[4] G. Agarwal, D. N. Pattanyak, and E. Wolf, Opt. Commun. 4, 225 (1971); 4, 260 (1971). See also an earlier work by the same authors: G. Agarwal, D. N. Pattanavak, and E. Wolf, Phys. Rev. Letters 27, 1022 (1971).

[5] See the discussions of the additional boundary condition and citations to the literature given by V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Interscience, London, 1966).

[6] D. L. Mills, R. A. Weiner, and M. T. Bêal-Monod, Phys. Rev. B 5, 4637 (1972).

[7] J. J. Hopfield, J. Phys. Soc. Japan Suppl. 21, 77 (1966).

[8] See the discussion in D. E. Beck and V. Celli, Phys. Rev. Letters 28, 1124 (1972).

[9] A. Bagchi, C. B. Duke, P. J. Feibelman, and J. O. Porteus, Phys. Rev. Letters 27, 998 (1971).

[10] A. Otto, Z. Physik 216, 398 (1968).

[11] See J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), Chap. 6.

[12] G. E. Hite, D. T. F. Marple, M. Aven, and B. Segall, Phys. Rev. 156, 850 (1967).

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Model-Pseudopotential Calculation of Electron States in Solids. I. Method*

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A model-pseudopotential method for calculating the states of a valence electron in a solid (such as a conduction or localized electron) is developed. This is done by using atomic model pseudopotentials and the expansion of the valence-electron state in terms of the complete orthonormal set of atomic model pseudo-wave-functions. By this expansion, the operation of the atomic-pseudopotential operator on the pseudo-wave-function of the valence electron is changed into the operation of the atomic pseutopotential on the atomic pseudo-wave-functions. A model pseudopotential suitable to this method is suggested. In the case of the positive ions where bound states are available, the quantum-defect data for them are used to determine the necessary parameters. In the case of a negative ion with no open cores the integro-differential equation for the electron scattering problem is solved. The necessary parameters are then determined from the solution. This method is tested in the case of a localized electron by calculating the optical ionization energy of the *F* center in the ground state for KCl. It is found that the method gives satisfactory results.

I. INTRODUCTION

The calculation of the states of a valence electron (i.e., a noncore electron) in a solid is a complicated problem. Among other things, one has to take into account the effect of the presence of the core electrons, such as direct and exchange interactions, correlations, etc. Since a complete solution of the many-body Schrödinger equation for the interacting electrons and nuclei is out of the question, one has to resort to different kinds of approximations.

In the usual Hartree–Fock (HF) approximation, the correlation and other minor effects, e.g., relativistic effects, have been neglected. The core states are just taken to be free-ion core states, thereby neglecting some crystal effects. Even in this approximation, the solution of the HF equation for a solid is still not easy, in that a large amount of computation has to be done. This is particularly true when the situation becomes more complicated, e.g., in impurity-state calculations.

Another method to tackle this problem is provided by the theory of pseudopotentials.[1] Already, a number of pseudopotentials have been suggested. These fall into two classes. In one, the core states are included explicitly. A well-known example is Austin's pseudopotential,[2] V_A^{ps}, which is defined by

$$V_A^{ps}|\phi\rangle = V_a|\phi\rangle - \sum_c \langle\psi_c|V_a|\phi\rangle|\psi_c\rangle \tag{1.1}$$

for an arbitrary ket $|\phi\rangle$. Here, as in the rest of the paper, we denote the spatial one-electron core states by $|\psi_c\rangle$, and the atomic-core potential operator by V_a.

Another well-known example of this class is the Philip and Kleinman[3] pseudopotential, which is defined by

$$V_{PK}^{ps}|\phi\rangle = V_a|\phi\rangle + \sum_c (E-E_c)\langle\psi_c, \phi\rangle|\psi_c\rangle \tag{1.2}$$

for arbitrary $|\phi\rangle$. Here E is the energy of the state $|\phi\rangle$ and E_c are the core energy levels.

For both of these, an exact form of V_a has to be known. In actual applications, V_a is usually taken as the HF potential, neglecting correlation and other minor effects. Even in this approximation, the solution of the pseudoeigenequation is by no means easy, especially in the solid case.

In the other class, it is assumed that the pseudopotential has some simple analytic form, with parameters to be determined by fitting to some atomic properties. In this way, the requirement of the core states in the calculation is bypassed and knowledge of the exact form of V_a is not necessary. To avoid confusion, we shall call pseudopotentials in this class "model pseudopotentials." Because of its simplicity, such an approach is very useful in studying the electronic states in solids. A well-known example is the Heine–Abarenkov model pseudopotential[4]

$$V_{\mathrm{HA}} = \begin{cases} \sum_{l=0} B_l P_l \ , & r < R_c \\ -Ze^2/r \ , & r > R_c \ . \end{cases} \tag{1.3}$$

Here B_l is an adjustable parameter for a given l valence state, P_l is the projection operator over the subspace of spherical harmonics of a given l, and R_c is a core radius.

However, it should be noted that the pseudopotential operator, like the atomic-potential operator V_a, is in general strongly state dependent. The parameter determined from the properties of an atomic eigenstate is applicable only when it operates on the corresponding pseudoeigenstate and, rigorously speaking, may not be used for any other pseudostate.

It is the main purpose of this paper to develop a model-pseudopotential method, by which atomic data can be employed in a solid-state calculation, consistent with the above situation. It is accomplished by making use of the fact that, if properly chosen, the set of pseudo-wave-functions can form a basis on which the pseudopotential can be represented. The theory is presented in Sec. II. There, a model pseudopotential suitable to our theory is also proposed. Determination of the necessary parameters and discussion of the appropriateness of this model pseudopotential for alkali and halogen ions is given in Secs. III and IV. A first application of the method to calculate the optical ionization energy of the F center in the ground state for the KCl crystal is presented in Sec. V. There, an approach to treat the effect of the crystalline electronic polarization on a point defect, based on Toyozawa's exciton description for this polarization,[5] is also presented. Finally, a summary of the work is given in Sec. VI.

II. THEORY

A. Atomic Pseudopotential

In this section, we consider the states of an extra electron outside a free ion with no open cores. We denote the spatial one-electron eigenstates for the core electrons by $|\psi_c\rangle$, for the extra (or valence) electron by $|\psi_v\rangle$, and the corresponding eigenvalues by E_v. Here c and v are abbreviations for the set of quantum numbers n, l, m, which have the usual meaning of principal, azimuthal, and magnetic quantum numbers, respectively, for bound states. For scattering states, n is related to the scattering wave vector k.

The Schrödinger equation for $|\psi_v\rangle$ can be written as

$$(p^2/2m + V_a)|\psi_v\rangle = E_v|\psi_v\rangle \ . \tag{2.1}$$

Here V_a is the atomic-potential operator. It contains all the effects that are due to the presence of the core electrons.

The corresponding atomic pseudo-wave-equation is given by

$$(p^2/2m + V_a + V_R)|\phi_v\rangle \equiv [-(\hbar^2/2m)\nabla^2 + V_a^{\mathrm{ps}}]|\phi_v\rangle = E_v|\phi_v\rangle \ . \tag{2.2}$$

Here V_a^{ps} is the atomic-pseudopotential operator. V_R is the repulsive part, which accounts for the orthogonalization effect when $|\psi_v\rangle$ is replaced by a smooth pseudoeigenstate $|\phi_v\rangle$.

In general, the pseudopotential V_a^{ps} is not unique. This can easily be seen from Austin, Heine, and Sham's[2] pseudopotential theory, in which the form of the atomic-pseudopotential operator is defined by

$$V_a^{\mathrm{ps}}|\phi\rangle \equiv (V_a + V_R)|\phi\rangle = V_a|\phi\rangle + \sum_c (F_c, \ \phi)|\psi_c\rangle \ . \tag{2.3}$$

Here F_c is a completely arbitrary function for each core label c. The relation between $|\psi_v\rangle$ and $|\phi_v\rangle$ is given by

$$|\phi_v\rangle = |\psi_v\rangle + \sum_c \langle\psi_c|\phi_v\rangle|\psi_c\rangle \ . \tag{2.4}$$

In order that the atomic pseudopotential derived from free-ionic or atomic data can be used in a calculation for a solid, we may choose V_a^{ps} in such a way that the energy spectrum of the pseudo-Hamiltonian is identical with the true valence energy spectrum and the corresponding pseudoeigenstates form a complete orthonormal set. Then this set forms a basis in the Hilbert space, on which the pseudopotential operator V_a^{ps} can be represented Thus, if we write out the valence-state label v in full, then from Eq. (2.2) we have

$$V_a^{\mathrm{ps}} = \sum_{n,l,m} [E_{nlm} + (\hbar^2/2m)\nabla^2]|nlm\rangle\langle nlm| \tag{2.5a}$$

$$\equiv \sum_{n,l,m} V_{nlm}(\vec{r})|nlm\rangle\langle nlm| \ . \tag{2.5b}$$

Here $|nlm\rangle$ is the pseudoeigenstate corresponding to the true eigenstate with quantum numbers n, l, m and energy level E_{nlm}.

It is interesting to note from Eq. (2.5a) that V_a^{ps} can be regarded as one and the same operator all the time. Only when one goes to different representations does one get different forms of $V_{nlm}(\vec{r})$. In this way, the model pseudopotential can be regarded as a special representation of the operator V_a^{ps} on the complete orthonormal set $\{|nlm\rangle\}$, with $V_{nlm}(\vec{r})$ to be determined for each pseudostate $|n, l, m\rangle$. However, such $V_{nlm}(\vec{r})$ can only be defined numerically point by point in space for each $\vec{r}$, and its use in actual calculations is not very convenient. We therefore follow another approach. We start with some suitable form of $V_{nlm}(\vec{r})$, so that the pseudoeigenstates form a complete orthonormal set and the corresponding energy spectrum coincides with the true valence energy spectrum to a good approximation. Then, the resulting model-pseudopotential operator, V_m say, is to a good approximation equivalent to a first-principles pseudopotential. Indeed, using Philip and Kleinman's type pseudopotential,[3] i.e., the pseudopotential in Eq. (2.3) with F_c given by $F_c = (E - E_c)\psi_c$, a first-principles pseudo-Hamiltonian can be written as

$$H^{ps} = H_M + H' , \tag{2.6a}$$

where

$$H_M = p^2/2m + V_M \tag{2.6b}$$

and

$$H' = (V_a - V_M) - \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c| , \tag{2.6c}$$

with E being the energy level of the state under consideration. Treating H' as a perturbation on H_M, the ith eigenvalue E_i of H^{ps} can be written in terms of the ith eigenvalue E_M^i of H_M as

$$E_i = E_M^i + \Delta E_i^{(1)} + \Delta E_i^{(2)} + \cdots , \tag{2.7}$$

where $\Delta E_i^{(1)}$ and $\Delta E_i^{(2)}$, etc., are, respectively, the first, second, and higher order of corrections. Since the main difference between H^{ps} and H_M may be only inside the core region where the amplitude of the pseudoeigenfunctions is small, the perturbation series should converge quickly and corrections higher than second order may be considered negligible compared with the first two. Since the difference between E_i and E_M^i is small and $\Delta E_i^{(1)}$ and $\Delta E_i^{(2)}$ are of different orders of magnitude, each of them is small compared to E_M^i. Then, if we denote the ith eigenstate of H_M by ϕ_i^M, we have, from the first-order correction

$$\Delta E_i^{(1)} = \langle\phi_i^M|H'|\phi_i^M\rangle \simeq 0 . \tag{2.8}$$

Therefore, all the diagonal elements of H' in the $\{\phi_i^M\}$ representation are small compared with E_M^i. Regarding the nondiagonal elements $\langle\phi_i^M|H'|\phi_j^M\rangle$, these are in general much smaller than the diagonal elements because of the orthogonality of the ϕ_i^M's. Therefore, H' is small compared to H_M, which is thus a good approximation to H^{ps} and enables us to write

$$V_M \simeq V^{ps} . \tag{2.9}$$

Hence, to a good approximation, V_M is equivalent to a first-principles pseudopotential.

