

Application of the Orthogonalized-Plane-Wave Method to Lithium Chloride, Sodium Chloride, and Potassium Chloride*

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(Received 30 January 1968; revised manuscript received 16 May 1968)

The orthogonalized-plane-wave method has been used to compute the energy bands of LiCl, NaCl, and KCl. General results are obtained that are valid for any diatomic lattice. Computer programs (which considerably reduce the labor of applying this method to a wide class of substances) have been developed and are discussed. The results are compared with those of recent calculations and experiments. In general, there seems to be a good correlation between the present results and those of experiment. It is suggested that the peculiar optical absorption of LiCl may be due to transitions from the valence band to the conduction band involving the line Λ and the point L in the Brillouin zone. The possibility of X excitons in NaCl and LiCl is explored.

I. INTRODUCTION

IN previous years, the orthogonalized-plane-wave (OPW) method^{1,2} has found its principal application in studying the band structure of metals^{3,4} or semiconductors.^{5,6} For tightly bound solids, such as the alkali halides or the solid rare gases, its principal use has been in calculations of the conduction states.⁷⁻⁹

This author has recently succeeded in applying the OPW method to selected symmetry points in the first Brillouin zone of sodium chloride for both the valence and conduction bands.¹⁰ It is the intent of the author in this paper to extend the OPW method to tightly bound solids in general, to discuss some of the important factors inherent to this method, and to relate the method to others commonly used for these substances. Calculations have been performed for lithium chloride, sodium chloride, and potassium chloride at selected symmetry points in the first Brillouin zone. Some powerful numerical techniques that were developed to handle the labor of this type of calculation are discussed. Computer programs have been written that will greatly reduce the labor of applying this method to a wide class of solids.

There are some advantages inherent to the OPW method as opposed to the tight-binding method¹¹ or the augmented-plane-wave (APW) method.¹² These advantages lie in the ability of the OPW method to include the lattice potential conveniently in an exact manner. In the tight-binding method, it is usual to

include only certain terms in the lattice potential, and this may lead to difficulties as to the accuracy of the bands considered.¹³ In the APW method, one usually assumes the potential about a given lattice site to be spherically symmetric, and the potential in the region between the spherical regions about each lattice site to be a constant.^{14,15} It is possible, however difficult, to overcome these assumptions in the APW method by a perturbation approach.¹⁴

The results obtained in this calculation for KCl are compared with those of previous calculations using other techniques. The results are, in general, compared with recent and not-so-recent experiments, and a fair amount of agreement is obtained between theory and experiment. There also seems to be a reasonable amount of correlation between the results of the several theoretical calculations available for comparison.

II. THEORETICAL DEVELOPMENT

As in previous calculations, it is assumed that the lattice potential may be given as a superposition of the potentials of the free ions that constitute that lattice.^{10,13,16} It is desired to solve the usual nonrelativistic Schrödinger equation for the lattice subject to the usual one-electron approximation. The method of solution to be used is the OPW method.¹² The core states are formed from the core-state solutions to the free-ion problem. These core states are then formed into Bloch functions, and linear combinations of the Bloch functions are formed to transform according to the l th row of the α th irreducible representation of the symmetry group of the wave vector \mathbf{k} , for the point in the first Brillouin zone for which a solution is desired.^{17,18} The states used as core states were those states for which $E(\mathbf{k})$ was a constant. The core states and the free-ion potentials were obtained by using

* Work supported in part by the U. S. Air Force Office of Scientific Research, Contract No. 1276-67.

¹ C. Herring, *Phys. Rev.* **57**, 1169 (1940).

² L. Mariot, *Group Theory and Solid State Physics* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962).

³ M. L. Glasser and J. Callaway, *Phys. Rev.* **109**, 1541 (1958).

⁴ R. H. Parmenter, *Phys. Rev.* **86**, 552 (1952).

⁵ F. Herman, *Phys. Rev.* **93**, 1214 (1953).

⁶ T. O. Woodruff, *Phys. Rev.* **98**, 1741 (1956).

⁷ W. Beall Fowler, *Phys. Rev.* **132**, 1591 (1963).

⁸ S. Oyama and T. Miyakawa, *J. Phys. Soc. Japan* **21**, 868 (1966).

⁹ M. H. Reilly, PhD. thesis, University of Rochester, 1966 (unpublished); *J. Phys. Chem. Solids*, **28**, 2067 (1967).

¹⁰ A. Barry Kunz, *Phys. Letters* **25A**, 538 (1967).

¹¹ J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).

¹² J. C. Slater, *Phys. Rev.* **51**, 846 (1937); **92**, 603 (1953).

¹³ A. Barry Kunz, *Phys. Rev.* **162**, 789 (1967).

¹⁴ P. D. DeCicco, *Phys. Rev.* **153**, 931 (1967).

¹⁵ David A. Liberman, *Phys. Rev.* **153**, 704 (1967).

¹⁶ A. Barry Kunz and W. J. Van Sciver, *Phys. Rev.* **142**, 462 (1966); A. Barry Kunz, *ibid.* **151**, 620 (1966).

¹⁷ R. S. Knox and A. Gold, *Symmetry in the Solid State* (W. A. Benjamin, Inc., New York, 1964).

¹⁸ J. C. Slater, *Rev. Mod. Phys.* **37**, 68 (1965).

modified Herman and Skillman computer codes for several choices of potential.¹⁹

In the usage of Herman and Skillman,¹⁹ one defines the potential of a free ion to be

$$V(r) = -\frac{2Z}{r} - \frac{2}{r} \int_0^r \sigma(r') dr' - 2 \int_r^\infty \sigma(r') \frac{dr'}{r'} - 6[-3/(8\pi)(4\pi r^2)^{-1}\sigma(r)]^{1/3}, \quad r \leq R_0 \quad (1a)$$

$$V(r) = -2(Z-N+1)/r, \quad r > R_0. \quad (1b)$$

In Eqs. (1), Z is the atomic number, N is the number of electrons centered on the ion, and R_0 is defined as that radius at which the value of $V(r)$ given by Eq. (1a) equals the value of $V(r)$ given by Eq. (1b).

