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Mixed approach of linear-combination-of-atomic-orbitals and orthogonalized-plane-wave methods to the band-structure calculation of alkali-halide crystals

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The energy-band structure of lithium chloride, sodium chloride, and potassium chloride has been calculated following a mixed approach of linear-combination-of-atomic-orbitals method for the valence bands and orthogonalized-plane-wave method for the conduction bands. The interpolation scheme developed by Slater and Koster has been used to calculate the matrix elements of the energy operator and the overlap integrals. The influence of the mode of admixture of wave functions to the crystal orbitals is extensively studied. For the different mode of admixture of states, the variations in the band parameters, viz. band gaps, widths, and locations, are noted. The calculated values are compared with experiments and the previous theoretical results.

I. INTRODUCTION

Recently[1–16] a number of authors have published calculations on the band structure of alkali-halide crystals. Shockley[1] for the first time calculated the valence-band structure of NaCl. Two other calculations on NaCl were reported by Tibbs[2] and Cassella.[3] Tibb's calculation gives only the approximate results and Cassella's calculation provides only the valence bands. In case of KCl, Howland's[4] linear-combination-of-atomic-orbital (LCAO) approach reports on the valence band for the first time. In that paper the author takes into account the contributions of the core states to the crystal orbitals although he does not show the core bands. Subsequently Oyama and Miyakawa[5] calculated the conduction bands of KCl adopting the orthogonalized-plane-wave (OPW) method, De Cicco[6] used the augmented-plane-wave method to calculate the valence and the conduction bands of KCl. In a semiempirical approach Phillips[7] explained the band structure of some alkali halides. On using the experimental data due to Eby *et al.*,[8] and Philipp *et al.*,[9] he empirically deduced the bands of alkali-halide crystals. His results for KCl are found to be consistent with those due to Howland.[4] Although his calculations are semiempirical, the optical properties obtained are found to be consistent with recent experimental interpretations.[10,11] In a more recent investigation, Kunz[12] adopted the OPW method to calculate the band structure of LiCl, NaCl, and KCl. His results are found to be consistent with the recent experiments due to Roessler *et al.*[13] Fong and Cohen[14] in a recent paper calculated the optical constants of NaCl and KCl using the empirical-pseudopotential-method. In the case of NaCl they adopted the empirical-pseudopotential-method approach but in the case of KCl they added a nonlocal d-wave potential. Their results provide a complete analysis of the band structure in optical spectrum. In a recent investigation, Shulichenco *et al.*[14a] adopted a simplified LCAO approach to deduce the valence band of KCl taking certain parameters from Ref. 13.

Very recently Kunz *et al.*[15] have calculated the band properties of LiCl, NaCl, and KCl using a mixed basis method developed by Kunz.[16] This method involves expanding an electronic wave function in terms of plane waves and tight-binding Bloch functions. Using local orbitals, the self-consistent Hartree-Fock energy bands are first obtained and correlation effects are then taken into account. To avoid excessive labor they considered only several points in the first Brillouin zone along some highly symmetric directions. Nevertheless their results are more favored by the recent experiments[13,17] than the calculations[14] using only the Hartree-Fock approach without the correlation effects.[18]

Experimentally the situation of the alkali halides is rather interesting. Among the considerable experimental measurements, the results of Parrett and Jossem[17a] were interpreted as yielding the valence widths of KCl. They found a half-width of 0.025 Ry. Many authors[1–6] have compared their results with those due to Parrett and Jossem, but Best[17b] has recently advanced convincing arguments to show that the results of Parrett and Jossem do not give correct valence widths. Severe localization effects of the hole prevent the true valence width being given in x-ray emission.

Moreover, the results of Parrett and Jossem are in conflict with x-ray emission data of O'Brian and Skinner[17c] and the recent experiments of Teegarden *et al.*,[19] Baldini *et al.*,[20] and Roessler *et al.*[13] provide information which is not consistent with the experiments of Parrett and Jossem. Of these the work of Roessler *et al.*[13] is consistent with the theoretical investigations.[15,16]

Among the very recent experimental information, the photoemission studies of LiCl, NaCl, and KCl by Pong and Smith[21] are likely to be the most interesting. The results which they obtained within the spectrum range (13–25 eV) provide data on the valence and conduction bands which disagree with the previous experiments. Since they were interested in the upper band regions, their results did not provide information about the core. In a very recent experiment Kowalczyk *et al.*[22] obtained optical properties of the localized as well as the valence bands of NaCl and KCl.

The present authors[23] calculated the band structure of KCl using an LCAO approach in the filled region. In this investigation it is noted that if one progressively adds core states to the crystal orbitals, the results obtained are in good agreement with experiment. The gradual introduction of the local orbitals to the final one-electron crystal orbital is noted to improve the band locations with respect to the vacuum level which is consistent with the recent experiments on alkali-halide crystals regarding low-energy-electron diffraction,[24] x-ray emission,[25] and optical studies.[26]

From the OPW approach due to Kunz[12] it is clear, however, that this treatment yields excellent band structure in the conduction region. On the other hand, the LCAO technique gives quite good results on the valence and inner bands. In view of these predictions, we have adopted a mixed approach to calculate the band structure of LiCl, NaCl, and KCl. For the filled regions we have used the LCAO method and for the conduction bands we have adopted the OPW approach due to Kunz.[12] In this respect we used the interpolation scheme developed by Slater and Koster[27] for the calculation of the matrix elements of the energy operator. The disposable parameters that appear in the interpolation scheme are classified into two groups: (a) those between the filled, i.e., valence, and localized states and (b) those between conduction and core-conduction states. It is to be noted that the matrix elements of the energy operator are developed with different basis functions while the crystal potential remains the same for both the valence and the conduction bands.

The consequences of the present mixed approach are that it provides information on the core states, their influences on the valence and conduction bands and shifting of the band locations which is noted to change the transition and the optical properties. It is noted that although the parameters and the optical constants in the core bands remain more or less constant during the changes of the mode of admixture, their appearance in the band system improves the upper-band parameters to some extent. The removal of degeneracies at certain highly symmetric points, the changes in the gaps and widths of the valence band are noted to attain improved values. The results obtained are compared with recent experiments and with theoretical calculations and it is noted that the present mixed approach yields better results for the band parameters than the LCAO and the OPW approaches can separately.

