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Band Structure and Cohesive Energy of Potassium Chloride*†

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The band structure of crystalline KCl has been calculated in an LCAO (linear combination of atomic orbitals) approximation. Interactions between free-ion Hartree-Fock functions are calculated directly from molecular-type integrals without reducing exchange interactions to an exchange potential. The structure of the filled bands of KCl is obtained by solving secular equations on a cubic mesh of points in k space. The valence band is found to be quite narrow, about 1.5 ev wide, but the band-structure results do not explain the observed x-ray emission data for KCl. The band structure is recalculated in less detail as a function of interionic distance. Numerical quantities for the band-structure calculation are used also to calculate the cohesive energy of KCl at its normal interionic distance by Löwdin's method. Inclusion of the second-neighbor interactions here is found to raise Löwdin's equivalent of the repulsive energy from 18.9 kilocalories per mole to 26.2 kilocalories per mole and thus to raise the total cohesive energy above the experimentally-determined value, in line with expectation.

1. INTRODUCTION

According to the results of x-ray measurements, crystalline KCl has a cubic lattice with K^+ and Cl^- ions occupying alternate lattice sites. The electronic structure of the crystal is expected to be closely related to that of the free ions. Both of these ions are isoelectronic with neutral argon, and both have ^1S, closed-shell electronic wave functions in their ground states. The KCl crystal is expected to have a ground-state wave function which also is closed-shell, being a singlet and having the full symmetry of the nuclei. This closed-shell structure is expected because of the large first excitation energy of about 7.65 ev which is observed for KCl.

In view of these features a Hartree-Fock procedure probably would give a reasonably good approximation to the ground-state wave function and total energy of the crystal. In addition, the array of the resulting Hartree-Fock one-electron energy parameters probably would give a fairly good representation of the structure of the filled energy bands of KCl. Since the Hartree-Fock procedure for a crystal is too difficult to be performed, however, an actual calculation of the band structure must involve some further approximations. In the existing calculations for such crystals[1,2] the exact Hartree-Fock operator is replaced by just its kinetic energy operator and a simple periodic potential. Recent investigations have shown that calculated band structure may depend quite critically on details of the starting potential, however.

The present calculation also represents an approximation to the Hartree-Fock procedure, but it obtains the structure of the filled bands without resort to a one-electron potential. The method is based directly on the use of a single determinant of one-electron functions, each of which is an LCAO (linear combination of atomic orbitals), and the interactions which are used to determine the functions and their energies are calculated directly from many-center integrals between the atomic orbitals.[3] Exchange effects are included automatically.

The band-structure calculation is performed fairly accurately for one value of the interionic distance (the normal value), and then more approximately for several other values. Numerical quantities determined for the band calculation at the normal distance are used also to redetermine the cohesive energy of KCl by the method of Löwdin,[4] but in a more accurate approximation. Unless otherwise specified the work to follow is in atomic units: atomic units (a.u., or Bohr radii) for length, rydbergs for energy, and e, the magnitude of the electron charge, for charge.

2. LCAO APPROXIMATION FOR KCl

(a) Basis of the Approximation

In the present calculation the Hartree-Fock functions for a KCl crystal are approximated by linear combinations of all of the occupied free-ion Hartree-Fock functions for K^+ and Cl^-,[5] centered on appropriate crystal lattice sites. This is the LCAO approximation mentioned above. It is expected to be fairly good for the reasons to be discussed.

In the first place the largest overlap integral between

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[1] D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936).

[2] W. Shockley, Phys. Rev. **50**, 754 (1936).

[3] This approximation might be called tight binding, except that that name generally connotes the use of a one-electron potential. The name LCAO is used here because it implies the direct use of one- and two-electron integrals between atomic functions, at least in the usage of current molecular work.

[4] P. -O. Löwdin, thesis, Uppsala, 1948 (unpublished). See also, P. -O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

[5] For Cl^- see D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936); for K^+ see D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

any two of the free-ion Hartree-Fock functions which are separated by a normal KCl lattice distance is only 0.07, as compared to one for maximum overlap. By the usual arguments, such small overlapping indicates narrow bands of energy parameters, and it indicates crystal Hartree-Fock functions which are nearly equal to linear combinations of just degenerate free-ion functions. These effects have been discussed by Slater and Shockley[6] in their analysis of the band structure of NaCl. The most important deviations from this simple result can be corrected by letting the crystal Hartree-Fock functions be approximated by combinations of all the occupied free-ion functions, as is done here.

In the second place, with the proposed LCAO approximation for the crystal Hartree-Fock functions, the resulting approximate Hartree-Fock determinant is just equivalent to a determinant of the free-ion Hartree-Fock functions themselves, according to a well-known transformation theorem.[7] Löwdin has calculated the cohesive energy of KCl (and other alkali halides) on the basis of just such a determinant of free-ion Hartree-Fock functions. The success of his calculation (and the recalculation in Sec. 6), provides another measure of justification for the equivalent determinant of approximate Hartree-Fock functions which is used here.

Additional justification for the LCAO approximation is provided by the large first excitation energy of KCl, by the emission and absorption spectra of KCl,[8] and by the cellular band structure calculations for LiF[1] and NaCl,[2] since all of these indicate that the filled energy bands of KCl should be fairly narrow and hence that the crystal functions should be made up largely of just free-ion functions.

(b) Equations

The equations for one-electron functions and energies in the LCAO approximation used here are obtained as follows. Let the usual large region for periodic boundary conditions contain N unit cells and $2M$ electrons, M of each spin. The approximate wave function for the crystal in its ground state then will be symbolized by $\Psi(1,2,\cdots j,\cdots 2M)$, where j stands for the space and spin coordinates of electron j. This function is taken to be a single determinant made from M doubly-occupied, orthonormal, one-electron space functions. Because of crystal translation symmetry these one-electron functions can all be taken to be Block functions $\psi_i(\mathbf{k}|\mathbf{r})$, where $\mathbf{k}$ is the usual wave vector (having N discrete values), and where i runs over all the occupied bands. In the present LCAO approximation each of these Bloch functions is to be written as a linear combination of Bloch sums of the Hartree-Fock space functions for the free-ions; thus each function is written

$$\psi_i(\mathbf{k}|\mathbf{r})=\textstyle\sum_m c_{mi}(\mathbf{k})b_m(\mathbf{k}|\mathbf{r}), \qquad (2\text{-}1)$$

where $b_m(\mathbf{k}|\mathbf{r})$ is the following Bloch sum:

$$b_m(\mathbf{k}|\mathbf{r})=(f_m/N^{\frac{1}{2}})\textstyle\sum_g{}^{(m)}\, e^{i\mathbf{k}\cdot\mathbf{R}_g}u_m(\mathbf{r}-\mathbf{R}_g). \qquad (2\text{-}2)$$

In the latter equation $u_m(\mathbf{r}-\mathbf{R}_g)$ is a real, free-ion space function of type m (specifying quantum numbers and ion type) centered on lattice site g at $\mathbf{R}_g$; the superscript (m) to the summation sign indicates that the sum is to run over only those sites g on which a function of type m can be located (all K^+ or all Cl^- sites); and the factor f_m is equal to i (the square root of minus one) if u_m is odd on inversion and one if u_m is even on inversion (it is included so that the matrix elements between Bloch sums will be real).

Let the Hamiltonian for the $2M$-electron crystal be

$$H=W+\textstyle\sum_j F_j+\sum'_{j,j'} G_{jj'}, \qquad (2\text{-}3)$$

where W is the Coulomb interaction energy of the static nuclei, where F_j is the one-electron operator for electron j, giving its kinetic energy and its Coulomb energy of interaction with the nuclei, where $G_{jj'}$ is the two-electron operator giving the Coulomb interaction of electrons j and j', and where the prime on the second sum means j' cannot equal j. On the basis of this Hamiltonian, Hartree-Fock space-functions for the crystal satisfy the following set of equations:

$$F_1\psi_i(\mathbf{k}|\mathbf{r}_1)+2\int G_{12}\psi_i(\mathbf{k}|\mathbf{r}_1)\rho(2|2)dv_2 - \int G_{12}\psi_i(\mathbf{k}|\mathbf{r}_2)\rho(2|1)dv_2=\epsilon_i(\mathbf{k})\psi_i(\mathbf{k}|\mathbf{r}_1), \qquad (2\text{-}4)$$

where $\epsilon_i(\mathbf{k})$ is the Hartree-Fock energy parameter for the function $\psi_i(\mathbf{k}|\mathbf{r})$ and where $\rho(2|1)$ is given by

$$\rho(2|1)=\textstyle\sum_{i',\mathbf{k}'}\psi_{i'}(\mathbf{k}'|\mathbf{r}_2)^*\psi_{i'}(\mathbf{k}'|\mathbf{r}_1). \qquad (2\text{-}5)$$

As Löwdin has shown,[4] when the functions ψ in Eq. (2-5) are constructed as LCAO of the type used here, the quantity $\rho(2|1)$ can be written out in a way which does not involve the coefficients of the atomic functions. Let the overlap integral between free-ion functions $u_m(\mathbf{r}-\mathbf{R}_g)$ and $u_n(\mathbf{r}-\mathbf{R}_{g'})$ be symbolized by

$$\Delta(m\mathbf{R}_g|n\mathbf{R}_{g'})=\int u_m(\mathbf{r}-\mathbf{R}_g)^*u_n(\mathbf{r}-\mathbf{R}_{g'})dv; \qquad (2\text{-}6)$$

this integral can be thought of as one element in the $M\times M$ matrix of all the overlap integrals. According to Löwdin's result, then, Eq. (2-5) for $\rho(2|1)$ can be

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[6] J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936).

[7] See for instance F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York and London, 1940), p. 301.

[8] L. G. Parratt and E. L. Jossem, Phys. Rev. **97**, 916 (1955). See also the summary of earlier work in H. H. Landolt and R. Bornstein, *Zahlenwerte und Functionen* (Springer-Verlag, Germany, 1955), sixth edition, Vol. 1, Part 4, pp. 786 and 864. In addition the author is indebted to Professor Jossem for communication of results from his as yet unpublished work on the Cl^- K_β emission of all the alkali chlorides.

written

$$\rho(2|1)=\sum_{m,n}\sum_{g,g'}\Delta^{-1}(m\mathbf{R}_g|n\mathbf{R}_{g'})\times u_m(\mathbf{r}_2-\mathbf{R}_g)^* u_n(\mathbf{r}_1-\mathbf{R}_g), \quad (2\text{-}7)$$

where $\Delta^{-1}(m\mathbf{R}_g|n\mathbf{R}_{g'})$ is an element in the $M\times M$ matrix which is the inverse of the overlap matrix. The validity of Eq. (2-7) depends on the following facts: first, the functions ψ are mutually orthonormal; second, the functions u are linearly independent; and third, the number of derived functions ψ is the same as the number of starting functions u.

If all the two-center overlap integrals are small compared to one, as they are for KCl, the overlap matrix $\mathbf{\Delta}$ differs only slightly from the unit matrix. In this case the inverse overlap matrix just defined also is very nearly equal to the unit matrix. In view of this the following definitions are useful:

$$\Delta_{mn}=\delta_{mn}+S_{mn}, \quad (\Delta^{-1})_{mn}=\delta_{mn}+P_{mn}, \quad (2\text{-}8)$$

where δ_{mn} is the Kronecker delta, and where for brevity each index m or n temporarily is taken to designate site as well as quantum numbers for the free-ion functions u (this shorter notation will be used interchangably with the original notation through the rest of this paper). These definitions will be used in Sec. 3.