If $P_{nl}(r)$ is the radial part of the solution to the nl orbital of the free ion multiplied by r , and W_{nl} is the number of electrons in the nl subshell, then $\sigma(r)$ is defined by

$$\sigma(r) = -\sum_{n,l} W_{nl} |P_{nl}(r)|^2. \quad (2)$$

The summation is over all filled levels in the free ion. In the cases considered here, the value of R_0 for the several free ions is such that the exchange parts of the potentials do not overlap when one forms the lattice potential by a summation of the free-ion potentials of the lattice. For example, R_0 for Na^+ was 1.5 Bohr units and R_0 for Cl^- was 3.2 Bohr units.

The use of these potentials deserves some discussion. This potential resembles that which the author has found most useful for studying the valence bands by tight-binding theory.¹⁶ It is assumed that the valence-electron wave function is that which arises chiefly from a Cl^- $3p$ orbital. To form the potential, one has an electron in a given unit cell associated with a Cl^- ion at the center of that cell. This cell center is considered to be the origin. There are five other valence electrons in that unit cell. In the other unit cells, there are six valence electrons. The Cl^- core electrons and the electrons associated with the alkali are the same in all unit cells. Thus, the valence electron in question sees a potential formed from three types of contributions. These are (i) the halogen ion at the origin, (ii) the short-range parts of the other alkali and halogen ions, and (iii) the long-range parts of the other alkali and halogen ions.

The three types of contribution are considered separately. The potential due to the halogen ions at the origin is evaluated using Eqs. (1) and (2), with $N=Z+1$. This contribution goes to zero rapidly as r goes to infinity. The effect of the remainder of the lattice is less simple. In the other halogen ions, one has $N=Z$, and for the alkali ions, one has $N=Z+2$. Thus, the electron sees potentials due to the other halogen

ions, which go as $+2/r$ Ry at large distances, and potentials due to the alkali ions, which go as $-2/r$ Ry at large distances. In order to evaluate the Fourier coefficients of this potential contribution it is necessary to separate the potential into long-range and short-range parts. The long-range parts are those that go as $\pm 2/r$ Ry.

The contribution of the halogen ion at the origin and of the short-range parts of the potentials to the Fourier coefficients can be evaluated in the usual ways with no difficulty.^{1,2,7} However, the Fourier coefficients of the long-range potential are more troublesome. In this case, one evaluates the Fourier coefficient for the entire potential by integrating over the unit cell at the origin.² In this case, the total long-range part of the potential in the unit cell about the origin converges and its contribution to $v(0)$ is simply the Madelung energy. All potential contributions to the Fourier coefficients may be evaluated in this way if one desires.

The author believes that the effect of this potential is to have the electron in question see a potential which is due to all the remainder of the electrons in the lattice and the nuclei. Thus, this potential is different from the one usually used in which the electron in question is considered to be an extra electron in the lattice. The type of potential used in this calculation seems to be especially suited to consideration of the valence levels.

In the usual OPW practice, the solution is found by solving the equation

$$\text{Det}(M_{pj,p'j'}) = 0, \quad (3)$$

where

$$M_{pj,p'j'} = \int \psi_p^{\alpha lj}(\mathbf{k}, \mathbf{r})^* H \psi_{p'}^{\alpha lj'}(\mathbf{k}, \mathbf{r}) d\tau - E \int \psi_p^{\alpha lj}(\mathbf{k}, \mathbf{r})^* \psi_{p'}^{\alpha lj'}(\mathbf{k}, \mathbf{r}) d\tau. \quad (4)$$

In Eq. (4), $\psi_p^{\alpha lj}(\mathbf{k}, \mathbf{r})$ is the function formed by symmetrizing a linear combination of plane waves to transform according to the j th column, the l th row of the α th irreducible representation of the group of the vector \mathbf{k} , and it is orthogonalized to the core states which are similarly symmetrized. H is the one-electron Hamiltonian and $\psi_{p'}^{\alpha lj'}(\mathbf{k}, \mathbf{r})$ is defined in a way similar to the other function. The integration is over the volume of the crystal. These equations reduce to a simpler form, which, if the crystal were a zinc-blende structure, would be the same as those of Bassani and Yoshimine.²⁰

III. DETAILS OF THE CALCULATION

Calculations have been performed for sodium chloride, lithium chloride, and potassium chloride. In order to perform this calculation, the ionic potentials and the core states for the free ions were obtained by solving the Hartree-Fock-Slater equations subject to

¹⁹ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

²⁰ F. Bassani and M. Yoshimine, *Phys. Rev.* **130**, 20 (1963).

the modification given by Herman and Skillman.¹⁹ To do this work, a computer program was prepared which computed the potentials and wave functions for the free ions and then performed the necessary group theory automatically for states of interest. The program then formed the determinant M_{p_j, p'_j} as defined in Eqs. (3) and (4), computed the roots of this determinant, and obtained the eigenvectors. The necessary group-theoretical data were obtained from standard sources^{21,22} and the results were seen to agree with those of Luehrmann.²³ The numerical techniques used are discussed in Appendix A.

These results neglect spin-orbit effects. These, however, may be included by a perturbation method.^{24,25} It is assumed that the spin-orbit effects are important only for the p -like valence band. This would be consistent with recent calculations on KI.^{26,27} It seems reasonable to expect that spin-orbit splittings in the conduction band will be even smaller in the chlorides than in the iodides.

In performing the computations, those states for which energy as a function of wave vector was essentially a constant were chosen as core states. For NaCl, an attempt was made to construct the valence band from tight-binding functions¹³ and then by orthogonalizing to them, to construct only the conduction states from OPW's. However, the lowest value of energy rather rapidly converged to the valence energy, and the next value converged to the conduction states.

Thus, one concludes that the tight-binding functions are not adequate to represent the valence states of NaCl and possibly the other alkali halides, at least not when these functions are used in their normal form.

