expression for $\partial D_{pq}/\partial V_{rs}$:

$$\partial D_{pq}/\partial V_{rs}=\tfrac{1}{2}\bar{\rho}(D^{(-1/2)}{}_{pr}\delta_{sq}+D^{(-1/2)}{}_{ps}\delta_{rq}+D^{(-1/2)}{}_{qr}\delta_{sp}+D^{(-1/2)}{}_{qs}\delta_{rp})\,. \tag{3.24}$$

Finally, from (3.7), (3.8), and (3.24), we have

$$\tau_{rs}=-pJD^{(-3/2)}{}_{rs}, \tag{3.25}$$

where $J=\bar{\rho}/\rho$ as in (3.13).

Even when the stress is not hydrostatic pressure, if the stress system is such as to preserve the eigenvectors of $D$, then the thermodynamic tensions are related to the stress through the expression obtained by substituting from (3.24) into (3.7).

As a special case, the initial state may be chosen to be a natural unstressed state, in which case $X_i=a_i$, and $D_{ij}$ and $\bar{\rho}$ in the preceding formulas become $C_{ij}$ and $\rho_0$. However, it is interesting to note that *any* hydrostatically compressed state may be chosen as the initial state, and the enthalpy as defined here will reduce to $U+p/\rho$ for *all* pressures, while with the $V_{ij}$ in (3.17), the thermodynamic tensions at the initial state will be equal to the initial stress.

In the special case of cubic crystals and isotropic media under hydrostatic pressure, $D_{ij}$ remains spherical, and the substate variables and thermodynamic tensions reduce to

$$V_{ij}=\tfrac{1}{3}V\delta_{ij}, \qquad \tau_{rs}=-p\delta_{rs}. \tag{3.26}$$

The simplification already mentioned at the end of the Introduction results from the fact that in this case constant pressure corresponds to constant thermodynamic tensions for all pressures.

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# Energy Bands and the Optical Properties of LiCl*

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Using a recently developed local-orbital theory of the author's, the ground-state eigenfunctions of the LiCl crystal in the Hartree-Fock approximation have been obtained. Using these functions to form the crystal charge density, the one-electron energy bands have been computed in essentially the Hartree-Fock approximation using the mixed-basis technique. Various levels of approximation within the local-orbital approximation are investigated. Polarization corrections to the energy bands are included by the method of Fowler. Finally, using tight-binding interpolation for the valence levels and empirical pseudopotentials for the conduction bands, the density of states for the valence and conduction states are obtained, and a joint density of states is computed. Extensive experimental comparisons are made. The principal results are the following: (1) The valence bands are very wide ($3p$ band is about 8 eV wide). (2) The soft x-ray spectrum can be interpreted in terms of the band structure. (3) Polarization corrections are significant.

## I. INTRODUCTION

In recent years, energy-band calculations on the alkali halide crystals have become common. While these calculations are extremely useful for qualitative interpretation of optical-absorption measurements and also electron energy-loss data, the theoretical situation is not fully satisfactory. Firstly, there is no general agreement as to how one chooses a model potential for computing alkali halide band structures, and different types of potentials can yield greatly differing results.[1] Secondly, when one chooses a model potential for such a calculation, Koopmans's theorem is violated, and the resultant one-electron eigenvalues are not the electron binding energies.[2] Thus the agreement of such a calculation with experiment is fortuitous. Most recent band calculations are of this nature.[3–6] Other recent calculations have attempted to use the correct Fock exchange.[7,8] In the cases in which the Fock exchange was used, no attempt at self-consistency was made. In addition, in the case of Oyama and Miyakawa[7] the Fock exchange was considered in an approximate way.[9] In the calculations by Kucher, Tolpygo, Tomasevich, and Evseev (KTTE),[8] the tight-binding method was employed for the conduction band, and so few states were included in the tight-binding expansion so that the accuracy of such calculations is in doubt and the $d$ states are neglected.

Only KTTE attempt to include polarization effects in their energy-band calculations. An excellent discussion of these techniques has been recently given by

Fowler.[10] This technique involves considering the polarization effect which an extra charge such as an electron or hole has on the surrounding ions using classical techniques.[11] Fowler has shown that this approximation is adequate for insulators.[10]

In this paper, a band calculation is performed for LiCl which avoids the difficulties associated with the previous calculations. The nonlocal Fock exchange operator, with only slight approximations as outlined in the text, is used, and thus difficulties with Koopmans's theory are essentially avoided.[2] The method of computing the energy band is the mixed-basis method recently described by the author.[12] In this method we expand the one-electron wave function in terms of Bloch functions formed from the core eigenfunctions and plane waves. Thus the limitations of the tight-binding method which limits KTTE are avoided. Using the local-orbital method of Adams[13] and Gilbert[14] as developed by the author[15] the calculations are carried out in a self-consistent manner. The effects of self-consistency and of various levels of approximation to the localized orbitals are investigated. In Sec. II these theories are summarized and the various approximations are discussed in detail. In Sec. III the numerical results are given and in Sec. IV the inclusion of polarization effects is discussed and a final LiCl band structure is presented.

Experimentally, the situation of LiCl is rather interesting. LiCl is hygroscopic and quite difficult to work with. Thin-film optical absorption data are available,[16,17] as are reflectivity data.[18] In addition, there are soft x-ray data relating to absorption from the lithium $K$ shell and the $L_{2,3}$ edges in the chlorine ion.[19,20] In the early work of Eby, Teegarden, and Dutton[16] no exciton transition is found preceding the onset of optical absorption. Thus LiCl was thought to be an anomaly and theoretical models were devised to explain the peculiar behavior of this substance.[10,21] The more recent optical work finds that LiCl does have an exceptionally sharp exciton peak preceding the onset of band-to-band absorption,[17,18] and thus the early theoretical models are not satisfactory. Experimentally LiCl is still somewhat different from the other alkali halides, excepting perhaps LiBr and LiI, in that the exciton peak is of the same strength as the band-to-band transitions and seems to immediately precede them. The band gap is not accurately known and a determination of it using two quantum techniques or photoconductivity would be of great value. In a previous paper, the author suggested that the great strength of the band-to-band absorption may be explained by the near degeneracy of the $\Gamma$ and $L$ absorption edges.[4] In Sec. V the available calculations are compared to this calculation and the final band results are used to interpret the available experiments. Densities of states for the various bands are obtained and a joint density is computed. In the final section (Sec. VI) the theoretical advances included in this calculation are discussed. Suggestions for further investigations are given.