Substitution of Eq. (2-7) into Eq. (2-4) gives the following set of Hartree-Fock-like equations for one-electron functions and their energies:

$$F_1\psi_i(\mathbf{k}|\mathbf{r}_1)+\sum_{m,n}(\Delta^{-1})_{mn}\left[2\int G_{12}\psi_i(\mathbf{k}|\mathbf{r}_1)u_n(2)^* u_m(2)dv_2-\int G_{12}u_m(1)u_n(2)^*\psi_i(\mathbf{k}|\mathbf{r}_2)dv_2\right]=\epsilon_i(\mathbf{k})\psi_i(\mathbf{k}|\mathbf{r}_1), \quad (2\text{-}9)$$

where a short notation for free-ion functions is used again. Solving Eqs. (2-9) above for general functions ψ would be a possible first stage in a self-consistent Hartree-Fock procedure which could lead finally to the exact Hartree-Fock functions and their energy parameters. In the present calculation, however, the functions ψ are assumed to be given by the LCAO approximation of Eq. (2-1). Equation (2-9) then yields the following sets of equations for the unknown coefficients, one set for each value of the wave vector $\mathbf{k}$:

$$\sum_n[H_{mn}(\mathbf{k})-\epsilon_i(\mathbf{k})\Delta_{mn}(\mathbf{k})]c_{ni}(\mathbf{k})=0, \quad (2\text{-}10)$$

where $H_{mn}(\mathbf{k})$ and $\Delta_{mn}(\mathbf{k})$ are matrix elements of energy and overlap, respectively, between the Bloch sums $b_m(\mathbf{k}|\mathbf{r})$ and $b_n(\mathbf{k}|\mathbf{r})$. Letting $M_{mn}(\mathbf{k})$ stand for either of these matrix elements, either element is given by

$$M_{mn}(\mathbf{k})=\sum_g{}^{(m)}\left\{\begin{matrix}\cos\mathbf{k}\cdot\mathbf{R}_g\\ p_m\sin\mathbf{k}\cdot\mathbf{R}_g\end{matrix}\right\}M(m\mathbf{R}_g|n), \quad \left\{\begin{matrix}p_m=p_n\\ p_m=-p_n\end{matrix}\right\}, \quad (2\text{-}11)$$

where p_m is the parity (plus or minus one) of the function u_m, and where $M(m\mathbf{R}|n)$ is an element of energy or overlap, as is appropriate, between a function u_n and another function u_m which is on a site at $\mathbf{R}$ relative to the site of u_n as an origin (for brevity the location vector of the origin site is not written in M). An element of overlap between free-ion functions is given by Eq. (2-6), and an element of energy is given by the following equation:

$$H(m\mathbf{R}|n)=\int u_m(\mathbf{r}_1-\mathbf{R})^*\left\{F_1+2\int G_{12}\rho(2|2)dv_2\right\}u_n(\mathbf{r}_1)dv_1-\int G_{12}u_m(\mathbf{r}_1-\mathbf{R})^*\rho(2|1)u_n(\mathbf{r}_2)dv_1dv_2, \quad (2\text{-}12)$$

where $\rho(2|1)$ is the approximate quantity in Eq. (2-7). This energy element is built up from one- and two-electron, one-, two-, three-, and four-center integrals of the same type as are encountered in complicated molecular problems.

In the foregoing discussion, Eqs. (2-10) for the approximate one-electron functions and their energies are obtained by making substitutions in the Hartree-Fock equations. Equations (2-10) cannot be obtained directly by the variation procedure as the Hartree-Fock equations are obtained, however, because the determinant $\Psi(1,2,\cdots 2M)$ is invariant under all variations of the coefficients $c_{ni}(\mathbf{k})$ which leave the functions $\psi_i(\mathbf{k}|\mathbf{r})$ in the determinant mutually orthonormal. Despite this, Eqs. (2-10) do have a meaning. The functions and energies determined by these equations are just those for which Koopmans' theorem[9] can be applied to predict the total wave functions and energies of the crystal with one electron missing. Stated in other words, Eqs. (2-10) can be obtained by a variation principle applied in the case of the crystal minus one electron; for this it should be assumed that the total wave function is either a single determinant made up from linear combinations of free-ion functions or a configuration series in the basis of the free-ion functions.[10] The functions and energies determined by Eqs. (2-10) therefore have the same important significance with respect to the band structure of KCl as the true Hartree-Fock functions and energies do, although in a lower approximation, and in this sense they approximate Hartree-Fock functions and energies.

The problem now is reduced to calculation of the elements of energy and overlap of which Eqs. (2-10) are made up. The reader who is not interested in the details of this work may proceed directly to Sec. 4.

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[9] T. Koopmans, Physica 1, 104 (1933).

[10] In this connection a theorem due to Meckler on performing configuration interactions in equivalent bases is useful; see A. Meckler, J. Chem. Phys. 21, 1750 (1953).

3. MATRIX ELEMENTS OF ENERGY AND OVERLAP

(a) Nature of the Energy Elements

First let us analyze an element of energy between free-ion functions as given in Eq. (2-12). In atomic units (with Rydbergs for energy) the one- and two-electron operators appearing in this equation are

$$F_1 = -\nabla_1^2 - \textstyle\sum_g 2Z_g/r_{1g} \quad \text{and} \quad G_{12} = 2/r_{12}, \qquad \text{(3-1)}$$

where ∇_1^2 is the Laplacian operating on the coordinates of electron 1, Z_g is the nuclear charge of the ion at site g (nineteen for K$^+$ and seventeen for Cl$^-$), r_{1g} is the distance of electron 1 from site g, and r_{12} is the distance between electrons 1 and 2.

An analysis of the energy element is facilitated by a consideration of the crystal charge density. In the present approximation the electronic part of this charge density is just equal to $-2\rho(2|2)$; let us symbolize this charge density by $\rho(2)$. On the basis of Eq. (2-7) for $\rho(2|1)$ and Eq. (2-8) for Δ^{-1} the charge density $\rho(2)$ can be split into two parts as follows:

$$\rho(2) = \textstyle\sum_g \rho_g(2) + \rho_{\text{ov}}(2). \qquad \text{(3-2)}$$

In this equation $\rho_g(2)$ is the spherical electron charge density of a free-ion at site g, given by

$$\rho_g(2) = -2\textstyle\sum_p(\text{on site } g)u_p(2)^*u_p(2), \qquad \text{(3-3)}$$

and $\rho_{\text{ov}}(2)$ is what will be called the overlap charge density, given by

$$\rho_{\text{ov}}(2) = -2\textstyle\sum_{p,q} P_{qp}u_p(2)^*u_q(2). \qquad \text{(3-4)}$$

On a particular site g, the free-ion electron charge density $\rho_g(2)$ and the nuclear charge Z_g together give a net charge of z_g, which is plus one for K$^+$ and minus one for Cl$^-$. Since the sum of z_g over the two ions in a single unit cell is zero, the sum of nuclear charges and free-ion charge distributions throughout the crystal gives a net charge of zero. As will be described later, the overlap charge density $\rho_{\text{ov}}(2)$ is neutral also; hence the complete crystal is neutral, as it should be.

The overlap charge density describes a shifting of electron charge from the density predicted by a simple superposition of free-ion charge densities. This shift decreases the electron charge density in regions of maximum overlap between pairs of free-ions, and it compensates by forcing an increase in the electronic charge in the region of a nucleus. This redistribution of charge arises from orthonormalizing the one-electron functions, and it can be described as an effect of the exclusion principle. In the present approximation it is essentially this redistribution of charge which provides the repulsion between ions in the crystal (see Sec. 6) and which causes the crystal energy bands to rise as the interionic distance decreases below its normal value (see Sec. 5).

Let us now return to the analysis of the general energy element given in Eq. (2-12). After substitution for F_1, G_{12}, $\rho(2|2)$ and $\rho(2|1)$ in that equation, the energy element can be written as a sum of terms which are convenient for calculation, as follows:

$$H(m\mathbf{R}_g|n) = [(\text{KE}+\text{C}+\text{EX}) + (\text{CPI}+\text{CCC} + \text{OVC}+\text{CEX}+\text{OVE})](m\mathbf{R}_g|n). \qquad \text{(3-5)}$$

Each term in this expression should individually bear the indices $(m\mathbf{R}_g|n)$, but for brevity the indices are written only once for all. The individual terms are defined as follows:

$$\text{KE}(m\mathbf{R}_g|n) = \int u_m^*(\mathbf{r}_1-\mathbf{R}_g)[-\nabla_1^2]u_n(\mathbf{r}_1)dv_1; \qquad \text{(3-6)}$$

$$\text{C}(m\mathbf{R}_g|n) = \textstyle\sum_{g'=0,g} \displaystyle\int u_m^*(\mathbf{r}_1-\mathbf{R}_g)\Big[-(2Z_{g'}/r_{1g'}) - \int \rho_{g'}(2)(2/r_{12})dv_2\Big]u_n(\mathbf{r}_1)dv_1, \qquad \text{(3-7)}$$

where the origin is designated as site 0;

$$\text{EX}(m\mathbf{R}_g|n) = -\textstyle\sum_{g'=0,g} \displaystyle\times \int\int u_m^*(\mathbf{r}_1-\mathbf{R}_g)\rho_{g'}(2|1)(2/r_{12})u_n(\mathbf{r}_2)dv_1dv_2, \qquad \text{(3-8)}$$

where $\rho_{g'}(2|1)$ is what will be called the exchange function of the ion at site g', defined by

$$\rho_{g'}(2|1) = \textstyle\sum_p(\text{on site } g')u_p(2)^*u_p(1); \qquad \text{(3-9)}$$

$$\text{CPI}(m\mathbf{R}_g|n) = \int u_m^*(\mathbf{r}_1-\mathbf{R}_g) \times[-\textstyle\sum_{g'\neq 0,g}2z_{g'}/r_{1g'}]u_n(\mathbf{r}_1)dv_1; \qquad \text{(3-10)}$$

$$\text{CCC}(m\mathbf{R}_g|n) = \textstyle\sum_{g'\neq 0,g}\displaystyle\int u_m^*(\mathbf{r}_1-\mathbf{R}_g) \times[-2Z_p'(g'|r_{1g'})/r_{1g'}]u_n(\mathbf{r}_1)dv_1, \qquad \text{(3-11)}$$

where $Z_p'(g'|r)$ is the effective-nuclear-charge-for-potential minus $z_{g'}$ for an ion of the type at site g' (it is a function which approaches zero rapidly with increasing r), and where $r_{1g'}$ is $|\mathbf{r}_1-\mathbf{R}_{g'}|$:

$$\text{OVC}(m\mathbf{R}_g|n) = \int u_m^*(\mathbf{r}_1-\mathbf{R}_g)\Big[-\int(2/r_{12}) \times\rho_{\text{ov}}(2)dv_2\Big]u_n(\mathbf{r}_1)dv_1; \qquad \text{(3-12)}$$

$$\text{CEX}(m\mathbf{R}_g|n) = -\textstyle\sum_{g'\neq 0,g}\displaystyle\int\int u_m^*(\mathbf{r}_1-\mathbf{R}_g) \times\rho_{g'}(2|1)(2/r_{12})u_n(\mathbf{r}_2)dv_1dv_2; \qquad \text{(3-13)}$$