One may discuss the implications of the convergence of the energies to the valence states when one attempted to use the Cl^- tight-binding functions for the valence bands. This implies that for purposes of orthogonalization, the tight-binding valence states are not adequately close to being eigenstates of the crystal Hamiltonian. One may ask, at what point are the tight-binding orbitals such poor eigenstates of the crystal Hamiltonian that they are unusable in an OPW calculation? It is not possible to give a definitive answer to this question at present; however, it is possible to begin to answer this question. In the case of KCl, calculations were made in which the $3p$ K^+ band was computed by OPW

²¹ G. F. Koster, *Space Groups and Their Representations* (Academic Press Inc., New York, 1957).

²² G. F. Koster, I. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (The M. I. T. Press, Cambridge, Mass., 1963).

²³ A. W. Luehrmann, thesis, University of Chicago, 1966 (unpublished).

²⁴ L. Liu, *Phys. Rev.* **126**, 1317 (1962).

²⁵ A. Barry Kunz, *Phys. Rev.* **159**, 738 (1967).

²⁶ Y. Onodera, M. Okazaki, and T. Inui, Technical Report of the Institute for Solid State Physics, University of Tokyo, Tokyo, Japan Ser. A, No. 209, 1966 (unpublished); *J. Phys. Soc. Japan* **21**, 2229 (1966).

²⁷ Y. Onodera and Y. Toyozawa, *J. Phys. Soc. Japan* **22**, 833 (1967).

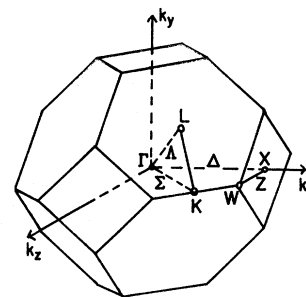


FIG. 1. The Brillouin zone for a fcc crystal. Points and lines of symmetry are given.

techniques and other calculations in which this band was assumed known from tight-binding theory. There was no significant deviation in the valence or conduction levels of KCl when the results of these two calculations were compared.

Figure 1 shows the Brillouin zone for the fcc lattice and points and lines of symmetry. The band structures including spin-orbit effects in the valence bands are given for LiCl, NaCl, and KCl in Figs. 2-4. In addition, the values of the energy are given in Tables I-III. The notation is that of Bouchaert, Smoluchowski, and Wigner.²⁸

The convergence of the energies was studied using second-order perturbation theory. It was required that the contributions of the last few sets of plane waves be smaller than 10^{-4} Ry. The second-order-perturbation-theory result was computed with respect to the dominant orthogonalized plane wave.

In addition, the convergence of the wave function was studied and it was required that the coefficients of the last few sets of plane waves be 10^{-2} or smaller. The normal convergence curves of energy as a function of the

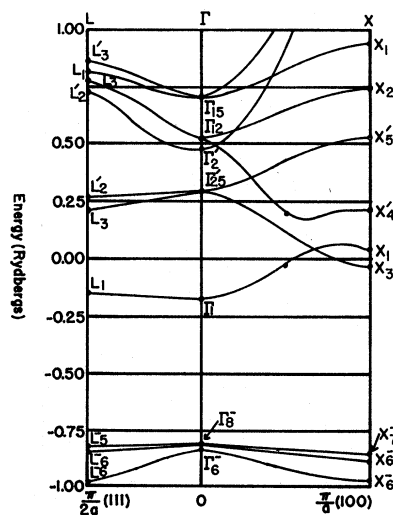


FIG. 2. The band structure of LiCl. The notation is that of Ref. 28. The points actually calculated are shown by a dot. The bands have been drawn using the compatibility relations and also the result of other calculations.

²⁸ L. P. Bouchaert, R. Smoluchowski, and E. Wigner, *Phys. Rev.* **50**, 58 (1936).

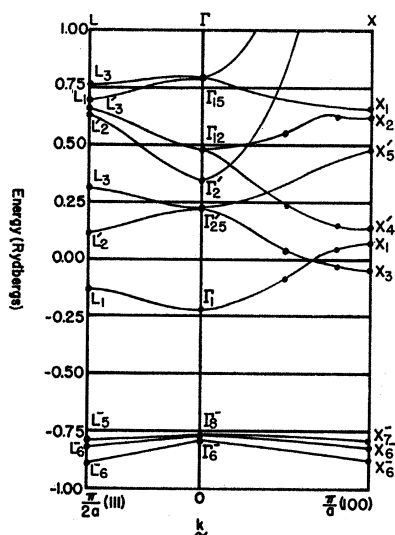


FIG. 3. The band structure of NaCl. The notation is that of Ref. 28. The points actually calculated are shown by a dot. The bands have been using the compatibility relations and also the results of other calculations.

number of plane waves used were not obtained for all states. The primary reason is that a rather large number of plane waves were used (300–600) and this required that rather large matrices (30×30 – 50×50) be diagonalized. It was not economical to diagonalize a large number of these matrices in order to check on the convergence of all states. However, for a few key levels such as Γ_{15} , Γ_{12} , Γ_{25}' , L_3' , and X_3 this information was obtained for the case of NaCl and for Γ_{12} and Γ_{25}' in KCl and LiCl. These results indicated that the states were well converged. Therefore, the author believes that the perturbation-theory results are an adequate indication of convergence.

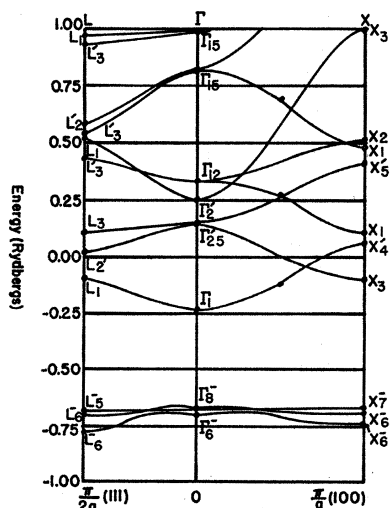


FIG. 4. The band structure of KCl. The notation is that of Ref. 28. The points actually calculated are shown by a dot. The bands have been drawn using the compatibility relations and also the results of other calculations.