## II. HARTREE-FOCK AND LOCAL-ORBITAL THEORY

In this section we summarize Hartree-Fock theory as it applies to energy-band calculations, summarize the results of local-orbital theory and discuss the several levels of approximation available. In doing this we remind ourselves of the fact that for insulators in the one-electron limit the Bloch and the Heitler-London picture are equivalent.[22] We shall make extensive use of the extended Hückel theory in obtaining the various levels of approximation. A recent review of this theory as it applies to solids has recently been given by Gilbert.[23] The excited or conduction-band states will be obtained using the invariant core approximation. This method is generally successful when applied to systems with many electrons[24] and is implied by Koopmans's theorem.

Using density-matrix notation we write the Fock operator for a solid in the form

$$F=-\nabla_1^2-\sum_B(2Z_B/|\mathbf{r}_{B1}|)+4\sum_{B,j}\int|\mathbf{r}_{12}|^{-1}\phi_{Bj}^2(\mathbf{r}_2)d\mathbf{r}_2 -2\sum_{B,j}|Bj\rangle\langle Bj||\mathbf{r}_{12}|^{-1}. \quad (1)$$

Here the Fock operator is in rydberg units. The subscripts $B$ refer to the nuclear coordinates and the subscripts $j$ refer to the electronic coordinates. The summations over $B$ are for all nuclei in the lattice and the sum over $j$ involves all occupied orbitals about site $B$. In the sum we include only one of a spin-up, spin-down pair of orbitals. Appropriate factors of 2 have been included in the summations to account for this. It is assumed that in the ground state only filled subshells occur and we write the Fock operator in the Heitler-London scheme using local orthonormal orbitals. Methods of obtaining the orbitals will be discussed a little later in this section. All occupied orbitals are included in the above representation of the Fock operator in the form of localized functions.

Having obtained the Fock operator in self-consistent form we must obtain its eigenvalue and eigenvectors. To do this, the mixed-basis method is used.[12] Here we write the one-electron eigenfunction $\psi_n^{\alpha\gamma}(\mathbf{k},\mathbf{r})$ as

$$\psi_n^{\alpha\gamma}(\mathbf{k},\mathbf{r})=\sum_{j,l}A_{njl}^{\alpha\gamma}\sum_m C_{lm}^{\alpha\gamma}(\mathbf{k})\Phi_{jlm}(\mathbf{k},\mathbf{r}) +\sum_q d_{nq}^{\alpha\gamma}\sum_t b_{qt}^{\alpha\gamma}\exp[i(\mathbf{k}+\mathbf{h})\cdot\mathbf{r}]. \quad (2)$$

In Eq. (2) the functions $\phi_{jlm}(\mathbf{k},\mathbf{r})$ are Bloch functions formed from those nonoverlapping local orbitals which are used in $F$ (i.e., the $\mathrm{Li}^+$ $1s$, $\mathrm{Cl}^-$ $1s$, $2s$, $2p$ shells). The $C_{lm}^{\alpha\gamma}$ are chosen so that the Bloch functions transform according to the $\gamma$th row of the $\alpha$th irreducible representation of the group of the wave vector $\mathbf{k}$. The vector $\mathbf{h}_t$ is a reciprocal-lattice vector. It is required that $|(\mathbf{k}+\mathbf{h}_t)|$ be constant for all $t$. One chooses $b_{tq}^{\alpha\gamma}$ so that the plane-wave part of the basis has the correct symmetry. The coefficients $A_{njl}^{\alpha\gamma}$ and $d_{nq}^{\alpha\gamma}$ are variational parameters. The quantities $l$ and $m$ refer to the angular momentum and its $Z$ component for the atomic states from which the Bloch sums are formed.

Thus the problem at hand is to evaluate the matrix elements of the Fock operator and the overlap matrix. These fall into three general classes of element, which are

$$\begin{aligned} A&=\int\Phi_{jl}^{\alpha\gamma *}O_p\Phi_{j'l'}^{\alpha\gamma}d\tau,\\ B&=\int\Phi_{jl}^{\alpha\gamma *}O_pS_q^{\alpha\gamma}d\tau,\\ C&=\int S_q^{\alpha\gamma *}O_pS_{q'}^{\alpha\gamma}d\tau,\end{aligned}\tag{3}$$

where

$$\Phi_{jl}^{\alpha\gamma}=\sum_{m=-l}^{l}C_{lm}^{\alpha\gamma}\phi_{jlm}(\mathbf{k},\mathbf{r})$$

and

$$S_q^{\alpha\gamma}=\sum_t b_{qt}^{\alpha\gamma}\exp[i(\mathbf{k}+\mathbf{h}_t)\cdot\mathbf{r}].\tag{4}$$

In Eqs. (3) when $O_p=1$ one obtains the overlap matrix $D$, and when $O_p=F$ one obtains the Fock matrix $F$. Thus we must evaluate Eqs. (3) and solve the matrix equation

$$F\psi=ED\psi.\tag{5}$$

The techniques to be used in evaluating the $D$ matrix are straightforward and need no discussion at this time. The difficulties involved are discussed in previous work by the author.[12] When $O_p=F$ the classes of elements $A$ and $B$ are also simple and straightforward to evaluate and the technique used is discussed in Appendix A. The evaluation of elements of class $C$ is somewhat more difficult and involves an approximation. These elements are given by substituting $F$ of Eq. (1) into the third of Eq. (3). We note that in practice the local orbitals used to form the Fock operator are not orthogonal. In actual calculations these nonorthogonalities are corrected to first order in overlap as described in Appendix A for elements of type $A$ and $B$ and as follows for those of type $C$:

$$\begin{aligned}F_{qq'}^{\alpha\gamma}&=\int S_q^{\alpha\gamma *}(\mathbf{r}_1)\\ &\times\Big[-\nabla_1^2-\sum_B(2Z_B/|\,\mathbf{r}_{B1}\,|)+4\sum_{B,j}\int|\,\mathbf{r}_{12}\,|^{-1}\phi_{Bj}^2(\mathbf{r}_2)d\mathbf{r}_2\Big]\\ &\times S_{q'}^{\alpha\gamma}(\mathbf{r}_1)d\mathbf{r}_1-2\sum_{Bj}\iint S_q^{\alpha\gamma *}(\mathbf{r}_1)|\,\phi_{Bj}(\mathbf{r}_1)\;|\,\mathbf{r}_{12}\,|^{-1}\\ &\times\phi_{Bj}^*(\mathbf{r}_2)|\;S_{q'}^{\alpha\gamma}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2.\end{aligned}\tag{6}$$

In this element, $C$, the nonorthogonality of the local orbitals, has been corrected for using the technique of symmetric orthogonalization. The first term on the right-hand side of Eq. (6) involves only the kinetic-energy term and the local part of the potential. This part is easily evaluated using standard techniques used in orthogonalized plane wave calculations.[25] The second term on the right-hand side is the exchange term which involves two plane waves. This is to be approximated. The plane waves are decomposed into cubic harmonics[26] and the evaluation proceeds quite easily. This is discussed in Sec. III. It is noted that states of all wave vectors $\mathbf{k}$ enter into the exchange calculation here. A sufficient number of terms is included to ensure reasonable accuracy. In any event, the time involved in considering additional exchange terms is sufficiently costly to be impractical at this point.

