

## Study of the electronic structure of twelve alkali halide crystals

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(Received 8 March 1982)

In this manuscript we use nonrelativistic self-consistent Hartree-Fock theory to compute the electronic structure of twelve alkali halides. Only compounds containing Cs or I are excluded because the author believes that relativistic effects should be included for such compounds. Correlation effects are included by our previously developed methods. The calculations are performed to compare to photoemission-type data. Extensive comparisons to such data are made. In this calculation a new version of the local-orbitals theory is used, and the bands are computed with the use of a modern development of the mixed-basis method.

## I. INTRODUCTION

Although lacking the intense technological interest of the compound or elemental semiconductors, the alkali halides have been of intense scientific interest. This is due to their utility as targets in scintillation detectors, for example, and as prototype systems for the development of theoretical models and experimental techniques. The alkali halides consist of the twenty compounds of the alkalis Li, Na, K, Rb, and Cs and the halogens F, Cl, Br, and I. The generic alkali halide may be symbolized as  $MX$ . These systems are highly ionic in nature as seen from either cohesive energies and elastic constants<sup>1</sup> or the Phillips ionicity scale,<sup>2</sup> and all form in the double interpenetrating fcc crystal structure (rocksalt or NaCl structure). It is noted that for CsCl, CsBr, and CsI, the simple cubic structure is the stable phase at STP and the rocksalt modification occurs only at elevated pressures. In this manuscript I concentrate on twelve of these compounds. That is, I exclude the compounds containing Cs or I. This is done because I employ a nonrelativistic theory, and relativistic modifications for such Cs or I containing compounds can modify valence or conduction levels by 1 eV or more, an unacceptable error at this point.<sup>3</sup> Thus here we consider LiF, LiCl, LiBr, NaF, NaCl, NaBr, KF, KCl, KBr, RbF, RbCl, and RbBr.

Due to the prototype nature of the  $MX$  systems, many band-structure calculations exist for these systems. However, the vast majority of such calculations are not self-consistent, and furthermore, most techniques employed have been for only one or two materials in the sequence, making identification of trends impossible. The only exception to this has been the series of studies performed by the

author over a decade ago.<sup>4</sup> This study was not self-consistent and included all except the simple cubic  $MX$  crystals. This study employed a Slater exchange-correlation potential and a crude self-interaction correction. Basically these results were in good accord with other non-self-consistent calculations for the same systems. Several definite trends emerged from such studies. These were that band gaps were usually 2–4 eV smaller than experiment and the valence-band widths were narrow ( $\sim 0.5$  eV for RbX, 0.67 eV for KX, 1.2 eV for NaX, 2 eV for LiX). The narrow valence widths accorded well with the common prejudices of this period.<sup>5</sup>

Potentially more accurate self-consistent techniques were first introduced for KCl by DeCicco.<sup>5</sup> In this calculation the Slater exchange was employed and predicted a band gap of 6.2 eV and a valence width of 0.67 eV. Later self-consistent calculations were by the author and Lipari<sup>6</sup> for LiCl, LiBr, NaCl, NaBr, and KCl, and by Mickish and the author for LiF.<sup>7</sup> These studies employed a Hartree-Fock (HF) formalism which overestimates the band gap by  $\sim 8$  eV or so. Correlation corrections were incorporated which reduced the gap error to about 1 eV or less. More recent self-consistent studies for the  $MX$ 's include LiF by Euwema *et al.*,<sup>8</sup> LiF by Brenner<sup>9</sup> employing Hartree-Fock methods, LiF, LiCl, NaF, NaCl, KF, and KCl by Perrot<sup>10</sup> using an approximate Hartree-Fock with a muffin-tin approximation to Coulomb and exchange integrals and correlation corrections, and for LiF by Zunger and Freeman<sup>11</sup> employing local density plus corrections for the exchange-correlation potential and for relaxation and self-interaction corrections.

The early work of Lipari and Kunz<sup>6</sup> used a

primitive version of the mixed-basis (MB) method, and likely an inadequate number of plane waves were included to guarantee convergence of the valence levels. The study by Perrot<sup>10</sup> is not truly self-consistent, and the muffin-tin effects in ionic crystals are capable of inducing 1 eV or greater errors in conduction levels.<sup>12</sup> The other cited self-consistent studies are, to my belief, accurate representations of their methodology.

The one striking feature of the Hartree-Fock method calculation is width of the valence bands (3–8 eV), in stark contrast with the older studies. These findings were not without basis, however, since older x-ray emission data of O'Brien and Skinner<sup>13</sup> had suggested such widths were to be expected. Unfortunately, at the time when most work was being expended on the *MX* system, photoemission data was unavailable. Recent photoemission data substantiates the idea of wide valence bands (3–4 eV) for *MX* systems<sup>14</sup> and also using angular resolved techniques provides evidence of the conduction-band structures as well. I believe it is therefore timely to present a series of studies on the *MX*'s which incorporates recent technology into the calculations and is compared with the recent photoemission data, optical data, and other high-quality calculations.

In the next section, the techniques employed are discussed. In Sec. III, the results are presented, and comparisons of these results to other theory and experiment is given. Finally, conclusions are given in Sec. IV.

## II. THE THEORETICAL APPROACH

One begins with the usual nonrelativistic Hamiltonian for the "infinite" solid after making the Born-Oppenheimer approximation. In this case,  $H$  is

$$H = - \sum_{i=1}^n \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i=1}^n \sum_{I=1}^N \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i,j=1}^n \frac{e^2}{|\vec{r}_i - \vec{r}_j|} . \quad (1)$$

In Eq. (1), one uses lower case letters to signify electron properties and upper case letters to signify nuclear properties. The mass of the electron is  $m$ , its charge magnitude  $e$ , and its position  $\vec{r}_i$ . If spin dependence were needed, then  $\vec{x}_i$  would be the position spin coordinate. The nuclear charge at site  $I$  is  $Z_I$ , and the coordinate is  $\vec{R}_I$ .

Ideally one wishes to solve, exactly,

$$H\Psi_\alpha(\vec{x}_1, \dots, \vec{x}_n) = E_\alpha\Psi_\alpha(\vec{x}_1, \dots, \vec{x}_n) , \quad (2)$$

for all relevant  $\alpha$  and  $n$ , but such is impossible for extended systems, and a series of systematic approximations is necessary. My approach is to employ the Hartree-Fock method and then to correct it in a potentially systematic way. For the *MX*'s in the ground state, one has filled shells, and hence the restricted or the unrestricted Hartree-Fock method (RHF or UHF) has the same solutions when iterated to self-consistence, and either solution is isomorphic with a Heitler-London (valence-bond) solution.<sup>1</sup> Therefore one approximates  $\Psi_\alpha$  by

$$\Psi_\alpha = (n!)^{-1/2} \text{Det}[\phi_i(\vec{x}_i)] . \quad (3)$$

The one-electron orbitals are constrained to be orthonormal and eigenstates of the  $z$  component of spin (Pauli  $\alpha$  or  $\beta$  dependence) and *all* pertinent crystal symmetry operations. In these cases such restrictions do not affect energy minimization for the ground state. If the  $\phi$ 's are chosen, optimally, one obtains the canonical RHF equation, defining the  $\phi$ 's

$$F\phi_i(\vec{k}, \vec{x}_i) = \epsilon_i(\vec{k})\phi_i(\vec{k}, \vec{x}_i) , \quad (4)$$

where

$$F = - \frac{\hbar^2}{2m} \nabla^2 - \sum_I \frac{Z_I e^2}{|\vec{r} - \vec{R}_I|} + e^2 \int \frac{\rho(\vec{x}^1, \vec{x}^1)}{|\vec{r} - \vec{r}^1|} d\vec{x}^1 - e^2 \rho(\vec{x}, \vec{x}^1) / |\vec{r} - \vec{r}^1| \hat{P}(\vec{x}^1, \vec{x}) , \quad (5)$$

and

$$\rho(\vec{x}, \vec{x}^1) = \sum_{\vec{k}} \sum_i \phi_i(\vec{k}, \vec{x}) \phi_i^\dagger(\vec{k}, \vec{x}^1) . \quad (6)$$

