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A CALCULATION OF THE ELECTRONIC ENERGY
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by

Tommy Dean Clark

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I. INTRODUCTION

The measurement of the optical absorption spectra of solids has long been recognized as one of the most direct methods of studying the electronic states of these materials. The alkali halides in particular were among the first solid types to be investigated by this technique in the pioneering work of Hilsch and Pohl (1929, 1930). These investigators were able to interpret their data to a reasonable degree of accuracy by a simple transfer model in which the absorption of a photon caused an electron in the outer shell of an halide ion to be transferred to an excited state of one of the nearby alkali ions. An abundance of additional data on the optical absorption and reflection spectra has subsequently appeared (Schneider and O'Bryan 1937, Hartman et al. 1957, Teegarden 1957, Eby et al. 1959, Teegarden and Baldini 1968, Philipp and Ehrenreich 1963, Baldini and Bosacchi 1967, Roessler 1965, 1966, Roessler and Lempka 1966, Roessler and Walker 1967) and it has become apparent that the simple transfer model of Hilsch and Pohl cannot explain the complex structure of these spectra adequately.

From a theoretical viewpoint the major problem in the interpretation of these optical spectra is that one must consider excitations of the crystal as a whole. First principle calculations of crystalline states are impossible from a practical viewpoint and certain approximations must be
employed. An approach to the problem of optical absorption which has had a great deal of success is to visualize the optical absorption as being associated with two related, but distinct, phenomena.¹

The first is the formation of conducting states of the crystal, visualized as the excitation of an electron from one of the normally filled valence bands to an excited state which is similar to that of an extra electron injected into the lattice. The excited electron and resultant hole in the valence band are thought of as moving more or less independently and can both contribute to conduction processes. Of course the electron and positive hole do interact, essentially through a Coulomb potential, and this gives rise to the second phenomenon of the optical absorption, the formation of localized, nonconducting states of the crystal called excitons. The usual formal approach to the exciton states of the crystal is to assume that the conducting states of the crystal, mentioned above, are known, to write the exciton states as a linear combination of these conducting states, and to diagonalize the Hamiltonian of the system. In one such approach, the Wannier model, one finds the conceptually satisfying result that, when the exciton state is formed from conduction

¹For a review of this work and the following material the reader is referred to the monograph The Theory of Excitons by R. S. Knox (1963).
states near a parabolic minimum of the conduction bands and the valence states near a parabolic maximum in the valence band, the exciton can be viewed as a bound electron-hole pair quite similar to the hydrogen atom.

Both of these phenomena are actually observed in the optical data. The formation of the exciton states are characterized by the peaks characteristic of localized states and the conducting states by the broad shoulders and continuous absorption of continuum states. It is apparent, then, that a detailed knowledge of the conducting states of the crystal is necessary for the interpretation of the experimental data.

However, in contrast to the large amount of experimental work, surprisingly few theoretical calculations of the electronic states of perfect alkali halide crystals have been performed. A few calculations of the unexcited or ground states of these materials have been performed (Ewing and Seitz 1936, Shockley 1936, Casella 1956, Kunz and Van Sciver 1966, Howland 1958, Kunz 1967a, 1967b). Generally these are tight-binding calculations in which the crystal is assumed to be a superposition of free ions and, since the excited states are not calculated, are of limited use in the interpretation of the optical data. Special mention should be made of the work of Tolpygo and his Russian co-workers (Tolpygo and Tomasevich 1961, Kucher and Tolpygo 1961, Evseev and Tolpygo 1963, Evseev 1964, Tolpygo and Sheka 1964, 1967), who have extended
the tightbinding techniques and have attempted to calculate, in addition to normal ground state, the lowest conducting states in NaCl. Their work is distinguished by the attempt to include the complicated many body effect of polarization of the lattice by the excited electron, an effect which is generally neglected in current band calculations. Although their work is presently limited in scope by the tightbinding approach, the Russians' work may prove to be the touchstone for future theoretical work in this field.

There are presently only three detailed calculations of the conduction bands of the alkali halides, two of KCl (DeCicco 1967, Oyama and Miyakawa 1966) and one of KI (Onodera et al. 1966). Certain details of the absorption spectra depend in a striking manner on which cation is present in the material. For example certain exciton peaks are present in the potassium and rubidium halides but are absent in the sodium halides. Recently several interpretations of this effect have been proposed (Phillips 1964, Onodera et al. 1966, Teegarden and Baldini 1967, Roessler and Walker 1967, Baldini and Bosacchi 1968), but all of these proposals are primarily of a speculative nature because of the limited knowledge of the conduction band structure of the alkali halides.

The purpose of this work is, then, to calculate the electronic energy and charge density structure of NaCl by a band theoretic approach and to use the results of this calculation,
as a complement to the above calculations in the potassium halides, in the interpretation of some of the features of the optical data.

Chapter II is devoted to establishing the notation and discussing the approximations and techniques used in the band theoretic calculation of the electronic states of NaCl. In Section A the periodic structure of the NaCl lattice and the resulting simplifications in the calculations are discussed. The one electron approximation, the use of the Bloch Theorem and the effects of these approximations upon the calculation are discussed in Section B. Essential assumptions and formulas of the numerical method chosen for the calculation, the augmented plane wave or APW method are presented in Section C. The methods used to construct the various potentials used in the calculation are presented in Section D.

The details and results of the calculation are presented and discussed in Chapter III. Section A consists simply of a presentation of the numerical results and a discussion only of those details necessary for the execution of the calculation. A detailed discussion of these results is postponed until Section B. In Section B, further, a comparison of these results with those of other alkali halides is made and the relation of these results to the optical data is discussed.
II. THE METHOD OF CALCULATION

A. The Periodic Structure

The ideal, ground state, NaCl crystal is shown in Fig. 1. The lattice is face-centered-cubic (FCC) with a basis of one sodium ion (Na\(^{+}\)) and one chlorine ion (Cl\(^{-}\)) separated by a distance \(a = 2.82\) Å, one half the length of the usual FCC cube edge. If we choose one of the points of the FCC lattice, e.g., one of the Na\(^{+}\) ions, as the origin of our co-ordinate system, all other lattice points are at positions given by the lattice vectors \(\mathbf{r}_n\)

\[
\mathbf{r}_n = \mathbf{a}(n_1, n_2, n_3) = n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3
\]  

where \(n_1, n_2, n_3\) are any integers. The vectors \(\mathbf{t}_i\), \(i=1,2,3\), are called the translation or basis vectors of the lattice and are given by (Slater 1965)

\[
\mathbf{t}_1 = a(\hat{i} + \hat{j})
\]

\[
\mathbf{t}_2 = a(\hat{i} + \hat{k})
\]

\[
\mathbf{t}_3 = a(\hat{j} + \hat{k})
\]

where \(\hat{i}\), \(\hat{j}\), and \(\hat{k}\) are unit vectors along the \(x\), \(y\), \(z\) crystallographic axes as shown in Fig. 1. The sodium and chlorine ion sites are at positions \(\mathbf{r}_1 = 0\) and \(\mathbf{r}_2 = a\hat{1}\), respectively, relative to the lattice points \(\mathbf{r}_n\). The ionic sites of the lattice are then given by