The starting point for obtaining the appropriate localized orbitals to be used in forming the Fock operator is the Adams-Gilbert equation of the form[13]

$$[F_A+U_A-\rho U_A\rho]\phi_{Ai}=\epsilon_{Ai}\phi_{Ai}.\tag{7}$$

In forming this equation one removes the restriction that the orbitals centered on different sites be orthogonal.

As Eq. (7) is rather difficult to evaluate exactly, we shall make a simplifying assumption that terms in the equation which are of second or higher order in interatomic overlap may be neglected. In this case the resulting equation is

$$[F_A+U_A-\epsilon_{Ai}]\phi_{Ai}=\sum_k{}'\phi_{Ak}\langle Ak\,|\,U_A\,|\,Ai\rangle,\tag{8}$$

where

$$\begin{aligned}F_A\phi_{Ai}&=\Big[-\nabla_1^2-2Z_A/\mathbf{r}_{A1}+4\sum_j\int\phi_{Aj}^2(\mathbf{r}_2)|\,\mathbf{r}_{12}\,|^{-1}d\mathbf{r}_2\Big]\phi_{Ai}\\ &\quad-2\sum_j\phi_{Aj}(\mathbf{r}_1)\int\phi_{Aj}^*(\mathbf{r}_2)\phi_{Ai}(\mathbf{r}_2)|\,\mathbf{r}_{12}\,|^{-1}d\mathbf{r}_2\end{aligned}\tag{9}$$

and

$$U_A=-\sum_B{}'(2Z_B/|\,\mathbf{r}_{B1}\,|)+4\sum_{B,j}{}'\int\phi_{Bj}^2(\mathbf{r}_2)|\,\mathbf{r}_{12}\,|^{-1}d\mathbf{r}_2.\tag{10}$$

Equation (8) is solved by the technique described in Appendix B.

There are a number of additional approximations which one might make to Eq. (8). These can be approached in a systematic way using the extended Hückel theory as it applies to local orbitals in polyatomic systems.[23] In the spirit of the Hückel theory one may replace $U_A$ as given by Eq. (10) with the point-ion potential for the lattice $V_A^{\mathrm{PI}}$. In this case one finds

$$F_A+V_A^{\mathrm{PI}}-\epsilon_{Ai}\phi_{Ai}=\sum_k{}'\phi_{Ak}\langle\phi_{Ak}\,|\,V_A^{\mathrm{PI}}\,|\,\phi_{Ai}\rangle.\tag{11}$$

We see that the above result is particularly convenient in that for a diatomic system the two subsystems have become decoupled and thus one need solve only a pair of Hartree-Fock equations only slightly more difficult than those for a free ion.

It may be possible to take the Hückel theory one step further and use a relation given by Gilbert when the wave functions are centered about a site of high symmetry.[23] In this case

$$\langle\phi_{Ak}\,|\,V_A^{\mathrm{PI}}\,|\,\phi_{Ai}\rangle=\delta_{ik}=0,\tag{12}$$

since $i\neq k$. Thus one reduces Eq. (11) to

$$[F_A+V_A^{\mathrm{PI}}-\epsilon_{Ai}]\phi_{Ai}=0.\tag{13}$$

It is noted that several years ago Wahl and Gilbert investigated several of these ideas in the case of diatomic molecules formed by the alkali halides.[27] Wahl and Gilbert computed the potential-energy surface for these

TABLE I. The valence bands of LiCl are given here. In column I the state is specified. In column II the bands obtained from solutions to Eq. (13) are given and in column III the bands obtained from solutions to Eq. (12) are given. Finally in column IV the bands revised according to polarization corrections are given relative to $\Gamma_{15}$. Because of its small effect, spin-orbit corrections are neglected. The BSW notation is used. Results are in eV. The difference in polarization correction for alkali and halogen is included in result of column IV for $Li^+1s$ state.

| I | II | III | IV |
|---|---|---|---|
| $Cl^-$ 1*s* | −2860 | −2854 | −2846 |
| $Cl^-$ 2*s* | −287 | −287.7 | −279.7 |
| $Cl^-$ 2*p* | −218 | −218.5 | −210.5 |
| $Li^+$ 1*s* | −66.4 | −66.74 | −54.49 |
| | | 3*s* valence band | |
| $\Gamma_1$ | −31.6 | −31.56 | −23.56 |
| $X_1$ | −28.6 | −28.79 | −20.79 |
| $L_1$ | −29.2 | −29.45 | −21.45 |
| | | 3*p* valence band | |
| $\Gamma_{15}$ | −7.3 | −8.00 | −0.00 |
| $X_5'$ | −9.9 | −10.44 | −2.44 |
| $X_4'$ | −14.5 | −15.25 | −7.25 |
| $L_3'$ | −8.2 | −8.69 | −0.69 |
| $L_2'$ | −15.2 | −15.96 | −8.96 |

systems using free-ion Hartree-Fock wave functions for the alkali and the halogen ions, and also using solutions to Eq. (13) for these systems. They were able to conclude that for the alkali halide diatomic molecules the free-ion wave functions produced better results than the solutions to Eq. (13). The author would note that this need not be the case in an alkali halide crystal. This may be seen by remembering that for an alkali halide molecule, neither the nuclear position of the alkali ion or the halide ion is a point of high symmetry and hence the reduction of Eq. (11) to Eq. (13) is not valid for a diatomic molecule. However, in a crystal, the alkali and halogen ion sites are points of high symmetry, and one expects that Eq. (13) may be valid.