II. THEORETICAL DEVELOPMENT

The formulation of the present investigation is oriented in such a way that the matrix elements of the energy operator between the functions representing the filled energy states are derived from the LCAO tight-binding approach and those between the remaining states are accounted from the OPW approach developed by Kunz[12] for the alkali-halide crystals. We start with a one-electron crystal orbital expressed as an LCAO of Bloch sums of Hartree-Fock space functions for free ions given by

$$\psi_i(\vec{k},\vec{r}) = \sum_m G_{mi}(\vec{k})\,\omega_m(\vec{k},\vec{r}) \tag{1}$$

for the wave vector $\vec{k}$ and where

$$\omega_m(\vec{k},\vec{r}) = \frac{C_m}{\sqrt{N}} \sum_g^{(m)} e^{i\vec{k}\cdot\vec{R}_g}\,\varphi_m(\vec{r}-\vec{R}_g) \ , \tag{2}$$

where $\varphi_m(\vec{r}-\vec{R}_g)$ is a real-space function of type m (specifying quantum number and ion type) centered on lattice site g at $\vec{R}_g$, the superscript m to the summation sign indicates that the sum is to be extended over only those sites g on which a function of type m can be located (all the anions Li^+, Na^+, K^+ sites or cation Cl^- site) and the factor C_m is equal to $i=\sqrt{-1}$ if φ_m is odd on inversion and $i=1$ if φ_m is even on inversion.

The Hamiltonian of the system of electrons is taken to be

$$H = W + \sum_j Q_j + \sum_{j\neq j'} Q_{jj'} \ , \tag{3}$$

where W is the Coulomb interaction between the nuclei, Q_j is the one-electron operator for electron j giving its kinetic energy and Coulomb energy of interaction with the nuclei, and $Q_{jj'}$ is the two-electron operator giving the interaction of electron j and j'. On the basis of this Hamiltonian, Hartree-Fock space functions for the crystal satisfy the following equation:

$$Q_1\psi_i(\vec{k},\vec{r}_1)+2\int Q_{12}\psi_i(\vec{k},\vec{r}_1)\,\rho(\vec{r}_2,\vec{r}_2)\,d\vec{v}_2 - \int Q_{12}\psi_i(\vec{k},\vec{r}_2)\,\rho(\vec{r}_2,\vec{r}_1)\,d\vec{v}_2=\epsilon_i(\vec{k})\,\psi_i(\vec{k},\vec{r}_1)\,, \tag{4}$$

where $\epsilon_i(\vec{k})$ is the energy parameter for the function $\psi_i(\vec{k},\vec{r})$ and $\rho(\vec{r}_2,\vec{r}_1)$ is given by

$$\rho(\vec{r}_2,\vec{r}_1)=\sum_{i',k'}\psi_{i'}(\vec{k}',\vec{r}_2)\,\psi_i(\vec{k}',\vec{r}_1)\,. \tag{5}$$

As Löwdin[28] has shown when the functions $\psi_i(\vec{k},\vec{r})$ are constructed as LCAO of the type used here the quantity $\rho(\vec{r}_2,\vec{r}_1)$ can be written out in a way which does not involve the coefficients of the atomic functions. Let the overlap integral between the free-ion functions $\varphi_m(\vec{r}-\vec{R}_g)$ and $\varphi_n(\vec{r}-\vec{R}_g)$ be symbolized by

$$\Omega_{mn}(\vec{r},\vec{R}_g,\vec{R}_{g'})=\int\varphi_m(\vec{r}-\vec{R}_g)^*\,\varphi_n(\vec{r}-\vec{R}_{g'})\,d\vec{v}\,. \tag{6}$$

This integral can be regarded as one element in the $M\times M$ matrices of all overlap integrals, M being the number of electrons of each spin. According to Löwdin's result, Eq. (5) for $\rho(\vec{r}_2,\vec{r}_1)$ can be written

$$\rho(\vec{r}_2,\vec{r}_1)=\sum_{m,n}\sum_{g,g'}\Omega^{-1}_{mn}\varphi_m(\vec{r}-\vec{R}_g)^*\,\varphi_n(\vec{r}-\vec{R}_{g'})\,, \tag{7}$$

where $\Omega^{-1}_{mn}(\vec{r},\vec{R}_g,\vec{R}_{g'})$ is an element in the matrix $M\times M$ which is the inverse of the overlap matrix Ω.

If all the two-center overlap integrals are small compared to the one-center integrals as they are found to be for alkali-halide crystals, the overlap matrix Ω differs slightly from the unit matrix. In this case the inverse overlap matrix Ω^{-1} is very nearly equal to the unit matrix. In view of this the following definitions are useful:

$$\Omega_{mn}=\delta_{mn}+\zeta_{mn}\,,\quad \Omega^{-1}_{mn}=\delta_{mn}+\xi_{mn}\,, \tag{8}$$

where δ_{mn} is the Kronecker δ and for brevity each index m or n is temporarily taken to designate site as well as quantum numbers for the free-ion function φ.

Substitution of Eq. (7) into Eq. (4) gives the following set of Hartree-Fock-like equations for one-electron functions and their energies:

$$Q_1\psi_i(\vec{k},\vec{r}_1)+\sum_{m,n}\Omega^{-1}_{mn}\Big(2\int Q_{12}\psi_i(\vec{k},\vec{r}_1)\,\varphi_m(\vec{r}_2-\vec{R}_g)^*\times\varphi_n(\vec{r}_2-\vec{R}_{g'})\,d\vec{v}_2-\int Q_{12}\psi_i(\vec{k},\vec{r}_1)\,\varphi_m(\vec{r}_2-\vec{R}_g)^*\times\varphi_n(\vec{r}_1-\vec{R}_{g'})\,d\vec{v}_2\Big)=\epsilon_i(\vec{k})\,\psi_i(\vec{k},\vec{r}_1)\,. \tag{9}$$

Equation (9) then yields the following set of equations for the unknown coefficients, one set for each value of the wave vector $\vec{k}$;

$$\sum_n[H_{mn}(\vec{k})-\epsilon_i(\vec{k})\,\Omega_{mn}(\vec{k})]\,G_{ni}(\vec{k})=0\,, \tag{10}$$

where $H_{mn}(\vec{k})$ and $\Omega_{mn}(\vec{k})$ are the matrix elements of the energy operator and overlap, respectively, between the Bloch sums $\omega_m(\vec{k},\vec{r})$ and $\omega_n(\vec{k},\vec{r})$ earlier defined.