It should be noted that the accuracy of such an approximation depends entirely on the accuracy to which the model pseudopotential can produce the true valence spectrum. In the limit when the energy spectrum of H_M exactly coincides with the true valence energy spectrum, H_M and H^{ps} must be equal. From this point of view, a first-principles pseudopotential based on the HF approximation need not give better results than a good model-pseudopotential calculation.

B. Pseudopotential for Valence Electron in Solid

In the following, we adopt the same definitions for symbols as in the previous sections. In addition, we denote the spatial one-electron pseudoeigenstate in a solid by $|\phi\rangle$ and the corresponding eigenvalue by E. In order to avoid repetition, in the following, when we say "atomic" we actually mean atomic or ionic.

Applying the pseudopotential theory of Austin, Heine, and Sham[2] to the case of a valence electron (which will be simply called the electron) in a solid, we obtain the pseudo-wave-equation

$$\left(\frac{p^2}{2m} + \sum_\alpha V_\alpha^{ps} + h\right)|\phi\rangle = E|\phi\rangle , \tag{2.10a}$$

with

$$V_\alpha^{ps}|\phi\rangle \equiv V_\alpha|\phi\rangle + \sum_c (F_{c\alpha}, \phi)|\psi_{c\alpha}\rangle . \tag{2.10b}$$

Here $|\psi_{c\alpha}\rangle$ is the cth core state of the αth ion. $F_{c\alpha}$ is a completely arbitrary function for each core label c of the αth ion. h accounts for the crystal effects, such as the electronic and ionic polarizations. V_α is the potential operator for the interaction of the electron with the αth ion when the ions making up the solid are at their equilibrium positions and the crystalline valence electrons are in the ground state. Rigorously speaking, V_α^{ps} is the pseudopotential of an ion in a solid. However, since h is supposed to take into account most of the crystal effects, it may not be a bad approximation to use the corresponding pseudopotential derived from free-ion data. As will be shown in Sec. III, this approximation is especially good in the case where the energy dependence of the pseudopotential is negligible. In this approximation, the matrix element M_{ij} of the solid pseudopotential $\sum_\alpha V_\alpha^{ps}$, between two pseudostates $|\phi_i\rangle$ and $|\phi_j\rangle$, can be calculated readily.

By definition M_{ij} is given by

$$M_{ij} = \sum_\alpha \langle\phi_i|V_\alpha^{ps}|\phi_j\rangle \equiv \sum_\alpha I_\alpha . \tag{2.11}$$

By Eq. (2.9), we can replace V_α^{ps} with a model pseudopotential and write

$$I_\alpha \simeq \sum_{n,l,m} \langle\phi_i|V_{nlm}^\alpha(\vec{r})|nlm\rangle\langle nlm|\phi_j\rangle . \tag{2.12}$$

Under normal circumstances, such as in the absence of magnetic fields or spin-orbit interaction, the solution of Eq. (2.2) is degenerate with respect to m, so that from Eq. (2.5), $V_{nlm}(\vec{r})$ is independent of m and we can write $V^{\alpha}_{nlm}(\vec{r})$ as $V^{\alpha}_{nl}(\vec{r})$. Furthermore, if the atoms in the solid are of rare-gas structure, $V^{\alpha}_{nl}(\vec{r})$ for the state nl would be spherically symmetric, so that if we choose the origin of integration at α, then $V^{\alpha}_{nl}(\vec{r})$ can be written as $V^{\alpha}_{nl}(r)$. Integrating over the angular parts first and denoting the angular integration $\langle \phi_i | lm \rangle$ by $\zeta^{i}_{lm}(r)$, we obtain

$$I_{\alpha}=\sum_{n,l,m} \langle \zeta^{i}_{lm} | V^{\alpha}_{nl} | nl \rangle_r \langle nl | \zeta^{j}_{lm} \rangle_r . \tag{2.13}$$

Here $\langle \, | \rangle_r$ means integration is only over the r part. $|nl\rangle$ is the radial component of $|nlm\rangle$.

In the special case when $V^{\alpha}_{nl}(r)$ is independent of n, we have a great simplification. In fact, when

$$V^{\alpha}_{nl}(r)=V^{\alpha}_{l}(r) \tag{2.14}$$

we have, from Eq. (2.13),

$$I_{\alpha}=\sum_{l,m} \langle \zeta^{i}_{lm} | V^{\alpha}_{l}(r) | \zeta^{j}_{lm} \rangle r \tag{2.15}$$

because $\sum_n |nl\rangle\langle nl| = 1$ for a complete orthonormal set of the radial pseudo-wave-functions. In this case, I_{α} is independent of the radial pseudo-wave-function and a lot of computational effort is saved. Indeed, for localized states, ϕ_i and ϕ_j can be expanded in terms of the Slater orbitals. In this case, $\zeta_{lm}(r)$ is related to the ζ functions.[6] For conduction states, ϕ_i and ϕ_j are plane waves, and $\zeta_{lm}(r)$ is related to the spherical Bessel functions. In both cases the calculation of I_{α} in Eq. (2.15) is easy. In fact, even the calculation of I_{α} in Eq. (2.13) would not be very difficult for most practical choices of the pseudopotential, because only one-dimensional integrals are involved. However, the rapidness of the convergence of the summation depends on the particular choice of the pseudopotential.

C. Choice of Model Pseudopotential

We now come to the practical choice of the model pseudopotential. As a preliminary step, let us lay down a few guidelines regarding the desired properties of the model pseudopotential we are looking for.

(i) The model pseudopotential must give the same set of eigenvalues as the valence eigenvalues of the true potential.

(ii) The model pseudopotential must be equal to the true potential at large distances from the atomic core, where the core states vanish. Since the true potential is local and Coulombic at such places, the model pseudopotential is expected to behave similarly.

(iii) Under the same condition as in (ii), i.e., the vanishing of the core states, the true eigenstates and pseudoeigenstates must be equal.

The above three rules follow directly from the discussion following Eq. (2.5). Furthermore, we have two more conditions.

(iv) The corresponding eigenstates must form a complete orthonormal set.

(v) In view of the great simplification in Eq. (2.15), it is more desirable that the $V_{nlm}(\vec{r})$ be independent of n.

Not all of these conditions are satisfied by existing model pseudopotentials. For example, the Heine–Abarenkov model potential (including Shaw's modification[7]) does not satisfy condition (v). Furthermore, in the case of bound states, it is not at all clear that the corresponding eigenstates form a complete orthonormal set, thus violating condition (iv). In addition to these difficulties, the Heine–Abarenkov potential has one internal weak point, which is the discontinuity in the model potential. This is unphysical and causes oscillations in the pseudopotential form factor at short wavelengths.[7] Shaw's modification reduces such oscillations but does not eliminate them.

Observing that the quantum defect data of the alkali atoms are almost n independent for the valence eigenstates,[8] one of us (S. W.)[9] proposed a model potential of the form

$$V^{M}=-Ze^2/r+Ce^2/r^2 , \tag{2.16}$$

where C is a parameter to be determined from the quantum-defect data or the ionization energies of the alkali atoms. Later, Simons[10] proposed a model pseudopotential of a similar form for alkali and alkalilike ions,

$$V^{M}=-\frac{Ze^2}{r}+\sum_{l=0}^{\infty}\frac{C_l e^2}{r^2}P_l , \tag{2.17}$$

where the C_l's are parameters determined by the ionization energies for the respective angular momenta, and P_l is a projection operator over the subspace of spherical harmonics of a given l. In fact, it can be shown, as we shall do in Sec. III, that the C_l values are simply related to the quantum-defect data in the case of bound states. Since the quantum-defect data in the case of alkali or alkalilike ions are almost n independent, the C_l's are almost n independent.

We propose to use a model pseudopotential along this line, with $V_{nlm}(\vec{r})$ given by

$$V_{nlm}(\vec{r})=-Ze^2/r+C_{nl}e^2/r^2 \tag{2.18}$$

not only for alkalilike ions, but also for other ions such as Cl^-. The C_{nl} are parameters to be determined from properties of the state n, l. Here we have implicitly assumed that the conditions for degeneracy in m are valid (e.g., no magnetic effects) and the atomic core is of rare-gas structure. These are supposed to be valid for a wide class of

TABLE I. Scheme for the assignment of n_r to different states for potassium.

State	n_r	$n-n_r$	State	n_r	$n-n_r$	State	n_r	$n-n_r$
4*s*	0	4	4*p*	0	4	3*d*	0	3
5*s*	1	4	5*p*	1	4	4*d*	1	3
6*s*	2	4	6*p*	2	4	5*d*	2	3

problems, e.g., the study of electronic states in the absence of magnetic fields in ionic crystals like alkali halides, or in simple metals like the alkali or alkali-earth metals.

The appropriateness of this model potential in the present theory is discussed in the case of alkali and halogens ions in Secs. III and IV. The determination of the necessary parameters for these cases is also given there.

III. MODEL PSEUDOPOTENTIAL FOR ALKALI IONS

A. Determination of Parameters

For the model pseudopotential of an electron in the field of a positively charged alkali or alkalilike ion as given by Eq. (2.18), the pseudo-wave-functions can be separated into radial and angular parts, and we can write

$$|nlm\rangle = Nr^{-1}y_{nl}(r)Y_{lm}(\theta,\ \phi). \tag{3.1}$$

Here $Y_{lm}(\theta,\ \phi)$ are spherical harmonics as in the hydrogen problem, N is a normalizing constant. $r^{-1}y_{nl}(r)$ is the radial part of the pseudo-wave-function. The equation for $y_{nl}(r)$ follows immediately from the model pseudo-wave-equation:

$$y''_{nl}+\{2/r-[l(l+1)+2C_{nl}](1/r^2)+2E\}y_{nl}=0\,. \tag{3.2}$$

This equation has eigenvalues

$$E=-2(2n_r+1+\alpha)^{-2} \tag{3.3}$$

and eigenfunctions

$$y_{nl}=e^{-x/2}x^{(\alpha+1)/2}L_{n_r}^{(\alpha)}(x) \quad \text{if } \alpha>-1 \tag{3.4a}$$

in which

$$x=2\lambda r;\ \lambda=(-2E)^{1/2};\ \alpha^2=(2l+1)^2+8C_{nl}\,. \tag{3.4b}$$

$L_{n_r}^{(\alpha)}$ is a Laguarre function[11] of order n_r where $n_r=0,\ 1,\ 2,\ 3,\ \ldots$, and becomes that in the hydrogen problem when C_{nl} vanishes.

It is well known from the Rydberg–Ritz equation[8] that in alkali atoms the valence eigenvalues can be written in terms of the quantum-defect data Δ_{nl} as

$$E_{nl}=-\tfrac{1}{2}(n-\Delta_{nl})^{-2}\,. \tag{3.5}$$

If we equate the eigenvalues in Eq. (3.3) to that in Eq. (3.5) by adjusting the value α, we obtain the following equation for α:

$$\alpha=2(n-n_r)-2\Delta_{nl}-1\,. \tag{3.6}$$

In order that the entire set of eigenvalues for Eq. (3.2) coincide with the entire set of true valence eigenvalues, we let $n_r=0$ for the first valence state, $n_r=1$ for the next one, and so on, for each value of l. An illustration for potassium is given in Table I. It is clear from this table that the value of $n-n_r$ is independent of n, regardless of its appearance. For example, in potassium, this value is equal to 4 for the *s* and *p* states, and equal to $l+1$ for the *d* and higher states. Since α and C_{nl} are connected by an equation in (3.4b), a value of C_{nl} is defined for each n and l. For this set of C_{nl}, the eigenvalues of Eq. (3.2) coincide exactly with the valence eigenvalues E_{nl} in Eq. (3.5).