In this paper these relations are studied for the LiCl crystal. The energy bands are computed for points and lines of high symmetry in the first Brillouin zone in several approximations. Firstly, wave functions which satisfy the free-ion Hartree-Fock equations are used, secondly, solutions to Eq. (13) are used, thirdly, solutions to Eq. (11) are used, and finally solutions to Eq. (5) are used. In presenting these results the group-theoretical notation of Bouchaert *et al.* is used.[28] These results are contrasted to previous calculations of LiCl where effective exchange approximations were used.[4] A halogen ion site is used as the origin of the coordinate system.

At this point a review of the principal methods is useful. Firstly the self-consistent Fock charge density in terms of local orbitals is obtained for the crystal to first order in interatomic overlap. These local orbitals are nonorthogonal on different sites and are linear combinations of the Bloch orbital solutions to the Fock operator for all wave vector **k**. Thus the Fock matrix formed of these local orbitals is nondiagonal. The Fock matrix is next put into diagonal form. In forming the Fock operator, Eq. (1), the nonorthogonality of the local orbitals is taken into account properly.[14,23] All the local orbitals computed are included in the formation of *F*, and hence all occupied levels in the crystals are included. Next the Fock matrix is diagonalized. This is done by using the more compact local orbitals which are formed into Bloch functions, and plane waves are used to represent the more diffuse of the local orbitals (these correspond closely to the 3*s* and 3*p* $Cl^-$ orbitals). Since this is not a minimum basis, virtual levels are obtained as well as the occupied levels, when the Fock matrix is diagonalized. Using Koopmans's theorem, we identify these virtual states as the conduction levels. It is stated that in evaluating matrix elements of the Fock operator between two local orbitals or a local orbital and a plane wave, terms to first order in interatomic overlap are retained as is described in Appendix A. In evaluating matrix elements between the Fock operator and two plane waves, only the exchange integral is approximated as is described in Sec. III. It is believed that none of these assumptions is serious in that only those local orbitals which were very compact (do not overlap) are retained in the basis and the expansion used in the case of the plane waves seems well converged.

It is observed that the matrix elements connecting two local orbitals on the same site, Table IV, are almost zero and hence the local orbitals for the lower states, $Cl^-$ 1*s*, 2*s*, 2*p*, and $Li^+$, should when formed into Bloch orbitals, be essentially the eigenfunction of the Fock

TABLE II. The conduction bands of LiCl are given. In column I the state is specified. In column II the bands obtained from solutions to Eq. (13) are given and in column III the bands obtained from solutions to Eq. (12) are given. Finally, in column IV the bands are given relative to the $\Gamma_{15}$ valence level after polarization corrections are made. Spin-orbit effects are ignored. The BSW notation is used. Results are in eV.

| I | II | III | IV |
|---|---|---|---|
| $\Gamma_1$ | 3.5 | 3.47 | 7.69 |
| $\Gamma_{25}'$ | 11.4 | 11.22 | 15.44 |
| $\Gamma_{12}$ | 14.2 | 14.07 | 18.29 |
| $\Gamma_{15}$ | 14.2 | 3.98 | 18.20 |
| $X_1$ | 5.5 | 5.37 | 9.59 |
| $X_3$ | 5.5 | 5.31 | 9.53 |
| $X_5'$ | 14.2 | 14.04 | 18.26 |
| $X_4'$ | 12.7 | 12.60 | 16.82 |
| $X_2$ | 17.6 | 17.41 | 21.63 |
| $L_1$ | 4.5 | 3.84 | 8.06 |
| $L_3$ | 7.9 | 7.55 | 11.77 |
| $L_2'$ | 13.8 | 13.61 | 17.83 |
| $L_2'$ | 16.5 | 16.42 | 20.64 |
| $L_3$ | 18.7 | 17.28 | 21.50 |
| $L_1$ | 12.0 | 18.51 | 22.73 |

operator for these levels. By checking the eigenvalues of Eq. (5) this was confirmed to be the case. This is additional reason to believe the solutions are self-consistent.

## III. CALCULATION

Initial calculations of the LiCl energy bands were made using free-ion $Cl^-$ function of Löwdin and Appell[29] and $Li^+$ free-ion wave functions computed by the author. In computing the bands the $Cl^-$ $1s$, $2s$, and $2p$ functions and the $Li^+$ $1s$ function were included in the basis. The plane-wave part consisted of 113 plane waves at $\Gamma$ and an appropriate number elsewhere. Convergence was adequate. The calculation at $\Gamma$ was repeated using 59 plane waves and about 300 plane waves. The conduction levels, including the difficult to converge $d$ levels[30] and the $3s$ valence level, remained essentially unchanged in these calculations (changes were about 0.05 eV at most). The $3p$ valence level was less well converged although its position should exhibit less than an absolute error of 0.25 eV. This calculation was repeated using functions which are solutions to Eqs. (11) and (13). The results of these three calculations were in good agreement, and in Tables I and II the results for the functions which satisfy Eq. (11) are given. A halogen ion is used as the origin here as is the BSW notation.[28] We note that the valence bands are extremely wide (7.84 eV for the $3p$ band and 3.03 eV for the $3s$ band). This result is consistent with that of Howland for KCl,[31] in that when the mixings of the $K^+$ band were neglected the $Cl^-3p$ band was about 3 eV wide and a considerable increase in width in going from KCL to LiCl may be expected owing to the change in lattice constant. It is noted that KTTE found a width of 5 eV for the LiCl $3p$ band[8] using a somewhat approximate tight-binding method. Their KCl results were narrower than those of Howland. The correlation of these results and x-ray emission studies will be performed later in this paper.[32–34]

In evaluating the exchange terms which occur in matrix elements of type $C$ of Eq. (3) we used the usual expansion for $|\,\mathbf{r}_{12}\,|^{-1}$ given by Hartree,[35]

$$|\,\mathbf{r}_{12}\,|^{-1}=\sum_{l=0}^{\infty}4\pi(2l+1)^{-1}\times\sum_{m=-l}^{l}Y_l^{m*}(\theta_1\phi_1)\,Y_l^m(\theta_2\phi_2)\,(r^{<l}/r^{>l+1}),\qquad(14)$$

where

$$\begin{aligned} r^{<l}/r^{>l+1}&=r_1^{\,l}/r_2^{\,l+1}, & r_1&<r_2\\ &=r_2^{\,l}/r_1^{\,l+1}, & r_1&>r_2. \end{aligned}\qquad(15)$$

In this calculation we used only the first five terms in the expansion given by Eq. (14). In order to test the accuracy of this, the calculation was repeated using only the first term of Eq. (14) and using only the first three terms of Eq. (14). Band points changed by as much as several volts in going from one term to three terms in the expansion. However, in going from three terms to five terms the change was of the order of 0.1 eV. Therefore the author concludes that the first five terms of Eq. (14) are sufficient and all remaining calculations are made using five terms. It should be noted that owing to the nonlocal nature of the exchange integral the time required to compute a Hartree-Fock energy band is considerably greater than that required to compute an energy band using a local exchange approximation.