Since we have used the interpolation scheme developed by Slater and Koster[27] for the matrix elements of the energy operator, each matrix element is written in the form

$$E_{mn}(\vec{k},\vec{r},\vec{R}_g)=\sum_g^{(m)}E_{mn}(\vec{r},\vec{R}_g)\times\begin{cases}\cos\vec{k}\cdot\vec{R}_g, & p_m=p_n\\ p_m\sin\vec{k}\cdot\vec{R}_g, & p_m=-p_n\end{cases} \tag{11}$$

where p_m is the parity of the function φ_m and $E_m(\vec{r},\vec{R}_g)$ is an element of the energy operator as is appropriate between a function φ_n and another function φ_m which is at site $\vec{R}_g$ relative to site φ_n as origin. In the present investigation we have considered the interaction up to the second-nearest neighbors. Equation (11) is written in terms of the second-nearest-neighbor approximation. The elements $E(\vec{r},\vec{R}_g)$ in Eq. (11) are considered as the disposable parameters in a Slater-Koster representation. In the filled region these parameters are calculated from the LCAO method, but since in the conduction region this method is not sound at all we have used the OPW approach of Kunz[12] to calculate the matrix elements between the conduction and other wave functions except those between the localized and the valence functions. The details of the construction of the crystal potential are given in the Appendix.

III. CALCULATIONS

The sequence of the computation of the present results is as follows: (a) the computations of the integrals in Eq. (6) for $\Omega_{mn}(\vec{k},\vec{r},\vec{R}_g)$ and in Eq. (11) for $E_{mn}(\vec{r},\vec{R}_g)$ are performed, (b) the secular determinantal equations are set up and these equations are diagonalized taking up OPW elements at the selected regions of the matrices, and (c) eigenvalues thus obtained are arranged in a regular array at the output. It is to be noted that the matrix elements of the energy operator are calculated with different basis functions while the crystal potential remains the same for both the valence and the conduction bands. This of course reduces the computation labor to some extent. In computing the integrals we have used the ζ function expansion technique due to Barnett and Coulson[29] while Corbato's[30] approach is adopted for the programming. In this respect the necessary Hartree-Fock space functions for the anions (Li$^+$, Na$^+$, K$^+$) and the cation (Cl$^-$) in analytic form are obtained by fitting the tabulated Hartree-Fock radial functions with a series of Slater's atomic orbitals.[29]

TABLE I. Slater–Koster parameters for KCl. The primed notations are for the K$^+$ functions. (All energies are in Ry.)

Valence states		Conduction states		Localized states	
$E_{xx}(000)$	−0.732 15	$E_{ss}(000)$	−0.049 31	$E_{x'x'}(000)$	−1.760 07
$E_{xx}(110)$	0.001 55	$E_{sx}(110)$	−0.021 79	$E_{x'x'}(200)$	−0.002 92
$E_{xx}(011)$	−0.003 01	$E_{ss}(200)$	0.009 31	$E_{y'y'}(200)$	0.000 72
$E_{xx}(200)$	−0.005 93	$E_{xy,xy}(110)$	−0.047 39	$E_{s'x'}(200)$	−0.000 17
$E_{yy}(200)$	0.005 13	$E_{xy,xy}(011)$	−0.014 37	$E_{s's'}(000)$	−3.035 12
$E_{xy}(110)$	0.004 37	$E_{xy,xz}(011)$	−0.035 71	$E_{s's'}(200)$	−0.000 11
…					
Valence–conduction states		$E_{3z^2-r^2,3z^2-r^2}(000)$	0.456 12	$E_{ss}(000)$	−2.013 20
$E_{z,3z^2-r^2}(002)$	0.003 71	$E_{3z^2-r^2,3z^2-r^2}(110)$	0.012 03	$E_{ss}(200)$	−0.000 09
$E_{z-r^2,x}(011)$	0.004 23	$E_{x^2-y^2,x^2-y^2}(110)$	−0.007 00	…	
$E_{3z^2-r^2,x}(011)$	−0.003 15	$E_{xy,xy}(000)$	0.223 12	Localized–valence states	
$E_{x,xy}(020)$	0.000 77	$E_{xy,3z^2-r^2}(110)$	0.052 93	$E_{s'x}(110)$	−0.000 35
$E_{x,xy}(110)$	−0.000 57	…		$E_{s'y}(110)$	−0.000 51
		$E_{xy,xy}(002)$	0.000 58	$E_{sx}(011)$	−0.000 21
$E_{x,xy}(011)$	0.000 52	…		…	
…				$E_{x'y}(110)$	−0.000 59

Some fits were made by Howland[4] and we made all the fits for our necessary functions. The fitted functions were adjusted slightly to make them mutually orthonormal (and orthogonal) to the numerical inner functions in the case of Cl$^-$. In the OPW portion the core states are formed from the core-state solutions to the free-ion problem. These core states are then formed into Bloch functions and linear combinations of the Bloch functions are formed according to the symmetry group of the wave vector $\vec{k}$ for the point ion in the first Brillouin zone for which a solution is desired. This symmetrization of the basis functions to the one-electron crystal orbital reduces the labor of computation. Our computer programs are oriented in such a way that secular determinants are set up for each $\vec{k}$ value before the call of the subroutine for diagonalization. Owing to the nonorthogonality of the free-ion Hartree-Fock functions $\epsilon(\vec{k})$ comes in the off-diagonal elements. This appearance of the energy parameter $\epsilon(\vec{k})$ in the off-diagonal elements creates a complication; but owing to the advantage that in the outer function approximation for the alkali-halide crystals overlapping of space functions for $n=2$, 3 and $l=0$ with respect to others is very small, some off-diagonal elements containing Ω_{mn} between functions of highest and lowest quantum numbers *viz.* $\Omega_{3x,3s}$, $\Omega_{3s,3xy}$, etc., may be neglected. In this respect it is noted that the largest overlap integral between any two of the free-ion functions which are separated by a normal KCl lattice distance is only ~ 0.70 as compared to one for the maximum overlap. Similar values are obtained for LiCl and NaCl. The overlap integrals for the basis functions located at the second-nearest neighbors are found to be below ~ 0.02 and in some cases, for example, $\Omega_{2s,3x}$, $\Omega_{3s,3y}$, etc., these values are not above ~ 0.001. Beside these small values of the atomic and diatomic overlap integrals, since most of the off-diagonal elements *viz.* $E_{sx}(\vec{k})$, $E_{xz}(\vec{k})$, etc., contain sine functions, they vanish automatically along the directions in which the components of the wave vector $\vec{k}$ are taken to be zero. It is noted that for the cases in which $\epsilon(\vec{k})$ appears in the off-diagonal elements the secular determinants are solved at those values of $\epsilon(\vec{k})$ for which the determinants are zero.

IV. RESULTS AND DISCUSSION

The numerical values of the matrix elements of energy operator are presented in Tables I–III. Since the effect of the admixture of inner states to crystal orbital is the principal aim of our investigation, we have calculated the band parameters from matrices of different orders and the results are plotted in the graphs on a comparison basis.

In the present mixed approach the valence-band widths of LiCl, NaCl, and KCl are found to be 0.14, 0.072, and 0.06 Ry, respectively, as shown in Tables IV–VI. But when the order of the matrices

TABLE II. Slater-Koster parameters for NaCl. The primed notations are for the Na$^+$ functions. (All energies are in Ry.)