TABLE I. The energy in rydbergs of selected symmetry points for LiCl. The notation is that of Ref. 28. For the p -like valence bands, energies with and without spin-orbit effects are given. $\Delta = (\pi/2a)$ (100), $A = 9.7$ Bohr units, $\xi = 0.00321$ Ry.

Γ	X	L	Δ	
s-like valence state				
Γ_1	-1.81150	X_1 -1.76290	L_1 -1.77687	Δ_1 -1.78923
p -like valence state without spin-orbit effects				
Γ_{15}	-0.82454	X_4' -0.98715	L_2' -0.98764	Δ_1 -0.89629
		X_5' -0.87666	L_3' -0.84134	
p -like valence state with spin-orbit effects				
Γ_6^-	-0.83096	X_6^- -0.98687	L_6^- -0.98770	
Γ_8^-	-0.82133	X_6^- -0.88015	L_6^- -0.84448	
		X_7^- -0.87345	L_8^- -0.83813	
All computed conduction states without spin-orbit effects				
Γ_1	-0.18548	X_1 0.05044	L_1 -0.15683	Δ_1 -0.02574
Γ_{25}'	0.29717	X_3 -0.04599	L_3 0.22063	
		X_5' 0.53980	L_2' 0.26342	
Γ_2'	0.48032		L_3' 0.72668	
Δ_{12}	0.54401	X_4' 0.22863	L_3 0.76154	Δ_1 0.19055
		X_2 0.75345		
Γ_{15}	0.71369	X_1 0.93666	L_1 0.82151	Δ_1 1.17949
		X_4' 1.40991	L_1' 0.84777	
			L_1 1.411757	

Some Fourier coefficients of the potentials are given in Table IV. It is due to the large number of plane waves needed that additional points in the first Brillouin zone such as K or some points along Λ have not been calculated. Some attempts were made to do this. However, to obtain good convergence, matrices greater than 50×50 needed to be diagonalized, and to do a sufficient number of them to obtain more useful information was not practical.

It is possible to compute the energy structure for other points in the Brillouin zone using the results presented here. To do this, the formalism of Slater and Koster¹¹ may be used. In the Slater-Koster method, hypothetical tight-binding-type functions are assumed

TABLE II. The energy in rydbergs of selected symmetry points for NaCl. The notation is that of Ref. 28. $\Delta = (\pi/2a)$ (100), $A = 10.6$ Bohr units, $\xi = 0.00313$ Ry.

Γ	X	L	Δ	
s-like valence state				
Γ_1	-1.72970	X_1 -1.71024	L_1 -1.71569	Δ_1 -1.72106
p -like valence states without spin-orbit effects				
Γ_{15}	-0.78210	X_4' -0.86747	L_2' -0.88112	Δ_1 -0.81036
		X_5' -0.79929	L_3' -0.79141	
p -like valence states with spin-orbit effects				
Γ_6^-	-0.78836	X_6^- -0.87076	L_6^- -0.88437	
Γ_8^-	-0.77897	X_6^- -0.79914	L_6^- -0.79129	
		X_7^- -0.79616	L_8^- -0.78828	
All calculated conduction states without spin-orbit effects				
Γ_1	-0.24356	X_1 0.07541	L_1 -0.13777	Δ_1 -0.10461
Γ_{25}'	0.23533	X_3 -0.05498	L_3' 0.12194	Δ_2' 0.02325
		X_5' 0.48843	L_3 0.29163	
Γ_2'	0.35804	X_3 1.31686	L_2' 0.63133	Δ_2' 0.73192
Γ_{12}	0.47112	X_4' 0.12516	L_3' 0.63853	Δ_1 0.24984
		X_2 0.66258		Δ_2 0.56679
Γ_{15}	0.80184	X_1 0.67150	L_1 0.67216	
		X_4' 1.42723	L_3 0.75117	
Γ_{15}	1.32859	X_4' 1.34732	L_1 1.17878	Δ_2 1.33698
			L_3' 1.27606	
Γ_1	1.43441		L_2' 1.39284	

and the values of the energies throughout the Brillouin zone are given in terms of the energy parameters of these hypothetical tight-binding functions and the crystal potential. In this case, the two-center approximation need not be made. Using the energy values computed by the OPW method and the equations of Table II of Slater and Koster, it is possible to compute the energy parameters needed to give the p -like valence band, the lowest s -like conduction band, the two lowest d -like conduction bands, and the p -like conduction band using a halogen ion as the origin. The values of the parameters needed have been obtained for LiCl, NaCl, and KCl, and are given in Table V. In obtaining these parameters, the interaction of the s , p , and d conduction levels is neglected. Using these results and the formulas of Slater and Koster, Table II, it is possible to compute approximate energies for the valence bands

TABLE III. The energy in rydbergs of selected symmetry points for KCl. The notation is that of Ref. 28. $\Delta = (\pi/2a)$ (100), $A = 11.8$ Bohr units, $\xi = 0.00303$ Ry.

Γ	X	L	Δ
s-like valence state			
Γ_1	-1.64038	X_1 -1.63583	L_1 -1.64121 Δ_1 -1.64238
p-like valence states without spin-orbit effects			
Γ_{15}	-0.71709	X_4' -0.74572	L_3' -0.77369 Δ_1 -0.70802
		X_3' -0.70756	L_2' -0.72023
p-like valence states with spin-orbit effects			
Γ_6^-	-0.72317	X_6^- -0.74611	L_6^- -0.77407
Γ_8^-	-0.71405	X_8^- -0.71020	L_8^- -0.72289
		X_7^- -0.70452	L_7^- -0.71719
All calculated conduction states without spin-orbit effects			
Γ_1	-0.24573	X_4' 0.06382	L_1 -0.10755 Δ_1 -0.13255
Γ_{25}'	0.15366	X_3 -0.08009	L_2' 0.02344
		X_6' 0.42196	L_3 0.10539
Γ_2'	0.24156	X_3 1.03582	L_1 0.51339
Γ_{12}	0.34128	X_1 0.09704	L_3' 0.43237 Δ_1 0.27889
		X_2 0.51174	
Γ_{15}	0.83054	X_1 0.47441	L_3 0.51807 Δ_1 0.70118
		X_5' 1.27238	L_2' 0.55834
Γ_{15}	0.99616	X_4' 1.16465	L_3' 0.90085
			L_1 0.95883
Γ_1	1.22874	X_1 1.38124	L_2' 1.10965
Γ_{12}	1.43415		L_3 1.08464

and the lower conduction bands throughout the first Brillouin zone.