In Eq. (5),  $\hat{P}$  is the operator which replaces coordinate  $\vec{x}$  with  $\vec{x}^1$ , and in Eq. (6) the sum is over all occupied orbitals [i.e., those contained in the determinant in Eq. (3)]. Other solutions to Eq. (4) not contained in the trial wave function are termed virtual orbitals. In the context of Koopmans's theorem, the eigenvalue of an occupied orbital  $\epsilon_i(\vec{k})$  is the negative of the energy needed to remove that electron from the crystal, and the eigenvalue  $\epsilon_a(\vec{k})$  for a virtual orbital is the negative of the energy gained by adding an electron to the system.<sup>15</sup>

In this context it is noted rigorously that the virtual eigenvalues represent a transition from an  $n$ -electron system to an  $(n+1)$ -electron system, whereas the occupied represent a transition from an  $n$ -electron system to an  $(n-1)$ -electron system.

This is because the Fock equation for occupied orbitals rigorously excludes the electron's self-interaction and that equation for the virtual orbitals includes the interaction of the virtual electron with the entire  $n$  electrons in the ground state. Therefore, energy differences between occupied and virtual levels do not truly represent excitation energies of the system unless the self-interaction term is negligible. This is reasonable as long as the transition is from an occupied Bloch function to a virtual Bloch function so that the size of the neglected term goes as  $N^{-1}$ ,  $N$  being the number of unit cells in the crystal.

It is clear from Eq. (5) that the Fock operator is a unique functional of the first-order density matrix  $\rho$ . It is also clear from Eq. (6) that  $\rho$  depends upon *all* occupied orbitals. In principle, the  $\vec{k}$  is a three-dimensional vector spanning the first Brillouin zone in the zone scheme used here. There are therefore an infinite number of points to be considered in forming  $\rho$ . Conventionally one uses a numerical quadrature in obtaining  $\rho$  over a three-dimensional mesh in  $\vec{k}$  space. Used carefully, such a procedure is accurate and acceptable. It is also unnecessary for closed-shell systems. One may exploit the isomorphism of the Bloch with the valence-bond picture and rotate into a system of local orbitals. The basic techniques have been developed by Adams,<sup>16</sup> Gilbert,<sup>17</sup> and the author.<sup>18</sup> This one solves the alternate equation

$$(F + A^F)\hat{\phi}_i(\vec{r} - \vec{R}_A) = \hat{\epsilon}_i \hat{\phi}_i(\vec{r} - \vec{R}_A), \quad (7)$$

where

$$A^F = \hat{\rho} A_A \hat{\rho} \quad (8)$$

and

$$\hat{\rho} = \sum_{\substack{Ai \\ Bj}} \hat{\phi}_i(\vec{x} - \vec{R}_A) S_{AiBj}^{-1} \hat{\phi}_j^\dagger(\vec{x}^1 - \vec{R}_B), \quad (9)$$

and

$$S_{AiBj} = \int \phi_i^*(\vec{x} - \vec{R}_A) \phi_j(\vec{x} - \vec{R}_B) d\vec{x}, \quad (10)$$

and (most importantly)

$$\rho(\vec{x}, \vec{x}^1) \equiv \hat{\rho}(\vec{x}, \vec{x}^1). \quad (11)$$

Thus solving Eq. (7) provides the unique values of  $\rho$  needed to obtain the Fock operator  $F$ , for *any* Hamiltonian choice of  $A$  in Eq. (8). Ideally, one picks a set of  $A$ 's to produce localized atomiclike, orbital solutions as implied by the four  $\hat{\phi}_i(\vec{r} - \vec{R}_A)$ . The method used to choose  $A$  is given in general by Gilbert.<sup>17</sup>

In the prior studies of the author with Lipari

and Mickish,<sup>6,7</sup> a single center localization choice for  $A^F$  was used. This choice imposes severe constraints on the basis sets used to solve Eq. (7) and can permit nonlocal solutions to occur. The ramifications of this were explored by Gilbert and the author.<sup>19</sup> In the time since the development of the local orbitals band method by the author and its use for the alkali halides, the method has been used for other systems, including FeO, CoO, NiO,<sup>20</sup> and TiO.<sup>21</sup> In the cases of FeO, CoO, and NiO, proper localization occurred, but in the case of TiO, a partially delocalized self-consistent solution was obtained which time has proven to be unsatisfactory. In order to ensure against delocalization, the choice of  $A^F$  has been modified in this series of studies.

One modifies here the prescription given by the author<sup>22</sup> some time ago. Let us define a site local part of  $\rho$  called  $\rho_A$

$$\rho_A = \sum_{i=1}^{n_A} \phi_i(\vec{x} - \vec{R}_A) \phi_i^\dagger(\vec{x}^1 - \vec{R}_A). \quad (12)$$

In Eq. (12) only occupied orbitals at site  $A$  are included. One has

$$\rho \rho_A = \rho_A \rho = \rho_A,$$

for all  $A$ . This implies, however, that

$$\rho = \sum_A \rho_A + \sum_{A,B} \rho_{AB} \neq \sum_A \rho_A.$$

As in the past, we divide  $F$  into two parts:  $F_A$ , the part containing only  $A$  site terms, and  $U_A$ , which contains the balance of  $F$ .  $U_A$  is then decomposed into terms for each  $\rho_B$  and  $\rho_{AB}$ . Consider here only  $\rho_B$  terms now and let  $V_B$  be the part of  $U_A$  which contains only  $B$ -site contributions. That is

$$V_B = -\frac{e^2 Z_B}{|\vec{r} - \vec{R}_B|} + \int \frac{\rho_B(\vec{x}^1, \vec{x}^1)}{|\vec{r} - \vec{r}^1|} d\vec{r}^1 - e^2 \rho_B(\vec{x}, \vec{x}^1) / |\vec{r} - \vec{r}^1| \hat{P}(\vec{x}^1, \vec{x}). \quad (13)$$

Then further split  $V_B$  into a Madelung or long-range part  $V_B^L$  and the rest or non-Coulomb part  $V_B^S$ . Pick  $A_A$  using the following prescription:

$$A_A = -\rho_A \sum_{B \neq A} V_B^S \rho_A - \sum_B \rho_B V_B^S \rho_B. \quad (14)$$

Thus  $A^F$  becomes

$$A^F = -\rho_A \sum_{B \neq A} V_B^S \rho_A - \sum_B \rho_B V_B^S \rho_B. \quad (15)$$

This formalism is so far exact and has full multi-

center localization. In addition, in keeping with the ideas of Ref. 23, all four-center integrals are eliminated in solving both the local orbital equation and in projecting energy bands using a linear combination of atomic orbitals (LCAO) technique in which the local orbitals are the basis set. This result is exact in the local orbital Hartree-Fock formulation. This procedure has been followed here for the first time, and well-localized solutions have been found for all 12 systems separately. In this case, Na, for example, is found separately for NaF, NaCl, and NaBr. The same applies to all ions here. Thus one has here solutions for 24 ions. It is unreasonable to use journal space to publish solutions for all 24 ions, but the author will provide any or all solutions to any interested party upon request.