Valence states		Conduction states		Localized states	
$E_{xx}(000)$	−0.819 31	$E_{ss}(000)$	−0.072 13	$E_{x'x'}(000)$	−1.1235
$E_{xx}(110)$	0.005 03	$E_{sx}(110)$	−0.021 31	$E_{x'x'}(200)$	−0.002 13
$E_{xx}011)$	−0.003 26	$E_{ss}(200)$	0.011 25	$E_{y'y'}(200)$	0.000 89
$E_{xx}(200)$	−0.003 71	$E_{xy,xy}(110)$	−0.050 21	$E_{s'x'}(200)$	−0.000 13
$E_{yy}(200)$	0.002 85	$E_{xy,xy}(011)$	0.017 93	$E_{ss}(000)$	−2.239 51
$E_{xy}(110)$	0.007 31	$E_{xy,xz}(011)$	−0.048 01	$E_{ss}(200)$	0.000 10
Valence-conduction states		$E_{3z^2-r^2,3z^2-r^2}(000)$	0.616 81	Localized-valence states	
$E_{z,3z^2-r^2}(002)$	0.002 78	$E_{3z^2-r^2,3z^2-r}(110)$	−0.011 23	$E_{s'x}(110)$	−0.000 42
$E_{z,3z^2-r^2}(011)$	0.002 49	$E_{x^2-y^2,x^2-y^2}(110)$	−0.013 25	$E_{s'y}(110)$	−0.000 63
$E_{x,xy}(020)$	0.000 83	$E_{xy,xy}(000)$	0.290 21	$E_{sx}(011)$	−0.000 28
$E_{xy,xy}(110)$	−0.000 49	...		...	
$E_{x,xy}(011)$	0.000 62	$E_{xy,3y^2-r^2}(110)$	0.179 92	$E_{x'y}(110)$	−0.000 67
$E_{z,3z^2-r^2}(110)$	0.003 21	$E_{xy,xy}(002)$	0.000 78	...	
...					

is changed these values are noted to change to some extent. From the heavily drawn curves in Figs. 1–3 it is noted that when the core and the inner functions are excluded from the one-electron crystal orbitals the valence bands broaden, followed by a change in the shape of the energy surfaces. This broadening of the valence bands is expected owing to the absence of the localized basis. But when we consider the uppermost filled *s* states of the anions and the three Cl$^-$ $3p$ states as the basis, then the valence bands are noted to contract. From this phenomenon it can be concluded that the center of gravity of the entire band system remains constant and the shifting in

TABLE III. Slater-Koster parameters for LiCl. The primed notations represent the Li$^+$ functions. (All energies are in Ry.)

Valence states		Conduction states		Localized states	
$E_{xx}(000)$	−0.898 72	$E_{ss}(000)$	−0.083 86	$E_{x'x'}(000)$	−0.703 11
$E_{xx}(110)$	0.009 85	$E_{sx}(110)$	−0.016 03	$E_{x'x'}(200)$	−0.001 87
$E_{xx}(011)$	−0.003 98	$E_{ss}(200)$	0.012 03	$E_{x'x'}(200)$	0.000 92
$E_{xx}(200)$	−0.003 16	$E_{xy,xy}(110)$	−0.053 32	$E_{s'x'}(200)$	−0.000 11
$E_{yy}(200)$	0.001 00	$E_{xy,xy}(011)$	0.019 87	$E_{s's'}(000)$	−1.003 95
$E_{xy}(110)$	0.012 08	$E_{xy,xy}(011)$	−0.065 32	$E_{ss}(200)$	−0.000 07
Valence-conduction states		$E_{3z^2-r,3z^2-r^2}(000)$	0.770 31	$E_{ss}(000)$	−0.987 15
$E_{z,3z^2-r^2}(002)$	0.001 39	$E_{3z^2-r^2,3z^2-r^2}(110)$	−0.007 52	...	
$E_{z,3z^2-r^2}(011)$	0.001 25	$E_{x^2-y^2,x^2-y^2}(110)$	−0.318 62	$E_{ss}(200)$	−0.000 03
$E_{x,xy}(020)$	0.009 11	$E_{xy,xy}(000)$	0.330 61	Localized-valence states	
$E_{x,xy}(110)$	−0.000 41	$E_{xy,3z^2-r^2}(110)$	0.110 07	$E_{s'x}(110)$	−0.000 47
$E_{x,xy}(011)$	0.000 73	...		$E_{s'y}(110)$	−0.000 71
$E_{z,3z^2-r^2}(110)$	0.004 23	$E_{xy,xy}(002)$	0.008 11	$E_{sx}(011)$	−0.000 31
...				...	
				$E_{x'y}(110)$	−0.000 73

TABLE IV. Comparison of the published parameters[a] with the present investigation for KCl. (All energies are in Ry.)

Ref. (Theor.)	Valence-band width	Gap $[E(\Gamma_1)-E(\Gamma_{15})]$	Valence-band location	Conduction band location lower upper
Ref. 4	0.1120	···	0.78 – 0.88	··· ···
Ref. 6	0.0604	0.500	0.40 – 0.50	0.18 – 0.73
Ref. 12	0.058	0.502	0.69 – 0.76	0.24 – 1.00
Ref. 15	0.190	0.640	0.71 – 0.90	··· ···
Ref. 14	0.064	0.651	0.68 – 0.73	··· ···
Ref. 14a	0.057	0.062	0.86 – 0.92	··· ···
Ref. 23	0.106	···	0.80 – 0.90	··· ···
Present	0.060	0.680	0.72 – 0.79	0.03 – 0.46
Ref. (Expt.)				
Ref. 17	0.050	···	0.68 – 0.74	··· ···
Ref. 7[b]	0.103	0.630	0.72 – 0.83	0.4 – 1.5
Ref. 13[b]	0.062	0.643	0.76 – 0.86	··· ···
Ref. 21	0.180	0.801	0.72 – 0.90	0.08 – 0.40
Ref. 22	0.350	···	0.40 – 0.60	··· ···

	s-d-like band gap			
Ref. (Theor.)	Γ	*K*	*L*	*X*
Ref. 12	0.37	···	0.13	···
Present	0.26	0.24	0.25	0.15

[a] Parameters for the localized bands not shown in the table.

[b] Semiempirically deduced results.

TABLE V. Comparison of the published parameters[a] with the present investigation for NaCl. (All energies are in Ry.)