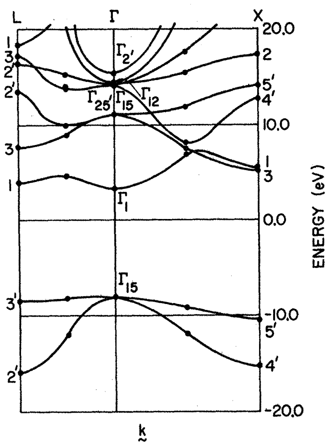

FIG. 1. Self-consistent Hartree-Fock energy bands for LiCl. Spin-orbit effects are neglected and the BSW notation is used.

The orbitals which are solutions to Eqs. (11) and (13) are obtained by analytic Hartree-Fock techniques.[36,37] This is described in Appendix B. Free-ion $Cl^-$ and $Li^+$ functions were obtained by this technique and the $Cl^-$ results compared with those of Watson and Freeman[37] and Hartree and Hartree.[38] The $Li^+$ results were compared to those of Fock and Petrashen.[39] In all cases agreement was satisfactory.

Finally, Eq. (8) was solved self-consistently. In doing this only nearest neighbors were included in the short-range part of the potential. In forming the crystal Fock operator, the overlapping of the wave functions was taken into account by symmetric orthogonalization. The energy bands were evaluated at the points $\Gamma$, $X$, $L$, the midpoints of $\Delta$ and of $\Lambda$. These results are presented in Tables I and II and the resultant energy bands are shown in Fig. 1. The band gap is computed to be 11.47 eV, the $3p$ band is 7.96 eV wide and the $3s$ band is 2.77 eV wide. The photoemission threshold is 8.99 eV and the electron affinity is $-3.47$ eV. Polarization corrections to the band gap are discussed in Sec. IV.

## IV. POLARIZATION CORRECTIONS

In this section we follow the work of Fowler.[10] Polarization corrections to this Hartree-Fock treatment occur for several reasons: (1) All electronic correlation is neglected except for that which arises from a totally antisymmetric wave function; (2) during an optical excitation we assume that the orbitals at the site from which the excitation occurs remain unchanged; (3) we assume the surrounding change bands remain un-

TABLE III. The tight-binding and pseudo-Hamiltonian parameters used for LiCl are given. The notation of Ref. 46 is used for the tight-binding parameters.

| Parameter | Value (eV) |
|---|---|
| $V_s$ | −29.5 |
| $V_{ss\sigma}$ | −0.713 |
| $V_p$ | −10.0 |
| $V_{pp\sigma}$ | 1.05 |
| $V_{pp\pi}$ | −0.15 |
| $\alpha$ | 1.383 |
| $v(000)$ | −15.87 |
| $v(111)$ | 6.59 |
| $v(200)$ | −3.76 |
| $v(220)$ | −0.845 |
| $v(311)$ | 2.17 |
| $v(222)$ | −1.03 |

changed during an excitation; (4) we assume the ionic position remains unchanged during excitation. Of these assumptions only (4) is justified. The method of Fowler allows us to include type (1) and (3) corrections.

The Fowler theory is a refinement of the theories of Haken and Schottky and of Toyozawa.[40] Fowler shows that for the insulators these theories reduce to a static limit, and this is evaluated using a Mott-Littleton approach.[11] This result which we apply in an appropriate manner lowers the conduction bands with respect to the valence bands by about 3.78 eV. As we apply this theory here the polarization correction is not **k** or energy dependent. This has been seen also in calculations by Lipari and Fowler[41] for solid argon. This technique is essentially similar to that employed by KTTE.[8] Having done this, the band gap reduces to 7.69 eV. The revised results measured with respect to the $\Gamma_{15}$ $3p$ valence band are given in Tables I and II. For transition from the $\text{Li}^+$ $1s$ shell the polarization correction is to decrease the energy by 5.03 eV.

The method of application is quite simple. One evaluates the amount of ground-state or excited-state wave function contained within the ionic radius of the $\text{Li}^+$ ion. The remainder is associated with the $\text{Cl}^-$ sublattice. One uses Fowler's tables to compute the polarization correction according to the formula

$$E_{\text{pol}}=\pm[d(+)E_{\text{elect}}+d(-)E_{\text{hole}}]. \qquad (16)$$

Here $E_{\text{pol}}$ is the polarization correction and the plus sign is used for the occupied levels and the minus sign for the conduction levels. The quantity $E_{\text{elect}}$ is the correction due to an extra electron on an alkali ion and $E_{\text{hole}}$ is the correction due to a hole on a halogen ion[10]; $d(+)$ is the wave-function density about the alkali ion and $d(-)=1-d(+)$.

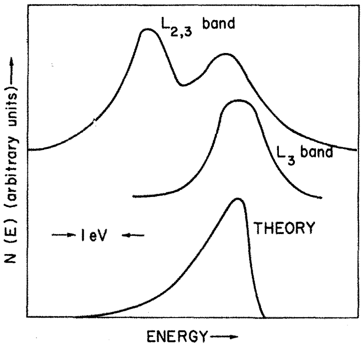

FIG. 2. Density of states for the $3s$ valence band and emission spectrum of this state to the $L_{23}$ shell in $\text{Cl}^-$ according to Ref. 44. The zero of energy is arbitrary.

One may estimate the correction due to correlation on the ion at which the transition takes place using the pair correlation theory of Allen *et al.*[42] They do not have results for the breaking of an orbital pair of $3p$ electrons; however, in the case in which a $2p$ electron is the outer electron, the energy per $2p$ electron pair is about 1.7 eV. Thus the effect of this intra-atomic correlation is to increase the band gap over the Hartree-Fock value. This trend is in qualitative agreement with the present result since the computed gap is about 1 eV too narrow.