We now discuss the n dependence of C_{nl}. As can be seen from Table II, the quantum-defect data for the alkali atoms are only weakly dependent on n. In fact, the same is true also for alkalilike ions. Consequently, the above α and thereby C_{nl} are ap-

TABLE II. Quantum-defect data for valence states of Li, Na, K, and Rb. The data listed for all the *s* and *f* states are taken from Ref. 12(a) (to three figures). (a) refers to data of Ref. 12(a). The other data were computed from Eq. (3.5) using the data for atomic energy levels of alkali atoms given in Ref. 12(b).

n	*s*	*p*	*d*	*f*
			Li	
2	0.412	0.0407	(a)	
3	0.404	0.0445	0.00148	−0.0003
4	0.402	0.0457	0.00168	−0.0037
5	0.401	0.0463	0.00176	
6	0.400	0.0470	0.00182	
			Na (a)	
3	1.37	0.882	0.0103	
4	1.36	0.867	0.0123	0.0008
5	1.35	0.862	0.0133	0.0015
6	1.35	0.859	0.0139	0.0013
7	1.35	0.858	0.0144	0.0015
			K	
3			0.146	
4	2.23	1.77	0.203	0.00686
5	2.20	1.74	0.231	0.0084
6	2.19	1.73	0.246	0.0084
7	2.19	1.72	0.254	0.0090
8	2.18	1.72	0.259	0.0096
9	2.18			
			Rb	
3			2.68	
4			1.23	0.0118
5	3.20	2.71	1.29	0.0136
6	3.15	2.67	1.32	0.0147
7	3.14	2.66	1.33	0.0155
8	3.14	2.66	1.33	0.0162
9	3.14	2.65	1.34	
10	3.14	2.65	1.34	

proximately n independent. In reality, it has been shown by Simons,[10] who used n independent C_{nl} values determined from the first-valence-state ionization energies for C_{nl} in the model pseudopotential considered here, that such a model pseudopotential is able to reproduce quite accurately the eigenvalues of the higher states.

B. Properties of Pseudo-Wave-Functions

The validity of the approximation that C_{nl} is n independent is essential in the case where the parameters are derived from bound-state properties, not only in the great simplification obtained, but also in that it allows the eigenfunctions of the pseudo-wave-equation to form a complete orthonormal set. Indeed, if the n dependence of the C_{nl} determined above is neglected, Eq. (3.2) has the form of a Sturm–Liouville equation[13] and the completeness and orthogonality of its eigenfunctions are thus guaranteed.

Next, let us show that with C_{nl} defined as above, the eigenfunctions of Eq. (3.2), just as first-principles pseudoeigenfunctions, are exactly equal to the true wave functions at sufficiently large r. It has been mentioned earlier that when r becomes sufficiently large, the true potential is local and Coulombic. At such places, the true wave function can be expressed as a linear combination of any two independent solutions of the Coulomb radial differential equation. It was shown by Wannier[14] and Kuhn[15] that two such independent functions are

$${}^0U_c^{l,\nu}(r) = \tfrac{1}{2} z\, J_{2l+1}^{\nu}(z)$$

and (3.7)

$${}^2U_c^{l,\nu}(r) = \tfrac{1}{2} z\, N_{2l+1}^{\nu}(z)\,,$$

where $z = (8r)^{1/2}$, $\nu = (-2E)^{-1/2}$, and the notation is that of Wannier. Therefore, the true wave function at an energy E for sufficiently large r is given by

$$U_l^{\nu}(r) = \alpha(\nu)\,{}^0U_c^{l,\nu}(r) + \gamma(\nu)\,{}^2U_c^{l,\nu}(r)\,. \tag{3.8}$$

It was shown by Brooks and Ham[16] that at an eigenvalue corresponding to the quantum numbers n and l,

$$\frac{\alpha(\nu)}{\gamma(\nu)} = -\frac{\Gamma(\nu+l+1)}{\nu^{2l+1}\Gamma(\nu-l)\tan(\pi\Delta_{nl})}\,. \tag{3.9}$$

The corresponding ratio for the pseudo-wave-functions can be obtained as follows. Let us denote the principal quantum number of the eigenfunctions in Eq. (3.2) by $M = n_r + l + 1$. Then, the corresponding eigenvalues can be expressed by

$$E_{Ml} = -\tfrac{1}{2}(M - \delta_{Ml})^2\,, \tag{3.10}$$

where $\delta_{Ml} = n - M - \Delta_{nl}$ are the quantum-defect data for Eq. (3.2). Proceeding exactly as in the case of the true wave functions, when r becomes sufficiently large, the eigenfunctions $W_l^{\nu}(r)$ corresponding to the quantum numbers M and l are given by

$$W_l^{\nu}(r) = \alpha_M(\nu)\,{}^0U_c^{l,\nu}(r) + \gamma_M(\nu)\,{}^2U_c^{l,\nu}(r)\,, \tag{3.11}$$

with the ratio $\alpha_M(\nu)/\gamma_M(\nu)$ given by

$$\frac{\alpha_M(\nu)}{\gamma_M(\nu)} = -\frac{\Gamma(\nu+l+1)}{\nu^{2l+1}\Gamma(\nu-l)\tan(\pi\delta_{Ml})}\,. \tag{3.12}$$

Here, the value of ν is the same as that in Eq. (3.9), because C_{nl} is chosen such that $E_{nl} = E_{Ml}$. Since δ_{Ml} and Δ_{nl} differ only by an integer, the ratios α_M/γ_M and α/γ as given by Eqs. (3.9) and (3.12) are exactly equal. Consequently, when C_{nl} is chosen as described, the eigenfunctions of Eq. (2.3) are equal to the true wave function for sufficiently large r.

C. Appropriateness of Model Potential

From the above, it is now possible to discuss the appropriateness of the model pseudopotential given by Eq. (2.18) in relation to the conditions set out in Sec. II C.

(i) With C_{nl} chosen in the way described, the eigenvalues of the pseudo-wave-equation coincides with the true valence eigenvalues.

(ii) Clearly, the model pseudopotential is local and Coulombic at large r.

(iii) Whether the pseudo-wave-function and the true wave function are equal for the region just outside the core is unknown. However, for sufficiently large r when $1/r \gg 1/r^2$, they are equal. Since the wave functions are continuous, it may not be a bad approximation to assume that they are equal also in the region just outside the core.

(iv) and (v) It is a good approximation to neglect the n dependence of C_{nl}. In that case, the pseudo-wave-functions form a complete orthonormal set.

Therefore, we have shown that in the case of alkali atoms or alkalilike ions the model pseudopotential given by Eq. (2.18) is a suitable one for our theory.

Before going on to another section, let us examine the statement we made earlier in Sec. II B that the approximation of using atomic pseudopotentials in the calculation of electronic states in solids may not cause significant error, if the used atomic pseudopotential is not strongly energy (or say, n) dependent. In general, it is inadequate to treat the pseudopotential simply as a sum of pseudopotentials for free ions; rather, the function $V_{nlm}^{\alpha}(\vec{r})$ in Eq. (2.9) should incorporate a contribution to the potential, at the site of ion α, owing to the influence of all other ions in the crystal. However the difference between a free ion and an ion in a solid may be most significant in the outermost electronic shell. An extra electron outside the free ion also affects the outermost electronic shell. When the extra electron is in states of different n, the outer-

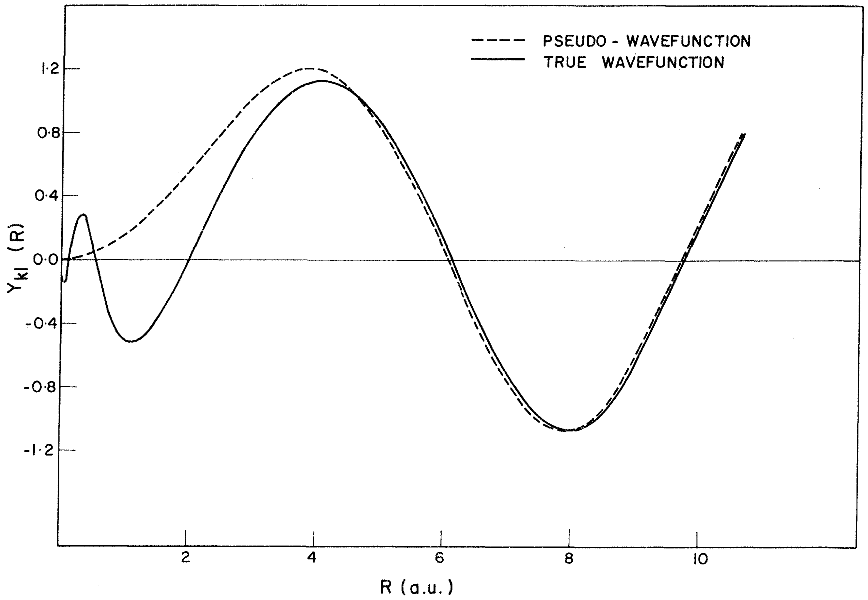

FIG. 1. Typical plot of the radial parts of the true wave function and corresponding pseudo-wave-function at $k=1$ a.u.$^{-1}$ and $l=0$. The pseudo-wave-function is smooth where typical core wiggles for the true wave function occur, and becomes approximately equal to the true wave function when R becomes large (outside the core).

most shell is affected to a different degree. Thus, if $V^{\alpha}_{nlm}(\vec{r})$ is almost n independent, it means that the pseudopotential is somewhat insensitive to effects on the outermost shell. This seems to imply that the model pseudopotential given by Eq. (2.18), being nearly n independent for a free alkalilike ion, may not be very different from that due to the same ion in a solid, although the latter ion is affected by its neighboring ions. This argument is further supported by a calculation done by Simons[10] on the alkali-earth atoms based on the model pseudopotential in Eq. (2.18) for the closed shell system of the corresponding doubly charged ion. The presence of one more electron in this case must affect the outermost shell of the ion core considerably. However, from the results he obtained, which agree quite favorably with experimental values, it seems that the model pseudopotential is not very much affected by effects of the presence of one more electron on the ion core. From the above, one may conclude that for the alkali ions, the model pseudopotential given in Eq. (2.18), with parameters determined from atomic properties, may be applied to solid-state calculations without significant error.

IV. MODEL PSEUDOPOTENTIAL OF HALOGEN IONS

A. Determination of Parameters

Determination of the parameters in a model pseudopotential for an electron in the field of a negative ion usually presents the greatest difficulty. Bound states are absent and scattering-state experimental data are scarce. In such cases we have to solve the HF equation for the electron scattering problem.[17] According to Burke and Seaton,[18] the HF equation for the lth partial wave for an electron scattered off an atomic core with closed shells is given by

$$\left(-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-\frac{2Z}{r}\right)f_l+2\sum_{n,L}(2L+1)\times\left(2y_0(P_{nL},P_{nL})f_l-\frac{1}{2}\sum_{\lambda}C_{lL\lambda}y_\lambda(P_{nL},f_l)P_{nL}\right)=k^2f_l\,, \qquad (4.1)$$

with

$$y_\lambda(A,B)=r^{-\lambda-1}\int_0^r A(x)B(x)x^\lambda\,dx+r^\lambda\int_r^\infty A(x)B(x)x^{-\lambda-1}\,dx\,.$$

Here Z is the charge of the atomic core, P_{nL} are the radial-core wave functions. An explicit expression for the coefficient $C_{lL\lambda}$ is given by Condon and Shortley[19] [their equation ($9^6 9$)].