Ref. (Theor.)	Valence-band width	Gap $[E(\Gamma_1)-E(\Gamma_{15})]$	Valence-band location	Conduction-band location lower upper
Ref. 1	0.30	···	0.80 – 0.84	···
Ref. 2	0.251	0.759	0.69 – 0.72	···
Ref. 3	0.2477	···	0.73 – 0.76	···
Ref. 31	0.082	0.550	0.81 – 0.90	0.08 – 0.80
Ref. 12	0.100	···	0.76 – 0.86	0.23 – 1.00
Ref. 15	0.195	0.700	0.80 – 0.92	0.15 – 1.5
Ref. 14	0.074	···	0.72 – 0.80	···
Present	0.072	0.730	0.82 – 0.90	0.04 – 0.65
Ref. (Expt.)				
Ref. 7[b]	0.100	0.723	0.81 – 0.91	···
Ref. 13[b]	0.070	0.70	0.80 – 0.87	···
Ref. 21	0.230	0.892	0.76 – 1.01	0.18 – 0.35
Ref. 22	0.360	···	0.53 – 0.90	···

	s-d band gap			
Ref. (Theor.)	Γ	*K*	*L*	*X*
Ref. 12	0.47	···	0.16 Ry	···
Present	0.34	0.32	0.32	···

[a] Parameters for localized bands have not been introduced in the table.

[b] Semiempirically deduced results.

TABLE VI. Comparison of the published parameters[a] with the present investigation for LiCl. (All energies are in Ry.)

Ref. (Theor.)	Valence-band width	Gap $[E(\Gamma_1)-E(\Gamma_{15})]$	Valence-band locations	Conduction bands lower upper
Ref. 12	0.160	0.64	0.82−0.98	0.15−1.00
Ref. 31	0.092	0.68	0.80−0.90	⋯ ⋯
Ref. 15	0.592	0.90	0.78−0.84	0.17−1.6
Present	0.140	0.780	0.88−1.00	0.02−0.81
Ref. (Expt.)				
Ref. 7[b]	0.120	0.750	0.86−0.89	⋯ ⋯
Ref. 13[b]	0.150	0.693	0.79−0.83	⋯ ⋯
Ref. 21	0.380	0.900	0.85−0.88	0.07−0.36

	s-*d*-like band gap			
Ref. (Theor.)	Γ	*K*	*L*	*X*
Ref. 12	0.47	⋯	0.30	⋯
Present	0.41	0.37	0.38	⋯

[a] Parameters for localized bands have not been introduced in the table.

[b] Semiempirically deduced results.

band location is confined within the key levels of different bands. Apart from the consideration of these changes it is noted that the widths obtained from the 14th ordered secular equations are in agreement with experiment.

There are several recent calculations available for the comparison of KCl band structure. In a very recent calculation the present authors[23] obtained a width of 0.1065 Ry from an LCAO approach. De Cicco[6] in his augmented-plane-wave approach obtained a width of 0.0620 Ry for the same band. On the other hand, Howland[4] by an LCAO tight-binding calculation obtained a width of 0.112 Ry. Of course, when the Cl^- 3*p* functions were taken only as the basis the bandwidth broadens considerably. In the OPW approach Kunz[12] obtained a width of 0.058 Ry. These values are not consistent with the recent *ab initio* band calculation of Kunz and Lipari[15,16] in which the correlation effects of polarization are taken into account.

Experimentally it is known that the very recent work of Pong and Smith[21] is the only published bandwidth which is a direct experimental result. In this measurement, the KCl valence band is found to be 0.18 Ry wide while our calculation gives 0.060 Ry.

A few theoretical predictions are available for the comparison of the valence-band width of NaCl. The present value of 0.072 Ry agrees well with Kunz's[12,31] result. But the *ab initio* approach of Kunz and Lipari[15,16] does not agree with the present value which might be due to the polarization effects taken into account by them. On the other hand, the semiempirical pseudopotential approach of Fong and Cohen[14] supports the present result as shown in Table IV. The widths obtained by Phillips[7] and Roessler *et al.*[13] are consistent with the present calculation. But the experimental value (0.23 Ry) for NaCl due to Pong and Smith[21] does not agree with our result (0.072 Ry).

In the case of LiCl the present valence-band width of 0.14 Ry is found to be consistent with 0.16 and 0.12 Ry due to Kunz[12] and Phillips,[7] respectively, whereas the *ab initio* approach of Kunz *et al.*[15] does not agree well with our calculations. The semiempirical interpretation due to Roessler and Walker[13] suggests that the value should be about 0.15 Ry. On the other hand, the optical data obtained recently[32,33] yield results consistent with present calculation. The experimental value (0.380 Ry) obtained by Pong and Smith[21] for LiCl does not agree with calculated value (0.14 Ry).

The values for the band gaps obtained are 0.78, 0.73, and 0.68 Ry for LiCl, NaCl, and KCl, respectively. The experimental gaps for LiCl, NaCl, and KCl as collected by Brown *et al.*[17d] are 0.69, 0.64, and 0.64 Ry, respectively. Our results are comparable to Kunz's[12] calculations. On the other hand, the *ab initio* values due to Kunz and Lipari[15] are 0.90, 0.70, and 0.64 Ry, respectively. They suggest that this improvement is due to their consideration of correlation effect and for NaCl they[15] have obtained a gap of 0.63 Ry using an improved dielectric function. The gap for KCl in our investigation is not in good agreement with 0.50 Ry due to De Cicco.[6] The empirical pseudopotential results for NaCl and KCl due to Fong and Cohen[14] are consistent with ours. Roessler and Walker[13] obtained a value of 0.64 Ry for KCl. Semiempirically, Phillips[7] obtained 0.635 and 0.63