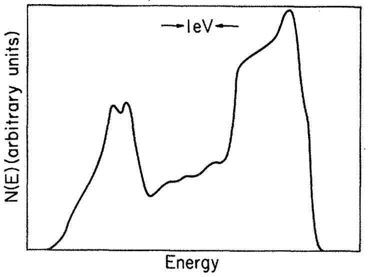

FIG. 3. Density of states for the $3p$ valence band. The zero of energy is arbitrary.

## V. COMPARISON WITH EXPERIMENT

The experimental situation for LiCl is not completely satisfactory. Thin-film optical-absorption measurements have been made by Eby, Teegarden and Dutton[16] and by Teegarden and Baldini.[17] In addition a reflectance spectrum has been obtained by Baldini and Bosacchi.[18] Soft x-ray absorption for the lithium $K$ shell have been measured by Haensel, Kunz, and Sonntag[19] and by Brown and Gahwiller[43] and for the $L_{23}$ edge by Sagawa[20] and by Brown and Gahwiller.[43] In addition, x-ray emission data from the $3s$ band in LiCl have been studied by O'Brian and Skinner along with other salts.[34,44] Two quantum-absorption experiments or photoconductivity experiments have not been performed for LiCl, and as a result the optical band gap is not known. In the measurement of Teegarden and

Baldini the exciton peak is at 8.6 eV at 10°K and strong absorption immediately follows the exciton. Thus the computed band gap is too small by about 1 eV or about 10%. This is not an unreasonable error.

In order to facilitate comparison of theory and experiment the 3*s* and 3*p* valence band have been fitted with tight-binding functions to permit interpolation of these bands throughout the zone. The conduction bands were fitted with a pseudo-Hamiltonian of the form

$$\mathcal{H}_{\mathrm{ps}}=\alpha(P^2/2m)+\sum_{\mathbf{k}} v(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}). \qquad (17)$$

In Eq. (17) $\alpha$ is an adjustable parameter as are the $v(\mathbf{k})$. $k$ is a vector in the direct lattice. The $v(\mathbf{k})$ were scaled from those given by Fong and Cohen for NaCl.[45] Slater and Koster theory was employed for the valence bands using tight-binding interpolation.[46] The tight-binding and pseudo-Hamiltonian parameters are given in Table III.

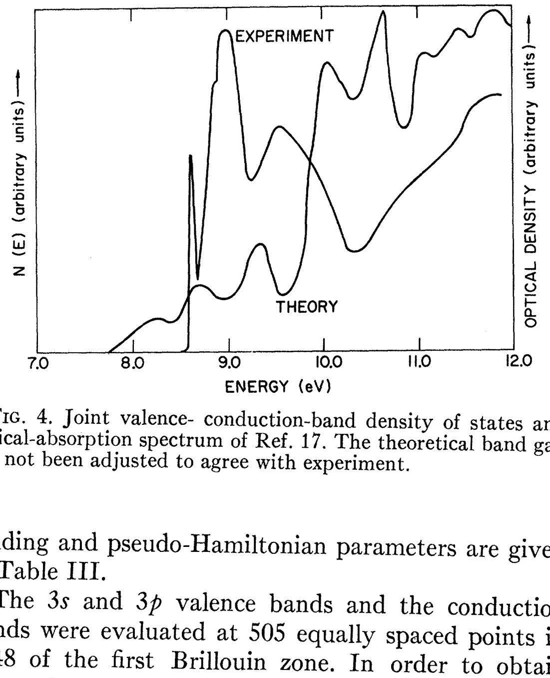

FIG. 4. Joint valence- conduction-band density of states and optical-absorption spectrum of Ref. 17. The theoretical band gap has not been adjusted to agree with experiment.

The 3*s* and 3*p* valence bands and the conduction bands were evaluated at 505 equally spaced points in 1/48 of the first Brillouin zone. In order to obtain reasonable results for the conduction bands 65 plane waves were used in the expansion. The pseudopotential bands fit the computed bands quite well up to 15 eV or so above the conduction-band minimum. In Fig. 2 the density of states for the 3*s* valence state is shown along with the emission spectrum for this state measured by O'Brian and Skinner.[44] It is noted that the final state in this emission is spin-orbital split and we also show the resultant emission to only one member of the final state. In general we see that the emission band is broader than the theoretical band. This may be due to lifetime broadening, and in general the agreement is reasonable.

In Fig. 3 the density of states for the 3*p* $\mathrm{Cl}^-$ band is given. The x-ray emission spectrum for this state is unknown. However the shape of this curve is in good agreement with those obtained previously for the alkali fluorides.[33]

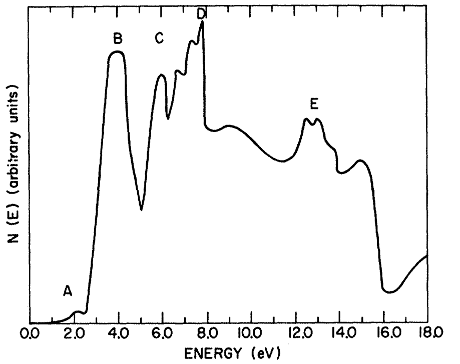

FIG. 5. Density of states for the conduction band. The zero of energy is arbitrary.

In Fig. 4, the computed joint density of states is shown as is the measured absorption spectrum of Teegarden and Baldini.[17] It may be seen that if the theoretical structure were shifted about 1 eV to the high-energy side, there would be fair correspondence between the maxima and minima in the theoretical curve and those of the experimental curve except that the third theoretical peak lies about 0.33 eV on the low-energy side of where it should. However, the heights are in poor agreement. This is most likely due to the complete neglect of transition matrix elements in the theoretical calculation. The theoretical peak at 8.6 eV arises from transitions from $L_3'\rightarrow L_1$ and the surrounding region. The peak at 9.4 eV arises from transitions $\Lambda_3$ to $\Lambda_1$ at the center of the line $\Lambda$ and the surrounding areas. The peaks at 10.0 eV and higher arise primarily from transitions to the regions around $X_3$, $X_1$, and $L_3$ and $K_1$. It is possible that some of the strong absorption measured at about 9.0 eV is due to excitonic effects associated with the conduction-band minimum at $L_1$.