IV. DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENT

It is found that the valence bands are 2.22, 1.35, and 0.77 eV in width for LiCl, NaCl, and KCl, respectively. These widths are increased by about 0.1 eV when spin-orbit effects are included. It is possible to compare these results with other recent calculations. For NaCl, the author¹³ has obtained a width of 1.4 eV using the tight-binding method and certain three-center integrals. For LiCl, the author obtained a width of about 1.2 eV using the tight-binding method but neglecting three-center effects.¹⁶ It is clear from the NaCl calculation¹³ that three-center terms would substantially widen the tight-binding LiCl results.

TABLE IV. The Fourier coefficients (in Ry) of the lattice potential for LiCl, NaCl, and KCl. The potential employed contained a modified Slater exchange.

$K^2(a/2\pi)^2$	$v(K)$, LiCl	$v(K)$, NaCl	$v(K)$, KCl
0	-1.40016	-1.23921	-1.15154
3	-0.44420	-0.27855	-0.10115
4	-0.40083	-0.39791	-0.41848
8	-0.26393	-0.29167	-0.32348
11	-0.19988	-0.11116	-0.02669
12	-0.19445	-0.22899	-0.25889
16	-0.15724	-0.19072	-0.21438
19	-0.13202	-0.06110	-0.00796
20	-0.13487	-0.16581	-0.18301
24	-0.11926	-0.14811	-0.16026
27	-0.10255	-0.04402	-0.00564
32	-0.09677	-0.12296	-0.12982
35	-0.08320	-0.03527	-0.00602
36	-0.08817	-0.11311	-0.11904
40	-0.08097	-0.10449	-0.11009
43	-0.06970	-0.02925	-0.00568
44	-0.07500	-0.09693	-0.10249
48	-0.07006	-0.09032	-0.09594
51	-0.06051	-0.02467	-0.00458
56	-0.06246	-0.07958	-0.08524
59	-0.05399	-0.02235	-0.00332
64	-0.05663	-0.07143	-0.07696
68	-0.05409	-0.06806	-0.07350
72	-0.05172	-0.06504	-0.07040
76	-0.04948	-0.06230	-0.06760

There are several recent calculations available for KCl. DeCicco, using the APW method, obtained a width of 0.82 eV for the KCl valence band.¹⁴ In a less

TABLE V. Tight-binding parameters (in Ry) are given for the valence bands and the lowest conduction bands. The notation is that of Table II, Ref. 11. Using these parameters and the formulas of Table II of Ref. 11 as it applies to a fcc crystal, it is possible to construct an energy-level diagram throughout the first Brillouin zone for these substances.

Parameter valence states	Substance	LiCl	NaCl	KCl
$E_{xx}(000)$		-0.89067	-0.81667	-0.72877
$E_{xx}(110)$		0.01016	0.00533	0.00179
$E_{xx}(011)$		-0.00364	-0.00318	-0.00298
$E_{xx}(200)$		-0.00239	-0.00361	-0.00585
$E_{yy}(200)$		0.00105	0.00296	0.00524
$E_{xy}(110)$		0.01219	0.00747	0.00445
Conduction states				
$E_{ss}(000)$		-0.08268	-0.07105	-0.04810
$E_{ss}(110)$		-0.01475	-0.01994	-0.02142
$E_{ss}(200)$		0.01235	0.01112	0.00991
$E_{xy,xy}(110)$		-0.05177	-0.04978	-0.04815
$E_{xy,xy}(011)$		0.02144	0.01814	0.01461
$E_{xy,zz}(011)$		-0.06110	-0.04786	-0.03550
$E_{3z^2-r^2, 3z^2-r^2}(000)$		0.76979	0.61806	0.45512
$E_{3z^2-r^2, 3z^2-r^2}(110)$		-0.00736	-0.01169	-0.01182
$E_{x^2-y^2, x^2-y^2}(110)$		-0.030265	-0.01280	-0.00715
$E_{xy,xy}(000)$		0.33269	0.28930	0.22937
$E_{xy,3z^2-r^2}(110)$		0.1077	0.1838	0.05350
$E_{xx}(000)$		0.65298	0.46633	0.29606
$E_{xx}(110)$		0.03032	0.04229	0.04792
$E_{xx}(011)$		-0.04546	-0.07083	0.03778
$E_{xy}(110)$		0.04869	0.04305	0.03407

recent calculation, Howland, by a LCAO (linear combination of atomic orbitals) tight-binding calculation, obtained a width of 1.5 eV.²⁹ It is noted that, when only $3p$ Cl^- functions were included in the basis, the width of the band according to Howland was 2.2 eV. Using only the $3p$ Cl^- functions as a basis, the author has performed a tight-binding calculation for KCl, and finds a width of 0.48 eV when three-center terms are neglected. The author feels that a value of 0.8 eV would be most reasonable for the width of the KCl valence band when one considers the present results, the results of DeCicco, and the author's tight-binding results.