It is worth making a few comments about the solutions. Basic observations are, the positive ion solutions in crystal differ by typically one part in  $10^4$  from free-ion solutions in terms of charge density. The negative-ion crystal solutions differ by up to one part in  $10^2$  in terms of charge density from the free-ion solutions. This deviation for the negative ion is significant; and in all cases considered here, the negative ion in the crystal is more compact than the same ion in free space. This is a strong indication of the efficacy of the multicenter localization used here. The other comment of practical nature is that the equations with multicenter localization converge much more rapidly than when single-center localization is employed. The enhancement is between a factor of 2 and 10. This is fortunate in that the need for fewer iterations helps offset the extra effort in performing the multicenter localization. In all cases the self-consistency in terms of charge density was two parts in  $10^7$ . A Slater-type basis set was used throughout of triple-zeta accuracy.

The output of the local orbital procedure is the first-order density matrix  $\rho$  which uniquely defines the Fock operator  $F$  [Eqs. (4)–(6)] and a set of local orbitals,  $\hat{\phi}_i(\vec{x} - \vec{R}_A)$  which exactly span the occupied part of the Fock space. That is, one can let a Fock occupied orbital  $\phi_j(\vec{k}, \vec{x})$  be given as

$$\phi_j(\vec{k}, \vec{x}) = (N)^{-1/2} \sum_{l=\text{occ}}^m \sum_A a_l^j(\vec{k}) \times e^{i\vec{k} \cdot \vec{R}_A} \hat{\phi}_l(\vec{x} - \vec{R}_A). \quad (16)$$

The coefficients  $a_l^j(\vec{k})$  are determined by diagonalizing the  $m \times m$  matrix for the Fock operator in

terms of the basis of Bloch projected local orbital solutions. Here one has  $m$  occupied orbitals per unit cell. That is, in terms of the local orbitals, the occupied Fock space is exactly determined by a minimum basis set.

This procedure does not provide for the virtual (conduction) bands at all. One may remedy this by adding additional tight-binding orbitals to the basis set. This was done by Mickish and Kunz<sup>7</sup> and is commonly done by others as well.<sup>8,9,11</sup> However, economic considerations compel one to use a small set of such additional orbitals, and obtaining accurate conduction bands is difficult but not impossible. It is the opinion of this author that plane waves form a much more natural basis set for the conduction levels. This was formally developed a long time ago into the mixed basis (MB) method.<sup>3,24</sup> That is, a LCAO basis, Eq. (16), and plane wave are used. The plane-wave set here is simply,

$$x(\vec{k}, \vec{K}_\mu, \vec{r}) = (N\Omega)^{-1/2} \exp[i(\vec{k} + \vec{K}_\mu) \cdot \vec{r}]. \quad (17)$$

In Eq. (17),  $\Omega$  is the unit cell volume,  $\vec{k}$  a vector in the first Brillouin zone, and  $\vec{K}_\mu$  a reciprocal-lattice vector. In order to keep the number of  $\vec{K}_\mu$  small (say 100 or less), it is essential to include all occupied LCAO orbitals in the basis set. If this is not done, one is facing a problem similar to that faced by orthogonalized-plane-wave practitioners. For the alkali fluorides, one would need  $\sim 6000$  plane waves for convergence and for the rest, 400–800 plane waves. If one solves general points in the Brillouin zone as the author does, this is far too many plane waves.

Past attempts to use valence tight-binding functions and plane waves have resulted in numerical instabilities which limited the utility of such a method.<sup>25–27</sup> In the previous work the problem was recognized and corrected by eliminating diffuse LCAO functions from the basis set and enlarging the plane-wave part. This solution eliminates accuracy problems but also limits one's ability to evaluate energy bands efficiently to points of high symmetry. It was assumed that the overcomplete nature of the basis set was responsible, and no successful attempt to circumvent the problem was reported. The author has investigated these problems in this study and concurs that the basis set is potentially overcomplete, *but* for the few plane waves used, this is *not* the source of the problem. The problem is entirely in evaluating the trivial overlap integral between a plane wave and an atomiclike orbital  $\hat{\phi}_i(\vec{x})$ . That is,

$$S_{iA}(\vec{k}, \vec{K}_\mu) = \int \exp[i(\vec{k} + \vec{K}_\mu) \cdot \vec{r}] \hat{\phi}_i(\vec{r} - \vec{R}_A) d\tau$$

is often in gross error. The error in numerically evaluating this integral may be in the first significant figure. This can cause the overlap matrix to become singular. Even if it is not singular errors of several eV are possible in energy eigenvalues. In all crystals studied the eigenvalues of the  $S$  matrix were never less than 0.1 using accurate evaluation of the overlap integral. Other ways of evaluating this integral are possible as well and also potentially accurate. The problem stems from using a linear or exponential mesh which, although accurate for the exponentially decaying  $\hat{\phi}_i$ , resonates with the oscillatory complex exponential, generating substantial errors. The solution is to go either to a very dense mesh which is too costly or to evaluate the overlap analytically. Since our LCAO basis is simply a contracted Slater-type orbital set, the analytic evaluation of the relevant integrals is trivial. Doing so eliminates completely the numerical instabilities, and this method is employed throughout in these studies. Thus all occupied local orbitals are used in the basis set. The number of plane waves was also explored here. I desire to obtain conduction bands for the first 20 eV above the conduction-band edge. The number tried was varied from one to 89. The net result is that in going from 15 to 27 plane waves, the conduction levels shift by about 0.25 eV over the first 20 eV, whereas in going from 27 to 89 plane waves, the shifts are 0.1 eV or less. Since errors of 0.1 eV or so are far less than the uncertainties in the physical model used, for this study a set of 27 plane waves was used.