Equation (4.1) has been solved numerically by means of the IBM 360/75 at the University of Waterloo using Seaton's algebraic method[18] for a Cl$^-$ ion. A typical solution is contained in Fig. 1. The Cl$^-$ core wave function used in this calculation was that due to Clementi.[20] The log derivative for the electron wave function at the place where the atomic potential becomes Coulombic was evaluated numerically from the solution. From the log derivative, the phase shift can then be calculated according to the following formula:

$$\tan\eta_l=-\left.\frac{q_l\,F_l(r)-F_l'(r)}{q_l\,G_l(r)-G_l'(r)}\right|_{r=r_0}\,. \qquad (4.2)$$

Here η_l is the phase shift, q_l is the log derivative

TABLE III. Phase shifts of the electron–Cl$^-$-ion scattering problem. They were calculated from the solution of the HF integro-differential equation of the scattering problem [Eq. (4.1)].

k (a.u.$^{-1}$)	η_0	η_1	η_2
0.325	-0.294×10^{-4}	0.185×10^{-4}	-0.160×10^{-5}
0.350	-0.104×10^{-3}	0.665×10^{-4}	-0.556×10^{-5}
0.375	-0.305×10^{-3}	0.195×10^{-3}	-0.181×10^{-4}
0.400	-0.757×10^{-3}	0.494×10^{-3}	-0.499×10^{-4}
0.425	-0.165×10^{-2}	0.110×10^{-2}	-0.123×10^{-3}
0.450	-0.325×10^{-2}	0.219×10^{-2}	-0.271×10^{-3}
0.475	-0.576×10^{-2}	0.400×10^{-2}	-0.546×10^{-3}
0.500	-0.937×10^{-2}	0.680×10^{-2}	-0.101×10^{-2}
0.525	-0.142×10^{-1}	0.108×10^{-2}	-0.179×10^{-2}
0.550	-0.201×10^{-1}	0.163×10^{-1}	-0.295×10^{-2}
0.575	-0.266×10^{-1}	0.234×10^{-1}	-0.474×10^{-2}
0.600	-0.334×10^{-1}	0.323×10^{-1}	-0.718×10^{-2}
0.625	-0.396×10^{-1}	0.430×10^{-1}	-0.105×10^{-1}
0.650	-0.443×10^{-1}	0.556×10^{-1}	-0.149×10^{-1}
0.675	-0.467×10^{-1}	0.700×10^{-1}	-0.205×10^{-1}
0.700	-0.461×10^{-1}	0.861×10^{-1}	-0.274×10^{-1}
0.725	-0.419×10^{-1}		-0.362×10^{-1}
0.750	-0.337×10^{-1}	0.123	-0.467×10^{-1}
0.775	-0.215×10^{-1}	0.144	-0.593×10^{-1}
0.800	-0.523×10^{-2}	0.165	-0.740×10^{-1}
0.825	0.149×10^{-1}	0.188	-0.913×10^{-1}
0.850	0.386×10^{-1}	0.212	-0.111
0.875	0.655×10^{-1}	0.236	-0.134
0.900	0.951×10^{-1}	0.261	-0.160
0.925	0.128	0.287	-0.189
0.950	0.162	0.313	-0.222
0.975	0.198	0.339	-0.259
1.000	0.230	0.365	-0.299
1.025	0.275	0.392	-0.344
1.050	0.315	0.418	-0.393
1.075	0.356	0.445	-0.446
1.100	0.397	0.471	-0.504
1.125	0.439	0.498	-0.565
1.150	0.482	0.524	-0.630
1.175	0.524	0.551	-0.697
1.200	0.567	0.577	-0.767
1.225	0.609	0.603	-0.838
1.250	0.651	0.629	-0.909
1.275	0.694	0.654	-0.980
1.300	0.736	0.679	-1.05
1.325	0.777	0.704	-1.12
1.350	0.819	0.729	-1.18
1.375	0.860	0.754	-1.24
1.400	0.901	0.778	-1.30
1.425	0.942	0.802	-1.36
1.450	0.982	0.825	-1.41
1.475	1.02	0.849	-1.46
1.500	1.06	0.872	-1.50
1.525	1.10	0.896	-1.54

from the internal solution, F_l and G_l are, respectively, the regular and irregular Coulomb wave functions,[21] and r_0 is the place where the internal solution is matched to the external solution. For the Cl$^-$ ion core, r_0 was taken to be 10 a.u. It has been verified that at such a distance, the atomic potential is equal to $0.999/r$. The phase shifts obtained this way are listed in Table III, and will be used to determine the parameters in the model pseudopotential suggested.

Similar to the case of the alkali ions, the radial part of the model pseudo-wave-equation can be written as

$$y''_{kl}+[-2/r-l'(l'+1)/r^2+k^2]y_{kl}=0\,, \qquad (4.3)$$

with

$$l'(l'+1)=l(l+1)+2C_{kl}\,.$$

Here, as well as in the following, the wave vector k will be used as a state label to replace n. Equation (4.3) has a solution that is regular at the origin. The asymptotic form of this solution is given by

$$y_{kl}\sim\sin[kr-(1/k)\ln 2kr-\tfrac{1}{2}l'\pi+\arg\Gamma(l'+1+i/k)]\,. \qquad (4.4)$$

Comparing with the asymptotic solution of the true wave function given by

$$f_{kl}\sim\sin[kr-(1/k)\ln 2kr-\tfrac{1}{2}l\pi+\arg\Gamma(l+1+i/k)+\eta_l]\,, \qquad (4.5)$$

we obtain the equation for determining l' and thus C_{kl}:

$$-\tfrac{1}{2}l\pi+\arg\Gamma(l+1+i/k)+\eta_l=-\tfrac{1}{2}l'\pi+\arg\Gamma(l'+1+i/k)\,. \qquad (4.6)$$

The C_{kl} so obtained is given in Table IV. It is rather strongly k dependent except for low values of k. In that case, C_{kl} remains small. When k increases, the penetration into the core region becomes greater, with the result that the state-dependent part of the model pseudopotential increases. This k dependence of the parameter in the model pseudopotential complicates the calculations, but for the time being, there is nothing we can do about it. Fortunately, for solid-state calculations in general, only small values of k for the model pseudopotential are involved. For example, for a conduction state $|\phi\rangle$, the coefficients $\langle\phi|klm\rangle$ in Eq. (2.12) are significant only when the wave vectors of $|\phi\rangle$ and $|klm\rangle$ match. The energy of a conduction electron in a solid seldom exceeds a few electron volts. This indicates that only small values of k have to be considered. The same is true also in the case of a localized electron if this electron spends relatively little time inside the core region. This situation will be discussed in more detail when we come to the F-center ground-state calculation (Sec. V). Under such circumstances, one never has to do the summation over all k (i.e., n) in Eq. (2.13). Further, the state-dependent part of the model pseudopotential remains small for most cases of interest. In situations where the calculation involving this term becomes too complicated, it is not a bad approximation to neglect this term completely. In fact, this is exactly what we did in calculating the first optical absorption energies of the F_2^+ and F_{2A}^+ centers in the following paper (II).[22] Furthermore, based on the observation that when l increases C_{kl} for low k decreases, we consider it may not be a bad approximation to neglect this term for l higher than 2. For such l, the model pseudopotential we propose just coincides with Shaw's modification of the Heine–Abarenkov model potential.[7]

B. Eigenvalues

Before going on, let us define the normalization condition for the pseudo-wave-functions. We require these functions be normalized to 1 in a sphere of radius L (L being arbitrarily large). With the normalization condition defined this way, the eigenvalues k become quasicontinuous. From Eq. (4.5), allowed values of k are given by

$$kL-(1/k)\ln 2kL-\tfrac{1}{2}l\pi+\arg\Gamma(l+1+i/k)+\eta_l=n\pi\,,\qquad n=0,\ \pm 1,\ \pm 2. \quad (4.7)$$

By Eq. (4.6), the asymptotic form of the true and pseudo-wave-functions are the same. Consequently, the allowed values of k for the pseudo-wave-equation are also given by Eq. (4.7). This guarantees that the true and pseudo-wave-equations have the same set of eigenvalues.

C. Properties of Pseudo-Wave-Functions

We denote the true and pseudo-wave-functions by $Ny_{kl}(r)$ and $Ny_{kl}^{ps}(r)$, respectively, where N is a normalizing constant. Let us determine N for the true wave function first. From Eq. (4.5), the asymptotic form of y_{kl}, $H_{kl}(r)$, is

$$H_{kl}(r)=\sin[kr-(1/k)\ln 2kr+\theta_l]\,,$$

where (4.8)

$$\theta_l=-\tfrac{1}{2}l\pi+\arg(l+1+i/k)+\eta_l\,.$$

The total probability P of finding the electron in a sphere of radius L is given by

$$P=N^2\int_0^L H_{kl}^2\,dr+N^2\int_0^L(y_{kl}^2-H_{kl}^2)\,dr\,. \quad (4.9)$$

The integrand in the second term of the right-hand side is arbitrarily small for sufficiently large r. In fact, given any $\epsilon>0$, no matter how small, there exists a radius R such that

$$|y_{kl}^2-H_{kl}^2|<\epsilon$$

for all $r>R$. Using this, it can be shown that

$$N^2\int_0^L(y_{kl}^2-H_{kl}^2)dr\,|\leq N^2|M_0R-\epsilon(L-R)|\,, \quad (4.10)$$

where M_0 is the maximum of $|y_{kl}^2-H_{kl}^2|$ in the range $0\leq r\leq R$. As y_{kl} is an eigenfunction, M_0 must be finite. Therefore, in the limit when L becomes very large, Eq. (4.10) becomes

TABLE IV. Values for the parameter in the model pseudopotential given by Eq. (2.15) for a Cl$^-$ ion, which were determined from the phase shifts in Table III according to Eqs. (4.6) and (4.3a).

k (a.u.$^{-1}$)	C_{k0}	C_{k1}	C_{k2}
0.3250	-0.905×10^{-4}	0.600×10^{-4}	0.0
0.3500	-0.298×10^{-3}	0.210×10^{-3}	-0.250×10^{-4}
0.3750	-0.813×10^{-3}	0.570×10^{-3}	-0.500×10^{-4}
0.4000	-0.189×10^{-2}	0.137×10^{-2}	-0.150×10^{-3}
0.4250	-0.387×10^{-2}	0.288×10^{-2}	-0.375×10^{-3}
0.4500	-0.722×10^{-2}	0.548×10^{-2}	-0.800×10^{-3}
0.4750	-0.120×10^{-1}	0.961×10^{-2}	-0.155×10^{-2}
0.5000	-0.187×10^{-1}	0.157×10^{-1}	-0.280×10^{-2}
0.5250	-0.269×10^{-1}	0.241×10^{-1}	-0.485×10^{-2}
0.5500	-0.363×10^{-1}	0.351×10^{-1}	-0.780×10^{-2}
0.5750	-0.461×10^{-1}	0.489×10^{-1}	-0.122×10^{-1}
0.6000	-0.553×10^{-1}	0.657×10^{-1}	-0.182×10^{-1}
0.6250	-0.627×10^{-1}	0.852×10^{-1}	-0.261×10^{-1}
0.6500	-0.674×10^{-1}	0.108	-0.363×10^{-1}
0.6750	-0.684×10^{-1}	0.133	-0.492×10^{-1}
0.7000	-0.651×10^{-1}	0.160	-0.650×10^{-1}
0.7250	-0.572×10^{-1}		-0.842×10^{-1}
0.7500	-0.446×10^{-1}	0.220	-0.107
0.7750	-0.276×10^{-1}	0.253	-0.134
0.8000	-0.654×10^{-2}	0.288	-0.165
0.8250	0.182×10^{-1}	0.323	-0.201
0.8500	0.462×10^{-1}	0.359	-0.242
0.8750	0.769×10^{-1}	0.396	-0.288
0.9000	0.110	0.434	-0.339
0.9250	0.145	0.472	-0.396
0.9500	0.182	0.511	-0.459
0.9750	0.220	0.549	-0.528
1.0000	0.259	0.588	-0.604
1.0250	0.299	0.626	-0.685
1.0500	0.340	0.665	-0.773
1.0750	0.382	0.703	-0.866
1.1000	0.424	0.724	-0.964
1.1250	0.466	0.780	-1.07
1.1500	0.509	0.818	-1.17
1.1750	0.552	0.855	-1.28
1.2000	0.595	0.893	-1.38
1.2250	0.637	0.930	-1.49
1.2500	0.680	0.967	-1.59
1.2750	0.723	1.00	-1.69
1.3000	0.766	1.04	-1.79
1.3250	0.808	1.08	-1.87
1.3500	0.851	1.11	-1.96
1.3750	0.893	1.15	-2.03
1.4000	0.935	1.18	-2.10
1.4250	0.977	1.21	-2.16
1.4500	1.02	1.25	-2.21
1.4750	1.06	1.28	-2.26
1.5000	1.10	1.32	-2.31
1.5250	1.14	1.35	-2.35

$$\left|N^2\int_0^L (y_{kl}^2 - H_{kl}^2)\,dr\right| \le N^2\epsilon L . \tag{4.11}$$

It can be shown that in the limit when L becomes very large, the first term on the right-hand side of Eq. (4.9) becomes

$$N^2\int_0^L H_{kl}^2\,dr = \tfrac{1}{2}N^2 L .$$

Since ϵ is arbitrarily small, we have

$$N^2\int_0^L y_{kl}^2\,dr = \tfrac{1}{2}N^2 L . \tag{4.12}$$

Letting the left-hand side of Eq. (4.12) equal unity leads to

$$N = (2/L)^{1/2} . \tag{4.13}$$

In the above derivation, only the asymptotic form is required explicitly; the normalizing constant for the pseudo-wave-function, which has the same asymptotic form as the true wave function, is also given by Eq. (4.13).