TABLE I. Parameters B and b specifying the analytic radial functions $P_{nl}(r)$ for the final free-ion Hartree-Fock functions. Each function $P_{nl}(r)$ is of the form

$$P_{nl}(r)=\sum_{n'=n-l}^{n}\left\{\Sigma_i B_i^{n'l}\phi_{n'}(b_i^{n'l},r)\right\},\quad \text{where}\quad \phi_n(b,r)=[b^{2n+1}/(2n)!]^{\frac{1}{2}}r^n e^{-br}.$$

The function in curly brackets is a nodeless part of the function $P_{nl}(r)$. All the nodeless parts of each function are given in the table. Each nodeless part is symbolized as follows: $+B_1^{n'l}(b_1^{n'l})+B_2^{n'l}(b_2^{n'l})+\cdots$.

nl	$n'=1$	$n'=2$	$n'=3$
Cl⁻ $3p$	none	$+0.0009162(22.314)+0.109634(8.4758)$ $+0.211019(4.2435)$	$-0.434233(2.9859)-0.554674(1.6658)$ $-0.221689(0.92436)$
Cl⁻ $3s$	$+0.136317(11.9700)$	$-0.036350(11.9700)-0.474747(5.28481)$	$+0.2033042(4.17031)+0.724822(2.50768)$ $+0.2892075(1.51175)$
K⁺ $3p$	none	$+0.0326356(13.4132)+0.432421(5.80137)$	$-0.1959866(5.80137)-0.658190(2.93199)$ $-0.397249(1.84562)$
K⁺ $3s$	$+0.132348(14.9166)$	$-0.656603(5.77856)$	$+0.237170(5.77856)+0.681630(3.31794)$ $+0.417020(2.26585)$
K⁺ $2p$	none	$+0.0514901(15.2448)+0.583429(8.11418)$ $+0.400579(5.54331)$	none
K⁺ $2s$	$+0.0012533(41.049)$ $+0.396536(14.9166)$	$-0.956261(7.36055)-0.1690558(5.27633)$	none
K⁺ $1s$	$+0.464074(20.9557)$ $+0.541205(16.5026)$	none	none

and, finally,

$$\mathrm{OVE}(m\mathbf{R}_g|n)=-\int\int u_m^*(\mathbf{r}_1-\mathbf{R}_g)\times\rho_{\mathrm{ov}}(2|1)(2/r_{12})u_n(\mathbf{r}_2)dv_1dv_2,\quad (3\text{-}14)$$

where $\rho_{\mathrm{ov}}(2|1)$ is what will be called the overlap exchange function, defined by

$$\rho_{\mathrm{ov}}(2|1)=\sum_{p,q}P_{qp}u_p(2)^*u_q(1).\quad (3\text{-}15)$$

The terms KE, C, and EX as defined above involve only contributions from site g and the origin; they are atomic or diatomic terms depending on whether $\mathbf{R}_g$ is or is not zero. The remaining terms CPI, CCC, OVC, CEX, and OVE, all depend on the presence of the atom or atom-pair in the crystal. The mnemonic significance of the initials used for all these terms is as follows: in the order in which they appear in Eq. (3-5), they stand for kinetic energy, Coulomb, exchange, crystal point ion, crystal Coulomb correction, overlap Coulomb, crystal exchange, and overlap exchange.

For the particular case of a one-center energy element, $H(m000|n)$, the terms KE, C, and EX add up to just the free-ion Hartree-Fock energy, ϵ_m, if m equals n and to zero if m does not equal n. Another simple contribution to the energy element can be extracted from the term CPI. The potential function in square brackets in Eq. (3-10) for CPI is just the Madelung potential, the potential due to all the ions in the crystal considered as point ions, excluding the origin ion. For KCl an expansion of this potential about the origin ion in spherical harmonics contains a spherical term and spherical harmonics of order four and higher. Since the free-ion functions u_m and u_n are built from spherical harmonics only of order zero and one, the spherical term in the Madelung potential provides the entire contribution to $\mathrm{CPI}(m000|n)$. Inside a sphere of radius a, where a is the interionic distance, this spherical term is just equal to the Madelung energy, $z_02\alpha/a$ rydbergs, where α is the Madelung constant[11] and z_0 is the net charge of the origin ion (plus or minus one). Term $\mathrm{CPI}(m000|n)$ then can be set equal to $(z_02\alpha/a)\delta_{mn}$ plus a correction term, $\Delta\mathrm{CPI}(m000|n)$, which is the integral of the difference between the actual spherical part of the Madelung potential and $z_02\alpha/a$ outside a sphere of radius a (it is zero if the function u_m is zero outside that sphere). With these results a one-center energy element from Eq. (3-5) may be rewritten as

$$H(m000|n)=[\epsilon_m+z_02\alpha/a]\delta_{mn}+[\Delta\mathrm{CPI}+\mathrm{CCC}+\mathrm{OVC}+\mathrm{CEX}+\mathrm{OVE}](m000|n).\quad (3\text{-}16)$$

(b) Calculation of Preliminary Quantities

Most of the actual calculations of the present work were performed on the Whirlwind digital computer with programs which had already been developed for other molecular and crystal problems. The techniques employed here were dictated largely by the nature of the programs available.

First the necessary Hartree-Fock functions for K⁺ and Cl⁻ were obtained in analytic form by fitting the tabulated Hartree-Hartree radial functions with a series of Slater orbitals.[12] The parameters for the final functions are given in Table I. The Hartree-Fock free-ion energy elements for these analytic functions then were calculated on Whirlwind using the same techniques which were to be used throughout the calculation of matrix elements (described below). The resulting energy

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[11] See, for instance, C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition, p. 72.

[12] A fit by Löwdin was used for the Cl⁻ $3p$ function, and new fits were used for the functions Cl⁻ $3s$, K⁺ $3p$, K⁺ $2p$, K⁺ $3s$, K⁺ $2s$, and K⁺ $1s$. Interpolated numerical tables were used for the other Cl⁻ functions. The fitted functions for each ion were adjusted slightly to make them mutually orthonormal (and orthogonal to the numerical inner functions in the case of Cl⁻).

TABLE II. Free-ion Hartree-Fock-type energy elements $H(n_1l_1m_1|n_2l_2m_2)$ between the analytic functions of Table I. The original Hartree-Fock values for all the diagonal energy elements are given in the rows labeled HF. All energies are in rydbergs.

$n_1l_1\|n_2l_2$:	$3s\|3s$	$3s\|2s$	$2s\|2s$	$3s\|1s$	$2s\|1s$	$1s\|1s$	$3p\|3p$	$3p\|2p$	$2p\|2p$
K^+ analytic:	−3.9281	+0.014144	−29.427	+0.0077	+0.1426	−267.505	−2.3417	−0.0064	−23.476
K^+ HF:	−3.930		−29.44			−267.55	−2.341		−23.49
Cl^- analytic:	−1.4744						−0.3060		
Cl^- HF:	−1.454		−20.47			−209.1	−0.2971		−15.39

elements are presented in Table II, and the diagonal elements in the table are used as the values of ϵ_m in Eq. (3-16).

The most important of the integrals required for the crystal calculation were evaluated by the well-known expansion method of Barnett and Coulson,[13] as adapted by Corbató for Whirlwind.[14] In Corbató's adaptation the radial expansion functions are generated in numerical form given the input atomic functions in analytic form; radial integrations then are done by Simpson's rule. The particular integrals calculated here are discussed below.

Using the expansion technique and the analytic functions of Table I overlap integrals between the free-ion functions were calculated. The normal interionic distance of KCl was taken to be 3.122 angstroms, or 5.9007 a.u.[15] Overlap integrals were calculated for all possible pairs of functions out to quite large separations. From the results, the overlap integral between a particular pair of functions, both on the z axis, was found to vary exponentially with separation distance down to the nearest distance at which the pair of functions occurs in the normal lattice and to somewhat smaller distances. This dependence is the basis for the calculation of band structure as a function of interionic distance in Sec. 5. The final values of the independent, nonzero overlap integrals which actually are used in the present calculation are listed in Table III.

TABLE III. The independent, nonzero elements of overlap, $\Delta(m\mathbf{R}|n)$, and of inverse overlap, $\Delta^{-1}(m\mathbf{R}|n)$, in the second-neighbor, outer-function approximation for KCl. The interionic distance, a, is 5.9007 a.u. The code for the function index is as follows: $\mathbf{z}$, $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{s}$ stand for Cl^- $3pz$, $3px$, $3py$, and $3s$, and z, x, y, and s stand for K^+ $3pz$, $3px$, $3py$, and $3s$. The vector $\mathbf{R}$ is given by its components measured in units of a. The values of $S(m\mathbf{R}|n)$ and $P(m\mathbf{R}|n)$ can be obtained from the values below by use of Eqs. (2-8).

$\mathbf{R}$	mn	$\Delta(m\mathbf{R}\|n)$	$\Delta^{-1}(m\mathbf{R}\|n)$
000	$\mathbf{zz}$	1.000 000	1.029 038
	$\mathbf{ss}$	1.000 000	1.008 997
000	zz	1.000 000	1.012 478
	ss	1.000 000	1.020 794
001	$\mathbf{x}x$	0.017 939	−0.014 702
	$\mathbf{z}z$	−0.070 841	0.071 761
	$\mathbf{s}z$	−0.025 275	0.024 855
	$\mathbf{z}s$	0.061 050	−0.055 014
	$\mathbf{s}s$	0.012 060	−0.008 875
$\bar{1}01$	$\mathbf{zz}$	−0.019 168	0.016 963
	$\mathbf{zx}$	0.030 576	−0.025 635
	$\mathbf{sz}$	−0.014 354	0.012 697
	$\mathbf{yy}$	0.011 408	−0.009 126
	$\mathbf{ss}$	0.002 578	−0.001 500

On the basis of the overlap calculations and of energy element estimates, the inner free-ion functions (functions with principal quantum numbers of one and two) of both K^+ and Cl^- were assumed not to overlap any other functions in the crystal. The assumption is quite good for the inner Cl^- functions but only fair for the inner K^+ functions. In this approximation Eqs. (2-10) need only be solved with m and n running over the eight indices of the outer free-ion functions (Cl^- $3pz$, $3px$, $3py$, and $3s$, and K^+ $3pz$, $3px$, $3py$, and $3s$); this will be called the outer-function approximation. Furthermore, the only elements of overlap and energy between these outer functions which are taken as nonzero are the following: all the one-center elements; the two-center elements between a Cl^- and a K^+ function which are first neighbors (to be called ClK elements); and the two-center elements between two Cl^- functions which are second neighbors (to be called ClCl elements). This will be called the second-neighbor approximation. The overlap elements listed in Table III are the independent, nonzero elements which are required in the outer-function and second-neighbor approximations.