\[\text{We shall use the index } \nu = 1(2) \text{ to refer to the sodium (chlorine) site throughout.}\]
Fig. 1. The sodium chloride lattice
When dealing with periodic structures, that is, structures with a property, \( P \), such that
\[
P(\mathbf{r} + \mathbf{L}_n) = P(\mathbf{r})
\]
where \( \mathbf{L}_n \) is a lattice vector, one usually associates with each lattice point, \( \mathbf{L}_n \), a region of space near \( \mathbf{L}_n \) of volume \( \Omega \), called the unit cell. Each of the unit cells has the same space, volume, and orientation. The essential property of the unit cell is that the entire space is filled without overlapping when a unit cell is placed at each of the lattice points. Our crystal of volume \( V \) can then be thought of as composed of \( N \) unit cells where \( N = V/\Omega \). The unit cell can be constructed in a variety of ways, but in each method the volume must be the same, in our case \( \Omega = 2a^3 \). When investigating the property, \( P \), defining the periodic structure, we need consider a unit cell associated with only one of the lattice vectors, \( \mathbf{L}_n = 0 \) say, since the property \( P \) of any point outside this unit cell can be obtained by a simple translation of the property \( P \) inside by Equation 3.

To eliminate surface problems which produce mathematical complications, it is convenient to consider the crystal as being of infinite volume. This can be accomplished easily by employing periodic boundary conditions. Let us imagine that the crystal under consideration is a cube of edge \( L \) such that \( L^3 = V \). We can conceptually construct our infinite crystal by
placing these cubes side by side. We impose periodic boundary conditions by requiring that any property \( P \) of the extended crystal at the point \( \mathbf{r} + \mathbf{L} \), where

\[
\mathbf{L} = \mathbf{L}(m_1 \hat{1} + m_2 \hat{j} + m_3 \hat{k})
\]

(4)

and \( m_i \), \( i = 1, 2, 3 \) are any integers, can be obtained from the same property at the point \( \mathbf{r} \) in the original crystal via

\[
P(\mathbf{r} + \mathbf{L}) = P(\mathbf{r}).
\]

(5)

The use of periodic boundary conditions produces the convenient result that when Fourier analyzing we perform sums in the complement space and integrals over finite volumes in the direct space, that is

\[
P(\mathbf{r}) = \sum_k F_k e^{i\mathbf{k} \cdot \mathbf{r}}
\]

(6)

and

\[
F_k = \int \frac{d^3r}{V} P(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}
\]

(7)

where since \( P(\mathbf{r}) = P(\mathbf{r} + \mathbf{L}) \), the sum over \( k \) is restricted to the values

\[
k = \frac{2\pi}{L} (\lambda_1 \hat{1} + \lambda_2 \hat{j} + \lambda_3 \hat{k}); \quad \lambda_i = 0, \pm 1, \pm 2, \ldots, i = 1, 2, 3
\]

(8)

We shall assume throughout this work that periodic boundary conditions are in effect.

Let us now define the reciprocal lattice, a periodic structure in the complement (\( \mathbf{k} \)) space of the above Fourier transform. This reciprocal lattice is a body-centered-cubic (B.C.C.) lattice consisting of the points defined by the vectors
\[ K_m = K(m_1, m_2, m_3) = m_1 S_1 + m_2 S_2 + m_3 S_3 \] (9)

where
\[ S_1 = \frac{\pi}{a} (\hat{i} + \hat{j} - \hat{k}) \]
\[ S_2 = \frac{\pi}{a} (\hat{i} - \hat{j} + \hat{k}) \]
\[ S_3 = \frac{\pi}{a} (\hat{i} + \hat{j} + \hat{k}) \] (10)

are the reciprocal lattice basis vectors and \( m_i \), \( i = 1, 2, 3 \), are any integers. The reciprocal lattice basis vectors, \( S_i \), \( i = 1, 2, 3 \), are defined in terms of the direct lattice basis vectors, \( t_i \), \( i = 1, 2, 3 \), by
\[ S_1 = 2\pi \frac{(t_2 \times t_3)}{t_1 \cdot (t_2 \times t_3)} \]
\[ S_2 = 2\pi \frac{(t_3 \times t_1)}{t_1 \cdot (t_2 \times t_3)} \]
\[ S_3 = 2\pi \frac{(t_1 \times t_2)}{t_1 \cdot (t_2 \times t_3)} \] (11)

and satisfy the important relations
\[ S_i \cdot t_j = 2\pi \delta_{i,j} \quad (i, j = 1, 2, 3). \] (12)

The symbol \( \delta_{i,j} \) is the Kroneker delta
\[ \delta_{i,j} = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases} \] (13)

The usefulness of these reciprocal lattice vectors can be illustrated by considering the Fourier analysis of a function \( P(\mathbf{r}) \) which has the periodicity of the FCC direct lattice as in Equation 3 and thus the periodicity of Equation 5. \( P(\mathbf{r}) \) may be Fourier analyzed by Equations 6 and 7.
But by Equation 3, $e^{ik \cdot \hat{R}_n} = 1$ when $F_k \neq 0$ and thus by Equations 12, $k$ must be a reciprocal lattice vector. Thus in Equation 6 the sum can be taken over only reciprocal lattice vectors. Further because $P(r)$ satisfies Equation 3, we need integrate only over the unit cell at the origin when evaluating Equation 7. In summary

$$P(r) = \sum_{k_m} F_{k_m} e^{ik_m \cdot r}$$

where

$$F_{k_m} = \int_{\Omega_0} \frac{d^3 r}{\Omega_0} P(r) e^{-ik_m \cdot r}.$$ (15)

We shall now quote an important theorem known as Bloch's or Floquet's Theorem. Proofs of this theorem may be found in standard mathematics or physics texts (Whittaker and Watson 1962, Kittel 1964). The theorem states that when an electron moves in a periodic potential $v(r)$, the solutions $\psi(r)$ of the Schrödinger equation

$$(\frac{\hbar^2}{2m} + v(r)) \psi(r) = E \psi(r)$$ (16)

have the property

$$\psi(r + \hat{R}_n) = e^{ik \cdot \hat{R}_n} \psi(r)$$ (17)

where $k$ is a real vector and the vectors $\hat{R}_n$ are the translation vectors of the periodic potential. An equivalent conclusion is that $\psi(r)$ may be written as

$$\psi(r) = e^{ik \cdot r} u(r)$$ (18)
where \( u(r) \) has the periodicity of the potential. The \( k \) in Equation 1? are not unique, for, if we assume that the potential has the periodicity of the FCC lattice, \( k \) may be replaced by \( k + \frac{2\pi}{a} \) and Equation 1? is unaltered. The \( k \) can however be made unique by restricting \( k \) to the so-called first Brillouin zone (BZ), a unit cell in reciprocal space centered at the origin (Kittel 1963). This unit cell is constructed by the Wigner-Seitz technique. That is one constructs planes which perpendicularly bisect the reciprocal lattice vectors and the resulting polyhedron centered at the origin is taken to be the first Brillouin zone. Any value of \( k \) outside this cell can be obtained by a translation of one or more reciprocal lattice vectors. The Brillouin zone for the BCC reciprocal lattice of the FCC direct lattice is shown in Fig. 2. The wave functions and energies of an electron can then be labeled with the appropriate value of \( k \) and a band index \( \alpha \), e.g. \( \psi_{k,\alpha}(r) \) and \( E_{k,\alpha} \). The band index \( \alpha \) is included to allow for the possibility that several different states might occur for a given value \( k \). This is in general the case in solids, and the spectrum of energies \( E_{k,\alpha} \) with \( \alpha \) fixed and \( k \) allowed to vary over the Brillouin zone is referred to as the "\( \alpha \) th energy band."