With the normalizing constant defined, we shall now go on to show that for sufficiently large r, the true and pseudo-wave-functions are equal. In fact, when r becomes large, say, larger than a certain R, both the true and pseudo-wave-equations are just Coulomb wave equations. The solutions of both equations at such places are linear combinations of F_l and G_l, the regular and irregular Coulomb wave functions, respectively, i.e.,

$$y_{kl} = N(F_l + \alpha_l G_l) , \tag{4.14}$$

and

$$y_{kl}^{\text{ps}} = N^{\text{ps}}(F_l + \alpha_l^{\text{ps}} G_l) \tag{4.15}$$

for $r > R$. (In fact, in the actual calculation, R is assumed equal to 10 a.u. for Cl^-, as mentioned earlier.) If both waves are normalized by the same normalization conditions, N and N^{ps} are equal from Eq. (4.13). α_l and α_l^{ps} are both equal to $\tan\eta_l$, where η_l is the phase shift mentioned earlier. Therefore, y_{kl} and y_{kl}^{ps} are equal when $r > R$. (See Fig. 1.)

We proceed to discuss the orthogonality of the pseudo-wave-functions corresponding to different k. The overlap integral between pseudo-wave-functions corresponding to k and k' can be written as

$$(2/L)\int_0^L y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}}\,dr = (2/L)\int_0^L y_{kl}\, y_{k'l}\,dr + (2/L)\int_0^L (y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}} - y_{kl}\, y_{k'l})\,dr . \tag{4.16}$$

Since the true wave functions form an orthonormal set, the first term on the right-hand side of Eq. (4.16) is just $\delta_{kk'}$. For the second term, we note that there exists an R such that for $r > R$, $y_{kl} = y_{kl}^{\text{ps}}$ and $y_{k'l}^{\text{ps}} = y_{k'l}$, so that

$$\int_0^L (y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}} - y_{kl}\, y_{k'l})\,dr = \int_0^R (y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}} - y_{kl}\, y_{k'l})\,dr . \tag{4.17}$$

It follows from Eq. (4.17) that

$$\left|(2/L)\int_0^L (y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}} - y_{kl}\, y_{k'l})\,dr\right| \le (2/L) M_0 R ,$$

where M_0 is the maximum of $|y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}} - y_{kl}\, y_{k'l}|$ in the range $0 \le r \le R$ and is finite. Therefore, as L becomes very large,

$$(2/L)\int_0^L (y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}} - y_{kl}\, y_{k'l})\,dr = 0 . \tag{4.18}$$

Thus, we have finally

$$\int_0^L y_{kl}^{\text{ps}} y_{k'l}^{\text{ps}}\,dr = \delta_{kk'} . \tag{4.19}$$

The pseudo-wave-functions therefore form an orthonormal set.

Observing that the true and pseudo-wave-functions are different only in a finite range, and that this difference becomes smaller and smaller when k increases, we assert that the pseudo-wave-functions, just as the true wave functions, form a complete set.

To conclude this section, we note from the above discussion that the model pseudopotential given by Eq. (2.18) for Cl^- has the most essential properties (cf. Sec. II C) suitable to our purpose. However, the energy dependence is strong. In addition to complicating the computation, such strong energy dependence makes the approximation of using the free-ion pseudopotential in calculating electron states in a crystal less justified. In fact, under such circumstances, the core wave functions corrected for the influence of other ion cores should be used in Eq. (4.1), instead of the free-ion-core wave functions. However, the calculation of such corrected wave functions itself is too involved and is out of the scope of the present work. Nevertheless, as mentioned earlier, the main difference between an ion in a crystal and a free ion may be most significant in the outermost shell. The inner shells are probably not very much affected by the presence of other ions. When the electron is well inside the core, the pseudopotential is mainly contributed from the inner shells and the error due to the discrepancy in the outermost shell may not be important. On the other hand, when the electron is well outside the core, the $1/r^2$ term itself is small. Therefore, the region where the present approximation may be bad is in the vicinity of the valence core of the ion. Thus, in cases where the electron spends relatively little time within such a region, the approximation used here may not cause significant error.

It should also be noted that the Heine–Abarenkov form of the model pseudopotential as given in Eq. (1.3) also has the same properties in the case of Cl^-. The same technique as described in Sec. IV A has been used to determine the necessary parameters in this type of model pseudopotential. The results are listed in Table V. The values of $B_l(k)$ are less k dependent and the summation in Eq.

TABLE V. Values for the parameter in the Heine–Abarenkov model potential for Cl^-. The log derivative q_l at $R_c = 5$ a.u. was first determined from the phase shifts in Table III by Eq. (4.2), and $B_l(k)$ was then calculated by Eq. (2.4) in Ref. 7.

k (a.u.$^{-1}$)	$B_0(k)$	$B_1(k)$	$B_2(k)$
0.3250	0.238	0.507	0.162
0.3500	0.250	0.498	0.187
0.3750	0.263	0.488	0.200
0.4000	0.277	0.481	0.215
0.4250	0.292	0.477	0.229
0.4500	0.307	0.474	0.244
0.4750	0.323	0.474	0.259
0.5000	0.340	0.477	0.276
0.5250	0.357	0.481	0.29
0.5500	0.376	0.487	0.309
0.5750	0.395	0.495	0.326
0.6000	0.414	0.505	0.344
0.6250	0.435	0.516	0.362
0.6500	0.456	0.529	0.381
0.6750	0.479	0.543	0.400
0.7000	0.502	0.558	0.419
0.7250	0.526	0.577	0.439
0.7500	0.551	0.593	0.459
0.7750	0.577	0.612	0.480
0.8000	0.605	0.632	0.500
0.8250	0.634	0.654	0.522
0.8500	0.664	0.677	0.543
0.8750	0.695	0.701	0.565
0.9000	0.728	0.726	0.588
0.9250	0.762	0.753	0.610
0.9500	0.798	0.781	0.633
0.9750	0.834	0.810	0.655
1.0000	0.875	0.841	0.678

(2.12) converges faster. However, the k dependence is still not weak enough to be neglected. Furthermore, as can be seen from Table V, the state-dependent part [referring to $B_l(k)$] is large compared to the state-dependent part (i.e., C_{kl}/r^2) in Eq. (2.18), and complicates the computation in some cases, as in the calculation of the F_2^+ centers.[22]

V. OPTICAL IONIZATION ENERGY OF F CENTER

In order to test the applicability of the theory developed above to electronic states in solids, we calculate the optical ionization energy of the F center. This, rather than the F-band energy, is chosen because, besides being simpler, it provides a more sensitive test to the method used. In fact, since the energy of the optically highest bound state is independent of the particular pseudopotential used, any error due to the pseudopotential method in the ground-state calculation cannot be cancelled by a similar error committed in the excited state in calculating transition energies, as often is the case in F-band calculations. This is perhaps the reason why many rather crude models, e.g., the point-ion model or the semicontinuum model, are able to produce reasonable F band, but fail to give a correct optical ionization energy.

In the following we shall first follow the model-pseudopotential theory developed previously to derive a pseudo-Hamiltonian for the F center in a typical alkali halide. We shall then used the derived pseudo-Hamiltonian and the corresponding trial wave function to calculate the ground-state energy of the F center with respect to its optical highest bound state and thereby the optical ionization energy of the F center in the ground state.

A. Hamiltonian

The F center consists of an electron localized around a negative-ion vacancy at $\vec{R}_0$ in an alkali-halide crystal. When ignoring both the crystalline electronic and ionic polarizations, the F center may be regarded as a perfect alkali-halide crystal minus a halogen ion at $\vec{R}_0$ plus an electron, and its Hamiltonian can be written as

$$H_b = T_e + \sum_\alpha V_0(\vec{r};\, \vec{R}_{\alpha 0}) - V(\vec{r};\, \vec{R}_0) + T_h - \sum_\alpha{}' V_0(\vec{R}_0;\, \vec{R}_{\alpha 0}) + H_{\mathrm{ion}}. \qquad (5.1)$$

T_e is the kinetic energy of the localized electron (or simply say the electron). The second term is the interaction of the electron at the position $\vec{r}$ with all the ions making up the perfect alkali-halide crystal. $V(\vec{r};\, \vec{R}_0)$ is the interaction of the electron with a halogen ion at $\vec{R}_0$. $-V(\vec{r};\, \vec{R}_0)$ becomes $-e^2/|\vec{r}-\vec{R}_0|$ for large $|\vec{r}-\vec{R}_0|$ and is an interaction similar to the interaction of the electron with a hole in the case of excitons. But the hole in the present problem, which is $-Cl^-$ for alkali-chloride crystals and $-Br^-$ for alkali-bromide crystals, is a massive hole. Hence, we may call $-V(\vec{r};\, \vec{R}_0)$ the interaction of the electron with the massive hole at $\vec{R}_0$. T_h is the kinetic energy of the massive hole and may be omitted, because the mass of the massive hole is infinite compared to the electronic mass. The term $-\sum_\alpha' V_0(\vec{R}_0;\, \vec{R}_{\alpha 0})$ is the interaction of the massive hole with all ions at the positions $R_{\alpha 0} \neq \vec{R}_0$, as indicated by the prime on the sum (see Ref. 23 for details). The last term, H_{ion}, is the Hamiltonian of the ions making up the perfect crystal.

When the electron and hole are present in an alkali halide, the system of crystalline valence electrons, in general, will be virtually excited by these particles to give the crystalline-electronic-polarization (CEP) field. In this case the second and fifth terms in Eq. (5.1) become, respectively,

$$\sum_\alpha V(\vec{r};\, \vec{R}_{\alpha 0}) = \sum_\alpha V_0(\vec{r};\, \vec{R}_{\alpha 0}) + V_e^{\mathrm{ep}} \qquad (5.2)$$

and

$$-\sum_{\alpha}{}'V(\vec{R}_0;\ \vec{R}_{\alpha 0})=-\sum_{\alpha}{}'V_0(\vec{R}_0;\ \vec{R}_{\alpha 0})+V_h^{\text{ep}}, \quad (5.3)$$

where V_e^{ep} is the electron potential due to the CEP field created by the electron itself and V_h^{ep} is the massive hole potential due to the CEP field created by the massive hole itself.

We now follow Toyozawa's theory for the CEP field due to an extra charged particle in a perfect insulator[5] to consider V_e^{ep} and V_h^{ep}. Within this theory the CEP field is described by the excitons, and its Hamiltonian is given by

$$H_{\text{ex}}=\sum_{\vec{w}} b_{\vec{w}}^{\dagger} b_{\vec{w}} E_{\text{ex}}, \quad (5.4)$$

where $b_{\vec{w}}^{\dagger}$ and $b_{\vec{w}}$ are, respectively, the creation and annihilation operators for a longitudinal exciton of wave vector $\vec{w}$ and of energy E_{ex} (whose $\vec{w}$ dependence is usually omitted). Further, the interaction of the CEP field with the extra particle which creates this field is given by

$$V_e^{\text{ep}}=\sum_{\vec{w}}\left(V_w b_{\vec{w}} e^{i\vec{w}\cdot\vec{r}}+\text{c.c.}\right) \quad (5.5)$$

for the extra particle negatively charged as the present localized electron, and is given by

$$V_p^{\text{ep}}=-\sum_{\vec{w}}\left(V_w b_{\vec{w}} e^{i\vec{w}\cdot\vec{r}_p}+\text{c.c.}\right) \quad (5.6)$$

for the extra particle positively charged. The coupling constant V_w takes the form

$$V_w=-i\left[\frac{2\pi e^2 E_{\text{ex}}}{\Omega w^2}\left(1-\frac{1}{\epsilon_\infty}\right)\right]^{1/2}, \quad (5.7)$$

where Ω is the volume of the crystal under consideration and ϵ_∞ is the usual high-frequency dielectric constant. This coupling constant is a renormalized one, which is renormalized such that the dielectric screening has the expected macroscopic behavior in the limit of large electron-hole separation. Thus, the coupling constant includes a host of other corrections, such as the approximation of replacing the excited states, which consist of bound and continuum states, by a single-exciton band in Toyozawa's theory of CEP.