The inverse-overlap elements $(\Delta^{-1})_{mn}$ [and hence the elements P_{mn} which come into Eqs. (3-12) and (3-14)] are calculated from the overlap integrals in Table III. As can be proved by group theory, each inverse-overlap element $(\Delta^{-1})_{mn}$ has all the symmetry properties of an integral of the crystal potential between the two free-ion functions u_m and u_n. Furthermore, as Löwdin has shown,[4] each element $(\Delta^{-1})_{mn}$ can be expressed as a power series in the elements S_{mn} which are defined by the first of Eqs. (2-8). On the basis of estimates made with this series, each element $(\Delta^{-1})_{mn}$ can be considered negligible if the corresponding overlap integral Δ_{mn} is negligible; thus the second-neighbor, outer-function approximation can be extended to elements of inverse-overlap. The list of independent, nonzero inverse-overlaps to be determined therefore corresponds exactly to the list of overlaps in Table III, and there are fourteen such elements. The working

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[13] M. P. Barnett and C. A. Coulson, Trans. Roy. Soc. (London) **A243**, 221 (1951).

[14] F. J. Corbató, thesis, Massachusetts Institute of Technology, 1956 (unpublished).

[15] This value of the interionic distance is appropriate to KCl at about −180 degrees centigrade, as the original purpose of the KCl work was an investigation of the V_1 color-center absorption, which is observed at that temperature.

TABLE IV. The independent, nonzero elements of energy $H(m\mathbf{R}|n)$ and all the terms contributing to those elements for KCl in the outer-function, second-neighbor approximation. The interionic distance, the code for the function index, and the notation for $\mathbf{R}$ are the same as in Table III. All energies are in rydbergs.

(a) One-center elements $H(m000\|m)$:									
mm	$\epsilon_m+z_0 2\alpha/a$			ΔCPI	CCC	OVC	CEX	OVE	H
$\mathbf{zz}$	−0.8983			0.0013	−0.0139	0.0662	−0.0347	0.0028	−0.8766±0.002
$\mathbf{ss}$	−2.0667			0.0000	−0.0027	0.0806	−0.0086	−0.0087	−2.0061±0.002
zz	−1.7494			0.0000	−0.0161	0.0217	−0.0184	0.0081	−1.7540±0.002
ss	−3.3358			0.0000	−0.0137	0.0247	−0.0238	0.0155	−3.3331±0.002
(b) Two-center ClK elements $H(m001\|n)$:									
mn	KE	C	EX	CPI	CCC	OVC	CEX	OVE	H
$\mathbf{x}x$	−0.0027	−0.0147	−0.0274	0.0026	0.0000	−0.0005	0.0000	0.0077	−0.0351±0.002
$\mathbf{z}z$	0.0017	0.0608	0.1241	−0.0029	0.0000	−0.0011	0.0000	−0.0307	0.1518±0.0025
$\mathbf{s}z$	0.0135	0.0172	0.0523	−0.0008	0.0000	−0.0008	0.0000	−0.0142	0.0672±0.002
$\mathbf{z}s$	−0.0120	−0.0999	−0.1404	0.0106	0.0000	−0.0010	0.0000	0.0278	−0.2149±0.0025
$\mathbf{s}s$	−0.0100	−0.0144	−0.0317	0.0013	0.0000	−0.0001	0.0000	0.0104	−0.0445±0.002
(c) Two-center ClCl elements $H(m\bar{1}01\|n)$:									
$\mathbf{zz}$	0.00013	−0.01259	0.02368	0.01788	0.00044	−0.0005	0.00210	−0.00635	0.0248±0.0012
$\mathbf{zx}$	−0.00128	0.01953	−0.03526	−0.02882	−0.00411	0.0005	−0.00624	0.00964	−0.0460±0.0012
$\mathbf{yy}$	−0.00115	0.00694	−0.01158	−0.00852	−0.00068	0.0003	−0.00208	0.00349	−0.0133±0.0015
$\mathbf{sz}$	0.00359	−0.00503	0.02478	0.01232	0.00054	−0.0008	0.00149	−0.00506	0.0319±0.001
$\mathbf{ss}$	−0.00196	0.00139	−0.00570	−0.00224	−0.00116	0.0001	−0.00049	0.00220	−0.0079±0.001

values of these fourteen elements were obtained here by setting up and solving on Whirlwind a set of fourteen simultaneous equations. These equations were obtained in a straightforward way from the basic equation $\mathbf{\Delta\Delta}^{-1}$ equals $\mathbf{1}$.[16] The calculation was repeated with larger sets of equations in order to test the assumptions about negligible elements. The best set of the fourteen desired inverse-overlap elements are listed in Table III.

The atomic and diatomic integrals besides overlap which were evaluated accurately for the crystal calculation are the following: the one- and two-center kinetic energy and nuclear attraction integrals, the one-center, two-electron integrals, and the two-center, hybrid and exchange integrals. Only integrals involving outer functions were calculated, and the expansion method was used throughout. The values of the final integrals and of other integrals to be described below are omitted from the present paper, but they are available upon request.[17] Due to a combination of factors involving convergence, integration mesh, and the number of exponentials in the analytic functions of Table I, it is not feasible to obtain adequate two-center Coulomb integrals directly by the expansion method. Coulomb integrals which are adequate for many purposes were obtained by neglecting the mutual penetration of the interacting charge distributions, however.[17] In this approximation the desired Coulomb integral is replaced by the Coulomb interactions of the multipoles for the two charge distributions. The errors in the approximate integrals thus obtained were compensated when necessary by methods to be described in Sec. 3(c) [in the discussion of CCC$(m000|m)$].

Certain three-center integrals also were obtained by the expansion method. These were the integrals of a spherical potential $V(r)$ on the origin against a function u_m at $\mathbf{R}_g$ and a function u_n at $\mathbf{R}_{g'}$. In the integrals which were calculated $V(r)$ is $2/r$, $2Z_p'(\mathrm{K}^+|r)/r$, or $2Z_p'(\mathrm{Cl}^-|r)/r$ [see Sec. 3(a)]. These integrals were calculated by expanding each of the free-ion functions about the origin in spherical harmonics with its own location vector as the z axis for its own expansion and by rotating the spherical harmonics of one expanded function to the coordinate system of the other. The coefficients for rotation of the spherical harmonics were generated on Whirlwind[14] on the basis of formulas due to Wigner.[18] Infinite series result for each three-center integral in this method, and the convergence of these series often is quite poor, especially for integrals of the extensive potential $2/r$. Final values for the integrals were obtained by extensive extrapolation.[17]

(c) Calculation of Energy Elements

The general formula for a one-center energy element is given in Eq. (3-16). In the outer-function approximation the only such elements which must be calculated are diagonal. The terms contributing to these elements are discussed below, and the final values of the elements with their uncertainties and the values of the contributing terms are listed in Table IV(a). The uncertainties arise mostly from integration errors and from neglecting the effects of inner free-ion functions.

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[16] This follows a procedure suggested by S. O. Lundquist and P. O. Froman, Arkiv Fysik 2, 431 (1950).

[17] A complete table of the one-, two-, and three-center integrals calculated here has been deposited as Document No. 5492 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

[18] E. P. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik* (Friedrich Vieweg und Sohn, Berlin, 1931), p. 182, p. 232.

From Eq. (3-16) the principal contribution to the one-center energy element $H(m000|m)$ is $\epsilon_m + z_0 2\alpha/a$. The energy parameters ϵ_m are given in Table II, and the Madelung constant for KCl is 1.747558.[11] The remaining terms contributing to $H(m000|m)$ are all overlap-dependent and small; they are discussed individually below.

The term $\Delta\text{CPI}(m000|m)$ is appreciable only if the function u_m is significantly large in regions outside a sphere of radius a, the first-neighbor lattice distance. Because of this the contribution is only appreciable when u_m is a Cl^- $3p$ function; in this case the correction term is essentially just $2Z_p'(\text{Cl}^-|a)/a$.

The term $\text{CCC}(m000|m)$ is given by Eq. (3-11). For calculation the right side of this equation can be rewritten as $\sum_{g'}(g'\neq 0)\text{CC}_{mm}(g')$, where $\text{CC}_{mm}(g')$ is a two-center Coulomb correction term whose definition should be clear on comparison to Eq. (3-11). The terms $\text{CC}_{mm}(g)$ were calculated by a modification of the usual expansion method for Coulomb integrals. In this modification a Cl^- ion always is taken as the displaced ion, because of its size. The charge density on the displaced Cl^- ion is then written out analytically using the parameters of Table I, but only those parts of the resultant expression are retained which penetrate significantly into the origin charge density. The quantity $\text{CC}_{mm}(g)$ then is taken to be the difference between the interactions of the origin density and the partial displaced density when the latter is treated exactly and when it is treated as a nonpenetrating, displaced multipole. These two interactions are calculated easily and fairly accurately by the expansion method.

The term $\text{OVC}(m000|m)$ is given by Eq. (3-12). As examination of Eq. (3-4) for the overlap density $\rho_{\text{ov}}(2)$ shows, a part of OVC can be obtained from the accurate one- and two-center two-electron integrals and the quantities P_{qp} in Table III. These contributions account for the effects of part of the overlap charge density. The remainder of the overlap charge density can be replaced by an appropriate array of point charges, and its contributions may be calculated approximately, as described below.

The complete overlap charge density in Eq. (3-4) consists of negative charge in spherical distributions on crystal lattice sites (different charges for K^+ and Cl^- sites), and positive charge in two-center overlap distributions between the sites. The net overlap charge in a spherical distribution on site g is $-2\sum_p(\text{on site } g)P_{pp}$, which will be symbolized by $q_{\text{ov}}(g)$, while the net overlap charge in the overlap distribution between sites g and g' is $-4\sum_p(\text{on } g)\sum_q(\text{on } g')P_{qp}\Delta_{pq}$, which will be symbolized by $q_{\text{ov}}(g,g')$. It can be shown that the charge $q_{\text{ov}}(g)$ must equal $-\frac{1}{2}\sum_{g'}(g'\neq g)q_{\text{ov}}(g,g')$, and the neutrality of the overlap charge density follows from this. When the approximate values of P and Δ from Table III are used, however, the left and right sides of this equality differ by about one percent. To avoid difficulties, then, the working value of each charge $q_{\text{ov}}(g)$ is taken to be the value calculated from the charges $q_{\text{ov}}(g,g')$. These values for $q_{\text{ov}}(g)$ turn out to be -0.190 and -0.116 electron charges for g a Cl^- and a K^+ site, respectively. In the point charge approximation for the overlap charge density that density is replaced by the charge $q_{\text{ov}}(g)$ on each lattice site g and the charge $q_{\text{ov}}(g,g')$ on a line between each pair of sites g and g'. The exact location for each charge $q_{\text{ov}}(g,g')$ is determined by calculating the center of gravity of the two-center overlap charge distribution between sites g and g'.

For the calculation of $\text{OVC}(m000|m)$, then, part of the overlap density is included accurately, and the remainder is approximated by the point-charge array just described. To obtain the contribution to OVC arising from the point charge remainder, the primary density $-u_m^*(1)u_m(1)$ is treated as a negative point charge at the origin, and the charges in the point-charge array are grouped to give an infinite NaCl-like array and an array of high-order, neutral multipole distributions. The desired contribution is evaluated easily in this approximation. As shown by the results in Table IV, $\text{OVC}(m000|m)$ is generally the largest of the overlap-dependent contributions to a one-center energy element.

The term $\text{CEX}(m000|m)$ given by Eq. (3-13) is obtained easily from the accurate two-center exchange integrals.