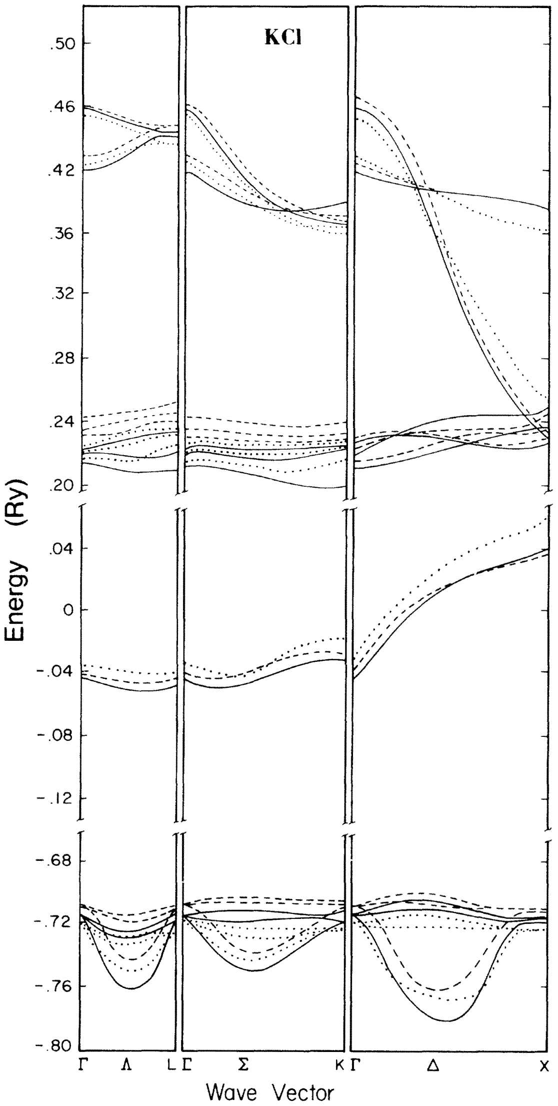

FIG. 1. Band structure of KCl. Heavily drawn and the dotted curves represent $E(\vec{k})$ for the 9th and the 14th ordered equations, respectively. Dashed curves in the valence band are obtained from the Cl^- $3p$ and K^+ $4s$ as the basis, while those in the conduction region are obtained from the five d states of the cation as the basis.

Ry for KCl and NaCl, respectively, which agree with the present calculation.

In the case of conduction bands, the s-like key levels in all the cases are found to lie below the vacuum level. For LiCl, NaCl, and KCl the possible s-like states that are obtained at the center of the Brillouin zone are 0.045, 0.121, and 0.065 Ry below the vacuum level. In this respect, Kunz's[12] OPW results are comparable. But De Cicco[6] obtained s-like conduction states above the vacuum level. Lately the *ab initio* approach due to Kunz and Lipari[15] suggests that states for s-like conduction bands are possible below the vacuum level. Of course the locations of the conduction states may be shifted upward by changing the order of admixture of basis functions. In Figs. 1–3 it is noted that when the inner functions are excluded from the crystal orbital the s-like conduction states shift upward over an energy range of about 0.004 Ry. In this respect when we have taken only the five d-states of Cl^- as the basis this upward shifting is noted. Thus it may be suggested that one may obtain the lower states of the conduction bands at or above the vacuum level by excluding the inner orbitals from the crystal orbital and taking into account the empty states in the

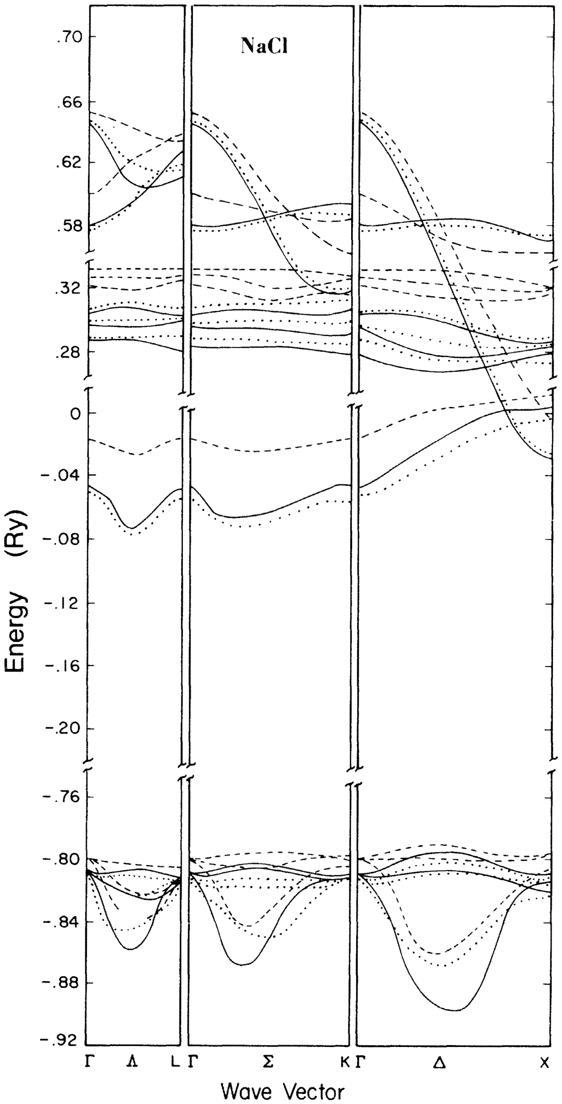

FIG. 2. Band structure of NaCl. Heavily drawn and the dotted curves represent $E(\vec{k})$ for the 9th and the 14th ordered equations, respectively. Dashed curves in the valence band are obtained from Cl^- $3p$ and Na^+ $3s$ states as the basis while those in the conduction states are obtained from the five d states of the cation as the basis.

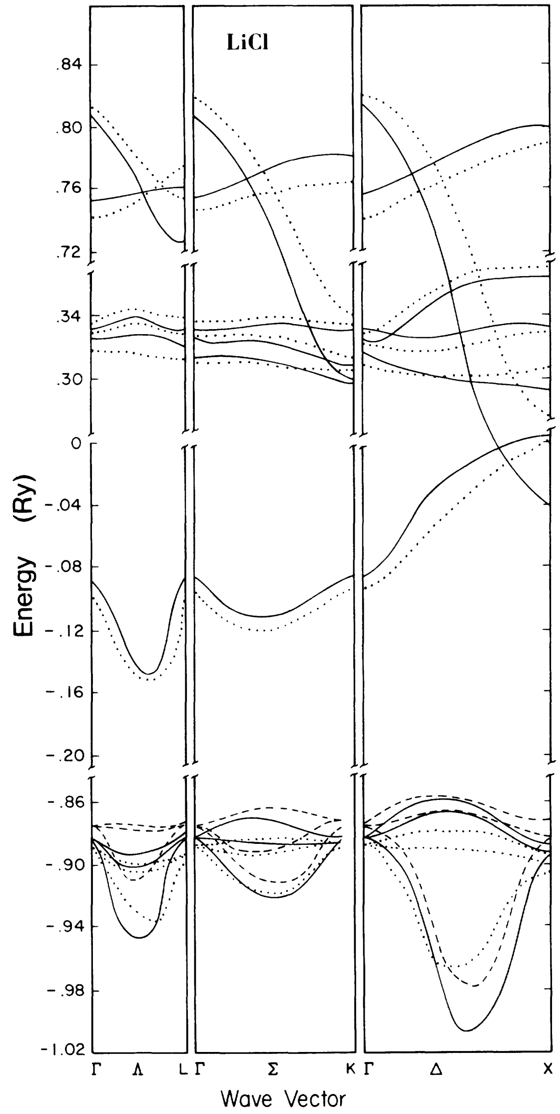

FIG. 3. Band structure of LiCl. Heavily drawn and the dotted curves represent $E(\vec{k})$ for the 9th and the 14th ordered equations, respectively. Dashed curves represent $E(\vec{k})$ only for the $3p$ states of the anion as the basis.