B. The One Electron Formalism

In order to discuss the phenomenon of optical absorption we would like to calculate the differences in energies between the ground state and the excited states of the system of
Fig. 2. The first Brillouin zone for the NaCl lattice
electrons and nuclei which constitute the NaCl crystal. Such a calculation is extremely difficult if attempted from a strictly first principles viewpoint and has never been solved. The major difficulty is that one must consider some $10^{23}$ electrons and nuclei interacting via the long range Coulomb interaction. Each of these particles responds to the detailed positions and motions of all of the other particles of the system. The solution of the appropriate Schrödinger equation will then be an intricate function of the co-ordinates of all of the particles which would be quite intractable in practice. An approximate solution to this "many body" problem can however be obtained by neglecting the detailed response of any given particle to the others. The nuclei of the system are assumed to be fixed at their equilibrium positions, $\rho$, $n$, $\nu$, where the $\rho$, $n$, $\nu$ are the ion site vectors defined in Section A. A given electron is then assumed to be in a one-electron state $\psi(r)$ associated with a potential arising from the fixed nuclei and the average motion of all other electrons. We note that $\psi(r)$ depends only on the co-ordinates of a single electron (hence the name "one-electron") as a result of averaging the motion of all other particles. The wave function of the entire system is taken to be a properly antisymmetrized function of the one electron functions $\psi$. This approximation, the Hartree-Fock approximation with the nuclei fixed, is used in most of the techniques current employed in the calculation
of the electronic states of solids and shall be used in the present calculation.

The many body Hamiltonian, $H$, of our system with the nuclei fixed is

$$H = \sum_i P_i^2 + \frac{1}{2} \sum_{i,j} \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,m} \frac{2Z_v}{|\mathbf{r}_i - \mathbf{r}_m, \nu|}$$

$$+ \sum_{m,m'} \frac{2Z_v Z_{\nu}'}{|\mathbf{r}_m, \nu - \mathbf{r}_m', \nu'|}$$

where the sums over $i$ and $j$ are over the $N$ electrons of the system, the sums over $m$ and $\nu$ are over all nuclei of charge $Z_{\nu}$, $\nu=1,2$ of the system, and the prime on $\sum$ for example means that terms with $i \neq j$ are excluded.

In this equation, as throughout this work, atomic units are used. That is, distance is measured in units of the first Bohr radius $a_0 = 0.529\AA$, angular momentum in units of $\hbar$, mass in units of the electron rest mass, and energy in units of Rydbergs (13.6eV). Further, potential energies shall be referred to as simply potentials throughout.

The first term in Equation 19 is the kinetic energy of the electrons; the second, the potential of the electron-electron interaction; the third, the electron-nucleus interaction; and the last, the nucleus-nucleus interaction. The nucleus-nucleus term is simply a constant which we shall take to be zero, or more precisely, relative to which we shall measure energies.
The stationary many body Schrödinger equation for the above system is
\[ H\psi(x_1, \ldots, x_N) = E\psi(x_1, \ldots, x_N) \]  
(20)
where \( x_i \) represents the spatial co-ordinates \( x_i \) of the \( i \text{th} \) electron and the spin co-ordinate \( \sigma_i \) of the \( i \text{th} \) electron. In the original Hartree one electron approach (Hartree 1928) it was assumed that the many body wave function \( \psi(x_1, \ldots, x_N) \) could be written as a simple product of the one electron functions \( \psi_i \).
\[ \psi_H(x_1, \ldots, x_N) = \psi_1(x_1) \ldots \psi_N(x_N). \]  
(21)
This approximation however violates the Pauli exclusion principle which requires that the state of a system of fermions must be antisymmetric under exchange of all pairs of electron co-ordinates. Slater (1929) showed that the unique antisymmetric many body wave function which can be constructed from \( N \) one electron functions \( \psi_i \) is the determinantal function
\[ \psi_{HF}(x_1, \ldots, x_N) = \begin{vmatrix} \psi_1(x_1) & \cdots & \psi_1(x_N) \\ \vdots & \ddots & \vdots \\ \psi_N(x_1) & \cdots & \psi_N(x_N) \end{vmatrix}. \]  
(22)
The one electron wave functions \( \psi_i \) in Equation 22 are not specified and may in principle take any functional form. Regardless of the choice of the one electron functions, the many body wavefunction \( \psi_{HF} \) will always be an approximation to the true wavefunction \( \psi \). Consequently, by the variational
principle (Seitz 1940, p. 200), the expectation value of the many body Hamiltonian of Equation 19 will always be greater than the energy eigenvalue, $E$, in Equation 20. That is

$$E < \epsilon = \frac{\langle \psi_{HF} | H | \psi_{HF} \rangle}{\langle \psi_{HF} | \psi_{HF} \rangle}.$$  \hspace{1cm} (23)

Slater (1930) and Fock (1930) independently proposed that the best choice of the one-electron functions would be those which minimize $\epsilon$ in Equation 22 in accordance with the variational principle. The results of this calculation (Seitz, 1940) are that the one electron functions which minimize $\epsilon$, subject to the $N^2$ orthonormalization constraints

$$\int d\tau_1 \delta^*_{i} (x_1) \delta_{j} (x_1) = \delta_{i,j} , \hspace{1cm} (24)$$

are those which satisfy

$$[- V_1 - \sum_{m,v} \frac{2Z_m}{|x_1 - x_m,v|} + \sum_{j} \int d\tau_2 \frac{2|\hat{\psi}_{j} (x_2)|^2}{|x_1 - x_2|}] \ \hat{\psi}_{i} (x_1)$$

$$- \sum_{j} \int d\tau_2 \frac{2\delta^*_{j} (x_2) \hat{\psi}_{i} (x_2)}{|x_1 - x_2|} \ \hat{\psi}_{i} (x_1) = \sum_{j} \lambda_{ij} \delta_{j} (x_1) . \hspace{1cm} (25)$$

The integration over $d\tau_1$ implies both an integration over spatial co-ordinates and a sum over spin co-ordinates. The $N^2$ quantities $\lambda_{ij}$ are the variational parameters or Lagrange multipliers associated with the orthonormalization constraints of Equation 24.
Now let us consider a unitary transformation, $U$, from the basis of the $\hat{\psi}$'s in Equation 22 to a new set $\hat{\psi}'$ with corresponding Slater determinant $\psi'_{HF}$ (Messiah 1962, p. 776). As $\psi'_{HF}$ is of determinental form,

$$\psi'_{HF} = (\det U) \psi_{HF} = \psi'_{HF}$$ (26)

since $U$ is unitary. That is, the Slater determinant is invariant with respect to unitary transformations. The quantities $\lambda_{ij}$ can be thought of as the elements of a certain $N \times N$ hermitian matrix $\Lambda$. Under the unitary transformation $U$, we shall obtain a new matrix $\Lambda'$,

$$(\Lambda')_{ij} = (U^* \Lambda U)_{ij}$$ (27)

We can always pick $U$ such that $\Lambda'$ is diagonal.