The extra particle mentioned above is not located at any particular lattice point and interacts with all the ions making up the perfect alkali halide, as is indicated by Eq. (5.2). Therefore, for the present problem, the V_e^{ep} may be given by Eq. (5.5). But V_h, for which the massive hole is at the lattice point $\vec{R}_0$ and interacts only with ions not at $\vec{R}_0$ [as is indicated by Eq. (5.3)], cannot be written exactly as Eq. (5.6). We now introduce a $\vec{w}$-dependent parameter z_w to write for V_h^{ep},

$$V_h^{\text{ep}}=-\sum_{\vec{w}} z_w\left(V_w b_{\vec{w}} e^{i\vec{w}\cdot\vec{R}_0}+\text{c.c.}\right). \quad (5.8)$$

The form of z_w will be discussed later.

Accordingly, the Hamiltonian, not including the crystalline ionic polarization, for the F center may be written as

$$H_e=H_0-V(\vec{r};\ \vec{R}_0)+\sum_{\vec{w}} b_{\vec{w}}^{\dagger} b_{\vec{w}} E_{\text{ex}}+V_e^{\text{ep}}+V_h^{\text{ep}}, \quad (5.9)$$

where the kinetic energy of the massive hole and a constant energy associated with the massive hole, $-\sum_{\alpha}' V_0(\vec{R}_0;\ \vec{R}_{\alpha 0})$, are omitted, and H_0 is given by

$$H_0=p^2/2m+\sum_{\alpha} V_0(\vec{r};\ \vec{R}_{\alpha 0}). \quad (5.10)$$

The first term in the last equation is the kinetic energy of the electron with momentum $\vec{p}$ and free-electron mass m.

In order to find an effective Hamiltonian for the electron, let us use the boson operator $B_{\vec{w}}$,

$$B_{\vec{w}}=b_{\vec{w}}-\frac{z_w V_w^{*} e^{-i\vec{w}\cdot\vec{R}_0}}{E_{\text{ex}}}, \quad (5.11)$$

and its complex conjugate $B_{\vec{w}}^{\dagger}$, to transform Eq. (5.9). This transformation yields

$$H_e=H_0-V(\vec{r};\ \vec{R}_0)+\sum_{\vec{w}}\frac{z_w|V_w|^2}{E_{\text{ex}}}\left(e^{i\vec{w}\cdot(\vec{r}-\vec{R}_0)}+\text{c.c.}\right)+\sum_{\vec{w}} B_{\vec{w}}^{\dagger} B_{\vec{w}} E_{\text{ex}}+\sum_{\vec{w}}\left(V_w B_{\vec{w}} e^{i\vec{w}\cdot\vec{r}}+\text{c.c.}\right)-\sum_{\vec{w}}\frac{z_w^2|V_w|^2}{E_{\text{ex}}}. \quad (5.12)$$

The fourth term is the Hamiltonian of the exciton system in the $B_{\vec{w}}$ representation (referring to a reference system here). The fifth term is the direct interaction of the electron with excitons characterized by the operator $B_{\vec{w}}$. The third term and the last term are, respectively, the dielectric screening interaction (i.e., the interaction between the electron and the massive hole via the CEP field) and the self-energy of the massive hole due to its own electronic polarization field (see Ref. 24 for details).

We are now in the position to discuss the form of z_w. If the z_w is chosen as

$$z_w=1/(1+v^2w^2), \quad (5.13)$$

where v is a parameter to be determined later, then the dielectric screening interaction, V_e say, can be written as follows:

$$V_e=\sum_{\vec{w}}\frac{|V_w|^2}{E_{\text{ex}}(1+v^2w^2)}\left(e^{i\vec{w}\cdot(\vec{r}-\vec{R}_0)}+\text{c.c.}\right). \quad (5.14)$$

This V_e can be evaluated as

$$V_e=\left(1-\frac{1}{\epsilon_\infty}\right)\frac{e^2}{|\vec{r}-\vec{R}_0|}\left(1-e^{-|\vec{r}-\vec{R}_0|/v}\right) \quad (5.15)$$

by replacing the summation over the wave vector $\vec{w}$ in the first Brillouin zone by the $\vec{w}$ integration with the upper limit of infinity, as in the polaron theory. Similarly, the self-energy of the massive hole, the last term in Eq. (5.12), may be evaluated as

$$E_{\mathrm{sh}}=-e^2\left(1-\frac{1}{\epsilon_\infty}\right)\left[\frac{d}{2(d^2+v^2\pi^2)}+\frac{1}{v\pi}\tan^{-1}\left(\frac{v\pi}{d}\right)\right]. \tag{5.16}$$

The above obtained dielectric screening interaction, Eq. (5.15), combines with the direct interaction between the electron and the massive hole, $-V(\vec{r};\vec{R}_0)$, to give $-e^2/\epsilon_\infty|\vec{r}-\vec{R}_0|$ for very large $|\vec{r}-\vec{R}_0|$, as is expected for the present problem. Therefore, to a good approximation, z_w in Eq. (5.12) may be set equal to that given by Eq. (5.13). The parameter v in it may be determined after the CEP effect on the electron itself is found from the electron-exciton interaction in Eq. (5.12).

This effect has been studied in Ref. 24 by taking the electron-exciton interaction as a perturbation for the case in which the binding energy of the electron is considerably less than the exciton energy (which is order of the band gap) as in the F-center problem. In this case, according to Ref. 24, the effect on the electron itself which is due to the electron-exciton interaction yields (i) a self-energy, (ii) a mass correction to the electronic mass, and (iii) a Lamb-shift-type correction. As discussed in Ref. 24, corrections (ii) and (iii) are unimportant for the case mentioned above. The self-energy, H_{se}, is given by

$$H_{\mathrm{se}}=-\alpha_1 E_{\mathrm{ex}}, \tag{5.17}$$

where

$$\alpha_1=\frac{e^2}{\pi E_{\mathrm{ex}}}\left(1-\frac{1}{\epsilon_\infty}\right)\left(\frac{2mE_{\mathrm{ex}}}{\hbar^2}\right)^{1/2}\tan^{-1}\left(\frac{\hbar^2}{2mE_{\mathrm{ex}}}\right)^{1/2} w_m \tag{5.18}$$

in which w_m is the maximum value of $|\vec{w}|$ in the first Brillouin zone and equals π divided by the nearest-neighbor distance d for alkali halides with NaCl structure.

Accordingly, the Hamiltonian for the electron plus the massive hole, corrected for the influence of the CEP field, may be written from Eq. (5.12) as

$$H=\frac{p^2}{2m}+\sum_\alpha{}' V_0(\vec{r};\vec{R}_{\alpha 0})+h \tag{5.19}$$

with h given by

$$h=\left(1-\frac{1}{\epsilon_\infty}\right)\frac{e^2}{r}(1-e^{-r/v})-e^2\left(1-\frac{1}{\epsilon_\infty}\right)\times\left[\frac{d}{2(d^2+v^2\pi^2)}+\frac{1}{v\pi}\tan^{-1}\left(\frac{v\pi}{d}\right)\right]-\alpha_1 E_{\mathrm{ex}}, \tag{5.20}$$

where the origin of the position vectors is chosen at $\vec{R}_0$, the center of the negative-ion vacancy. Hereafter we shall call H given by Eq. (5.19) simply the electronic effective Hamiltonian, since the energy associated with the massive hole in this equation is constant.

The parameter v involved in the above h may be determined in the following way. When $r\to 0$, i.e., when the electron approaches the center of the negative-ion vacancy, the crystal under consideration is close to a perfect crystal and the electronic polarization is negligible. Hence the parameter v can be approximately determined by setting the total electronic polarization equal to zero. Letting only the above h equal to zero for $r\to 0$ and using the values listed in Table VI for the crystal parameter, we obtain $v^{-1}=0.1949$ a.u.$^{-1}$ for KCl. We note that v determined in this way also includes a host of other corrections. We also note that the expression of the dielectric screening interaction, the first term in Eq. (5.20), with the above determined v is the same as that used in Ref. 27. But that expression in that reference was derived from the Haken–Schottky interaction for a Wannier exciton consisting of an electron with the effective mass m_e^* and a hole with the effective mass m_h^*, i.e.,

$$V_{\mathrm{HS}}=\left(1-\frac{1}{\epsilon_\infty}\right)\frac{e^2}{r}\left(1-\frac{e^{-\rho_e r}+e^{-\rho_h r}}{2}\right), \tag{5.21}$$

with $\rho_e=(2m_e^*E_{\mathrm{ex}}/\hbar^2)^{1/2}$ and $\rho_h=(2m_h^*E_{\mathrm{ex}}/\hbar^2)^{1/2}$, by putting $\rho_e=\rho_h$.

Now we have to discuss the ionic polarization effect on the ground state and on the optically excited states to which the optical transitions from the ground state occur. When the electron is inside a spherical region of radius R_0 ($\simeq d$, the nearest-neighbor distance of the crystal in question), centered at the massive hole, it moves much faster than the ions, and the Coulomb field of the massive hole is shielded by the electron so that the electron-hole system hardly polarizes the lattice.[23] This implies that only when the electron is outside the spherical region the lattice will be polarized by the electron and hole to give an appreciable ionic polarization. For the ground state of the F center in a typical alkali halide such as KCl, however, the electron spends most of its time inside the spherical region mentioned above, and the ionic polarization effect is not important in the calculation of the eigenenergy and eigenfunctions. This effect on the corresponding optically excited states is not important either, since the optical transitions from the ground state to these excited states in a typical alkali halide satisfies the Franck–Condon principle.

TABLE VI. Input data for the numerical calculation for KCl. The first three entries were taken from Ref. 25. The superscript (a) refers to the data of Ref. 26. The data for the electron affinity $-|\chi|$ were taken from Ref. 30.

d (Å)	ϵ_∞	α (Å^3)	$E_{\mathrm{ex}}^{(a)}$ (eV)	$-|\chi|$ (eV)
3.14	2.13	0.83	7.8	−0.6

B. Calculation of Ground State of *F* Center by Model-Pseudopotential Method

We take H given by Eq. (5.19) as the Hamiltonian for the problem considered in this section and write the corresponding wave equation in the form

$$\left(\frac{p^2}{2m}+\sum_{\alpha}{}' V_0(\vec{r};\ \vec{R}_{\alpha 0})+h\right)\psi(\vec{r})=E\psi(\vec{r}), \qquad (5.22)$$

where $\psi(\vec{r})$ and E are, respectively, the eigenfunction and eigenenergy of the F-center electron. The prime on the summation means that the summation is taken over all ions except the missing halogen ion.

According to the theory described in Sec. II, the corresponding pseudo-wave-equation may be written as

$$\left(\frac{p^2}{2m}+\sum_{\alpha}{}' V_{\alpha}^{\text{ps}}+h\right)\phi(\vec{r})=E\phi(\vec{r}), \qquad (5.23)$$

where $\phi(\vec{r})$ is the pseudo-wave-function for the F-center electron. Equation (5.23) may be solved by a variational method using a trial wave function expanded in terms of Slater atomic orbitals (STO). From continuum approximation, the F-center ground state should not be very different from the 1s hydrogen function, and we cut off the expansion at the 2s STO, so that

$$\phi_g(\vec{r})=N[u_{1s}(\beta_1)+\mu u_{2s}(\beta_2)], \qquad (5.24)$$

where N is a normalizing constant such that $\langle\phi(\vec{r})|\phi(\vec{r})\rangle=1$. $u_{1s}(\beta_1)$ and $u_{2s}(\beta_2)$ are the 1s and 2s STO's with parameters β_1 and β_2, respectively, i.e.,

$$u_{1s}(\beta_1)=(\beta_1^3/\pi)^{1/2}e^{-\beta_1 r}, \qquad (5.25a)$$

$$u_{2s}(\beta_2)=(\beta_2^5/3\pi)^{1/2}re^{-\beta_2 r}. \qquad (5.25b)$$

Here μ is also a variational parameter. When $\beta_1=\beta_2=\lambda$, and $\mu=\sqrt{3}$, we have the usual modified 1s function, $N(1+\lambda r)e^{-\lambda r}$.