Experimentally, Parratt and Jossem have found that the valence band of KCl has a half-width of about 0.33 eV.³⁰ This result is in disagreement with the experimental interpretations given by Phillips,³¹ which are based on the optical data of Eby, Teegarden, and Dutton.³² The results of Phillips rest heavily on the work of Howland and also on the free-electron picture for the conduction bands, and may be subject to error. Using the results of Slater and Koster and the values given in Table V, the author has computed the density of states for the KCl valence band. The energies for the valence bands were obtained at 512 nonequivalent points in the first Brillouin zone and a density-of-states curve obtained. The valence bands have a half-width of 0.4 ± 0.1 eV. This result is similar to that of DeCicco and does not compare unfavorably to the result of Parratt and Jossem.³⁰

Values for the band gaps [$E(\Gamma_1) - E(\Gamma_{15})$] have been obtained, and are 8.7, 7.4, and 6.5 eV for LiCl, NaCl, and KCl, respectively. The value of 6.5 eV for the KCl band gap compares favorably with the value of 6.3 eV obtained by DeCicco. In many features the present results compare well with the results of DeCicco, at least for the valence states and the lowest conduction levels. It is noted that the results of DeCicco are presented using a different origin than that of the present calculation and this causes a slight notational difficulty. At the point L , a state given here as L_1 would be given as L_2' by DeCicco. One also has the following interchanges: $L_2' \rightarrow L_1$, $L_3' \rightarrow L_3$, and $L_3 \rightarrow L_3'$. Keeping these identities in mind, the present results compare favorably with those of DeCicco. It is seen that the point X_3 lies lower than X_1 for all three substances. Thus, there is a possibility of excitons associated with X_3 for NaCl and LiCl as there is for KCl. However, since X_3 lies not as far below X_1 in LiCl or NaCl as in KCl, it is possible that any X_3 exciton in these substances would be considerably broadened by coupling to the continuum.

There is a wealth of optical data available for comparison. These data are of five types: the absorption

of photons by thin films of the alkali halide,^{32,33} the reflectance spectra of alkali-halide crystals,^{34,35} two-photon absorption processes,³⁶ the absorption of soft x rays by alkali-halide films,^{37,38} and electron energy-loss experiments.³⁹ The problem is to reduce the available data to a form in which they are useful.

Let us consider the band gap in KCl first. The band gap in KCl is thought to occur at about 8.5 eV.^{34,35} The present result is too small by about 2.0 eV. This is nearly the amount by which our value for the free-ion $3p$ Cl^- energy differs from the experimental value. It may be possible to shift our valence band downward by about 2.0 eV and then to continue the comparison to experiment. The justification of this is twofold. First, the approximate position of the valence band with respect to the vacuum is given by the sum of the Madelung energy and the energy of a $3p$ Cl^- electron. Thus an error in the free Cl^- electron would change the position of the band with respect to the vacuum.⁴⁰ Secondly, the position of the conduction band with respect to the vacuum remains essentially the same for changes of potential.

To investigate these effects, the band structure of NaCl was recomputed for several potentials. An attempt was made to use the Kohn and Sham potential⁴¹ but was frustrated by the author's inability to obtain convergent solutions for the free Cl^- ion using modified Herman-Skillman computer codes. The atomic Lindgren potential⁴² was used, and convergent results were obtained for the free Na^+ and Cl^- ions. The band structure of NaCl remained essentially unchanged for two sets of Lindgren parameters, with one exception. The position of the valence band with respect to the vacuum changed by the amount which the Cl^- $3p$ energy changed in the free-ion calculations. In other respects the valence bands seemed rigid. The conduction bands remained unchanged to all practical purposes by these changes of potential. For example, while the valence band changed position by about 1.0 eV for the various potentials, the lowest conduction band shifted by less than 0.1 eV and other conduction-band points by 0.2 eV or less. The change in valence-band width was less than 0.05 eV. Thus, the author feels justified in shifting the valence band downward in order to bring the band-gap results into agreement with

³³ K. Teegarden and G. Baldini, *Phys. Rev.* **155**, 896 (1967).

³⁴ G. Baldini and B. Bosacchi, *Phys. Rev.* **166**, 803 (1968).

³⁵ D. M. Roessler and W. C. Walker, *Phys. Rev.* **166**, 599 (1968).

³⁶ D. Forhlich and B. Stagninus, *Phys. Rev. Letters* **19**, 496 (1967).

³⁷ R. Haensel, C. Kunz, and B. Sonntag, *Phys. Rev. Letters* **20**, 262 (1968).

³⁸ R. Haensel, C. Kunz, T. Sasaki, and B. Sonntag (to be published).

³⁹ C. Gout and F. Pradal, *J. Phys. Chem. Solids* **29**, 581 (1968).

⁴⁰ T. L. Gilbert, in *Molecular Orbitals in Chemistry, Physics and Biology*, edited by P. O. Löwdin and B. Pullman (Academic Press Inc., New York, 1964); see also an unpublished paper.

⁴¹ W. Kohn and L. J. Sham, *Phys. Rev.* **140**, 1133 (1965).

⁴² I. Lindgren, *Arkiv Fysik* **31**, 59 (1965).

²⁹ L. P. Howland, *Phys. Rev.* **109**, 1927 (1958).

³⁰ L. G. Parratt and E. J. Jossem, *Phys. Rev.* **97**, 916 (1955).

³¹ J. C. Phillips, *Phys. Rev.* **136**, 1705 (1964).

³² J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959).

TABLE VI. Transition energies are given for several critical points in the bands of KCl both experimentally and theoretically. These energies are with respect to the transition Γ_{15} to Γ_1 . The identification of the states responsible for these transitions given by the several authors is given. Energies are in eV.

Ref. a		Experimental				Theoretical			
Transition	Energy	Ref. b	Ref. c	Ref. d	Present work	Transition	Energy	Transition	Energy
Γ_{15}, Γ_1	0.0	Γ_{15}, Γ_1	Γ_{15}, Γ_1	Γ_{15}, Γ_1	Γ_{15}, Γ_1	Γ_{15}, Γ_1	0.0	Γ_{15}, Γ_1	0.0
X_5', X_3	1.4	L_3', L_1	0.3						
		X_5', X_3	1.2			X_5', X_3	1.2	L_3', L_1	1.8
		X_5', X_1	2.2			L_3', L_1^*	2.5	X_5', X_3	2.2
		L_3', L_3	2.5			$\Gamma_{15}, \Gamma_{25}'$	2.7		
		$\Gamma_{15}, \Gamma_{25}'$	2.9			X_5', X_1	2.9		
				X_5', X_3	3.2				X_5', X_1
		X_5', X_1	4.0				L_3', L_3	4.8	
		$\Gamma_{15}, \Gamma_{25}'$	8.6			L_3', L_3	6.1	$\Gamma_{15}, \Gamma_{25}'$	5.4

* Reference 34.