Thus, choosing the basis, $\varphi_i$, such that the quantities $\lambda_{ij}$ satisfy

$$\lambda_{ij} = E_i \delta_{ij}$$ (28)

Equation 25 can be written

$$\left[ -\nabla^2 - \sum_{m,v} \frac{2z_v}{|x_1-x_m,v|} + \sum_j \int d\tau_2 \frac{2|\tilde{\psi}_j(x_2)|^2}{|x_1-x_2|} \right] \tilde{\psi}_i(x_1)$$

$$- \sum_j \int d\tau_2 \frac{2\tilde{\psi}_j(x_2)\tilde{\psi}_i(x_2)}{|x_1-x_2|} \tilde{\psi}_j(x_1) = E_i \tilde{\psi}_i(x_1).$$ (29)

Defining the operators

$$T = -\nabla^2$$ (30a)

$$V = - \sum_{m,v} \frac{2z_v}{|x_1-x_m,v|}$$ (30b)
and \( A \) by the relation

\[
A_{j}(\mathbf{r}_{1}) = - \sum_{j} \int d\tau_{2} \frac{2 \phi^{*}_{j}(\mathbf{r}_{2}) \phi_{j}(\mathbf{r}_{2})}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} \phi_{j}(\mathbf{r}_{1})
\]

Equation 29 may be rewritten

\[
H^{F} \phi_{1}(\mathbf{r}_{1}) \equiv (T + V + U + A) \phi_{1}(\mathbf{r}_{1}) = E_{1} \phi_{1}(\mathbf{r}_{1}).
\]

\( H^{F} \) is linear and hermitian. Thus the \( \phi_{j} \) are orthonormal eigenfunctions of the operator \( H^{F} \) with eigenvalues \( E_{1} \). This is consistent with our choice of \( \lambda_{1j} \) in Equation 28.

The Equations 29 or 31 are usually called the Hartree-Fock equations and describe the properties of an electron in the state \( \phi_{1} \). The first term, \( T \), of the Hartree Fock Hamiltonian, \( H^{F} \), represents the kinetic energy of the electron and the second term, \( V \), the electron-nuclei interaction energy. The third term, \( U \), can be regarded as the energy resulting from the Coulomb interaction of the electron in the state \( \phi_{1} \) with all the electrons of the system distributed in the classical charge distribution \( \rho_{e}(\mathbf{r}) \)

\[
\rho_{e}(\mathbf{r}) = \sum_{j} |\phi_{j}(\mathbf{r})|^{2}.
\]

If only these first terms were present the electron in the state \( \phi_{1} \) would interact with itself through the energy \( V_{SI} \).
appearing in the coulomb interaction $U$. An identical term, but with opposite sign, appears in the forth or exchange term of the Hartree-Fock equations and removes this self interaction.

The exchange term, in addition, represents the energy of correlation of two electrons of like spin. This correlation appears in the Hartree Fock theory as a consequence of the inclusion of the Pauli principle antisymmetrization condition. It is apparent from the orthogonality of the $\phi$'s that only those electrons in a spin state identical to the electron under consideration will contribute to the exchange term.

The exchange term can be given a more physical interpretation by introducing the concepts of the exchange charge density and the exchange potential. Let us write $\phi_e(x_m)$ as

$$\phi_e(x_m) = \psi_e(x_m) x_e(\sigma_m)$$

where $\psi_e$ is a spatial wave function and $x_e$ is a spin function. We shall use the notation $\Sigma$ to mean a summation over the electron $j$ whose spin is identical to $i$. The exchange term is then

$$\sum \int d\tau_2 \frac{2\phi_e^*(x_2)\phi_1(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$= \int d^3r_2 \sum_j \frac{\psi_1^*(x_2)\psi_1(x_2)\psi_1^*(x_1)\psi_1(x_1)}{|\psi_1^*(x)|^2} \frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_1(x_1)$$
\[ V_x^i(\mathbf{r}_1) = \sum_j \frac{\psi_j^*(\mathbf{r}_2)\psi_j^*(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\psi_j(\mathbf{r}_1)}{|\psi_j(\mathbf{r}_1)|^2}. \] (36)

Now at the point \( \mathbf{r}_2 = \mathbf{r}_1 \)

\[ \rho_x^i(\mathbf{r}_2, \mathbf{r}_1) = \frac{\rho_e(\mathbf{r}_1)}{2} \] (37)

where we assume that the total electronic charge density \( \rho_e(\mathbf{r}_1) \) given by Equation 32 consists of equal populations of spin up and down electrons. The exchange charge density thus has the effect, when calculating the total HF potential, of removing electrons of like spin from the vicinity of the electron under consideration. Although the total charge associated with this exchange distribution is that of one electron

\[ \int d^3r_2 \rho_x^i(\mathbf{r}_2, \mathbf{r}_1) = 1, \] (38)

the exchange density is localized about the point \( \mathbf{r}_2 = \mathbf{r}_1 \) (Slater 1951) and the associated exchange potential should
contribute significantly to the total potential which an electron senses.

In practice, the Hartree Fock exchange potential is extremely difficult to use as it depends on the state under consideration. Slater (1951) observed that, as the exchange charge density has the same volume integral (Equation 38) and the same value at $z_2 = z_1$ (Equation 37) for each of the states $\psi$, the exchange charge density and resultant potential should not differ greatly from state to state and should depend primarily on the total charge density, $\rho_e(r)$, at any point $r$. In the case of a uniform gas of electrons, the one electron wave functions are plane waves $\psi = \frac{1}{\sqrt{V}} e^{iK \cdot R}$ and the exchange potential is (Seitz 1940)

$$V_x(k) = -8 \left(\frac{\rho_o}{3\pi^2}\right) F(k)$$

(39)

where

$$F(k) = \frac{1}{2} + \frac{k_F^2 - k^2}{4kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right|$$

and $k_F$ is the wave vector of the electrons at the top of the filled fermi sphere. The free electron exchange potential is independent of $r$ of course since the gas is uniform with density $\rho_o = N/V$ but is proportional to $\rho_o^{1/3}$. The dependence on the state of the electron, the $k$ dependence, is not strong since the function $F(k)$ varies smoothly from $F(k) = 1$ at $k = 0$ to $F(k) = \frac{1}{2}$ for $k = k_F$. Averaging $F(k)$ over the occupied free electron states, one finds that the exchange potential of an
average free electron is
\[ \overline{V_x} = -6\left(\frac{3\rho_e}{8\pi}\right)^\frac{1}{3}. \]  

(40)

Slater proposed further that the Hartree-Fock exchange potential for a general system of electrons with total charge density \( \rho_e(r) \) at the point \( r \) could be approximated by the average free electron exchange, Equation 40, with \( \rho \) replaced by \( \rho_e(r) \). That is
\[ V_x^i(r) = -6\left(\frac{3\rho_e(r)}{8\pi}\right)^\frac{1}{3}. \]  

(41)

This is the Slater exchange or "\( \rho^{1/3} \)" approximation to the actual exchange potential. The accuracy of this approximation has not been established in solids, but in free atoms the results obtained with the Slater exchange approximation compare favorably with those using the actual Hartree-Fock exchange (Liberman et al. 1965).