The energy E in Eq. (5.23) for the ground state is given by

$$\begin{aligned}E_g&\equiv\langle\phi_g(\vec{r})|H^{\text{ps}}|\phi_g(\vec{r})\rangle\\&=-\tfrac{1}{2}\langle\phi_g(\vec{r})|\nabla^2|\phi_g(\vec{r})\rangle+\sum_{\alpha}{}'\langle\phi_g(\vec{r})|V_{\alpha}^{\text{ps}}|\phi_g(\vec{r})\rangle\\&\quad+\langle\phi_g(\vec{r})|h|\phi_g(\vec{r})\rangle. \qquad (5.26)\end{aligned}$$

Here, as well as in the rest of this paper, the calculations will be done in atomic units (a.u.). The first term can be calculated as usual. For the calculation of the second term, we adopt the model pseudopotential proposed earlier in this paper. According to Eqs. (2.15) and (2.18), the contribution due to a K$^+$ ion is given by

$$\begin{aligned}I_{\alpha}\equiv\langle\phi_g(\vec{r})|V_{\alpha}^{\text{ps}}|\phi_g(\vec{r})\rangle&=-\langle\phi_g|\frac{1}{r_{\alpha}}|\phi_g\rangle\\&\quad+\sum_{l,m}C_l\langle\zeta_{lm}|\frac{1}{r_{\alpha}^2}|\zeta_{lm}\rangle_r, \qquad (5.27)\end{aligned}$$

where

$$\zeta_{lm}=\langle\phi_g|lm\rangle,\quad r_{\alpha}=|\vec{r}-\vec{R}_{\alpha 0}|.$$

Since the most important contribution in the expansion of ϕ_g in terms of the atomic pseudo-wave-functions is expected to come from the lowest valence states, such as those corresponding to 4s and 5s, 4p and 5p, 3d and 4d, etc., for potassium, we may calculate C_l in Eq. (5.27) for the s states from an average of the 4s and 5s quantum-defect data, for the p states from an average of the 4p and 5p quantum-defect data, and so on in the case of potassium halides. The results are given in Table VII.

The contribution due to the Cl$^-$ ions can be written, from Eq. (2.13), as

$$I_{\alpha}=-\langle\phi_g|\frac{1}{r_{\alpha}}|\phi_g\rangle+\sum_{k,l,m}\langle\zeta_{lm}|\frac{C_{kl}}{r_{\alpha}^2}|kl\rangle_r\langle kl|\zeta_{lm}\rangle_r. \qquad (5.28)$$

The $|kl\rangle$'s are Coulomb wave functions and can be calculated numerically by a number of methods depending on the values of k, l, and r_{α}. A detailed discussion on this has been given by Fröberg.[21] For a typical case in which the Cl$^-$ ion is in the second-neighboring shell and $\beta_1=\beta_2=0.6$ a.u.$^{-1}$, a plot of $\langle kl|\zeta_{lm}^{(i)}\rangle$ vs k is given in Fig. 2. Here $i=1$ and 2, respectively, for 1s and 2s STO's. It is very interesting to note there that the expansion coefficients are important only over a rather short range of k from $k\simeq 0.325$ a.u.$^{-1}$ to $k\simeq 0.8$ a.u.$^{-1}$. This is to be expected. Indeed, the ζ_{lm}'s are rather slowly varying functions while $|kl\rangle$ becomes more and more oscillatory as k increases, so that the integral resulting from the product of these two functions would diminish rapidly as k increases. Therefore, in doing the summation over k, it may not be a bad approximation to replace the infinite upper limit by a finite upper limit k_m. This, in our case, is taken to be 1.5 a.u.$^{-1}$ (corresponding to an energy ~30 eV) and is believed to contain the most important components of k in the summation. As the radius L of the normalization sphere approaches infinity, the summation over k becomes an integral and we have

$$\sum_{k}^{km}\sum_{l,m}\langle\zeta_{lm}^{(i)}|\frac{C_{kl}}{r_{\alpha}^2}|kl\rangle_r\langle kl|\zeta_{lm}^{(j)}\rangle_r$$

TABLE VII. Parameters for the model pseudopotential in Eq. (2.18) for potassium.

C_0 (a.u.)	C_1 (a.u.)	C_2 (a.u.)
0.702	0.405	−0.422

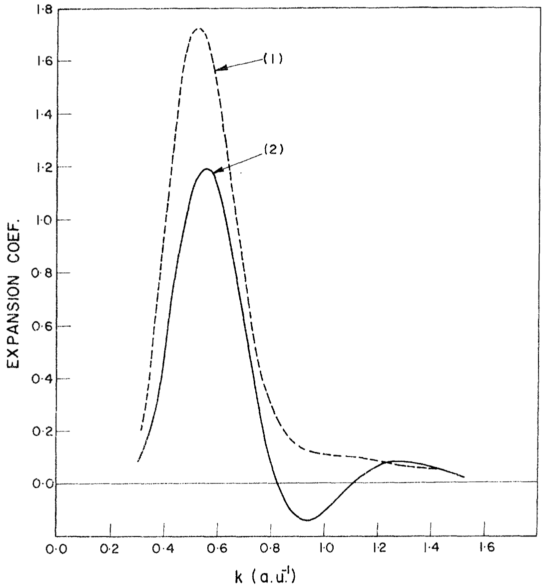

FIG. 2. Typical plot of the expansion coefficients $\langle kl\,|\,\zeta_{lm}^{(1)}\rangle$ and $\langle kl\,|\,\zeta_{lm}^{(2)}\rangle$ vs k of the $1s$ [curve (2)] and $2s$ [curve (1)] STO's in terms of the pseudo-wave-functions $|\,kl\rangle$ for $l=0$ and $\beta_1=\beta_2=0.6$ a. u.$^{-1}$.

$$=\int_0^{k_m}\rho(k)dk\sum_{l,m}\langle\zeta_{lm}^{(i)}\,|\,\frac{C_{kl}}{r_\alpha^2}\,|kl\rangle_r\langle kl\,|\,\zeta_{lm}^{(j)}\rangle_r\,. \qquad (5.29)$$

Here $\rho(k)$ is the density of states. This may be calculated from the allowed values of k and can be shown to be given by

$$\rho(k)=L/\pi$$

in the limit when L becomes very large. Since ϕ_g for the F-center electron in a typical alkali halide like KCl is very localized, for sufficiently far-away ions the state-dependent term C_{kl}/r_α^2 is small compared with the term Z_α/r_α (Z_α, the charge of the αth ion, is $+1$ for K$^+$ and -1 for Cl$^-$). Therefore, for ions farther away from vacancy than the three-nearest-neighboring shells, we may neglect the state-dependent term. In this way, the second term in Eq. (5.26) can be written as

$$\sum_\alpha{}'\langle\phi_g(\vec{r})|\,V_\alpha^{\text{ps}}\,|\,\phi_g(\vec{r})\rangle=E_{\text{pi}}+E_{\text{sd}}\,, \qquad (5.30\text{a})$$

where

$$E_{\text{pi}}=-\sum_\alpha{}'Z_\alpha\langle\phi_g(\vec{r})|\,\frac{1}{r_\alpha}\,|\,\phi_g(\vec{r})\rangle\,, \qquad (5.30\text{b})$$

$$E_{\text{sd}}=6T_{\text{K}1}+12T_{\text{Cl}}+8T_{\text{K}2}\,. \qquad (5.30\text{c})$$

Here $T_{\text{K}1}$ and $T_{\text{K}2}$ are the second term in Eq. (5.27) for a K$^+$ ion in the first- and third-neighboring shells, respectively, and T_{Cl} is the second term in Eq. (5.28) for a Cl$^-$ ion in the second-neighboring shell. The calculation of E_{pi} is similar to that in the usual point-ion calculation and will not be mentioned here.

Since the calculation of the third term of Eq. (5.26) is straightforward, we merely give the result

$$\langle\phi_g|h|\phi_g\rangle=E_{\text{se}}+E_{\text{sh}}$$
$$+\left(1-\frac{1}{\epsilon_\infty}\right)\left\{\beta_1\left[1-\left(\frac{\beta_1}{\beta_1+\gamma}\right)^2\right]+\mu^2\frac{\beta_2}{2}\left[1-\left(\frac{\beta_2}{\beta_2+\gamma}\right)^4\right]\right.$$
$$\left.+\mu(1+\tau)^{3/2}(1-\tau)^{5/2}\frac{2\beta}{\sqrt{3}}\left[1-\left(\frac{\beta}{\beta+\gamma}\right)^3\right]\right\}\,, \qquad (5.31)$$

where E_{se} is given by Eq. (5.17) and E_{sh} by Eq. (5.16), and $\gamma=(2v)^{-1}$. The value for v should be somewhat different from that determined previously, when we simply required $h=0$ as $r\to0$ for the F center. This is because the parameter C_l used here for potassium ions in the first- and third-neighboring shells includes also the atomic electronic polarization effect, part of which may have been accounted for through the renormalization of the coupling constant in Toyozawa's theory for the crystalline electronic polarization [see a discussion following Eq. (5.7)]. We now redetermine v by requiring that as $r\to0$ the total electronic polarization effect, i. e., h plus the electronic polarization potential due to the atomic polarization of the potassium ions in the first- and third-neighboring shells (which is $-\alpha_e e^2/2d^4$ for a nearest K$^+$ as $r\to0$,[28] α_e, being the electronic polarizability), equals zero. In this way v^{-1} is determined to be 0.228 a.u.$^{-1}$ for KCl. Correspondingly, the above E_{sh} is -0.02941 a.u. for KCl. This E_{sh} is no longer just the self-energy of the massive hole, because v in it contains a host of other corrections.

C. Results

Substitution of the different terms into Eq. (5.26) yields an expression of E_g in terms of the variational parameters β_1, β_2, and α. The variational equation is solved by Rosenbrook's "hill climbing" method.[29] The results obtained are given in Table VIII.

In addition to using the three-parameter trial wave function in Eq. (5.24), we also repeat the calculation for less flexible types of trial wave functions, e.g., the simple $1s$, the modified $1s$, and the two-parameter functions (β_1 and β_2 are kept equal). The results are also given in Table VIII.

It is interesting to note that the simple $1s$ trial function gives a ground-state energy almost 1 eV higher than the other three. The main contribution of this difference comes from the kinetic energy, and the state-dependent terms of K$^+$ and Cl$^-$. It is remarkable to see how these terms change when the wave function deviates farther from the true wave function (the one that gives lowest energy for all trial functions). This seems to justify the fact that these state-dependent parts do depend rather sensitively on the shape of the wave function.

TABLE VIII. Numerical results of the variational parameters and energies for the F center in the ground state in KCl. E_k, E_r^{-1}, $(E_{r^{-2}})_{K^+}$, $[E_{r^{-2}}]_{Cl^-}$, and E_{ep} refer to the total contribution to the ground-state energy E_g from the kinetic energy term, r^{-1} term, r^{-2} term due to K^+ ions, r^{-2} term due to Cl^- ions, and from h, respectively. The value for E_g is given relative to the vacuum level. All the energies are given in eV.

ϕ_g	β_1(a.u.$^{-1}$)	β_2(a.u.$^{-1}$)	μ	E_k	$E_{r^{-1}}$	$[E_{r^{-2}}]_{K^+}$	$[E_{r^{-2}}]_{Cl^-}$	E_{ep}	E_g
Three parameter	0.458	0.707	1.21	2.25	−7.69	1.88	0.113	−0.596	−4.05
Two parameter	0.611	0.611	1.53	2.26	−7.66	1.98	0.127	−0.599	−3.89
Modified 1s	0.623	0.623	$\sqrt{3}$	2.26	−7.67	2.00	0.124	−0.596	−3.88
1s	0.435	0	0	2.57	−7.56	2.3	0.150	−0.587	−3.07

Another point to note is that the state-dependent term of Cl^- is small compared to the total energy and may be neglected without committing great error.