It is well known that Hartree-Fock calculations overestimate the optical band gap by sizeable amounts.<sup>6-10</sup> The inclusion of correlation corrections is essential if one is to compare the experiment.<sup>28</sup> Correlation corrections are therefore included here. The basic method is an update of the method described by Pantelides *et al.*<sup>22</sup> A molecular-cluster calculation is used to evaluate the relaxation<sup>29</sup> or short-range correlation, and the electronic polaron, the long-range, or polarization corrections. This is fully described in the literature and needs no elaboration here. There is a point of interpretation, though, which is not well known. If one considers the formation of hole states, for example (i.e., the valence bands as defined for photoemission measurements), the presence of strong relaxation effects imply that the hole state in the *best* single determinant UHF model is a localized hole. In this event, the constraint of Bloch

symmetry applies to the entire many-electron state, not the individual orbitals. This point was recognized after the necessity of including relaxation corrections was discovered and hence merits emphasis here.<sup>30</sup> All results here include these correlation corrections. Probably the earliest recognitions of this point in a calculation was for the core hole states of O<sub>2</sub> by Bagus.<sup>30</sup>

The actual calculation of the  $\vec{k}$ -dependent correlation (polarization corrections) corrections for the valence band was carried out using the actual valence local orbitals to describe the valence wave functions and the formalism of the electronic polaron as derived for hole states by the author in 1972.<sup>22</sup> The computation of the  $\vec{k}$ -independent correlation correction for conduction electrons was carried out using the electronic polaron formalism as originally derived by Toyozawa.<sup>22</sup> A discussion of the  $\vec{k}$  independence for conduction electrons has been given by the author.<sup>22</sup> The relaxation corrections are evaluated by computing the difference in total energy for a molecular cluster embedded in a self-consistent environment potential simulating the remainder of the solid and then taking the difference by the binding energy of that electron obtained by the total energy difference and subtracting from it the equivalent Koopmans's theorem binding energy. This technique and its derivation has been given by Kunz and Klein.<sup>30</sup> The relaxation correction is  $\vec{k}$  independent provided the hole state is represented by a local hole in the best single-determinant approximation and provided there is not substantial  $\vec{k}$ -dependent hybridization between bands originating from different atomic energy levels. It is noted that if the relaxation corrections for differing atomic energy levels are the same then hybridization considerations become irrelevant. In the current systems all bands are narrow in the sense that relaxation corrections are as large or larger than a bandwidth, thus making the local hole description viable in the best single-determinant case. In these cases except for the RbX system and a lesser degree the KX systems the various valence bands do not strongly hybridize. In the case of RbX and KX some outer-level hybridization is present. However, the relaxation energy of the outer levels is comparable enough so that the neglect of  $\vec{k}$  dependence is minimal. The author believes this effect is less than 0.2 eV here at worst. In principle the conditions for  $\vec{k}$  independence of relaxation are not satisfied by the conduction bands. In this case however the small size of this correction is sufficient to allow one to ignore the  $\vec{k}$ -dependent part of the effect.

There is another point worth making here. This concerns the self-interaction terms in the Coulomb potential. As is well known, this term should not be present, and in the Hartree-Fock model it is exactly cancelled by a like term in the exchange potential. This is not true in local density approaches, and much effort is being expended in making such corrections to these models.<sup>31</sup> The tight-binding Hartree-Fock method based upon the local orbitals method can provide a model upon which to structure such a self-interaction correction. For simplicity consider a tightly bound solid

such that *at least* initially one may neglect local orbital overlap. Thus, here

$$\rho(\vec{x}, \vec{x}^1) \cong \sum_A \rho_A(\vec{x}, \vec{x}^1). \quad (18)$$

Consider a basis of *local orbitals*  $\hat{\phi}_i(\vec{x} - \vec{R}_A)$ . The effect of self-interaction is most pronounced for the diagonal element of  $F$  with this basis set. Therefore, consider here this element,  $F_{AiAi}$ , where

$$F_{AiAi} = \langle \phi_i(\vec{x} - \vec{R}_A) | F | \phi_i(\vec{x} - \vec{R}_A) \rangle.$$

Again neglecting overlaps, this reduces to

$$F_{AiAi} = \left\langle \phi_i(\vec{x} - \vec{R}_A) \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2 Z_A}{|\vec{r} - \vec{R}_A|} + e^2 \int \frac{\rho_A(\vec{x}^1, \vec{x}^1)}{|\vec{r} - \vec{r}^1|} d\vec{x}^1 \right. \right. \\ \left. \left. - e^2 \rho_A(\vec{x}, \vec{x}^1) / |\vec{r} - \vec{r}^1| \hat{P}(\vec{x}^1, \vec{x}) \right| \phi_i(\vec{x} - \vec{R}_A) \right\rangle. \quad (19)$$

It is clear that the self-interaction part here behaves exactly as in the atomic case. That is, for the diagonal element, the Fock operator behaves like that for  $n - 1$  electrons and the "hole" is atomiclike. This may be generalized for cases in which overlap is not to be ignored by simply including the overlap correction in forming  $F$ . The effect of this is to reduce the strength of the self-interaction correction. Nonetheless, for tightly bound systems such as  $MX$  in which the greatest overlap is 0.05 or less (1.0 would be the maximum possible overlap), one may expect the self-interaction correction to be atomiclike to great precision.

### III. RESULTS OF THIS STUDY

The self-consistent Hartree-Fock energy bands were computed for LiF, NaF, KF, RbF, LiCl, NaCl, KCl, RbCl, LiBr, NaBr, KBr, and RbBr. Correlated energy bands were also computed for these 12 systems. The energies of selected points in the first Brillouin zone for all 12 systems are given in Table I. The Hartree-Fock and the correlated energy bands are shown in Figs. 1–12. In Table II, the theoretical and experimental band gaps and valence-band widths are given. Finally, in Table III, the band structure for NaCl as determined by angular resolved photoemission is also given and compared to present results as well as other band calculations. Since only NaCl has had angular resolved photoemission data available, I

begin the discussion with NaCl. In Table IV the lattice parameters used are given. In Table V sample RHF, correlation, and relaxation correction data are given for NaCl and KCl.

#### A. NaCl

Optical absorption experiments determine a fundamental band gap for NaCl of 9.0 eV,<sup>32</sup> and photoemission data finds a valence-band width of 3 eV.<sup>33</sup> The present calculation predicts a band gap of 10.0 eV and a valence-band width of 3.0 eV. The bands are seen in Fig. 1. These predictions are in reasonable agreement with prior correlated Hartree-Fock results.<sup>6,9,10</sup> It is noted here that the valence bands found by Lipari and Kunz were a bit wider. I interpret this problem to be due to the MB method used then in which valence local orbitals were excluded and insufficient plane waves could be used to insure complete convergence of the valence states. This criticism is consistent with the absolute energy of the valence levels found by Lipari and Kunz which is somewhat too high. The inaccuracy here is  $\sim 1$  eV or less. Similar criticism may be leveled at the other early MB Hartree-Fock studies.

There are other high-quality NaCl calculations using local density corrections<sup>34,35</sup> or empirical pseudopotentials.<sup>36</sup> The local density calculation of Ref. 34 has the muffin-tin potential adjusted to produce the experimental band gap as does the empirical calculation of Ref. 36. The not adjusted lo-

TABLE I. Partial list of energies for some valence and conduction levels in the 12 alkali halides. Energies are in Ry and include correlation. Upper valence levels and lower conduction levels of a given symmetry are given.