In Fig. 5, the computed density of states for the conduction band is shown. In Fig. 6, the $\mathrm{Li}^+$ $K$ shell absorption after Brown and Gahwiller is shown,[43] and in Fig. 7

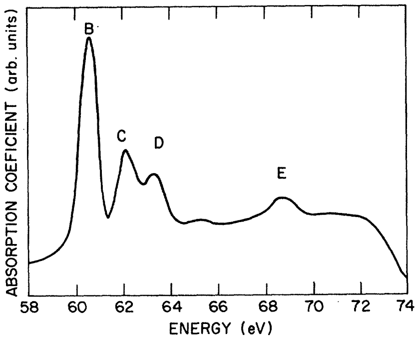

FIG. 6. Absorption from the $\mathrm{Li}^+$ $K$ shell in LiCl (Ref. 43).

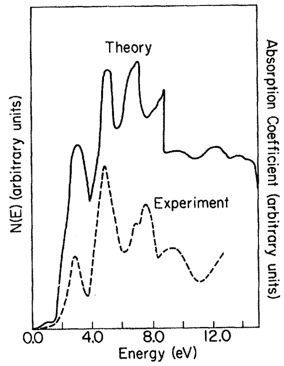

FIG. 7. Absorption from the $L_{2,3}$ shell of LiCl (Ref. 43), and a joint density for this transition obtained from the theoretical conduction density.

the $Cl^-$ $L_{2,3}$ absorption is shown along with a theoretical joint density of states for this transition. In forming the theoretical curve, a value of 1.6 eV is used for the spin-orbit splitting of the $Cl^-$ $2p$ shell. A constant transition matrix element is assumed in these comparisons. We suggest that the peaks labeled *B, C, D, E* in the *K* absorption correspond to the peaks in the density of states labeled *B, C, D, E* and shown in Fig. 5. The differences in relative heights in both theory and experiment are probably related to differing transition matrix elements. It is possible that transition matrix effects due to electron-hole interaction cause the experimentally strong absorption near the fundamental edge. The peaks are generally complex in terms of what type of states are included in their composition and generally include *s*, *p*, *d* states as well as states of higher angular momentum. In any event, density-of-states considerations alone, without additional exciton lives, seem to provide a satisfactory explanation of the x-ray spectra, the principal excitonic effects being in the matrix elements for the transitions. The rising absorption after the $L_{23}$ edge probably is due to a $p \rightarrow d$ transition resonance.[47]

It is possible to compare these results to those of a previous calculation using an effective exchange approximation.[4] The conduction bands in the present case agree well with those obtained using a model potential. However, the agreement for the valence bands is extremely bad. The present calculation produces valence bands which are about four times broader than those previously obtained.[4] However, as has been noted, the present valence results are probably consistent with those of Howland[31] and of KTTE.[8]

Using numerical differentiation, we have computed the effective mass for an electron at $\Gamma_1$ in the conduction band and find it to be 0.5 electron masses, and for a valence hole at $\Gamma_{15}$ in the $\Delta_5$ direction and find it to be 0.5 electron masses. If one uses these values and a hydrogenic model and the static dielectric constant, the exciton binding energy is given by[48]

$$E_B = 13.6(\mu/\epsilon_0^2), \qquad \mu = m_e m_h/(m_e + m_h). \quad (18)$$

$E_B$ is the binding energy in volts, $\mu$ is the exciton reduced mass, and $\epsilon_0$ is the static dielectric constant. Here $\epsilon_0$ is 11.05 and $E_B$ is 28 meV. This value is consistent with the previous experimental interpretations and also with the measured exciton binding energies of other large dielectric constant substances.[49] Using the polaron theory of Lee, Low, and Pines,[50] the polaron masses for both the valence hole and the conduction electrons are found to be 0.64 electron masses.

## VI. CONCLUSIONS

It has been possible to obtain nearly exact self-consistent Hartree-Fock energy bands for the LiCl crystal. Polarization corrections have been included by the technique of Fowler.[10] Such a technique produces a band gap which is in reasonable agreement with experiment (10%). In general the density-of-states curves for $3s$ and conduction bands are in agreement with available experiments and the joint valence conduction density is consistent with the optical spectrum.

The most significant results are that the valence bands are considerably broader than effective exchange approximation calculations lead one to believe. The soft x-ray absorption data may be satisfactorily explained in terms of band-to-band transitions. Polarization corrections are large and essential. The effects of self-consistency are small but not negligible.

The method of including polarization corrections should be extended to include effects due to relaxation of the ion from which absorption takes place. Efforts should be expanded on making calculations of this type more economical since the quality of the results tends to justify the effort expended.

There is a need for experimental studies on this system. Two photon spectroscopy or photoconductivity experiments should be performed to determine the band gap accurately. Cyclotron resonance measurements of the effective mass of conduction electrons would be useful. The x-ray emission spectrum of the $3p$ band of LiCl should be measured either to confirm or deny the broad valence-band results of this calculation.

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## APPENDIX A

Here we discuss the evaluation of the matrix elements of Eq. (3). We are concerned with the case in which

$$O_P = F_A + U_A. \quad (A1)$$

Thus, the operator in question is the Fock operator for

TABLE IV. The energy parameters, defined as $\epsilon_{nn'}=\langle\phi_n \mid F_A+U_A \mid \phi_n\rangle$, are given for a variety of cases. In column 1 the particular parameter is specified. In column 2 the parameters for the solutions to Eq. (14), in column 3 for the solutions to Eq. (13′), and in column 4 for the solution to Eq. (12) are given. In column 5 the free-ion parameters computed by the author are given. In column 6 the results of Fock and Petrasken (Ref. 39) are given for Li$^+$ and of Hartree and Hartree for Cl$^-$ (Ref. 38). In column 7 the results of Watson and Freeman (Ref. 37) are given for Cl$^-$.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| | | | Cl$^-$ | | | |
| $\epsilon_{1s,1s}$ | −209.9 | −209.9 | −210.0 | −209.2 | −209.0 | −209.0 |
| $\epsilon_{2s,2s}$ | −21.14 | −21.14 | −21.16 | −20.48 | −20.46 | −20.46 |
| $\epsilon_{3s,3s}$ | −2.151 | −2.19 | −2.162 | −1.473 | −1.454 | −1.471 |
| $\epsilon_{1s,2s}$ | 0.0 | $21\times10^{-7}$ | $11\times10^{-7}$ | 0.0 | 0.0 | 0.0 |
| $\epsilon_{1s,3s}$ | 0.0 | $-5\times10^{-7}$ | $18\times10^{-7}$ | 0.0 | 0.0 | 0.0 |
| $\epsilon_{2s,3s}$ | 0.0 | $21\times10^{-7}$ | $17\times10^{-7}$ | 0.0 | 0.0 | 0.0 |
| $\epsilon_{2p,2p}$ | −16.06 | −16.06 | −16.07 | −15.39 | −15.39 | −15.40 |
| $\epsilon_{3p,3p}$ | −0.9857 | −0.9852 | −0.9965 | −0.3035 | −0.2970 | −0.3036 |
| $\epsilon_{2p,3p}$ | 0.0 | $-159\times10^{-7}$ | $-155\times10^{-7}$ | 0.0 | 0.0 | 0.0 |
| | | | Li$^+$ | | | |
| $\epsilon_{1s,1s}$ | −4.875 | −4.875 | −4.910 | −5.597 | −5.56 | |