The term $\text{OVE}(m000|m)$ given by Eq. (3-14) is the exchange interaction of the primary exchange function with the overlap exchange function $\rho_{\text{ov}}(2|1)$. As examination of Eq. (3-15) for the overlap exchange function shows, a part of $\text{OVE}(m000|m)$ is obtainable from the accurate one- and two-center two-electron integrals and the quantities P_{qp} in Table III. The remainder of the overlap exchange function provides only small contributions to the over-all term $\text{OVE}(m000|m)$. These are included by approximating the more important many-center integrals as Coulomb interactions between appropriate point charges. This is the last of the terms contributing to a one-center energy element.

The general formula for a two-center energy element $H(m\mathbf{R}|n)$ is given in Eq. (3-5). The terms contributing to such an element are discussed below, and the final values of the elements with their uncertainties and the values of the contributing terms are listed in Table IV, (b) and (c).

The terms $\text{KE}(m\mathbf{R}|n)$, $\text{C}(m\mathbf{R}|n)$, and $\text{EX}(m\mathbf{R}|n)$ as given in Eqs. (3-6), (3-7), and (3-8) all are obtained easily from the standard two-center molecular integrals discussed in Sec. 3(b). As shown by the values listed in Tables IV, (b) and (c), the term EX is the most important of all the terms contributing to each two-center energy element, and its sign determines the sign of the element (the seemingly large contributions C and CPI in the ClCl elements necessarily tend to cancel one another, as will be shown).

The term CPI($m\mathbf{R}|n$) given by Eq. (3-10) is calculated differently depending on whether the pair m, n designates a ClK or a ClCl element. In the ClK case the potential energy due to the primary chlorine as a point ion is added and subtracted to the potential in the square brackets in Eq. (3-10). The term CPI then is given by the Coulomb interaction of the primary density with the KCl crystal as a crystal of point ions, excluding the primary K^+ ion, minus its interaction with the primary chlorine as a point ion. The latter interaction is calculated easily from the accurate, two-center nuclear-attraction integrals. The former is calculated by expanding both the Madelung potential and the primary Cl^- function about the K^+ site as an origin and evaluating the lead terms in the resultant infinite series. As shown by actual calculation of several terms in this series, the term $(2\alpha/a)\Delta(m\mathbf{R}|n)$ which arises from the spherical term in the expansion of the Madelung potential is the only significant contribution to CPI from this infinite series.

In the case in which the pair m, n designates a ClCl element, the above method for calculating CPI($m\mathbf{R}|n$) is not expected to be good due to poor convergence of the infinite series. For this case the contributions of the two nearest K^+ ions to CPI are calculated explicitly by use of the accurate three-center integrals involving the potential $2/r$, and the contributions due to all further ions are found to be negligible. The net charges of the two potassiums which are included neutralize the net charges of the two primary chlorines, and, as a result, the term CPI($m\mathbf{R}|n$) tends to cancel an important part of the corresponding term C($m\mathbf{R}|n$), as was anticipated.

The term CCC($m\mathbf{R}|n$) given by Eq. (3-11) is entirely negligible in ClK elements, and in ClCl elements its only significant contributions are from the two nearest K^+ ions. The latter contributions are calculated by use of the accurate three-center integrals of the neutralized nuclear charge for potential of a potassium ion [see Sec. 3(b)].

The term OVC($m\mathbf{R}|n$) given by Eq. (3-12) is the Coulomb interaction of the primary charge density with the overlap charge density $\rho_{\mathrm{ov}}(2)$. As with the corresponding contribution to one-center energy elements, a part of this term is given by combinations of standard two-center integrals and the quantities P_{qp} in Table III. The remainder of the term is calculated approximately by considering the primary charge density $-u_m{}^*u_n$ to be a point charge of magnitude $-\Delta(m\mathbf{R}|n)$ located at its own center of gravity and by finding the interaction of this point charge with the remainder of the overlap density as an array of point charges. As shown by the results in Table IV, the terms OVC are all small, but the smallness results from the cancellation of the two-center contributions against the remainder contributions.

TABLE V. List of k points. The values of $\mathbf{k}$ are given by the components k_x, k_y, and k_z, and each component is given in units of $\pi/4a$.

k-point	$\mathbf{k}$	k point	$\mathbf{k}$	k point	$\mathbf{k}$
1	0,0,0	13	0,3,3	26	0,8/5,8/5
2	0,0,1	14	1,1,1	27	0,9/5,9/5
3	0,0,2	15	1,1,2	28	0,11/5,11/5
4	0,0,3	16	1,1,3	29	0,12/5,12/5
5	0,0,4	17	1,1,4	30	0,13/5,13/5
6	0,1,1	18	1,2,2	31	0,14/5,14/5
7	0,1,2	19	1,2,3	32	0,8/5,10/5
8	0,1,3	20	2,2,2	33	0,7/5,11/5
9	0,1,4	21	1/2,1/2,1/2	34	0,4/5,14/5
10	0,2,2	22	3/2,3/2,3/2	35	1/5,9/5,9/5
11	0,2,3	23	1,5/2,3/2	36	2/5,9/5,9/5
12	0,2,4	24	0,6/5,6/5	37	1,9/5,9/5
		25	0,7/5,7/5		

The term CEX($m\mathbf{R}|n$) given by Eq. (3-13) is entirely negligible in ClK elements, and it is small in ClCl elements. Its values were obtained by approximating many-center integrals as interactions between appropriate point charges.

The term OVE($m\mathbf{R}|n$) given by Eq. (3-14) can be broken into two parts, one which is easily calculable from the accurate two-center integrals, and another which is small and can be estimated by the use of approximate two-electron integrals. This is the last of the terms contributing to a two-center energy element.

4. BAND STRUCTURE AT THE NORMAL INTERIONIC DISTANCE

(a) Calculation and Results

In the present calculation the electronic structure of KCl is determined by solving the set of eight simultaneous equations (2-10) in the outer-function, second-neighbor approximation. The set of equations is solved for representative values of the wave vector $\mathbf{k}$ lying in the central Brillouin zone of KCl. This Brillouin zone is the well-known Wigner-Seitz truncated octahedron; it is illustrated in Fig. 1(a). The coordinates of k space in this figure are given as ξ, η, and ζ, equal to ak_x, ak_y, and ak_z respectively, where a is the interionic distance; the alternative coordinates ξ_1, ξ_2, and ξ_3 in the figure will be used later. An independent segment of the zone is illustrated in Fig. 1(b). Its volume is one forty-eighth that of the entire zone, forty-eight being the number of operations of the cubic point group.

The representative wave vectors chosen for use in the present calculation are the twenty which define points on a cubic mesh of interval $\pi/4$ in the independent segment of the central Brillouin zone, plus certain others which are required for particular details. The first twenty k points are illustrated in Fig. 1(b), and all the points are listed in Table V. None of the first twenty points is general.

Equations (2-10) have been solved on Whirlwind for all the wave vectors listed in Table V, and the solutions in complete form (energies and coefficients) are avail-

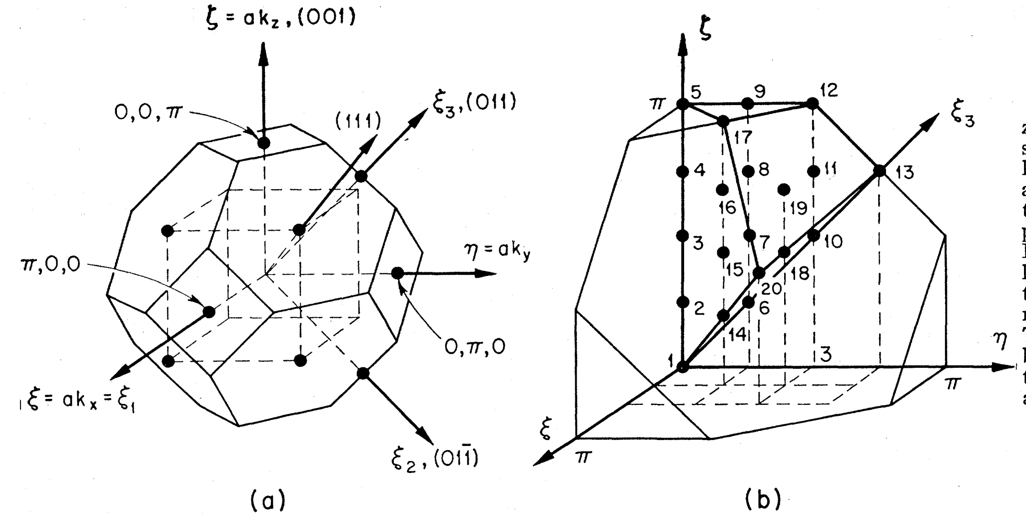

FIG. 1. (a) Brillouin zone for KCl. The inscribed cube in dotted lines and the axes ξ_1, ξ_2, and ξ_3 are described in the text. (b) An independent segment of the Brillouin zone (in heavy lines) and k points in that segment on a cubic mesh of interval $\pi/4$. The k points are numbered in sequence along the dotted lines which are parallel to the ζ axis.

able upon request.[19] In general these solutions bear out the expectations expressed in Secs. 1 and 2. Each final one-electron function is made up predominantly of a linear combination of some particular set of degenerate free-ion functions, and each band of one-electron energies is narrow compared to the energy differences between the bands. The energy parameter results are summarized in fairly complete form in Figs. 2 and 3 and are discussed in some detail below.

In Fig. 2 the seven highest energy parameters for each wave vector are plotted on a vertical energy scale, and the vertical scales for the different wave vectors are arranged close together across the page to allow easy comparison. By the choice of indexing the k points, they run in short sequences along lines in k space parallel to the k_z axis. Energy curves are drawn through these sequences in the figure.

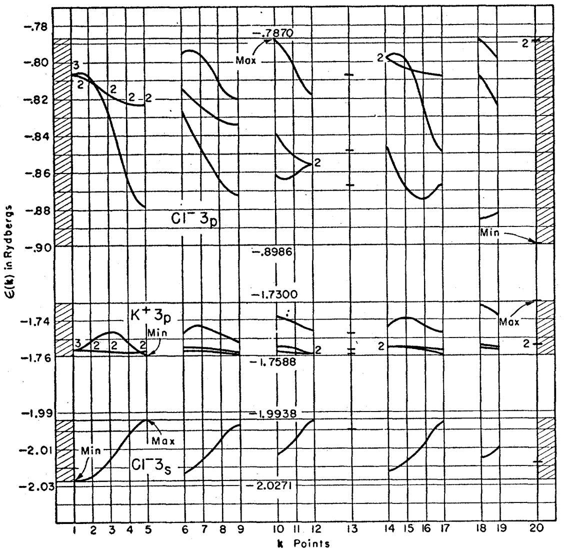

FIG. 2. Band structure of KCl at the normal interionic distance (5.9007 a.u.). The values $\epsilon(\mathbf{k})$ plotted vertically for each k point are the highest seven roots of the eighth-order secular equations. The k points are identified in Fig. 1(b) and in Table V. The degeneracy of each root is given unless it is one.