Level	System											
	LiF	NaF	KF	RbF	LiCl	NaCl	KCl	RbCl	LiBr	NaBr	KBr	RbBr
Valence States												
$\Gamma_{15}$	-0.77	-0.69	-0.60	-0.51	-0.55	-0.63	-0.63	-0.61	-0.46	-0.64	-0.56	-0.44
$X_5^1$	-0.85	-0.74	-0.62	-0.50	-0.62	-0.70	-0.67	-0.66	-0.60	-0.75	-0.57	-0.44
$X_4^1$	-1.00	-0.82	-0.67	-0.52	-0.82	-0.85	-0.78	-0.71	-0.70	-0.86	-0.65	-0.45
$L_3^1$	-0.80	-0.72	-0.62	-0.53	-0.59	-0.67	-0.66	-0.67	-0.51	-0.69	-0.60	-0.45
$L_2^1$	-0.94	-0.89	-0.76	-0.56	-0.79	-0.81	-0.72	-0.72	-0.75	-0.91	-0.69	-0.46
Conduction States												
$\Gamma_1$	0.26	0.19	0.20	0.30	0.16	0.11	0.11	0.15	0.16	0.10	0.08	0.08
$\Gamma_{25}^1$	1.56	1.20	0.85	0.76	0.77	0.65	0.52	0.49	0.64	0.52	0.45	0.33
$X_1$	0.87	0.83	0.68	0.61	0.20	0.30	0.40	0.46	0.16	0.18	0.33	0.29
$X_3$	0.92	0.72	0.51	0.46	0.40	0.34	0.27	0.27	0.33	0.25	0.23	0.22
$X_4^1$	1.34	1.08	0.87	0.76	0.94	0.75	0.58	0.59	0.93	0.69	0.52	0.36
$L_1$	1.53	1.16	0.77	0.73	0.96	0.76	0.53	0.36	0.35	0.64	0.23	0.11
$L_2^1$	0.41	0.54	0.58	0.49	0.16	0.20	0.29	0.48	0.27	0.17	0.48	0.43
$L_3$	1.20	1.31	1.11	0.95	0.53	0.61	0.70	0.71	0.74	0.46	0.59	0.26

cal density calculation of Ref. 35 predicts a band gap of 5.0 eV. The older HF + correlation result of Lipari and Kunz is 10.0 eV, and the muffin-tinned Hartree-Fock result of Perrot is 8.4 eV. The effect of muffin-tinning the Fock exchange is to reduce exchange and thus to underestimate the self-interaction correction. Therefore, the smaller band gap obtained in Ref. 10 is understandable as are other deviations from a non-muffin-tin calculation.

The valence-band width of Lipari and Kunz is

3.8 eV with the criticism leveled earlier, and Perrot predicts a width of 1.5 eV, again subject to the above criticism. The present result was stated earlier as 3.0 eV. The local density results are 0.6 eV from Ref. 34 and 1.7 eV from Ref. 35. The empirical potential result is 1.0 eV. Clearly here the adjustments made to match the band gap in Refs. 34 and 36 have a deleterious effect on the valence-band structure. The detailed results for NaCl may be seen in Table III, comparing all calculations to the angular resolved photoemission data.<sup>32</sup> It is

TABLE II. Theoretical band gap and valence-band width, including correlation corrections for the 12 alkali halides, is presented along with pertinent experimental data. Results are in eV.

System	Quantity			
	Theoretical band gap	Experimental band gap	Theoretical valence width	Experimental valence width
LiF	14.0	14.2	3.1	3.5–6.0
NaF	12.0	11.5	2.7	
KF	10.9	10.8	2.2	
RbF	11.0	10.3	1.7	
LiCl	9.7	9.4	3.6	5 ± 0.5
NaCl	10.0	9.0	3.0	3.0 ± 0.3
KCl	10.0	8.7	2.4	2.3 ± 0.3
RbCl	10.3	8.5	2.2	1.6 ± 0.2
LiBr	8.4	7.6	3.9	
NaBr	10.0	7.1	3.6	3.5 ± 0.5
KBr	8.7	7.4	2.5	
RbBr	7.1	7.2	1.3	1.6 ± 0.2

TABLE III. Internal band transitions for NaCl as given by angular resolved photoemission data, compared to the present calculation and to other calculations. Energies are in eV.

Transition	Expt.	This paper	Ref. 36	Ref. 34	Ref. 6	Ref. 10	Ref. 35
Valence Levels							
$\Gamma_{15}-\Gamma_{15}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\Gamma_{15}-X_5^1$	$-1.4\pm 0.2$	-1.1	-0.2	-0.2	-1.3	-0.6	-0.5
$\Gamma_{15}-X_4^1$	$-2.4\pm 0.2$	-2.9	-1.0	-0.6	-3.8	-1.5	-1.7
Conduction Levels							
$\Gamma_1-\Gamma_1$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$X_1-\Gamma_1$	$2.4\pm 0.5$	2.6	1.0	3.1	2.9	3.4	3.4
$X_3-\Gamma_1$	$3.0\pm 0.5$	3.1	1.0	4.0	3.0	2.0	2.6
$\Delta_{1\text{min}}-\Gamma_1$	$4.7\pm 0.5$	5.2	3.6	5.0	6.0		5.2
$X_4^1-\Gamma_1$	$8.0\pm 0.5$	8.7	8.8	5.2	7.4	5.2	5.7
$X_5-\Gamma_1$	$12.0\pm ?$	11.7	7.3	9.0	11.3	10.3	
$\Gamma_{25}^1-\Gamma_1$	$8.2\pm 0.2$	7.3	3.7	6.9	7.6	5.6	6.0
$\Gamma_{12}-\Gamma_1$	$9.7\pm ?$	11.1	4.2	8.4	10.0	8.1	

quite clear from this table that the correlated Hartree-Fock models overall provide the best fit to this data and the empirical potential model<sup>36</sup> is the worst. The local density models are of intermediate success, although the nonadjusted calculation of Ref. 35 fails to order the levels at  $X$  correctly. This failure is in common with the author's own nonempirical local density results.<sup>4</sup> The author feels that the present calculation is the one to be preferred based upon these comparisons.

The difference between present results and those of Lipari and Kunz or Perrot are not unreasonable, given the numerical expedients employed by the older work. As was seen in Sec. II, this current

TABLE IV. Lattice parameters used for the present study are given. Units used are a.u. (1 a.u.  $\approx$  0.53 Å). Bands are not sensitive to small variations in lattice constant.

System	$a$
LiF	7.600
LiC	9.700
LiBr	10.380
NaF	8.723
NaCl	10.620
NaBr	11.260
KF	10.083
KCl	11.858
KBr	12.424
RbF	10.650
RbCl	12.349
RbBr	12.953

calculation employs much better technique in solving the Fock equation. We will also see in the next discussion that for LiF, for which other very high accuracy Fock results are available, the present results agree very well indeed with other calculations.

