(L-l)$ being the greatest even number that does not exceed $L-l$. Our problem is to determine the coefficients $b_\nu^{(c)}(lm)$ and $b_\nu^{(s)}(lm)$. It is worth noting that the greater the value of l, the smaller the number of terms in the polynomial g_c or g_s. If we took the polynomials for $l=0$ to be given by Eq. (A3) and defined the polynomials for greater values of l so that they contained the same number of terms, this would be equivalent to including in the three-dimensional expansion some of the functions $x^\mu y^\nu z^\sigma$ with $\mu+\nu+\sigma = l > L$ without, how-

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[17] H. Weyl, *The Theory of Groups and Quantum Mechanics* (Dover Publications, New York, 1949), Chap. II, Sec. 4.

ever, including *all* such functions for a given value of l; therefore, the accuracy is not likely to be significantly improved, but the amount of calculation required would certainly be increased.

We can here given only an outline of the method; otherwise this Appendix would be too lengthy. Before we begin the calculation, we decide on the radius R of a spherical volume, centered at the point O, within which the expansion is to be accurate. We construct spherical surfaces, centered at O, of radii $\rho_1, \rho_2, \cdots, \rho_N$, such that

$$0 \quad \rho_N<\rho_{N-1}<\cdots<\rho_1<R;$$

the number N depends on L, the maximum value of l used in the expansion (A1). On each of these spherical surfaces the function $f(\mathbf{r})$ is a function of the angular coordinates only, and will be expanded in spherical harmonics. The expansion on the νth spherical surface, which is of radius ρ_ν, is carried out under the assumption that terms with $l>L_\nu$ are negligible, where, for the largest of the spherical surfaces, $L_\nu=L_1=L$, and for the other spherical surfaces the values of L_ν are determined by a somewhat complicated rule so that

$$L_{\nu'}\leq L_\nu \quad \text{for} \quad \rho_{\nu'}<\rho_\nu.$$

The smaller the radius of the spherical surface, the less important, according to Eq. (A3), are terms with large values of l, and it would not be economical to use the same number of terms in the expansion on a small spherical surface as on a large surface.

Considering now one of the spherical surfaces, we draw on it a number of parallel circles, the plane of each of these being perpendicular to the z axis. On each of these circles the function $f(\mathbf{r})$ is a function of the angle ϕ and is expanded in terms of the normalized functions $\epsilon_m\pi^{-1/2}\cos m\phi$ and $\pi^{-1/2}\sin m\phi$ under the assumption that, on the μth parallel circle, terms with $m>M_\mu$ are negligible, where, again, M_μ is in general smaller on a circle of small radius than on one of large radius. Each of the expansion coefficients is calculated as a linear combination of the values of the function $f(\mathbf{r})$ at $2M_\mu+1$ equally spaced points on the circle; the coefficients in the linear combination were precalculated when the program was being written, and are permanently stored in the program.

The coefficients, say $a_c(m)$ and $a_s(m)$, of these trigonometrical functions of ϕ are themselves functions of $\cos\theta$ and are now expanded in the normalized functions $\mathcal{P}_l^m(\cos\theta)$. Each coefficient of such an expansion is calculated as a linear combination of the values of $a_c(m)$ or $a_s(m)$ on the parallel circles, again with permanently stored coefficients.

We have, thus, obtained the values of $g_q(lm|\rho_\nu)$ (where $q=c$ or s), i.e., the values of the functions g_q of Eq. (A1), on the spherical surfaces that we have constructed. Each coefficient $b_\kappa^{(q)}(lm)$ of Eq. (A3) is now calculated as a linear combination, again with permanently stored coefficients, of the values of $g_q(lm|\rho_\nu)$ for different ν.

In the preparation of the program, great care was taken to select the ratios ρ_ν/R so as to minimize the errors arising from the neglected terms with $l>L$, as far as this was possible without unduly increasing the machine time required for the expansion. The method of selecting these ratios is based on the theory of orthogonal polynomials and cannot be described without making this Appendix too long. Suffice it to say that in each expansion it was found necessary to use not one but *two* different sets of radii ρ_ν: one for even and the other for odd values of l. Also, on each spherical surface we use two different sets of parallel circles: one for even and the other for odd values of m.

Certain kinds of symmetries of the function $f(\mathbf{r})$, if present, can be taken into account by the program to shorten the calculation.

This expansion program is very fast: on the CDC 1604, it takes between a fraction of a second and a few seconds to carry out an expansion of a smooth-component trial function (see text, Sec. II), even with L as high as 12. Tests of the program on this type of function have indicated that it is sufficiently accurate for our purposes, i.e., the errors arising from its use are much smaller than the errors arising from the unavoidable approximations in the physics of the problem. In most of our calculations we have used the value $L=8$ for nearest neighbors, and $L=6$ for second and third neighbors; the results do not differ significantly from those obtained with $L=12$, and this fact by itself is evidence that the program is sufficiently accurate for our purposes.