^b Reference 35.

^c Reference 39.

^d Reference 14.

experiment before further testing his prediction. The potential is discussed in Appendix B.

Certain features of the absorption spectra of the alkali halides may be understood in terms of band-to-band transitions, while others are explained best by an exciton model. In terms of band-to-band transitions, there are points of interest, called critical points,⁴⁸ which are singularities in the joint density of states for the valence and conduction bands. Some of these critical points are a consequence of symmetry. In terms of the fcc alkali chlorides, Roessler and Walker³⁵ identify several critical points that are symmetry-required, and these include the transitions Γ_{15} to Γ_1 , L_3' to L_1 , X_5' to X_1 , X_5' to X_3 , L_3' to L_3 , and Γ_{15} to Γ_{25}' . Here, the notation at L has been changed to conform to that of this paper. These critical points are of the type M_0 according to Roessler and Walker³⁵ and should correspond to a shoulder in the absorption spectrum. It is possible to identify some of these shoulders, and in Tables VI and VII these shoulders are given according to several experimental papers. In doing this, the energy of the transition Γ_{15} to Γ_1 has been subtracted out so that it is possible to compare the results of these measurements to the theoretical results of this paper and those of DeCicco for KCl.

It is obvious from Table VI that there is no general agreement either in experiment or theory as to the features of the KCl spectrum. This is due in part to the difficulty of identifying M_0 critical points in absorption curves. In the reflectance data for KCl, there is a broad strong absorption between 3 and 6 eV above the onset of absorption, which would tend to mask out any M_0 edges in this range. In addition, DeCicco found that his d -like conduction bands moved with respect to his s -like conduction band when he altered the strength of the constant term in the APW potential outside the spheres, so that there is several tenths of an eV uncertainty in the location of critical points in his calcula-

tion involving the states X_3 , Γ_{25}' , and L_3 . In this calculation, there is about 0.2 eV uncertainty due to the effects of altering the form of the exchange potential. It is not possible to evaluate this effect for DeCicco's calculation. The identification of critical points in the spectrum as being due to any given transition should be regarded skeptically when such identification is based upon purely speculative grounds.

The results for NaCl are much clearer. Here there is a much better agreement between experiments and also a much better agreement between theory and experiment. It is noted that there may be other M_0 critical points than those required by symmetry and in the present theoretical calculation these would not be observed. Insufficient information exists about the wave functions throughout the zone to permit a calculation of the absorption spectra of these substances. The author feels there are some remarks possible about the identifications of Roessler and Walker. They find that L_1 is slightly higher than Γ_1 , but the small energy difference which they obtain (0.3 eV for KCl and 0.5

TABLE VII. Transition energies are given for several critical points in the bands of NaCl both experimentally and theoretically. These energies are with respect to the transition Γ_{15} to Γ_1 . The identification of the states responsible for these transitions given by the several authors is given. Energies are in eV.

Experimental		Theoretical	
Ref. a	Ref. b	Present work	
Transition	Energy	Transition	Energy
Γ_{15}, Γ_1	0.0	Γ_{15}, Γ_1	0.0
L_3', L_1	0.5		
X_5', X_1	1.5	L_3', L_1	1.5
X_5', X_3	2.8	X_5', X_3	2.7
L_3', L_3	3.9	X_5', X_1	3.8
$\Gamma_{15}, \Gamma_{25}'$	4.2	$\Gamma_{15}, \Gamma_{25}'$	8.7
		X_5', X_1	4.3
		$\Gamma_{15}, \Gamma_{25}'$	6.5
		L_3', L_3	7.3

* Reference 35.

^b Reference 39.

⁴⁸J. C. Phillips, Phys. Rev. 133, A452 (1964).

eV for NaCl) seems to be unreasonable if the currently available calculations are considered. In addition, the labels given need not be unique, since at the present level of experimental accuracy the identification of transition symmetry is pure speculation. It is also observed that recent measurements by Fröhlich and Stagninus³⁶ indicate that the identification of the band gap in the alkali halides may be in error, and may be smaller than currently believed.

Because of the lack of well-defined structure in the LiCl absorption spectrum, analyses of these theoretical results are difficult. It is observed that, in this calculation, the conduction band is almost flat from Γ_1 to L_1 , as is the valence band from Γ_{15} to L_3' . Because of this, it seems likely that the strong absorption immediately after the first exciton transition^{32,33} may be due to band-to-band transitions involving quasicritical points along the entire line from Γ to L . As in previous calculations, the spin-orbit splitting at Γ in the valence band for the alkali chlorides is about 0.1 eV and is in good agreement with experiment.^{13,16,25}

The analysis may be continued by examining Roessler's statement that the various singularities are of type M_0 . In the case of KCl, the present calculation indicates that the transitions Γ_{15} to Γ_1 , X_5' to X_3 , X_5' to X_1 , and L_3' to L_3 are of the type M_0 . Thus, in table VI the theoretical transitions L_3' to L_1 and Γ_{15} to Γ_{25}' should be discounted. When this is done, the present results are in better agreement with experiment. It is clear from the results of DeCicco that he finds the transitions from L_3' to L_1 , Γ_{15}' to Γ_{25}' , and X_5' to X_1 not of type M_0 . In the case of NaCl, the present results indicate that, of the transitions given in Table VII, only the transitions Γ_{15} to Γ_1 , X_5' to X_3 , and X_5' to X_1 are of the type M_0 .

Additional information which is obtained from these calculations indicates that the half-width of the NaCl valence band is 0.50 ± 0.05 eV and that that of the LiCl valence band is 0.55 ± 0.05 eV.