## B. LiF

In recent years, LiF has received the most theoretical attention of all the alkali halides. Unfortunately, the basic experimental data is not yet as well developed as for NaCl. Hartree-Fock or studies beyond Hartree-Fock are reported by Mickish *et al.*,<sup>7</sup> Euwema *et al.*,<sup>8</sup> Brenner,<sup>9</sup> and Perrot.<sup>10</sup> Self-consistent local density studies are reported by Menzel *et al.*<sup>37</sup> and by Zunger and Freeman.<sup>11</sup>

The calculation by Menzel *et al.*<sup>37</sup> is a conventional LCAO self-consistent-field (SCF) local density calculation. In this calculation, a prediction of 10.6 eV is made for the fundamental band gap. This result is somewhat smaller than the currently accepted value of 14.2 eV.<sup>37</sup> This calculation also obtains a valence-band width of about 2.45 eV. The calculation of Zunger and Freeman<sup>11</sup> obtains similar initial results. However, much effort is expended in this study to transcend the limitations of the local density model. Long-range correlation corrections are included, as are self-interaction corrections and relaxation effects. The inclusion of these corrections raise the computed band gap to 13.9 eV, which compares favorably with experi-



TABLE V. RHF energy eigenvalues, the correlation corrections, the relaxation corrections, and the final correlated band energies are given for both NaCl and KCl. Since correction terms to RHF for the conduction band (c.b.) are  $\vec{k}$  independent, only the  $\Gamma_1$  conduction level is given. For occupied levels several selected symmetry points are given for the outermost valence band (v.b.). Results are in Ry (1 Ry = 13.6 eV).

System	Level	$\epsilon$ (RHF)	Correlation correction	Relaxation correction	Correlated energy
NaCl	c.b. $\Gamma_1$	0.33	-0.17	-0.05	0.11
NaCl	v.b. $\Gamma_{15}$	-0.84	0.10	0.11	-0.63
NaCl	$X'_5$	-0.92	0.11	0.11	-0.70
NaCl	$X'_4$	-1.09	0.13	0.11	-0.85
NaCl	$L'_3$	-0.88	0.10	0.11	-0.67
NaCl	$L'_2$	-1.04	0.12	0.11	-0.81
KCl	c.b. $\Gamma_1$	0.30	-0.16	-0.03	0.11
KCl	v.b. $\Gamma_{15}$	-0.82	0.08	0.11	-0.63
KCl	$X'_5$	-0.86	0.08	0.11	-0.67
KCl	$X'_4$	-0.94	0.09	0.11	-0.78
KCl	$L'_3$	-0.85	0.08	0.11	-0.66
KCl	$L'_2$	-0.91	0.08	0.11	-0.72

ment. The valence-band width is essentially unmodified by this set of corrections.

The Hartree-Fock level calculations are all in excellent agreement with one another. That level of agreement includes the current calculation. The Perrot calculation is a muffin-tin one and is in general in poorest agreement with the other three. The Mickish *et al.* and the Euwema *et al.* calculations both employ a SCF LCAO method, whereas the current calculation employs the updated MB technique. At the Hartree-Fock level, these latter three calculations agree within 0.1 to 0.2 eV

throughout the valence range and the first 15 eV or so of the conduction structure. The Hartree-Fock band gap is, for example, 22.8 eV, according to Mickish *et al.*, 23 eV according to Euwema *et al.*, 22.5 eV according to Perrot, and 22.7 eV in the present study. Valence-band details also compare well with a theoretical width of 3 eV being obtained by all but Perrot. The Perrot value is about 1 eV less and probably reflects the effects of muffin-tinning the exchange. Agreement within the conduction bands is also good. Therefore, based upon LiF, for which many high-quality results are available, we conclude the current technique is highly accurate.

The inclusion of correlation substantially reduces the Hartree-Fock band gap. In the present case a band gap of 14.0 eV is obtained, which compares well with the prediction of 14.1 eV of Mickish *et al.* and the experimental value of  $14.2 \pm 0.2$  eV. The computed valence width is 3.1 eV. In this case the experimental width is not well established. Early x-ray emission data of O'Brien and Skinner<sup>13</sup> suggests a width of  $3.5 \pm 0.5$  eV. Other x-ray photoemission spectroscopy studies predict a width of  $\sim 6$  eV.<sup>38,39</sup> Photoemission studies find a narrower width of about 4.5 eV.<sup>40</sup> These results strongly suggest that all calculations, except perhaps the Fock ones, underestimate the bandwidth by significant amounts. These results, ambiguous as they are, also establish the broad nature of the valence levels in the alkali halides. The LiF results from this study are seen in Fig. 2.

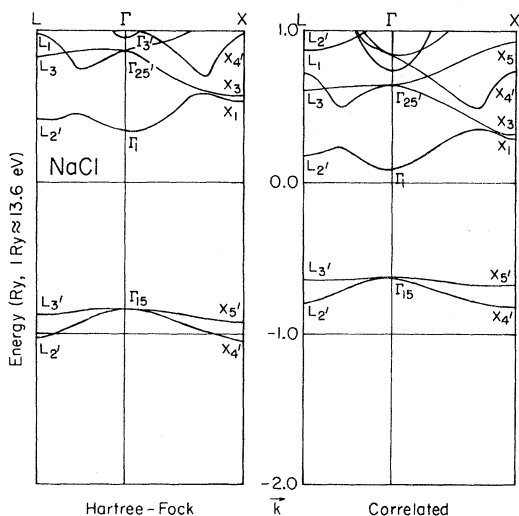


FIG. 1. Hartree-Fock and correlated energy bands for NaCl are seen.

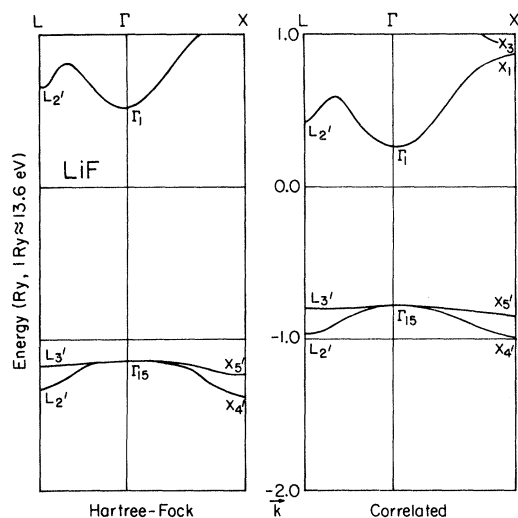


FIG. 2. Hartree-Fock and correlated energy bands for LiF are seen.

### C. LiCl and LiBr

The results for LiCl and LiBr are given in Figs. 3 and 4. The only other available self-consistent calculations are early ones and are subject to the type of errors previously discussed and are not further discussed. In these calculations, band gaps of 9.7 and of 8.4 eV are obtained for LiCl and LiBr, respectively. The experimental values respectively are 9.4 and 7.6 eV.<sup>41</sup> The computed valence-band width is 3.6 eV for LiCl and 3.9 eV for LiBr. The author is not aware of any experimental values for this parameter for LiBr but LiCl has a width of  $5 \pm 0.5$  eV.<sup>14</sup>

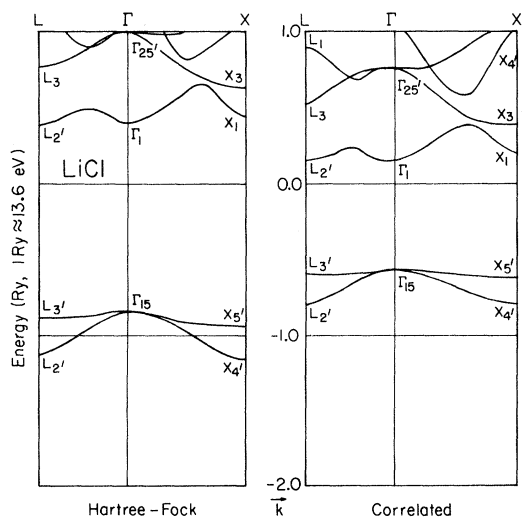


FIG. 3. Hartree-Fock and correlated energy bands for LiCl are seen.