the crystal. The case in which $O_P=1$ need not be included, as has been considered previously.[4] The essential matrix elements are of the form

$$A'=\int\phi_{Bnl}(\mathbf{r})(F_A+U_A)\phi_{An'l'}(\mathbf{r})d\tau,$$

$$B'=\int\exp[i(\mathbf{k}+\mathbf{h})\cdot\mathbf{r}](F_A+U_A)\phi_{Anl}(\mathbf{r})d\tau, \quad \text{(A2)}$$

$$C'=\int\exp[i(\mathbf{h}-\mathbf{h}')\cdot\mathbf{r}](F_A+U_A)d\tau.$$

These matrix elements are evaluated using the Eq. (7) defining local orbitals, and if we retain terms linear in interatomic overlap one has

$$[F_A+U_A]\phi_{Ai}=\epsilon_{Ai}\phi_{Ai}+\sum_k{}'\phi_{Ak}\langle Ak \mid U_A \mid A_i\rangle. \quad \text{(A3)}$$

If one substitutes this result into $A'$ and $B'$ of Eq. (A2) one obtains

$$A'=\epsilon_{An'l'}\langle Bnl \mid An'l'\rangle + \sum_{n'',l''}{}'\langle Bnl \mid An''l''\rangle\langle An''l'' \mid U_A \mid An'l'\rangle \quad \text{(A4)}$$

and

$$B'=\epsilon_{Anl}\int\exp[i(\mathbf{k}+\mathbf{h})\cdot\mathbf{r}]\phi_{Anl}(\mathbf{r})d\tau + \sum_{n',l'}{}'\langle An'l' \mid U_A \mid Anl\rangle \times\int\exp[i(\mathbf{k}+\mathbf{h})\cdot\mathbf{r}]\phi_{An'l'}(\mathbf{r})d\tau. \quad \text{(A5)}$$

These matrix elements do not depend in any way on the orbitals being orthogonal and are valid for overlapping or nonoverlapping basis functions.

The nonlocal part of element $C'$ has been discussed in the text. The evaluation of the local part is done along the same lines as one uses to evaluate the matrix element between two plane waves in the usual mixed-basis theory.[4] Thus one evaluates the kinetic-energy matrix element between two plane waves and evaluates the element of two plane waves and the local potential by evaluating the Fourier coefficients of that potential.

## APPENDIX B

In this Appendix we describe the technique used to solve the localized-orbital equation. The method used is the analytic Hartree-Fock method in the form used by Watson and Freeman for Cl$^{-37}$. It is assumed that the local orbital $\phi_{Ai}(\mathbf{r})$ may be given in the form

$$\phi_{Ai}(r)=R_{Ail}(r)\,Y_l^M(\theta,\phi)\begin{Bmatrix}\alpha\\ \beta\end{Bmatrix},$$

$$rR_{Ail}=\sum_j C_{Ailj}P_{lj}(r), \quad \text{(B1)}$$

$$P_{lj}(r)=N_{lj}r^{l+1+A_{lj}}\exp(-Z_{lj}r),$$

$$N_{lj}=[(2Z_{lj})^{2l+2A_{lj}+3}/(2l+2A_{lj}+2)!]^{1/2}.$$

The $Y_l^M$ are the usual spherical harmonics, $\alpha$ and $\beta$ are the spin-up, spin-down functions, and the parameters $A_{lj}$ and $Z_{lj}$ were those used by Watson and Freeman. The localized-orbital equation in its integrated form is given, using the standard notation of Hartree[35] for the $1s$ shell of Li$^+$ as

$$\epsilon_{1s}=K_{1S}+2F^0(1s,1s)-G^0(1s,1s)+V_{1s}, \quad \text{(B2)}$$

for the $ns$ shell of Cl$^-$ as

$$\epsilon_{ns}=K_{ns}+2F^0(ns,1s)+2F^0(ns,zs)+2F^0(ns,3s) +6F^0(ns,2p)+6F^0(ns,3p)-G^0(ns,1s)-G^0(ns,2s) -G^0(ns,3s)-G^1(ns,2p)-G^1(ns,3p)+V_{ns}, \quad \text{(B3)}$$

and for the $np$ shell of $\mathrm{Cl}^-$ as

$$\begin{aligned}\epsilon_{np}=K_{np}&+2F^0(np,1s)+2F^0(np,2s)+2F^0(np,3s)\\&+6F^0(np,2p)+6F^0(np,3p)-\tfrac{1}{3}G^1(np,1s)\\&-\tfrac{1}{3}G^1(np,2s)-\tfrac{1}{3}G^1(np,3s)-G^0(np,2p)\\&-G^0(np,3p)-0.4G^2(np,2p)-0.4G^2(np,3p)+V_{ns}.\end{aligned}\tag{B4}$$

In this notation we use the term $V_{nx}$ to specify the term

$$V_{nx}=\langle nx\mid U_A\mid nx\rangle.\tag{B5}$$

In Table IV the energy parameters $\epsilon_{nx}$ are given for the various calculations. The computations were performed using double-precision computer codes written for the IBM 360-75 computer by the author.

In iterating to self-consistency, the charge density from the $i$th iteration and the $(i-1)$st iteration was averaged before obtaining the $(i+1)$st iteration. This prevented the solutions from diverging. All pertinent integrals were evaluated numerically since the author had accurate, tested codes for this purpose. The integrals could have been evaluated analytically. The author checked a number of matrix elements evaluated numerically against the same elements evaluated analytically and found the results to be in good agreement. The computer codes generated by the author for this problem did not seem to be particularly efficient. About five minutes of computer time were required to obtain solutions for the free $\mathrm{Cl}^-$ and $\mathrm{Li}^+$ ions. Using numerical integration of the same equations, only about one minute would have been needed. Nonetheless in the crystal problem the analytic expansion technique proved to be easiest to apply.

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