Kohn and Sham (1965) have recently shown that if one replaces the term corresponding to exchange in Equation 23 by the free electron result and then performs the variational calculation, the exchange term in the one electron equation analogous to Equation 29 is 2/3 of the Slater exchange approximation. The key assumption in the Kohn-Sham approach is that the electronic charge density of the system is slowly varying over distances of the order of an atomic radius, i.e. \( \gamma \rho \ll \rho \), which is certainly not the ease in the region of atomic sites. In both the Slater and Kohn-Sham approximations one assumes
essentially that the exchange is free electron like and independent of the state under consideration and there is no a priori reason for choosing one over the other. A series of papers (Tong and Sham 1966, Cowan et al. 1966) investigating the relative merits of these two approximations in atomic systems have been published recently. The results indicate that both yield a reasonable approximation to the actual Hartree-Fock exchange. The full Slater exchange yields eigenvalues which approximate the Hartree-Fock eigenvalues somewhat better than those obtained with the Kohn-Sham exchange, whereas the wave functions obtained with the Kohn-Sham exchange approximate the Hartree-Fock wave functions better than those obtained with the full Slater exchange. As there seems to be neither fundamental reasons nor empirical evidence that one is preferable to the other, we shall use the full Slater exchange approximation.

We shall assume further that the total Hartree-Fock potential modified by the use of the Slater exchange approximation is periodic with the periodicity of the ground state lattice for all configurations of interest. We can then write our one electron wave functions as

\[ \psi_i(x_1) = \psi_{k,\alpha}(\mathbf{r}_i) x(\sigma_i) \]  

(42)

where \( \psi_{k,\alpha}(\mathbf{r}) \) is a Bloch function and \( x \) is a spin function. The \( \psi_{k,\alpha} \) are determined by the Hartree-Fock-Slater equations
\[
\begin{align*}
\frac{1}{8\pi} \left\{ \frac{1}{3} \left( \sum_{\kappa',\alpha' \in \text{occ}} \left| \psi_{\kappa',\alpha'}(\mathbf{r}) \right|^2 \right)^{1/3} \right. \\
\left. - 6 \sum_{\kappa' \in \text{occ}} \frac{\left| \psi_{\kappa',\alpha}(\mathbf{r}) \right|^2}{2 |\mathbf{r} - \mathbf{r}'|^2} \int d^3 \mathbf{r}' \right\} \psi_{\kappa,\alpha}(\mathbf{r}) = E_{\kappa,\alpha} \psi_{\kappa,\alpha}(\mathbf{r}).
\end{align*}
\]

Explicit reference to spin has been dropped and it is assumed in the summations over \( \kappa' \) and \( \alpha' \) that two electrons, one of spin up and the other spin down, may occupy each state \( \psi_{\kappa,\alpha}(\mathbf{r}) \).

Since the one electron states are Bloch functions, \( \psi_{\kappa,\alpha}(\mathbf{r}) \), we may, by Koopman's Theorem (Kittel 1963), identify the eigenvalues \( E_{\kappa,\alpha} \) with the negative of the energy required to remove an electron initially in the state \( \psi_{\kappa,\alpha}(\mathbf{r}) \) from the solid (within the one electron Hartree Fock approximation).

The energy required to excite an electron from the state \( \psi_{\kappa,\alpha}(\mathbf{r}) \) to the state \( \psi_{\kappa',\alpha'}(\mathbf{r}) \), which in the Hartree-Fock approximation is the quantity desired for the discussion of optical absorption, is \( E_{\kappa',\alpha'} - E_{\kappa,\alpha} \).

We have now discussed all the basically physical assumptions which are normally made in a band calculation. Virtually all band calculations performed to the present time start with Equation 43. There are, however, various methods of solution, one of which will be discussed in Section C. Further approximations are made in obtaining solutions, but these are of a more numerical than physical nature and hopefully do not affect
the results of the calculation.

It should be emphasized that, when we employ the static Hartree-Fock one electron approximation even without the requirement that the one electron functions be Bloch functions, we treat a given electron as one of a sea of electrons distributed according $|\psi|^2$ in which are imbedded the nuclei. With the exception of the exchange spin correlation, this sea of electrons and nuclei does not respond to the detailed motion of the electron under consideration but only to its average distribution. Similarly the electron does not respond to the detailed motion of the sea. We have thus eliminated all polarization related to the detailed response of the system to any given electron. A static contribution to polarization can occur in this approximation but only when we destroy the symmetry of the crystal in some manner, for example by impressing an external field on the system or by introducing a fixed charge into the system. We in fact eliminate even this static polarization effect when, in addition to the Hartree-Fock approximation, we require, as we have done, that the potential of any electron has the periodicity of the perfect ground state lattice or, equivalently that the one electron states be Bloch functions. Let us for example introduce an extra electron into our system. It is not inconceivable that this electron could polarize its surroundings to such an extent that it becomes self trapped or localized in some region of the crystal.
(Mott and Gurney 1964). However, with the approximations that we have made this cannot occur. In fact this extra election will not polarize the original lattice at all, since we require that the extra electron be in a Bloch state, an extended function in the sense that the probability of its presence at two points differing by one or more lattice translation vectors be the same. Thus in the first place the extra electron cannot become localized. In addition, in order for polarization to occur, the states of the other electrons of the system must be perturbed upon introduction of the extra electron. The Hartree-Fock potential determining these states is however unchanged by any detectable degree ($\frac{1}{N}$) by the introduction of this extra, extended electronic state into the sea of the other $10^{23}$ electrons. Consequently the one electron states are effectively unchanged by the introduction of the extra electron. These remarks are also true when an electron is removed from the system or when a single electron changes state. The insensitivity of the one electron states to the change in state of a single electron is the key assumption made in Koopmann's theorem used earlier. Observe that we have thus eliminated all exciton effects in the above approximations and that we treat the excited or conduction electron as having the same interaction with the rest of the lattice as an electron in the normally filled valence bands.

The elimination of polarization effects (and the exciton effect) is a serious deficiency of this type of calculation.
Fowler (1966) has estimated that the type of calculation which we shall perform here for NaCl should yield an optical band gap which is about 4eV larger than the observed value. We would of course like to include these polarization effects in the calculation, but to do so and remain in the general framework of a first principles calculation would produce a problem of immense difficulty.