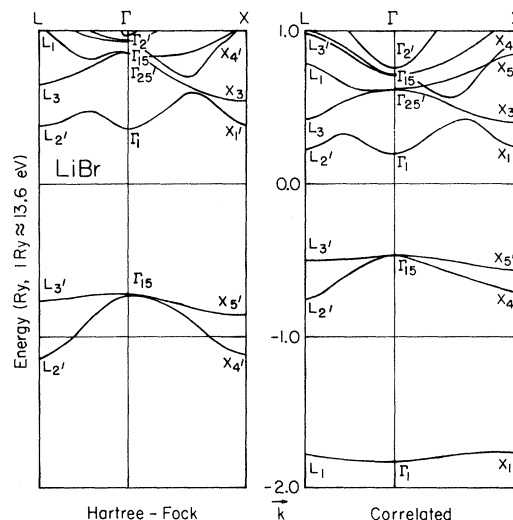


FIG. 4. Hartree-Fock and correlated energy bands for LiBr are seen.

### D. NaF and NaBr

The current bands for NaF are seen in Fig. 5 and for NaBr in Fig. 6. Again, only early self-consistent results are available and a comparison is not useful. The computed band gaps are 12.0 eV for NaF and 10.0 eV for NaBr. The experimental values are 11.5 and 7.1 eV, respectively.<sup>41</sup> The computed valence width is 2.7 eV for NaF and 3.6 eV for NaBr. Unpublished SCF results for NaF due to Mickish and available to the author agree well with the current study. NaBr has an experimental valence width of  $3.5 \pm 0.5$  eV.<sup>14</sup>

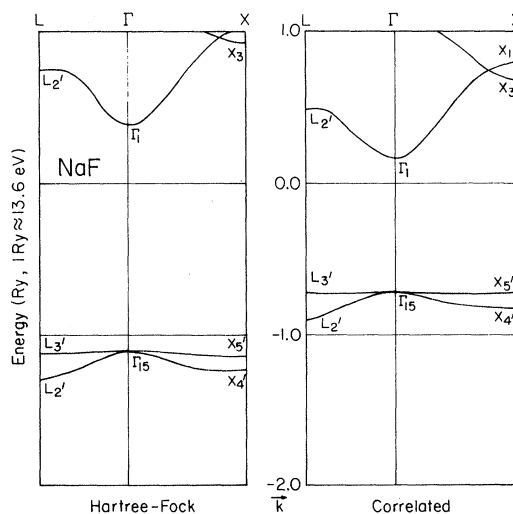


FIG. 5. Hartree-Fock and correlated energy bands for NaF are seen.

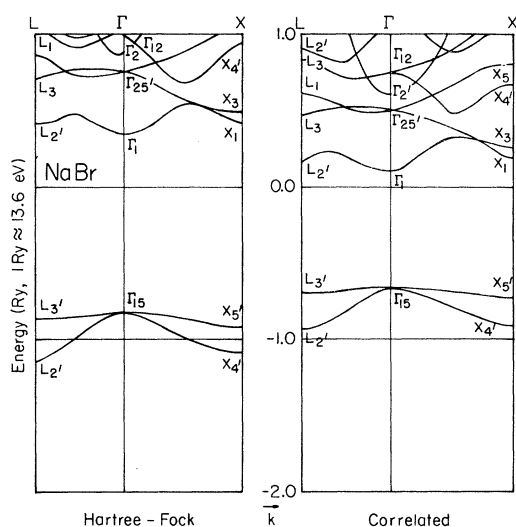


FIG. 6. Hartree-Fock and correlated energy bands for NaBr are seen.

#### E. KF, KCl, and KBr

KCl has received a high quality SCF augmented-plane-wave local density band study by DeCicco.<sup>5</sup> This study finds a valence-band width of 0.67 eV and a band gap of 6.2 eV. The corresponding experimental values are 2.75 (Ref. 42) and 8.7 eV.<sup>41</sup> This study finds a valence width of 2.4 eV and a band gap of 10.0 eV. This case points out an often found feature of local density calculations for insulators. That is, very narrow valence widths are found except for LiF. This was seen in early studies by this author and others.<sup>3,4</sup> For KF and KBr the valence widths are 2.2 and 2.5 eV, and the band gaps are 10.9 and 8.7 eV. The experimental gaps are known and are 10.8 eV for KF and 7.4 eV for KBr.<sup>41</sup> The bands are seen in Figs. 7–9.

#### F. RbF, RbCl, and RbBr

The current calculations are the only self-consistent ones for these substances. The predicted band gaps are 11.0 eV for RbF, 10.3 eV for RbCl, and 7.1 eV for RbBr. The corresponding experimental values are 10.3 eV, 8.5 eV, and 7.2 eV. The theoretical valence widths are found to be 1.7 eV for RbF, 2.2 eV for RbCl, and 1.3 eV for RbBr. Experimental determinations of the valence widths are  $1.6 \pm 0.2$  eV for RbCl and RbBr.<sup>42</sup> The bands are shown in Figs. 10–12.

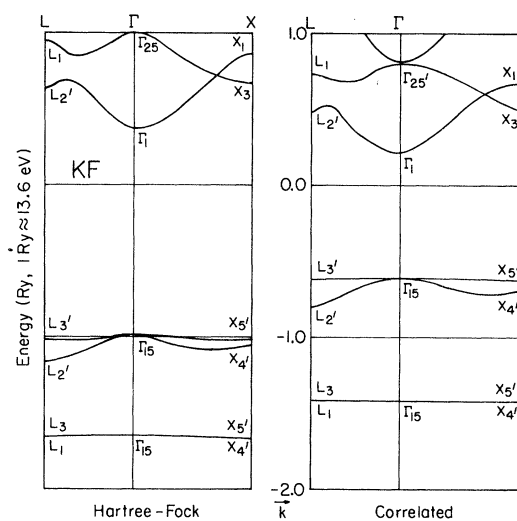


FIG. 7. Hartree-Fock and correlated energy bands for KF are seen.

#### IV. DISCUSSION AND CONCLUSIONS

In this paper a comprehensive study of the energy bands for the 12 fcc alkali halide crystals containing neither Cs nor I has been presented. The calculations are fully self-consistent in the RHF limit. Self-consistency has been achieved using a newly developed version of the local orbitals technique in which full multicenter localization is employed. This method has been found to converge rapidly and to produce orbital rotations usually more compact than those for the equivalent free ions. The degree of change from free-ion to crys-

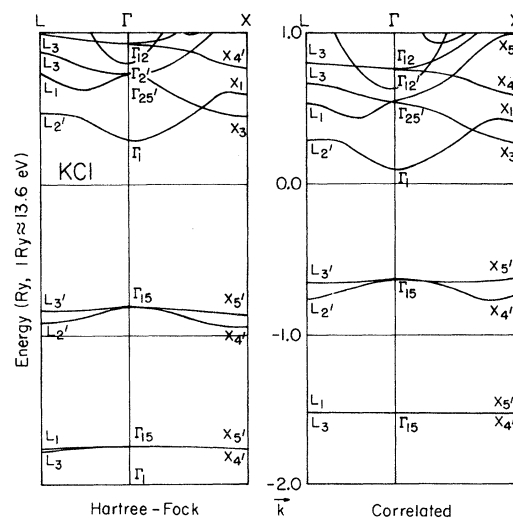


FIG. 8. Hartree-Fock and correlated energy bands for KCl are seen.