The order of the energy bands of KCl in Fig. 2 is just that predicted by the order of the free-ion, Hartree-Fock energy parameters plus or minus the Madelung energy. The filled band of highest energy, the valence band, is Cl^- $3p$. From data in the figure this band has a total width of 0.112 rydberg or 1.52 ev. Proceeding downward in one-electron energies, the next bands are K^+ $3p$, with a width of 0.029 rydberg or 0.39 ev and about 0.8 rydberg below the bottom of the valence band; Cl^- $3s$, with a width of 0.033 rydberg or 0.45 ev and about 0.23 rydberg below the bottom of the K^+ $3p$ band; and K^+ $3s$ (which is omitted from the figure), with a width of less than 0.001 rydberg and about 1.3 rydbergs below the bottom of the Cl^- $3s$ band.

In the outer-function approximation the energy bands corresponding to inner free-ion functions have no width at all, and they are given by the appropriate free-ion Hartree-Fock energies plus or minus the Madelung energy. To the scale of Fig. 2 this result almost certainly is valid for the inner-function Cl^- bands, and from the narrowness of the K^+ $3s$ band, it probably is correct for the inner-function K^+ bands as well.

Let us go on to consider the details of the valence band. In Fig. 2 the minimum of this band in the independent segment of the Brillouin zone is seen to be a nondegenerate energy at the zone boundary in the [1,1,1] direction (k point 20). It is quite distinct in that all the other energies on the cubic mesh of k points are appreciably higher than it. The minimum is illustrated further in Fig. 3(b).

The maximum of the valence band in the independent

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[19] A complete table of one-electron energies and functions for KCl at the k points listed and at the normal interionic distance can be obtained from the Library of Congress by the procedure which is outlined in footnote 17. This table is in the same document as the table of integrals described there.

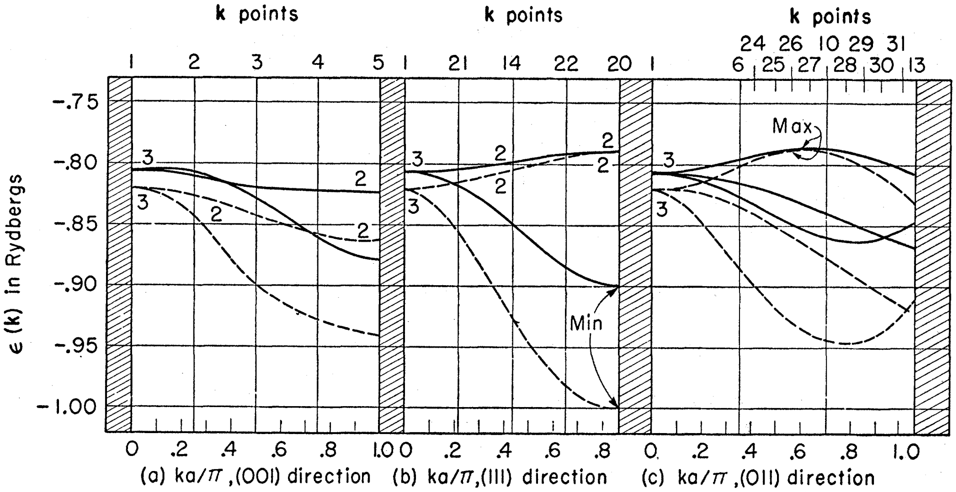

FIG. 3. Band structure of KCl at the normal interionic distance (5.9007 a.u.) along three directions in k space. The solid curve is obtained by the eighth-order equations, and the dashed curve is obtained by the third order equations. The degeneracy of an energy curve is given unless it is one.

segment appears to be a nondegenerate level at k point 10, inside the Brillouin zone and along the [0,1,1] direction. This maximum is not distinct, however, since the maximum energies for points 18 and 20 are only slightly below it. Inclusion in the calculation of interactions between free-ion functions on more distant neighbors might result in a shift of the calculated maximum from point 10 to one of these other two points. The maximum energies at these three points are distinctly higher than the energies at the other points on the cubic mesh, however, and a more accurate calculation probably could not shift the band maximum to one of these other points. From Table V or Fig. 1(b), the points 10, 18, and 20 in question are seen to lie along a straight line parallel to the k_x axis; this line, when extended, connects the centers of two adjacent hexagonal faces of the Brillouin zone, and point 10 is its midpoint. Taken together the twelve lines like this are edges of a cube inscribed in the truncated octahedron which is the Brillouin zone; this cube is indicated by dotted lines in Fig. 1(a).

Even if a band maximum actually occurs for a wave vector in the [0,1,1] direction, however, there is no reason of symmetry why it should be exactly at point 10. To obtain detailed information about the location of the band maximum, Eqs. (2-10) were solved at k-points 24 through 37 (see Table V) near point 10. Some of the resulting energies are included in the curve of Fig. 3(c). As shown by the results, the maximum band energy still occurs along the [0,1,1] direction, but at ξ_3 [defined in Fig. 1(a)] equals 0.631 π, rather than exactly at ξ_3 equals 0.707π, which is point 10. The actual value of the maximum band energy then is -0.7862 rydberg, rather than -0.7870 rydberg, as obtained at point 10.

In view of the results above, a surface of constant energy for an energy somewhat below the Cl^- $3p$ band maximum is a tubular framework almost describing the inscribed cube of Fig. 1(a), but having the tubes bent slightly toward the origin while their joints are fixed at the cube corners. For a higher energy this surface of constant energy breaks into twelve ellipsoids, each centered on one of the equivalent maxima. For the ellipsoid centered in the [0,1,1] direction the principal axes are parallel to the ξ_1, ξ_2, and ξ_3 axes (directions [1,0,0], $[0,1,\bar{1}]$, and [0,1,1], respectively), which are shown in Fig. 1(a). The corresponding components of the diagonalized effective mass tensor were found to be 10.0, 0.93, and 2.0 electron masses, respectively.

The results discussed above all are based on solutions of Eqs. (2-10) in the outer-function, second-neighbor approximation. In this approximation the equations are of order eight because the eight Bloch sums built from the eight different types of outer free-ion functions are allowed to mix to form each one-electron function $\psi_i(\mathbf{k}|\mathbf{r})$. As shown by the results obtained, however, the functions $\psi_i(\mathbf{k}|\mathbf{r})$ which have energies in the Cl^- $3p$ band are built up predominantly of Cl^- $3p$ free-ion functions with only small admixtures of the other types of functions. To separate the effects of these small admixtures, a third-order secular equation also has been solved for each of the wave vectors 1 through 23 in Table V. The third-order equation is obtained by allowing only Cl^- $3p$ Bloch sums to mix, but using the same matrix elements between them as were used before (these would be changed only slightly if ClK contributions were neglected fully). Energies in the Cl^- $3p$ band obtained by solving this third-order secular equation are plotted in Figs. 3(a), (b), and (c) along with those obtained by solving the eighth-order equation. The principal feature to note is that the band width predicted by the third-order equations is too large by a factor of about two.

The uncertainty in the final results obtained by solving the eighth-order equations is difficult to estimate. The significant uncertainties in a particular energy parameter arise from the following sources: omission of interactions with inner free-ion functions, omission of interactions between second-neighbor K^+ functions and interactions between all functions separated by more than the second-neighbor distance, and uncertainties in the values of the energy elements which are actually included in the calculation. In view of the estimated errors arising from these causes and in view of the nature of the equations to be solved, the uncertainty in a particular energy parameter probably is about ±0.015 rydberg. The absolute errors of energy parameters in different regions of reciprocal space are not independent, however, and a more accurate calculation based on the same model probably would give an energy band only slightly different though somewhat displaced from the band obtained here.

(b) Discussion of Results

The theoretical work most comparable to that presented here is Shockley's cellular calculation for the Cl^- $3p$ band of NaCl.[2] Shockley obtains a Cl^- $3p$ bandwidth of about 4 ev for NaCl, while the present calculation gives about 1.5 ev for KCl. The narrower band of the present calculation is somewhat more in line with expectation, since narrow bands are observed in the appropriate x-ray emission spectra of the alkali-halides.[8]

The difference between the band widths probably has several causes. In the first place Shockley's best results are obtained with the $Cl^- - Na^+$ matching conditions either neglected or included only approximately. In the present work the third-order equations in which only Cl^- $3p$ Bloch sums are allowed to mix involve an analogous omission of $Cl^- - K^+$ interactions (except as they are built into the ClCl energy elements), and these solutions give a band width of 2.9 ev (see Fig. 3), almost twice the final calculated band width. By implication, then, Shockley's relatively wide band might be largely a result of inadequate treatment of the $Cl^- - Na^+$ matching conditions. As a second cause of the difference in band widths, the KCl calculation is based on Hartree-Fock functions for Cl^- while Shockley's calculation is based on potentials obtained from the more extensive Hartree functions. A part of the difference between the calculated band widths for the two crystals may well be real, of course, since interactions between the second-neighbor Cl^- functions are relatively more important in NaCl than in KCl, but this probably cannot account for the entire difference.

Except for scale and the absolute values of energies, the Shockley NaCl valence band and the new KCl valence band are quite similar. Since Shockley did not calculate energy curves for the [0,1,1] direction in reciprocal space, however, it is not possible to compare the locations of the predicted band maxima. In view of the fact that for KCl an energy maximum occurs in the [0,1,1] direction away from k equals zero even in the third-order solutions, it is quite possible that in an extended Shockley-calculation for NaCl the same thing would occur.

Another theoretical study which is somewhat comparable to the present work is the cellular calculation for LiF by Ewing and Seitz.[1] The valence band of LiF is F^- $2p$ rather than Cl^- $3p$, and exchange effects were neglected in this calculation. In spite of these facts, however, the final curves of the valence band energies of LiF in the [1,0,0], the [1,1,1], and the [1,1,0] directions bear many resemblances to the corresponding curves for KCl in Fig. 3 and to Shockley's [1,0,0] and [1,1,1] curves for NaCl. In the [1,1,0] curve for LiF in particular the upper branch of the band rises as k increases from zero, as the corresponding KCl branch does. This result tends to support the suggestion made above that the NaCl band maximum also might occur in the [1,1,0] direction. Instead of going through a maximum inside the zone as the upper KCl branch does, however, the LiF branch goes to a maximum at the zone boundary. In addition, the LiF band has a width of about 0.4 rydberg or 5.5 ev.

The principal experimental work to which the present results can be compared is the study of the x-ray emission spectrum of KCl made by Parratt and Jossem.[8] This emission spectrum was observed in ranges around the K_β emissions of the free ions K^+ and Cl^-, and similar results were found in the two regions. Theoretically some part of the spectrum observed in the Cl^- K_β region should arise from band-to-band transitions of the crystal-minus-one-electron in which a hole in the Cl^- $1s$ band jumps to the Cl^- $3p$ band. From the experimental results this spectrum consists of a high, narrow peak called β_1, at the low-energy end of a lower, broader band called β_x. There is some reason to believe that the β_1 peak by itself represents the band-to-band transitions.[20] This peak has a width at half maximum of 1.20 ev, and it also is quite smooth, at least on its low-energy side.