A problem of a more practical nature is the self consistent solution of Equations 43. That is, the wave functions used to determine the Hartree Fock Slater potential must be solutions of the HFS equations. One generally attempts the solution of these equations by an iterative approach. That is, the charge density is initially assumed to be well approximated by that of a collection of free ions. The Hartree-Fock-Slater potential of this distribution is then calculated, and the eigenfunctions of Equation 43 with this potential are used to construct the charge density and potential necessary for the next iteration. This process is continued until the wave functions and potential of one iteration differ from those of the preceding iteration by less than some predetermined tolerance. Thus in the following sections we shall assume that the potential is known at any step of the iteration and seek solutions of Equation 43 using this potential.
C. Augmented Plane Wave Method

We now seek solutions of the one electron Hartree Fock Slater equation (Equation 43). Since the one electron wave functions are Bloch functions we may write

$$\psi_k(r) = e^{ik \cdot r} u_k(r)$$  \hspace{1cm} (44)

where $u_k(r)$ is a function having the periodicity of the potential. We shall temporarily drop explicit reference to the band index $a$. As $u_k(r)$ is periodic, with the periodicity of the lattice, we can expand $\psi_k(r)$ in a Fourier series of reciprocal lattice vectors

$$\psi_k(r) = e^{ik \cdot r} \sum_{i} C_k(k_i)e^{i k_i \cdot r}$$  \hspace{1cm} (45)

$$= \sum_{i} C_k(k_i)e^{i k_i \cdot r}$$

where we define the vectors $k_i$ by

$$k_i = k + K_i.$$  \hspace{1cm} (46)

The $C_i$ could then be determined by substituting this expansion for $\psi_k(r)$ into the Schrödinger equation thus obtaining a formally exact solution to the problem. However the function $u_k(r)$ oscillates rapidly in the core region, or region near a nucleus, and, consequently, the expansion of Equation 45 converges very slowly to $\psi_k(r)$ in this region. In a numerical calculation, the large number of terms which must be included in the above expansion for an accurate reproduction of $\psi_k(r)$
makes this technique impractical. On the other hand $u(r)$ is slowly varying and the plane wave expansion does converge rapidly outside the core region. Most of the methods currently used in the calculations of band structures (Callaway 1964) make use of this fact and attempt to find solutions of the Schrödinger equation by expanding $\psi_k(r)$ in the finite expansion

$$
\psi_k(r) = \sum_{i=1}^{M} C_{k_i} X_{k_i}(r)
$$

where $X_{k_i}(r)$ are plane waves outside the core region and are functions which reproduce or approximate the oscillations of $\psi_k(r)$ inside the core region. The $C_{k_i}$ are treated as variational parameters. Different methods differ primarily in the manner in which the functions $X_{k_i}(r)$ are chosen in the core region.

One such technique which has recently become popular is the augmented plane wave (APW) method originally proposed by Slater (1937). In this approach the crystal potential is replaced by a "muffin-tin" potential as shown schematically in Fig. 3. This muffin-tin potential is a constant, $V_o$, outside spheres centered at the nuclear sites of the lattice and is spherically symmetric inside these spheres. We shall call the region inside (outside) the spheres region I (II). The constant $V_o$ is generally taken to be the volume average of the crystal potential over region II; and the spherically symmetric potential, the spherical average of the crystal potential in
Fig. 3. Schematic of the muffin-tin potential approximation. Part a represents the crystalline potential contours near two lattice sites. Part c represents the muffin tin potential contours. Part b shows the crystalline potentials (dashed line) and muffin-tin potentials (solid line) along the line AA' in Parts a and c, respectively.
region I. A key assumption in this approach is of course that the muffin tin potential approximates the crystalline potential adequately. Exact solutions to the Schrödinger equation can now be found in both regions I and II which, when suitably matched at the sphere boundaries, can be used as variational functions in an expansion of the form in Equation 47. This method has the advantage that quite accurate solutions of the Schrödinger equation with the muffin tin potential can be found, but has the disadvantage of requiring a relatively large amount of computer time.

In a recent monograph by Loucks (1967) on the APW method, there appears a summary of the literature, a discussion of the relation of the APW method to other methods, derivations of most of the essential formulas and a detailed discussion of the numerical techniques used in this method. The purpose of this section is not to present a complete exposition of the APW method, but to present those results and formulas which are essential for understanding the philosophy and procedure of the method. The reader is therefore referred to this monograph for the details omitted here.

Let us now assume that we have a Bravais lattice of points located by the vectors \( \mathbf{R}_n \) with a basis of two ions whose nuclei are located by the vectors \( \mathbf{I}_v, v = 1,2 \), relative to \( \mathbf{R}_n \) as discussed in Section A. Let us further imagine that a sphere of radius \( R_v \) is centered at each of the points
The only restriction on the $R_v$ at this point in the discussion is that they be of such a magnitude that different spheres do not overlap. Since the potential and charge density are invariant under translations by $\mathbf{L}_n$, we shall restrict our attention in the following to the unit cell for which $\mathbf{L}_n = 0$.

Now as shown schematically for a two dimensional lattice in Fig. 4, points inside the sphere of type $\nu$ can be represented by the vector $\mathbf{r}_\nu$ where

$$\mathbf{r}_\nu = \mathbf{r} - \mathbf{r}_\nu$$

and $\mathbf{r}_\nu \leq R_\nu$.

We shall adopt the convention throughout that when inside the $\nu$th sphere, points are represented by $\mathbf{r}_\nu$ rather than $\mathbf{r}$.

The muffin tin potential inside sphere $\nu$, $V_\nu(r_\nu)$, is

$$V_\nu(r_\nu) = \int \frac{d\Omega_\nu}{4\pi} \ V_{\text{cr}}(\mathbf{r}_\nu)$$

where $V_{\text{cr}}(\mathbf{r})$ is the crystal potential in the Hartree Fock Slater approximation appearing in Equation 43, and the integral is over the solid angle associated with $\mathbf{r}_\nu$.

The muffin tin potential outside the spheres, $V_o$, is

$$V_o = \int d^3r \frac{V_{\text{cr}}(\mathbf{r})}{\Omega_o - \frac{4\pi}{3} R_1^3 - \frac{4\pi}{3} R_2^3}$$

where $\Omega_o$ is the volume of the unit cell and the integration is over the unit cell excluding the spheres. In order to simplify expressions in this section, we shall measure energies relative
Fig. 4. Illustration of co-ordinate convention used in the calculation
to \( V_0 \), so that in the following we may write \( V_0 = 0 \), realizing that \( V(\mathbf{r}) \) and \( E_k \) are actually \( V(\mathbf{r}) - V_0 \) and \( E_k - V_0 \) respectively.