basis. The uppermost d-like conduction states for LiCl, NaCl, and KCl are obtained around 0.81, 0.65, and 0.64 Ry, respectively. Of course, for different modes of admixture these values are found to change symmetrically. This phenomenon suggests that as long as one is concerned with the conduction bands, the range of energy for the locations of the key levels does not significantly respond to the entrance of the inner states to the crystal orbital. This phenomenon is expected due to the appearance of lower values of the off-diagonal elements in the conduction region. Experimentally the locations of the conduction bands have some interesting features. Phillips[7] in his semiempirical approach predicts that the conduction states below the vacuum level are possible which is interpreted as a consequence of photon energy around 12 eV. But in a very recent photoemission study by Pong and Smith[21] it is predicted that when photon energy in the range 19–23 eV is used no conduction state exists below the vacuum level. In this experiment the bottom of the conduction bands is always found above 1.0 ± 0.2 eV of the vacuum level for LiCl and KCl crystals. Of course, this value of the bottom energy for NaCl is found to be 1.0 ± 0.3 eV. This interpretation does not agree with our calculation.

In the present investigation the gaps between the s- and d-like conduction bands for KCl, NaCl, and LiCl are found to be 0.26, ~0.34, and ~0.41 Ry, respectively. On the other hand, at K the respective values are 0.22, 0.32, and 0.38 Ry. It is interesting to note that at X in the lower part of the conduction bands for NaCl and LiCl the key levels of the s- and d-like bands are found to undergo hybridization, whereas a distinct gap of 0.15 Ry for KCl is obtained. From the topological viewpoint of the conduction bands, the present results are comparable to those due to Kunz,[12] although there are certain qualitative disagreements. A comparison of gaps at certain highly symmetric points is presented at the lower parts of Tables IV–VI.

We may also mention that the band structures for KCl, NaCl, and LiCl that we have obtained exhibit an indirect band gap which has not been obtained by other authors. Unfortunately this indirect band gap is not supported by known experimental data. The optical absorption data of Teegarden and Baldini[19] or, Eby *et al.*[8] do not exhibit any low-energy temperature-dependent tail which would be present if an indirect band gap were present.

It is interesting to compare the ranges of energy in which the key levels are found to occur with those[32,33] experimentally measured. In Tables IV–VI a comparison is given from which it is noted that our results are consistent with most of the recent experiments. The deviations which are noted in case of localized bands might be due to our outer function approximation in the filled region. It is clear, however, that in cases where correlation effects are negligible the mixed approach can produce a better description of the valence and the lower part of the conduction bands than the LCAO and OPW methods can independently. And if correlation effects are greater, then to satisfy Pong and Smith's[21] experimental prediction one must take into account the polarization effect exclusively. Of course, we are waiting for further interpretations of their results since these conflict with most of the previous experiments.

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APPENDIX: CONSTRUCTION OF THE CRYSTAL POTENTIAL

In this Appendix we give a brief analysis of the construction of the crystal potential and develop the matrix elements of the energy operator. The matrix elements $E_{mn}(\vec{r}, \vec{R}_g)$ that appear in Eq. (11) are given by the following equation:

$$E_{mn}(\vec{r}, \vec{R}_g) = \int \varphi_m(\vec{r}_1 - \vec{R}_g)^* \left(Q_1 + 2\int Q_{12}\rho(\vec{r}_1, \vec{r}_2)\right) \times \varphi_n(\vec{r}_1)\, d\vec{v}_1 - \int Q_{12}\varphi_m(\vec{r}_1 - \vec{R}_g)^* \times \rho(\vec{r}_2, \vec{r}_1)\, \varphi_n(\vec{r}_2)\, d\vec{v}_1\, d\vec{v}_2\,, \qquad \text{(A1)}$$

where we have taken one and two electron, one- and two-center integrals to build up the energy elements.

In constructing the crystal potential and introducing the correlation effects to it we start from the expression of the crystal charge density. The electronic part of this charge density is split into two parts:

$$\rho(\vec{r}_2) = \sum_g \rho_g(\vec{r}_2) + \rho_{\mathrm{OV}}(\vec{r}_2)\,. \qquad \text{(A2)}$$

In Eq. (A2), $\rho_g(\vec{r}_2)$ is the spherical electronic charge density of a free ion at site g and is given by

$$\rho_g(\vec{r}_2) = -2\sum_p \varphi_p(\vec{r}_2)^*\, \varphi_p(\vec{r}_2) \qquad \text{(A3)}$$

and $\rho_{\mathrm{OV}}(\vec{r}_2)$ is what is called the overlap charge density, given by

$$\rho_{\mathrm{OV}}(\vec{r}_2) = -2\sum_{p,q} \xi_{pq}\varphi_p(\vec{r}_2)^*\, \varphi_q(\vec{r}_2)\,. \qquad \text{(A4)}$$

On a particular site g, the free-ion electron charge density

$$-2\sum_p \varphi_p(\vec{r}_2)\, \varphi_p(\vec{r}_2)$$

and the nuclear charge Z_g together give a net charge z_g which is $+1$ for Li^+, Na^+, or K^+ and -1 for Cl^-. Since the sum of z_g over the two ions in a single unit cell is zero, the sum of nuclear charge and free-ion charge distributions throughout the crystal gives a net charge zero. The effect of the overlap charge density

$$-2\sum_{p,q} \xi_{pq}\varphi_p(\vec{r}_2)\, \varphi_q(\vec{r}_2)$$

is to shift the electron charge from the density predicted by a simple superposition of free-ion charge densities. This shift decreases the electron charge density in regions of maximum overlap between pairs of free ions and it compensates by forcing an increase in the electronic charge in the region of a nucleus. This redistribution of charge arises from orthonormalizing the one electron functions and it can be described as an effect of the exclusion principle. In the present approximation it is essentially this distribution of charge which provides the repulsion between ions in the crystal and which causes the crystal energy bands to rise as the interionic distance decreases below its normal values.

In atomic units, the one- and two-electron operators are given by

$$Q_1 = -\nabla_1^2 + V(\vec{r}) = -\nabla_1^2 - \sum_g \frac{2Z_g}{\vec{r}_{1g}}, \quad Q_{12} = \frac{2}{\vec{r}_{12}}\,, \qquad \text{(A5)}$$

where ∇_1^2 is the Laplacian operating on the coordinates of electron one, Z_g is the nuclear charge of the ion at site g, and $\vec{r}_{12}$ is the distance between two electrons.