With energies and functions determined by the present type of calculation, a theoretical spectrum for the Cl^- K_β band-to-band emissions can be determined. This has been done here by interpolating to obtain valence-band energy parameters on a mesh half the size of that described earlier and by simply counting energies in subdivisions of the band to get a rough density-of-states curve. The latter curve would have roughly the same form as the desired Cl^- K_β emission spectrum if the effects of natural line-broadening and of the experimental apparatus were negligible, since the transition probability is fairly constant through k space, and since the Cl^- $1s$ band is flat. This theoretical density-of-states curve exhibits a dip near the middle of its 1.5-ev energy range, but, on the the basis of values given by Parratt and Jossem,[8] natural broadening and the experimental spectral window would smooth out this dip almost completely in the actual emission spectrum. The form of the theoretical density-of-states curve is not inconsistent with the form of

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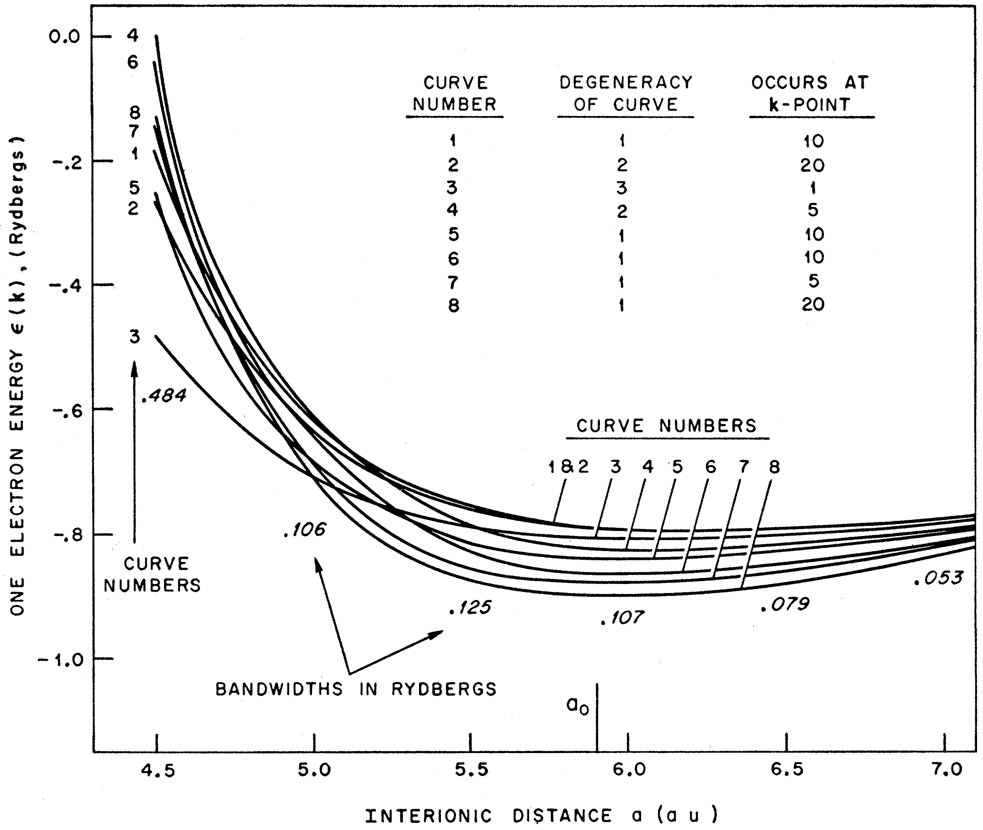
[20] L. G. Parratt (private communication).



CURVE NUMBER	DEGENERACY OF CURVE	OCCURS AT k-POINT
1	1	10
2	2	20
3	3	1
4	2	5
5	1	10
6	1	10
7	1	5
8	1	20

FIG. 4. Structure of the valence band of KCl as a function of the interionic distance a. Each curve represents a particular energy at a particular k point as a function of a. Values of the band width at intervals of 0.5 a.u. are given below the curves. The individual curves are numbered 1 through 8 in order of decreasing energy at 7.0 a.u. The k point for which a particular curve occurs and the degeneracy of a particular curve may be found from the table included in the figure.

the observed β_1 peak, therefore. When corrected for natural broadening, however, the theoretical curve predicts an emission spectrum with a width at half-maximum of about 1.32 ev, and this is appreciably larger than the true width of 0.78 ev obtained by Parratt and Jossem for the β_1 peak after correction for their spectral window.

The experimental $K^+ K_\beta$ emission spectrum of Parratt and Jossem is more readily explained by the present theoretical results than is the $Cl^- K_\beta$ spectrum discussed above. In view of the difficulties in explaining the latter, however, the $K^+ K_\beta$ agreements may be fortuitous, and they will not be discussed here.

5. BAND STRUCTURE AS A FUNCTION OF INTERIONIC DISTANCE

(a) Description of the Calculation

To provide some information about density-dependent effects in KCl as well as about band structure in general, the band structure of KCl was recalculated as a function of the interionic distance. For this the matrix elements of energy and overlap between free-ion functions (those in Tables III and IV) were taken to vary in simple analytic ways as functions of the distance.

On the basis of the observations mentioned in Sec. 3(b), the two-center overlap integrals all were taken to vary exponentially with distance. The exponential factor for a given integral was obtained by fitting one exponential to the curve of each overlap as a function of distance. The two-center energy elements each were taken to vary as an exponential divided by the interionic distance, and the exponential factors were chosen to be the same as those for the corresponding overlap integrals. The overlap-dependent contributions to each of the one-center energy elements [the second set of brackets in Eq. (3-16)] were taken to vary together as an exponential divided by the interionic distance, and the exponential factors were derived from those for the overlap integrals. All of the elements were made to equal the accurate elements at the normal interionic distance of 5.9007 a.u. The elements obtained by use of these analytic approximations probably are reasonable for interionic distances greater than about 5 a.u. The second-neighbor, outer-function approximation may not be very reasonable for distances less than 5.5 a.u., however.

(b) Results and Discussion

With the approximate elements discussed above the band structure of KCl was calculated for interionic distances from 4.5 to 7.0 a.u. at intervals of 0.5 a.u. The eighth-order equation (2-10) was solved only at k-points 1, 5, 10, and 20 (see Table V), since it was judged

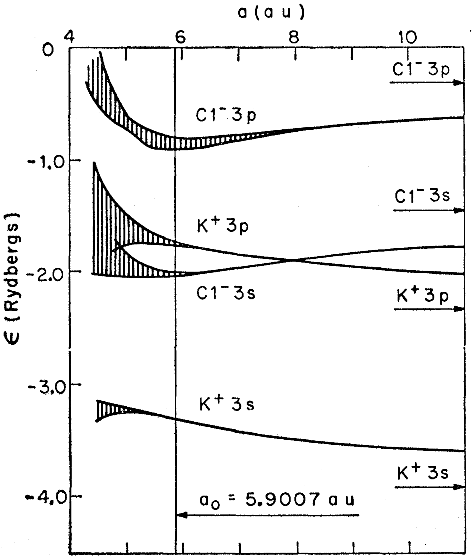


FIG. 5. The upper four filled bands of KCl as a function of the interionic distance *a*. The values of the free-ion Hartree-Fock energy parameters are given at the right of the figure; the bands approach these parameters in the limit as the interionic distance approaches infinity.

by Fig. 2 that the results for these points would characterize the dependence of band structure on distance fairly well.

The properties of interest in the results are most easily found by comparing the solutions of the secular equations for a given *k* point as a function of interionic distance. The functions and energies for large distances are easily identified with free-ion functions and energies. By matching the coefficients for one-electron functions from one value of the interionic distance to the next smaller value, it is possible to follow a particular energy as a function of distance. Smooth curves are obtained for the variation of each energy.

Figure 4 shows the superposed curves of all the calculated energy parameters in the Cl^- $3p$ band. The envelopes of these curves are approximate curves of the upper and lower limits of the Cl^- $3p$ band. For interionic distances greater than normal in the figure the band maximum is at point 10 (or near it), the minimum is at point 20, and the energies obtained are rather uniformly distributed throughout the band. As the distance decreases from infinity, however, the energies all decrease, pass through minima in the neighborhood of the normal distance, and then increase rapidly. During this variation, the energy for *k*-point 1 (*k* equals zero) shifts from a value near the band maximum for large distances to become the band minimum for distances less than 5.0 a.u. Although the results for a distance of 4.5 a.u. are not reliable, the trends indicate that the band minimum at *k* point 1 becomes deeper and the density of states in its vicinity decreases as the distance decreases below 5.0 a.u. In addition, as the interionic distance decreases through the neighborhood of 5.0 a.u., an energy at *k* point 5 takes over the role of band maximum from the energy at *k* point 10. Because of the shifting of energies relative to one another in the band, the width of the Cl^- $3p$ band does not vary smoothly with decreasing interionic distance; the band widths for various interionic distances are given in the figure.

The upper and lower bounds of all the bands as functions of interionic distance have been obtained, and they are plotted in Fig. 5. This plot shows many similarities to the plot of the NaCl energy bands which was constructed by Slater and Shockley.[6] The reasons for the behavior of the bands in Fig. 5 may be understood by consideration of the analytic forms of the elements of energy and overlap. As the interionic distance *a* decreases from 7.0 to 4.5 a.u. the two-center elements all increase essentially exponentially, and this increase is responsible for the observed broadening of the bands. At the same time each Cl^- band first falls because of the negative Madelung energy in the Cl^- one-center energy elements, and then it rises rapidly as the positive, exponentially-increasing, overlap-dependent contributions to the one-center elements come to overweigh the Madelung energy. The K^+ $3p$ band first rises due to the positive Madelung energy in the K^+ one-center energy elements and then rises much more rapidly as the positive overlap-dependent contributions become predominant. The K^+ $3s$ band probably should behave in the same general way as the K^+ $3p$ band, but due to calculation inaccuracies the small overlap-dependent contributions to its normal one-center energy element come out to be negative; the magnitudes of these contributions are less than their uncertainties, however.

The rapid rise of the three upper bands in Fig. 5 at small distances outweighs the band broadening. This is because the overlap-dependent contributions to the one-center energy elements vary roughly as the square of the largest overlaps while the two-center elements, which cause broadening, vary only as the overlaps themselves. Orthogonality requirements probably account for the particularly rapid rise of the Cl^- $3p$ band.

6. COHESIVE ENERGY OF THE NORMAL CRYSTAL

(a) Equations

The calculation of cohesive energy in the present section is performed both for its own interest and also to provide checks on the quantities used in the electronic structure work of the preceding sections. It is modeled after the comprehensive cohesive energy calculations of Löwdin.[4] The cohesive energy is defined as the energy of the crystal at 0°K relative to the energy of the infinitely-separated, static, free ions, K^+ and Cl^-. The fact that the interionic distance which is used here is not quite correct for 0°K will introduce only a negligible error in the total calculated cohesive energy.

On the basis of the definitions in Sec. 2 and Löwdin's

TABLE VI. The quantum-mechanical cohesive energy of KCl in various approximations as obtained with a determinant of free-ion Hartree-Fock functions. Energies are in kilocalories per mole and are obtained for an interionic distance of 5.9007 a.u.