We now seek solutions of the form given in Equation 47 of the Schrödinger equation

\[
[- \nabla^2 + V(\mathbf{r})] \psi_k(\mathbf{r}) = E_k \psi_k(\mathbf{r})
\]  

(51)

where \( V(\mathbf{r}) \) is the muffin tin potential defined by Equation 49 and 50. In region II, the solutions of Equation 51 are plane waves. Thus we pick

\[
X_{k_1}^1(\mathbf{r}) = e^{i \mathbf{k}_1 \cdot \mathbf{r}}
\]  

(52)
in region II. In region I, the muffin tin potential is spherically symmetric about \( \mathbf{r}_\nu = 0 \) so that inside sphere \( \nu \) the solutions of Equation 51 may be expanded in spherical harmonics and we write

\[
X_{k_1}^\nu(\mathbf{r}) = \sum_{\ell, m} A_{\ell, m}^{\nu, k_1, E'} R_{\ell, m}^\nu(\mathbf{r}_\nu, E') Y_{\ell, m}(\Omega_\nu)
\]  

(53)

where the \( Y_{\ell, m} \) are spherical harmonics, the \( A_{\ell, m} \) are constants to be determined and the radial functions \( R_{\ell, m}^\nu(\mathbf{r}_\nu, E') \) satisfy

\[
-\frac{1}{r_\nu^2} \frac{d}{dr_\nu} \left[ r_\nu^2 \frac{dR_{\ell, m}^\nu(\mathbf{r}_\nu, E')}{dr_\nu} \right] + \frac{\ell(\ell+1)}{r_\nu^2} + V_\nu(\mathbf{r}_\nu) R_{\ell, m}^\nu(\mathbf{r}_\nu, E') = E' R_{\ell, m}^\nu(\mathbf{r}_\nu, E').
\]  

(54)

The energy \( E' \) is a parameter which as of yet is undetermined. We impose the boundary condition that \( R_{\ell, m}^\nu(\mathbf{r}_\nu, E') \) be regular at \( r_\nu = 0 \).
By requiring that the solution inside the spheres, 

\[ X_{K_1}^v(r_v), \text{ (Equation 53) } \]

be continuous with the plane wave 

\[ X_{K_1}(r) \text{ of Equation 52 at the sphere boundaries, the constants } \]

\[ A_{\xi m} \] 

are found to be 

\[
A_{\xi m}(v, k_1, E') = 4\pi e^{ik_1 \cdot r_v} \frac{1}{\xi m(k_1)} \frac{j_\xi(k_1 r_v)}{R_\xi^v(r_v, E')} \tag{55}
\]

where \( j_\xi(x) \) is a spherical Bessel function of order \( \xi \). Thus our APW function \( X_{K_1}^v(r) \) is

\[
X_{K_1}^v(r) = \begin{cases} 
\frac{1}{\sqrt{V}} e^{ik_1 \cdot r} & \text{outside the spheres} \\
\frac{4\pi}{\sqrt{V}} \sum_{m} j_\xi(k_1 r_v)^* Y_{\xi m}(k_1) Y_{\xi m}(r_v) \frac{R_{\xi}(r_v, E')}{R_{\xi}^v(r_v, E')} & \text{inside sphere } v. 
\end{cases} \tag{56}
\]

where \( \frac{1}{\sqrt{V}}, V = N_0 \), the volume of the crystal is included for later convenience. The expansion constants \( C_{K_1} \) in Equation 46 are determined by a variational calculation. The variational principle, in its usual form, states that if we seek the ground state eigenvalues of the equation 

\[ H\psi(r) = \epsilon \psi(r) \tag{57} \]

then

\[
\epsilon \leq E = \frac{\int \phi^*(\varkappa_{\lambda_1} \cdots \lambda_m) H\phi(\varkappa_{\lambda_1} \cdots \lambda_m) \, d^3r}{\int \phi^*(\varkappa_{\lambda_1} \cdots \lambda_m) \bar{\phi}(\varkappa_{\lambda_1} \cdots \lambda_m) \, d^3r} \tag{58}
\]

where \( \phi \) is any function of the variational parameters \( \lambda_i \) and \( \varkappa \) subject to the restrictions that \( \bar{\phi} \) and \( \bar{\phi} \) are continuous
functions of $r$. In other words the value of $E$ determined by

$$E d^3 r \psi \psi^* = \int \psi \hat{H} \psi d^3 r$$

(59)

which best approximates $\phi$ is that for which

$$\frac{\partial E}{\partial \lambda_i} = 0 \quad i = 1, \ldots, M$$

(60)

In our case the function $\psi$ is the expansion of Equation 47. The $C_{K_i}$ are the variational parameters $\lambda_i$. The $X_{K_i}(r)$ of Equation 56, however, are continuous only in magnitude and not in slope at the sphere boundaries. Thus the function $\psi$ will be discontinuous in slope at the sphere boundaries and the variational expression of Equation 59 is invalid. Schlosser and Marcus (1963) have shown that the expression to be used in place of Equation 59 for functions, $\psi$, whose derivatives are discontinuous across a spherical surface $S$ between regions I and II is

$$E \int_{I+II} d^3 r \psi \psi^* = \int_{I+II} \hat{H} \psi \psi d^3 r - \frac{1}{2} \int_S (\psi_{I+II}^+ \psi_{I+II}^-) (\frac{\partial}{\partial \rho} \psi_{I+II}^- - \frac{\partial}{\partial \rho} \psi_{I+II}^+) dS$$

(61)

Volume integrations are over the unit cell, the derivative $\frac{\partial}{\partial \rho}$ is in the direction of the outward normal from region I to region II, and $\psi_{I}$ and $\psi_{I+II}$ are the wave functions in regions I and II respectively. Substituting the expansion 47 for $\psi$ into Equation 61 one obtains

$$\sum_{i,j}^{M} (H_{ij} + S_{ij} - \Delta_{ij}) C_i^* C_j = 0$$

(62)

where
\[ H_{ij} = \int_{\Omega_{I+II}} X^I_{k_1}(r) H X^I_{k_j}(r) \, d^3r \]

\[ \Delta_{ij} = \int_{\Omega_{I+II}} X^I_{k_1}(r) \Delta X^I_{k_j}(r) \, d^3r \] (63)

\[ S_{ij} = -\frac{1}{2} \int_S (X^{II}_{k_1}(r) + X^I_{k_1}(r)) \left( \frac{\partial}{\partial \rho} X^{II}_{k_j}(r) - \frac{\partial}{\partial \rho} X^I_{k_j}(r) \right) \, dS \]

\[ X^I_{k_1}(r)(X^{II}_{k_1}(r)) \] is the expression for \[ X^I_{k_1}(r) \] given by Equation 56 appropriate to region I(II). When the variational conditions

\[ \frac{\partial E}{\partial C_{k_1}} = 0 \quad i = 1, \ldots, M \] (64)

are applied to Equation 62, the set of M homogeneous equations

\[ \sum_{j} (H_{ij} + S_{ij} - E \Delta_{ij}) C_{k_j} = 0 \] (65)

is obtained. This set of equations will have non trivial solutions for the \[ C_{k_1} \] only when \( E \) is such that the secular determinant is zero,

\[ \det \begin{vmatrix} H_{ij} + S_{ij} - E \Delta_{ij} \end{vmatrix} = 0. \] (66)

When Equation 66 is satisfied, Equation 65 may be solved for M-1 of the \[ C_{k_1} \] 's in terms of the \( M^{th} \) whose value can be fixed by a normalization condition on \[ v_{k_1}(r) \].