Now we go on to the estimation of the energy level of the optically highest bound state. The difference between this energy level and that of the ground state will give an estimation of the optical ionization energy of the F-center electron in the ground state. For the highest bound state, the electronic wave function is completely diffused and the energy in Eq. (5.23) may be written as

$$E_h = -\,|\chi| - e^2\left(1 - \frac{1}{\epsilon_\infty}\right)\left[\frac{2\gamma^2 d}{(4\gamma^2 d^2 + \pi^2)} + \frac{\gamma}{\pi}\tan^{-1}\left(\frac{\pi}{2\gamma d}\right)\right]. \tag{5.32}$$

Here $-|\chi| = E_0 - \alpha_{1b} E_{ex}$, where E_0 is the lowest level of the conduction band relative to the vacuum level and α_{1b} is given by Eq. (5.18) with the free-electron mass replaced by the electronic band mass. Therefore $-|\chi|$ is the electron affinity and has a value of about −0.6 eV for KCl.[30] For KCl, $E_h \simeq -1.4$ eV, so that the magnitude of the optical ionization energy for the F electron $|E_g - E_h|$ is about 2.65 eV.

D. Discussion

The K band at 2.71 eV in KCl has been known both experimentally and theoretically to be due to optical transitions from the ground state of the F center to its excited states just below and above the conduction band.[31] From this observation, the experimental optical ionization energy of the F center in the ground state may be regarded to be of the order of 2.71 eV. The corresponding result of the present calculation is 2.65 eV, which is in good agreement with the above estimation. Since this calculation is done by a variational method, the actual eigenvalue for the pseudo-wave-equation should be a little bit lower than the ground-state energy level calculated above, so that the actual optical ionization energy calculated by this method should be a little bit greater than 2.65 eV, if a more flexible type of trial functions has been used.

A number of calculations on the F-center ground state, including the ion-size effect explicitly, exist in the literature.[25,32–35] In the following, we shall compare the result of the present calculation with some of them. To this effect, we list in Table IX the F-center ground-state energies calculated by Öpik and Wood using a HF-like method,[25] by Kübler and Friauf using the Austin-type of first-principles, pseudopotential,[32] and by Evarestov using the Heine–Abarenkov model potential.[33] In the third column, we estimate the energy level of the optically highest bound state for each individual case. In the work of Ref. 27, the electronic polarization was included explicitly and the hole self-energy due to this polarization was given by $-\frac{1}{2}(1-\epsilon_\infty^{-1})\rho_h \simeq -1.42$ eV, so that the highest-bound-state energy level is this value plus the electron affinity, i.e., −2.02 eV. This value is considerably different from the corresponding energy level we calculated (~−1.4 eV). Such a difference has its origin in the approach used to treat the CEP effect. A discussion of this was presented in Sec. V A. Despite this difference, the calculation of the optical ionization energy is not affected, because any error here merely shifts the ground and excited states by the same amount.

In both the work of Refs. 32 and 33, the CEP effects on the ground state are neglected, amounting to letting $h = 0$ for all r in Eq. (5.20). Note that h cannot vanish at all in a diffused state. Since the hole self-energy has not been calculated in any of the last two references, we just adopt our value of E_h and estimate the optical ionization energies in

TABLE IX. Some results on KCl based on calculations by other authors and the present authors. All energies are given in eV. Both the ground-state energy E_g and the energy of the optically highest bound state E_h are measured from the vacuum level. Experimental value for the optical ionization energy of the F center in the ground state, W_0, is about 2.71 eV for KCl (see text for details).

	E_g	E_h	W_0
Öpik & Wood	−4.81	−2.02	2.79
Kübler & Friauf	−4.08	−1.4	2.68
Evarestov	−3.67	−1.4	2.27
Present work	−4.05	−1.4	2.65

their cases (see Table IX). The discrepancy in the calculated and experimental results in Ref. 33 probably is due to the neglect of the CEP effect in the ground state, which according to our calculation is about − 0.5 eV. If this amount were added, the ground state might be lowered considerably to bring the calculated ionization energy closer to the experimental value.

Good agreement with experimental value is obtained by the result in Ref. 32 despite the omission of the CEP effect on the ground state. This does not necessarily mean the CEP effect is not important, because according to both Ref. 27 and the present work the contribution to the ground-state energy due to this effect is quite significant. Therefore, the good agreement between experimental and calculated values in this case probably is due to a mutual cancellation between the errors resulting from the approximation used in the calculation of the pseudopotential and that from the omission of the CEP effects.

Although ion-size effect has been included in the calculations in Refs. 34 and 35, the *F*-center ground-state energies obtained are not much different from those in the point-ion-model calculation, which are rather too deep compared with the results obtained by the above mentioned three calculations and the present one. Such discrepancies may partly be due to the effect of dielectric screening not being treated properly and partly to the approximation in the pseudopotential used in these two references.

From the discussion above, it seems that the method of model pseudopotentials, introduced here as a special representation of the pseudopotential operator in the Hilbert space, is a satisfactory method for calculating the state of a localized electron trapped in an electrically neutral point defect. Whether this method can be applied to a non-neutral system will be seen in Paper II. Further applications to diffused states, with some modification, and to the conduction electrons will be discussed in forthcoming papers.

VI. SUMMARY

A method of calculating the states of a valence electron in a solid (such as a conduction electron or a localized electron) was developed using atomic-model pseudopotentials. This was based on the possibility of representing the pseudopotential operator on the basis of the complete orthonormal set of atomic-model pseudo-wave-functions. A form of the model pseudopotential suitable to our theory was suggested and the necessary parameters for it were determined. In the case of alkali ions, the determination was effected using quantum-defect data. In the case of a negative ion with no open cores, such as Cl^-, the determination was designed to use phase shifts of the electron scattering problem.

The method proposed was tested by applying it to calculate the optical ionization energy of the *F* center in the ground state for KCl. It is found to give satisfactory results.

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[1] V. Heine, Solid State Phys. **24**, 1 (1970); M. L. Cohen and V. Heine, Solid State Phys. **24**, 37 (1970).

[2] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

[3] J. C. Philips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[4] I. V. Abarenkov and V. Heine, Philos. Mag. **12**, 529 (1965); V. Heine and I. V. Abarenkov, Philos. Mag. **9**, 451 (1964).

[5] T. Toyozawa, Prog. Theor. Phys. **12**, 421 (1954).

[6] M. P. Barnett, Methods Comput. Phys. **2**, 95 (1963).

[7] R. W. Shaw, Jr., Phys. Rev. **174**, 769 (1968).

[8] L. Pauling and S. Goudsmit, *The Structure of Line Spectra* (McGraw-Hill, New York, 1930).

[9] S. Wang, Phys. Status Solidi **23**, 387 (1967).

[10] G. Simons, J. Chem. Phys. **55**, 756 (1971).

[11] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1965).

[12] (a) F. S. Ham, Solid State Phys. **1**, 127 (1955); (b) C. E. Moore, Natl. Bur. Stds. (U. S.) Circ. No. 467 (1952), Vols. I and II.

[13] G. Birkhoff and G. Rota, *Ordinary Differential Equations* (Blaisdell, Waltham, Mass., 1969).

[14] G. H. Wannier, Phys. Rev. **64**, 358 (1943).

[15] T. S. Kuhn, Q. Appl. Math. **9**, 1 (1951).

[16] H. Brooks and F. S. Ham, Phys. Rev. **112**, 344 (1958).

[17] Another approach was used to tackle this problem by Abarenkov [I. V. Abarenkov and I. M. Antonova, Phys. Status Solidi **20**, 643 (1967)].

[18] P. G. Burke and M. J. Seaton, Methods Comput. Phys. **10**, 1 (1971).

[19] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Oxford U.P., London, 1951).

[20] E. Clementi, IBM J. Res. Dev. **9**, 2 (1965).

[21] C. E. Fröberg, Rev. Mod. Phys. **27**, 399 (1955).

[22] C. H. Woo and S. Wang, following paper, Phys. Rev. B **7**, 2827 (1973).

[23] S. Wang, Phys. Rev. **153**, 939 (1967).

[24] S. Wang, H. L. Arora, and M. Matsuura, Phys. Rev. B **4**, 3685 (1971).

[25] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Dover, New York, 1948).

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

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

[28] J. H. Van Vleck, *The Theory of Electronic and Magnetic Susceptibilities* (Oxford U. P., London, 1932).

[29] H. H. Rosenbrook, Comput. J. **3**, 175 (1960).

[30] T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).

[31] G. Spinolo and D. Y. Smith, Phys. Rev. A **140**, 2117 (1965).

[32] J. K. Kübler and R. J. Friauf, Phys. Rev. A **140**, 1742 (1965).

[33] R. A. Evarestov, Opt. Spektrosk. **28**, 712 (1970) [Opt. Spectrosc. **28**, 384 (1970)]; also M. I. Petrashen, I. V. Abarenkov, A. A. Berezin, and R. A. Evarestov, Phys. Status Solidi **40**, 433 (1970).

[34] R. H. Bartram, A. M. Stoneham, and P. Gash, Phys. Rev. **176**, 1014 (1968).

[35] W. Weber, and B. G. Dick, Phys. Status Solidi **36**, 723 (1969).

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Model-Pseudopotential Calculation of Electron States in Solids. II. Low-Lying States of the F_{2A}^{+} Center*

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With a correction due to the crystalline ionic polarization, the formalism of the preceding paper is applied to calculate the low-lying states of an F_{2A}^{+} center in an alkali-halide crystal containing impurity ions, such as KCl containing sodium. The theoretical absorption energy obtained from the difference between the energies of the ground and first excited states of the F_{2A}^{+} center in KCl is in reasonable agreement with the experimentally observed absorption band appearing at 0.98 eV in KCl containing sodium. In addition, our results lead us to assume the existence of the F_{2B}^{+} center. Calculations on the corresponding ground and first excited states of this configuration in KCl are performed. From these energies, the $1s\sigma \rightarrow 2p\sigma$-like transition energy is deduced to be at ≈ 1.07 eV.

I. INTRODUCTION

This paper deals with the second application of the model-pseudopotential method developed in the preceding paper I[1] to study theoretically low-lying states of an F_{2A}^{+} center in an alkali-halide crystal containing impurity ions, such as KCl containing sodium. The F_{2A}^{+} center under study consists of an F_2^{+} center (also known as an M^{+} center) with an impurity ion Na^{+} at a nearest-neighbor site in the (100) plane containing the F_2^{+} center.[2]

In this application we first derive in Sec. II the Hamiltonian for the F_{2A}^{+}-center electron corrected for the influence of the crystalline electronic polarization by using an approach described in paper I. We then obtain the corresponding pseudo-Hamiltonian employing the model-pseudopotential method developed in Paper I. The obtained pseudo-Hamiltonian is then corrected for the influence of the ionic polarization.

The resulting pseudo-wave-equation is then solved in Sec. III by the variational method, to obtain the ground state and the first optically excited state (to which the optical transition from the ground state occurs) of the F_{2A}^{+} center for KCl.

Finally, in Sec. IV, the theoretical optical absorption energy of the F_{2A}^{+} center, obtained by taking the difference between the calculated energies of the ground state and the first optically excited state, is discussed and compared with the absorption band observed by Schneider[2] occurring at ~0.98 eV (~0.09 eV higher than the corresponding M^{+} band) in KCl containing sodium. In addition, in view of the conclusions drawn there, we assume the existence of a color center (called the F_{2B}^{+} center) in KCl, consisting of an F_2^{+} center with two Na^{+} impurity ions at the two nearest-neighbor sites in the (100) plane, and calculate its ground state and the first optically excited state. A conclusion of this paper is also included in Sec. IV.

II. HAMILTONIAN

The F_{2A}^{+} center is an F_2^{+} center, consisting of two adjacent negative-ion vacancies plus an electron, with an impurity ion Na^{+} at a nearest-neighbor site in the (100) plane containing the F_2^{+} center in KCl.[2] In other words, the F_{2A}^{+} center is an electron in a crystal consisting of the perfect crystal KCl minus two adjacent Cl^{-} ions and plus an ion Na^{+} replacing a potassium ion at the mentioned position. Therefore, when ignoring the crystalline electronic polarization (CEP), the Hamiltonian for the F_{2A}^{+} center in KCl may be written as

$$H_b = T_e + \sum_{\alpha} V_0(\vec{r};\ \vec{R}_{\alpha 0}) - \sum_{i=1}^{2} V(\vec{r};\ \vec{R}_i) - V(\vec{r};\ \vec{R}_3)$$