Approximation	E_{Mad}	E_{corr}	E_{exch}	E_S	E_{ov}	E_{coh}
(*A*) 1st-neighb., out-fn, Löwdin	−185.8	−16.5	−48.6	84.0	18.9	−166.9
(*B*) 1st-neighb., out-fn, Howland	−185.8	−17.2	−49.5	(89.3)	(22.6)	...
(*C*) 2nd-neighb., out-fn, Howland	−185.8	−20.4	−60.0	106.6	26.2	−159.6
(*D*) Exact	−185.8	...	...	...	26.2 to ∼28.2	−159.6 to ∼−157.6

work the cohesive energy of KCl in the LCAO approximation is given by

$$E_{\mathrm{coh}}=E_{\mathrm{elstat}}+E_{\mathrm{exch}}+E_S, \tag{6-1}$$

where the three terms on the right are

$$E_{\mathrm{elstat}}=W+\sum_g\Big[2\sum_m(\text{on } g)\sum_{g'\neq g}\int u_m(1)^* \times(-2Z_{g'}/r_{1g'})u_m(1)dv_1+2\sum_m(\text{on } g) \times\sum_p(\text{not on } g)(G|mm|pp)\Big], \tag{6-2}$$

$$E_{\mathrm{exch}}=\sum_g[-\sum_m(\text{on } g)\sum_p(\text{not on } g) \times(G|mp|pm)], \tag{6-3}$$

and

$$E_S=\sum_g\sum_m(\text{on } g)\sum_n P_{nm}\{2(F|mn) +\sum_{p,q}[2(G|mn|pq)-(G|mq|pn)]P_{qp} +2\sum_p[2(G|mn|pp)-(G|mp|pn)]\}. \tag{6-4}$$

In these equations $(F|mn)$ is the integral of the operator F_1 between functions u_m and u_n, and $(G|mn|pq)$ is given by

$$(G|mn|pq)=\int\int u_m(1)^*u_n(1)G_{12}u_p(2)^* \times u_q(2)dv_1dv_2. \tag{6-5}$$

The three energy terms above are called the "electrostatic energy," the "exchange energy," and the "S-energy," respectively.

The electrostatic energy given by Eq. (6-2) represents the total Coulomb energy of interaction of all the free-ions in the lattice (electrons plus nuclei). It can be split up as follows:

$$E_{\mathrm{elstat}}=E_{\mathrm{Mad}}+E_{\mathrm{corr}}, \tag{6-6}$$

where E_{Mad} is the Madelung energy, which is equal to $-2\alpha/a$ per unit cell, and where E_{corr} is Löwdin's correction energy, which can be obtained from the effective charges for potential of the K^+ and Cl^- ions and from the Coulomb correction terms $\mathrm{CC}_{mm}(g)$, which were discussed in Sec. 3(c). The exchange energy given by Eq. (6-4) can be obtained as a sum of two-center exchange integrals, which were discussed in Sec. 3(b).

The *S* energy given by Eq. (6-4) can be rewritten to contain the energy elements H_{mn} of Eq. (2-12) explicitly. This is desirable both for ease of calculation and to provide checks on the energy elements. The *S* energy then is given by

$$E_S=\sum_{m,n}P_{nm}Q_{mn}, \tag{6-7}$$

where

$$Q_{mn}=2H_{mn}-\mathrm{OVC}_{mn}-\mathrm{OVE}_{mn}. \tag{6-8}$$

This equation for the *S* energy is not very satisfactory for calculational purposes, however. A product $P_{nm}Q_{mn}$ in the equation is negative if the functions *m* and *n* are on the same site (in which case *m* equals *n*) and positive if they are on different sites; the final *S* energy is an undesirable difference between large numbers. A better equation is obtained by the following considerations. From the definitions of P_{nm} and S_{nm} in terms of $(\Delta^{-1})_{nm}$ and Δ_{nm}, it can be proved easily that

$$P_{nm}=-S_{nm}-\sum_p\tfrac{1}{2}[P_{np}S_{pm}+S_{np}P_{pm}]. \tag{6-9}$$

On substitution of this expression for each one-center element P_{nm} in Eq. (6-7), the *S* energy becomes

$$E_S=\tfrac{1}{2}\sum\nolimits'_{g,g'}\sum_m(\text{on } g)\sum_n(\text{on } g')P_{nm}T_{mn}, \tag{6-10}$$

where

$$T_{mn}=2Q_{mn}-\sum_p(\text{on } g \text{ and } g')[S_{mp}Q_{pn} +Q_{mp}S_{pn}]. \tag{6-11}$$

Equation (6-10) for the *S* energy is satisfactory because each contribution $P_{nm}T_{mn}$ is positive. The differences which occur in Eq. (6-7) have been transferred into the quantity T_{mn}, as shown by Eq. (6-12), and in this form they can be taken in such a way as to avoid difficulty.

As described above, then, all of the quantities involved in Eq. (6-1) for the cohesive energy can be calculated simply from quantities which were determined in the course of the work on band structure. This has been done here only within the outer-function, second-neighbor approximation which was used for the band calculation.

(b) Results and Discussion

The results of the calculation described above are presented in Table VI. In addition to the quantities already defined, a quantity E_{ov}, the overlap energy, also is included in the table. This energy is the sum of the three overlap-dependent terms, E_{corr}, E_{exch}, and E_S; it is listed because it corresponds quite closely to the repulsive energy of the Born-Madelung type of calculations.[21] The notation in the first column of the table indicates the approximation in which the results are obtained.

From the results of the present outer-function, second-neighbor calculation in row C of the table, the Madelung energy is seen to be the predominant term in the cohesive energy. The correction and exchange energies are both negative also, but the S energy is positive and of such a magnitude that the total overlap energy is positive. It is this positive overlap energy which keeps the ionic lattice from collapsing under the influence of the ionic attractions. The overlap energy is positive because the S energy is large and positive, and the S energy arises from the existence of the overlap charge density, which in turn is an effect of the exclusion principle.

The cohesive energy and its individual components have been calculated again in a lower approximation by omitting the second-neighbor, ClCl contributions to E_{corr}, E_{exch}, and E_S almost completely. The values thus obtained are shown in row B of Table VI. The values of the correction and exchange energies thus obtained are exactly the values appropriate to a first-neighbor, outer-function calculation of the cohesive energy, as the notation in the first column of the table indicates. The value of the S energy thus obtained contains some dependence on the second-neighbor, ClCl overlapping, however, since the ClK elements of inverse-overlap and energy of Tables III and IV were used without correction. The values of both the S-energy and the overlap energy in row B therefore are given in parentheses.

Löwdin's results[4] for the cohesive energy of KCl are given in row A of Table VI; the values shown are obtained by interpolating Löwdin's published values to the interionic distance 5.9007 a.u. As is indicated in the first column of the table, Löwdin's results are obtained in the first-neighbor, outer-function approximation. The new values of the correction energy and the exchange energy in row B of the table are seen to agree fairly well with Löwdin's corresponding values in row A. The observed differences of two and four percent are reasonably explained by the slightly different functions used in the two calculations. The value of the S energy in row B does not agree very well with Löwdin's value, but the difference in the values is compatible with the sign and probable size of the ClCl contributions to the value in row B. The agreement with Löwdin's results is taken as providing a rough check on some of the numerical quantities used in the band-structure calculations of the preceding sections.

On comparison of the second-neighbor results in row C of Table VI with Löwdin's first-neighbor results in row A, the ClCl interactions are seen to provide an appreciable contribution to E_{ov} and E_{coh}. They provide about 7.3 kilocalories per mole as compared to the 18.9 kilocalories per mole which the ClK interactions provide.

In an exact calculation of E_{coh}, interactions between more distant neighbors in the lattice and interactions which involve inner free-ion functions would have to be included also. Such interactions would raise the overlap and cohesive energies to even higher values than those given in row C of Table VI, but probably by not more than about 2 kilocalories per mole. The values of the overlap and cohesive energies in an exact calculation on Löwdin's model therefore should lie in the ranges indicated in row D of Table VI. These ranges are included in the table to emphasize that the accurate cohesive energy as predicted by Löwdin's model (the single determinant of free-ion functions in the crystal) must be even higher than the value obtained in the present calculation. It should be added that there is a calculational uncertainty of about one kilocalorie per mole in the values in row C of the table and that this uncertainty carries over to the range values indicated in row D.

The experimental value of the cohesive energy of KCl is given by Huggins[21,22] as -167.8 ± 2 kilocalories per mole. Since the exact value of Löwdin's quantity E_{coh} is between -159.6 and -157.6 kilocalories per mole, Löwdin's model appears to give a cohesive energy which is between 8.2 and 10.2 kilocalories per mole too high. The source of this error can be seen by consideration of the problem of calculating the cohesive energy of an alkali halide in a general quantum-mechanical way, as shown below.

In principle the cohesive energy of an alkali halide should be calculated by performing complete configuration interactions for both normal crystal and separated free ions (with static nuclei), by subtracting the total energy of the free-ions from that of the crystal, and by adding the zero-point energy for lattice vibrations to the result. In practice the configuration interaction for the crystal is too difficult to be performed. The required difference between the configuration-interaction energies can be approximated, however. It can be considered as equal to the Hartree-Fock energy of the crystal minus the Hartree-Fock energy of the free ions plus a correction which is defined by the equality. This correction is just the contribution to the cohesive energy which arises from correlations of the motions of electrons in the two systems.

This correlation contribution is essentially just the energy due to the correlation of electrons which are on different ions in the crystal; thus it should be about equal to the van der Waals energy of interaction for ions in the crystal. On the basis of these remarks the complete cohesive energy of KCl should be given approximately by the following equation:

$$U=\Delta E_{\text{HF}}+E_{\text{vdW}}+E_{\text{zp}}, \qquad (6\text{-}12)$$

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[21] M. L. Huggins, J. Chem. Phys. 5, 143 (1937). See also the discussion in M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), p. 19.

[22] New values of -171 ± 3 and -166.4 ± 3 kilocalories per mole have been obtained by Morris, but these essentially substantiate Huggins' value. See D. F. C. Morris, Acta Cryst. 9, 197 (1956).

where U is the total cohesive energy, ΔE_{HF} is the difference between the Hartree-Fock energies of the crystal and the free ions, E_{vdW} is the van der Waals energy for ions in the crystal, and E_{zp} is the zero-point energy of the crystal.

Löwdin's quantity E_{coh} can be looked on as an approximation to the difference in Hartree-Fock energies, ΔE_{HF}, in Eq. (6-12). If the van der Waals and zero-point energies in this equation then are taken to be -6.2 and 0.9 kilocalorie per mole, respectively,[21] the total cohesive energy U as predicted by Eq. (6-12) is found to be between -164.9 and -166.9 kilocalories per mole. This result is only between 2.9 and 4.9 kilocalories per mole above the experimental value. This final discrepancy should be just equal to the error in the energy of Löwdin's single determinant of free-ion functions as an approximation to the true Hartree-Fock energy of the crystal. Löwdin's determinant therefore seems to have an energy which is between 2.9 and 4.9 kilocalories per mole higher than the true Hartree-Fock energy. The sign of this error is consistent with the definition of the Hartree-Fock energy,[23] and its magnitude is seen to be small. The results therefore provide a certain amount of justification for the LCAO approximation which has been used in the preceding sections.

It would not be too difficult to repeat the present cohesive energy calculation at other interionic distances, using the approximations of Sec. 5, but this has not been done. The results of such a calculation probably would predict very nearly the same equilibrium interionic distance for KCl which Löwdin found by his first-neighbor calculation, however. This is because the second-neighbor ClCl contributions to the correction, exchange, and S energies are all in about the same proportion to the corresponding first-neighbor ClK contributions and because, by an accident, the dependence on interionic distance of the largest ClCl overlap integral is almost the same as that of the largest ClK overlap integral.

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[23] On the basis of Löwdin's original results for E_{coh}, the sign of the corresponding error is not consistent with the definition of the Hartree-Fock energy.