The density of states for the LiCl p -like conduction band was computed using the results in Table V and one thousand nonequivalent points in the first Brillouin zone, and was compared to the Li^+ K edge absorption results for LiCl of Haensel, Kunz, and Sonntag.³⁷ Since these transitions are from the flat $1s$ Li^+ band to the lowest p -type conduction band, there should be similarities between the absorption spectrum and the density of states for the p -like conduction band. The results here indicate that if the first peak in the density of states is lined up with the first peak in the absorption spectrum, then the density of states has maxima where the absorption spectrum has maxima and the same is true of the minima. However, there are discrepancies between the magnitudes of the peaks. For example, in experiment the first peak is highest by a factor of 2 compared to the second peak. For the density of states the reverse is true. The transition probabilities have not been computed, due to a lack of information about the wave

functions throughout the zone, so that more detailed comparison is not possible.

The density-of-states calculation for the conduction band is highly speculative and of qualitative interest chiefly. That is, the mixing of the different conduction levels has been neglected, terms other than those involving nearest neighbors have been neglected, and only Wannier functions about a halogen ion site are included in this approximate tight-binding analysis. It is felt that for certain qualitative uses these parameters are of some value.

V. CONCLUSIONS

The OPW method has produced results for the valence and conduction bands of NaCl, KCl, and LiCl that are consistent with other recent calculations and are also consistent with recent experiment, except in the matter of the band gaps, which are too narrow. These calculations make it seem likely that X excitons are important in NaCl, and possibly in LiCl, just as they are important in KCl. The band shapes and splittings, except for the band gap, are seen to be insensitive to the choice of exchange potential. Possibly a better choice of exchange potential would improve the band-gap calculation. It has also been seen that tight-binding functions of the most common type are not good eigenfunctions of the Hamiltonian for the NaCl valence band. It seems reasonable that this will be true for other alkali halides as well. This technique produces useful results for the valence and conduction states of the alkali halides, and seems to be limited only by the size of matrices that one is able to afford to diagonalize.

ACKNOWLEDGMENTS

The author wishes to thank Professor W. Beall Fowler for several useful and stimulating discussions during the progress of this work. He thanks Professor W. J. Van Sciver for his advice and encouragement. He extends his deepest appreciation to Dr. R. Haensel of Institut für Experimentalphysik der Universität Hamburg and to Dr. F. Pardal of the Faculté des Sciences de Toulouse for several very helpful discussions and for providing him with copies of their experimental data prior to publication. He also extends his most hearty appreciation for the hospitality rendered him by the staff of the Courant Institute, where these calculations were made.

APPENDIX A

A brief discussion of the numerical techniques involved is presented here. All single integrations were performed using Simpson's rule. Both 111 and 441 mesh points were used in the interval with a negligible difference in the final energies. The energies were evaluated using a matrix diagonalizer, pioneered by

Fowler, which looks for changes of sign in the value of the determinant M_{p_i, p'_i} as a function of energy. This technique extracts roots accurate to ± 0.0 and -0.00001 Ry. This also produces the eigenvectors corresponding to the eigenvalue found. The program used to construct the potentials and core functions is basically due to Herman and Skillman, although it has been extensively modified for the present application.

The basic computer used was the Control Data 6600 at the Courant Institute. This machine has a 60-bit word length (about 14.5 significant figures); this was a real advantage. Using a short form of the OPW program, which needs potentials and core functions as data (hence avoiding any iterative calculation), energies and eigenvectors were obtained using the IBM 360-65 at the University of Pennsylvania. In this case, the word length is 32 bits (7.5 significant figures), and energies were produced with no better than four-figure agreement to the CDC 6600 results. The eigenvectors agreed only to about two figures. It was felt that the disagreement was due to round-off error in the IBM 360-65. It is also felt that the full program, which does iterative calculations as well as the usual OPW calculations, should be used only on a machine having a 60-bit word length or on smaller machines by using double precision, or the results would be worthless because of excess round-off error.

APPENDIX B

The choice of the form of the exchange potential is discussed in this Appendix. In all cases, the final ionic potential is subjected to the modification as discussed by Herman and Skillman.¹⁹ The principal exchange potential used is the Slater exchange potential given as¹⁹

$$rV_{\text{ex}}(r) = -\{[81/(4\pi^2)]r\rho(r)\}^{1/3}. \quad (\text{B1})$$

In Eq. (B1), rydberg energy units are used, and $\rho(r)$ is the radial charge density. This potential term is

derived from a free-electron approximation. Using some slightly different assumptions, Kohn and Sham⁴¹ have obtained the following form for

$$rV_{\text{ex KS}}(r) = \frac{2}{3}rV_{\text{ex}}(r). \quad (\text{B2})$$

In Eq. (B2), $V_{\text{ex KS}}(r)$ is the Kohn-Sham exchange potential and $V_{\text{ex}}(r)$ is the Slater exchange potential given by Eq. (B1).

Another form for this potential term has been developed by Lindgren.⁴² This is a more empirical type of potential, and has the form

$$rV_{\text{ex L}}(r) = C[81/(4\pi^2)]^{1/3}r^{n/3}\rho(r)^{m/3}. \quad (\text{B3})$$

The quantities C , n , and m are to be considered as disposable parameters. Lindgren adjusts these parameters so that the total system energy evaluated by solving the Hartree-Fock equation with the Lindgren form of exchange is as close as possible to the total system energy obtained solving the Hartree-Fock equation. For the systems on which Lindgren worked the range of parameters was not very great for optimizing results. It is found that $C=0.80\pm 0.10$, $n=1.15\pm 0.15$, and $m=1.0$. In the present calculation for NaCl, $C=0.80$ and $C=0.90$, and $n=1.15$ and $m=1.0$ are used. The results for the ionization potential of the Na^+ ion and the electron affinity for the Cl^- ion were found to be in poorer agreement with experiment than for the Slater potential. However, most band features are seen to be insensitive to the change of exchange potential. The only quantity which changes is the position of the valence band with respect to the vacuum. This is approximately given as the sum of the binding energy of a 3ρ electron on a Cl^- free ion and the depth of the Madelung well which that ion finds itself in. Other band features are insensitive to the choice of exchange potential. This is not unreasonable, as is seen from recent theoretical results due to Gilbert.⁴⁰