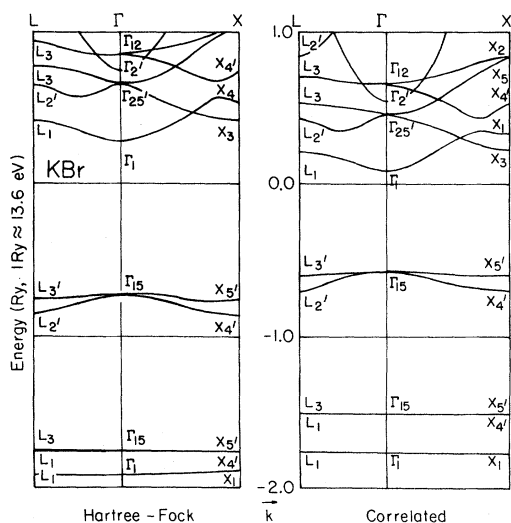


FIG. 9. Hartree-Fock and correlated bands for KBr are seen.

tal orbitals was small. This is in keeping with the original local orbital philosophy of Gilbert<sup>17</sup> in which atoms in a crystal were postulated to be merely weakly distorted atoms in free space. One, however, finds Cl in RbCl, say, to differ enough from Cl in LiCl so that it is not advisable to use the same set of Cl<sup>-</sup> orbitals for all chlorides. This is unfortunate and forces one to obtain each ion individually in each system.

Energy bands were then computed at 256 points in the first Brillouin zone using a newly revised, highly efficient version of the mixed basis method. Owing to the better basis set possible with the new

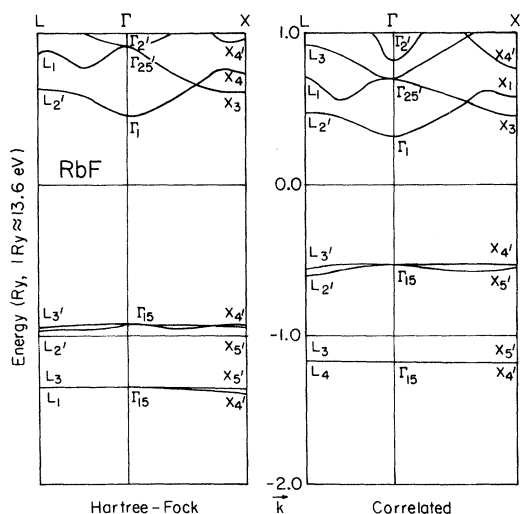


FIG. 10. Hartree-Fock and correlated bands for RbF are seen.

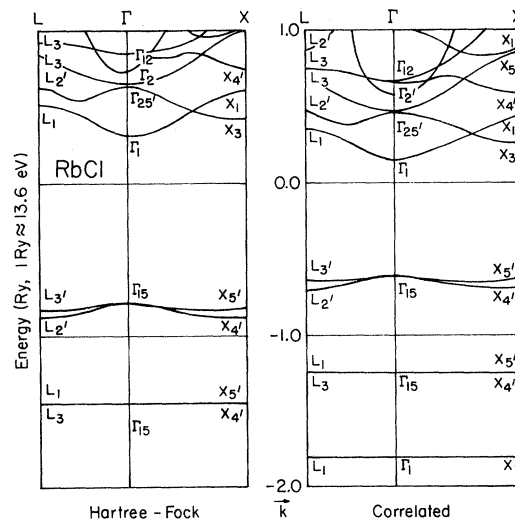


FIG. 11. Hartree-Fock and correlated energy bands for RbCl are seen.

code, results are not fully comparable to the older, not well converged, results of Lipari and the author.<sup>6</sup> This was fully developed in the text. However, the not quite as sensitive conduction bands are in reasonable agreement for the cases of LiCl, LiBr, NaCl, KCl, and NaBr. This is seen here in Table III for the case of NaCl.

The agreement with experiment for the band gap is usually quite reasonable as is seen in Table II. Similar comments apply to the width of the upper most occupied valence bands. In general, local density studies are not as successful on either band gap or valence width. The gaps are usually sub-

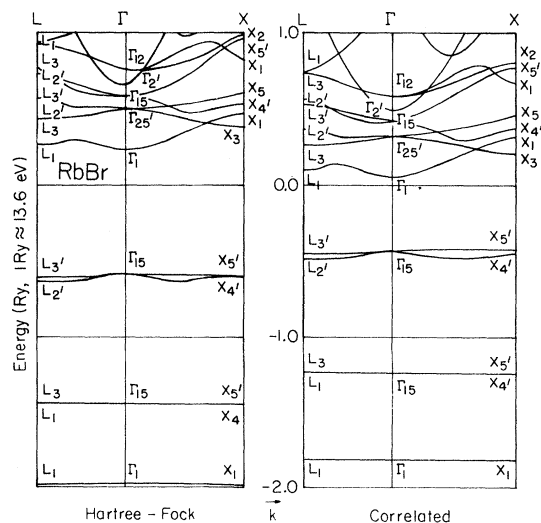


FIG. 12. Hartree-Fock and correlated energy bands for RbBr are seen.

stantially underestimated and the bandwidths are often especially poor. The calculation of LiF by Zunger and Freeman which includes corrections beyond the normal local density method is a substantial improvement over the usual local density result. It would be nice to use the Zunger-Freeman method on a more difficult case like NaCl. NaCl has other properties to commend it as well. I refer to the excellent angular resolved photoemission data for this system.<sup>32</sup> This set of measurements provides quite a bit of detailed information for NaCl valence and conduction bands. As is seen from Table III, the current calculation is in fine agreement with this study as was the earlier computation of Lipari and Kunz.<sup>6</sup> The same comment does not apply to the other studies for NaCl.

As is always true, Hartree-Fock band gaps are far too wide. Correlation corrections have been included using standard techniques.<sup>22</sup> In this paper, no attempt at detailed comparison to optical absorption data is attempted. This is because much of the absorption strength comes from exciton absorption lines<sup>7,11,43</sup> and such effects are omitted in traditional band theory. Work on the optical ab-

sorption, including excitons, is under way, and some preliminary studies by Kunz, Boisvert, and Woodruff<sup>44</sup> on these systems are in hand. This series of calculations will be extended and presented subsequently.

Nonlocal exchange methods are often avoided due to presumed expense and difficulty of calculation. This avoidance may be unnecessary. All these studies were performed on a DEC system 11/23 microcomputer using 64K bytes of core, 5M bytes of disc, and Fortran IV using the RT11 operating system. The total computational time varies with system, but a medium-sized calculation such as NaCl takes about 8 h on this system. A very large system such as AgBr takes 22 h. Solid Ne requires 1 h. This is a modest cost in reality and points to the practicality of such non-local-type calculations.

#### ACKNOWLEDGMENT

This research has been supported in part by the U. S. Navy under Grant No. ONR N00014-81-K-0620.

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