On using Eq. (A1) and the electronic charge density represented by Eq. (A2) the matrix element takes the form

$$\begin{aligned} E_{mn}(\vec{r}, \vec{R}_g) = {} & \int \varphi_m(\vec{r}_1 - \vec{R}_g)^* (-\nabla_1^2)\, \varphi_n(\vec{r}_1)\, d\vec{v}_1 + \sum_{g'=0,g} \int \varphi_m(\vec{r}_1 - \vec{R}_g)^* \left(-\frac{2Z_{g'}}{\vec{r}_{1g'}} - \int \rho_{g'}(\vec{r}_2)\frac{2}{\vec{r}_{12}}\, d\vec{v}_2\right) \varphi_n(\vec{r}_1)\, d\vec{v}_1 \\ & - \sum_{g'=0,g} \iint \varphi_m(\vec{r}_1 - \vec{R}_g)^*\, \rho_{g'}(\vec{r}_2, \vec{r}_1)\frac{2}{\vec{r}_{12}}\, \varphi_n(\vec{r}_2)\, d\vec{v}_1\, d\vec{v}_2 + \int \varphi_m(\vec{r}_1 - \vec{R}_g)^* \left(-\int \frac{2}{\vec{r}_{12}}\rho_{\mathrm{OV}}(\vec{r}_2)\, d\vec{v}_2\right) \varphi_n(\vec{r}_1)\, d\vec{v}_1 \\ & - \sum_{g'\neq 0,g} \int \varphi_m(\vec{r}_1 - \vec{R}_g)^*\, \rho_{g'}(\vec{r}_2, \vec{r}_1)\frac{2}{\vec{r}_{12}}\, \varphi_n(\vec{r}_2)\, d\vec{v}_1\, d\vec{v}_2 - \iint \varphi_m(\vec{r}_1 - \vec{R}_g)^*\, \rho_{\mathrm{OV}}(\vec{r}_2, \vec{r}_1)\frac{2}{\vec{r}_{12}}\, \varphi_n(\vec{r}_2)\, d\vec{v}_1\, d\vec{v}_2 \\ & + \int \varphi_m(\vec{r}_1 - \vec{R}_g)^* \left(\sum_{g'\neq 0,g} \frac{2[\rho_{g'}(\vec{r}_2) + Z_{g'}]}{\vec{r}_{1g'}}\right) \varphi_n(\vec{r}_2)\, d\vec{v}_2 + \sum_{g'\neq 0,g} \int \varphi_m(\vec{r}_1 - \vec{R}_g)^* \frac{2Z_{g'} + \rho_{g'}(\vec{r}_2) - \rho_{\mathrm{OV}}(\vec{r}_2)}{\vec{r}_{1g'}} \\ & \times \varphi_n(\vec{r}_1)\, d\vec{v}_1\,, \end{aligned} \qquad \text{(A6)}$$

where the basis with quantum number n is taken to be at the origin and where the exchange and overlap exchange charge densities $\rho_g(\vec{r}_2, \vec{r}_1)$ and $\rho_{OV}(\vec{r}_2, \vec{r}_1)$ are defined by

$$\rho_g(\vec{r}_2, \vec{r}_1) = \sum_p \varphi_p(\vec{r}_2)^* \, \varphi_p(\vec{r}_1) \tag{A7}$$

and

$$\rho_{OV}(\vec{r}_2, \vec{r}_1) = \sum_{p,q} \xi_{pq} \varphi_p(\vec{r}_2)^* \, \varphi_q(\vec{r}_1) , \tag{A8}$$

respectively. In Eq. (A6) the exchange energy terms are named as follows: Exchange energy

$$\langle V\rangle_{ex} = -\sum_{g'=0,g} \iint \varphi_m(\vec{r}_1 - \vec{R}_g)^* \rho_{g'}(\vec{r}_2, \vec{r}_1) \times \frac{2}{\vec{r}_{12}} \varphi_n(\vec{r}_2) \, d\vec{v}_1 \, d\vec{v}_2 . \tag{A9a}$$

Coulomb exchange energy

$$\langle V\rangle_{Cex} = -\sum_{g'\neq 0,g} \iint \varphi_m(\vec{r}_1 - \vec{R}_g)^* \rho_{g'}(\vec{r}_2, \vec{r}_1) \times \frac{2}{\vec{r}_{12}} \varphi_n(\vec{r}_2) \, d\vec{v}_1 \, d\vec{v}_2 . \tag{A9b}$$

Overlap exchange energy

$$\langle V\rangle_{ov\,ex} = -\iint \varphi_m(\vec{r}_1 - \vec{R}_g)^* \rho_{OV}(\vec{r}_2, \vec{r}_1) \times \frac{2}{\vec{r}_{12}} \varphi_n(\vec{r}_2) \, d\vec{v}_1 \, d\vec{v}_2 , \tag{A9c}$$

where $\langle V\rangle_{ex}$ involves only contributions from site g and the origin; it is atomic or, diatomic terms depending on whether $\vec{R}_g$ is or is not zero. The last two terms $\langle V\rangle_{Cex}$ and $\langle V\rangle_{ov\,ex}$ depend on the presence of the atoms or, atom pair in the crystal. The crystal Coulomb correction term that appears in the matrix elements in Eq. (A6) as an autocorrelation effect is given by

$$\langle V\rangle_{cor} = \sum_{g'\neq 0,g} \int \varphi_m(\vec{r}_1 - \vec{R}_g)^* \left(-\frac{2Z_{g'}}{\vec{r}_{1g'}}\right) \varphi_n(\vec{r}_2) \, d\vec{v}_1 , \tag{A10}$$

whose physical significance is that it is a nonlocal term and it approaches zero rapidly with increasing $\vec{r}$.

The crystal potential which is developed by the crystal charge density consideration requires some discussion owing to its usage both in the valence and the conduction bands. It is assumed that the valence electron wave function is that which chiefly arises from a Cl^- $3p$ orbital. To form the potential one had an electron in a given unit cell associated with a Cl^- ion at the center of that cell. This cell center is considered to be the origin. There are five other valence electrons in that unit cell. In the other unit cells there are six valence electrons. The Cl^- core electrons and the electrons associated with the alkali are the same in all unit cells. Thus the valence electrons in question see a potential formed from three types of contributions. These are (i) the halogen ion at the origin, (ii) the short-range part of the other alkali and halogen ions, and (iii) the long-range parts of the other alkali and halogen ions. In this regard it is to be noted that the degree of self-consistency of the potential that we have used has not been checked.

The effect of this potential is that the electron in question sees a potential which is due to all the remainder of the electrons in the lattice. Thus this potential is different from the one usually used in which the electron in question is considered to be an extra electron in the lattice.

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