The parameter \( E' \) which appears implicitly in Equation 66 through \( R_y^\gamma(r, E') \), defined by Equation 54, may in principle take on any fixed value and the value of \( E \) determined from Equation 66 will be a variational minimum for a given value of
E'. However, as emphasized by Schlosser and Marcus (1963), the value of the variational E which best approximates \(\epsilon\), the actual eigenvalue, is obtained when \(E' = E\). In order to see why this is so, let us assume that \(\epsilon\), the actual eigenvalue for the muffin tin potential under consideration, is known. If \(E'\) were chosen to be equal to \(\epsilon\), the wave functions using the \(R^y(r,\epsilon)\) determined from Equation 54 would be, inside the spheres, actual eigenfunctions of the Schrödinger equation with the muffin tin potential. The variational functions would then be very good approximations to the actual wave function and, in the limit of a large basis of plane waves, \(M \rightarrow \infty\), the variation energy, \(E\), should approach \(\epsilon\). For any other choice of \(E'\), the variational wave function would not approximate the actual wave function as well and the variational \(E\) would not be as good an approximation to \(\epsilon\). In practice, one could, as Schlosser and Marcus have done, perform an iterative calculation. That is, first estimate \(E'\) and determine a variational \(E, E_1\) say, from Equation 66. Since \(E_1\) is presumably a better approximation to \(\epsilon\), one could obtain better variational functions by choosing \(E' = E_1\) and then repeat the cycle obtaining a new and better \(E\). In the limit of many cycles and an infinite basis, we would obtain \(E' \rightarrow E \rightarrow \epsilon\). Rather than perform this tedious iterative cycle, we shall simply take \(E' = E\) in the matrix elements as did Slater in his original paper (Slater 1937). The final results are unaffected by this choice.
With \( E' = E \), then, the matrix elements \( H_{ij} + S_{ij} - EA_{ij} \) can be written in the form

\[
H_{ij} + S_{ij} - EA_{ij} = \Omega_0 (k_i^2 - E) S_{ij} - 4\pi \Sigma R_\nu^2 e^{ik_{ij} \cdot \nu \cdot \gamma} \zeta_{ij}^\nu
\]

where

\[
\zeta_{ij}^\nu = \left( k_i \cdot k_j - E \right) \frac{j_\nu(k_i R_\nu)}{k_{ij}}
\]

\[
- \Sigma(2\lambda + 1) \Sigma \frac{k_i \cdot k_j}{k_i k_j} j_\nu(k_i R_\nu) j_\nu(k_j R_\nu)
\]

\[
x \left[ \frac{d}{dr} \ln R_\nu(r, E) \right]_{r = R_\nu}
\]

and \( k_{ij} = k_j - k_i \).

Note that, with our choice of \( \lambda_1 = 0 \) and \( \lambda_2 = a^\dagger \), the matrix elements \( H_{ij} + S_{ij} - EA_{ij} \) are real since the only complex quantity appearing in Equation 67, \( e^{ik_{ij} \cdot \nu \cdot \gamma} \), is real for this particular choice of \( \nu \). Thus the expansion coefficients \( C_{k_i} \) are real.

The formal solution has now been obtained. We need only normalize the wave function \( \psi_k(r) \) and determined the crystalline charge density

\[
\rho(r) = 2 \Sigma \Sigma \psi_k^*(r) \psi_{k', \alpha}(r),
\]

the factor of two arising from spin degeneracy. In Equation 68 and subsequent related expressions the summation is understood to be only over occupied states.
For normalization we require that only one electron of a given spin occupy \( \psi_{\mathbf{k}} \), that is

\[
l = N \int \frac{d^3r}{\Omega_0} \psi_{\mathbf{k},\alpha}^*(\mathbf{r}) \psi_{\mathbf{k},\alpha}(\mathbf{r})
\]

\[
= \sum_{i,j} C_i C_j \frac{4\pi}{\Omega_0} R_v e^{\frac{i\mathbf{k}_i \cdot \mathbf{r}_j}{\mathbf{k}_i}} \frac{\mathbf{j}_i (\mathbf{k}_i, R_v)}{\mathbf{k}_i}
\]

\[
- \sum_{i,j} C_i C_j \frac{4\pi R_v^2}{\Omega_0} e^{\frac{i\mathbf{k}_i \cdot \mathbf{r}_j}{\mathbf{k}_i}} \sum_\mathbf{\tau} \mathbf{j}_i (\mathbf{k}_i, R_v) \mathbf{j}_j (\mathbf{k}_j, R_v)
\]

\[
x \mathbf{P}_\mathbf{\Lambda} (\mathbf{k}_i, \mathbf{k}_j) \times \frac{\partial}{\partial E_\alpha} \left[ \frac{d}{dR_v} \ln R_v (\mathbf{r}_v, E_\alpha) \right]_{R_v=R_v}
\]

(69)

as shown in Appendix A. As discussed earlier this equation and the Equations 65 determine all the \( \mathbf{G} \)'s in our expansion 47.

Although the evaluation is straightforward in principle, the computation time necessary for an accurate evaluation of the crystalline charge density \( \rho(\mathbf{r}) \) given by Equation 68 is prohibitive in practice. A muffin tin charge density defined in much the same manner as the muffin tin potential can however be found with relative ease. We take the charge density outside the APW spheres to be a constant, \( \rho_0 \), given by the volume average of the charge density given by Equation 68 over this region. Thus

\[
\rho_0 = \frac{1}{(\Omega_0 - \frac{4\pi}{3} R_1^3 - \frac{4\pi}{3} R_2^3)} \int d^3r \frac{1}{k,\alpha} \psi_{\mathbf{k},\alpha}^*(\mathbf{r}) \psi_{\mathbf{k},\alpha}(\mathbf{r})
\]

(70)

The muffin tin charge density, \( \rho_v (\mathbf{r}_v) \), in the sphere \( \nu \), is defined to be the spherical average of the charge density given
by Equation 68
\[ \rho_v(r_v) = \int \frac{d\psi^*}{4\pi} \rho(r_v). \] (71)

The evaluation of these expressions and others related to the muffin tin charge density using the APW form of \( \psi_k(r) \) is carried out in Appendix A. It should be noted that all of the resulting expressions are quite similar in form to the normalization Equation 69, differing primarily in the dependence on the radial functions \( R_k^r(r_v,E) \).

One other benefit is derived from the evaluation of the muffin tin charge density rather than the charge density of Equation 68. The muffin tin potential resulting from this muffin tin charge density is easily obtained since only charge distributions which are either spherically symmetric or constant need be considered. Certain errors are of course introduced by this approximation, but as discussed in Section C where explicit expressions for the potential are derived, these errors are probably small for the case of NaCl.

D. The Muffin Tin Potential

The potential used to initiate the self consistent calculation of the bands of NaCl is taken to be that derived from a superposition of the free, closed shell Na\(^+\) and Cl\(^-\) ions arranged in the manner discussed in Section A. In the Hartree-Fock-Slater approximation, the resultant superimposed free ion (SFI, henceforth) potential, \( V_{SFI}(z) \), is given by
The sums are over all ionic sites of the crystal. \( V^{\nu}_{PI}(\mathbf{r}) \) is the Coulombic or electrostatic potential of both the nucleus and the electronic charge density, \( \rho^{\nu}_{PI}(\mathbf{r}) \), of the free ion of type \( \nu \). The first term on the right of Equation 72, \( V_{e}(\mathbf{r}) \), defined by

\[
V_{e}(\mathbf{r}) = \sum_{n,\nu} V^{\nu}_{PI}(\mathbf{r} - \mathbf{R}_{n,\nu}) - 6 \left( \frac{2}{3\pi} \right)^{\frac{1}{3}} \left[ \sum_{n,\nu} \rho^{\nu}_{PI}(\mathbf{r} - \mathbf{R}_{n,\nu}) \right]^{\frac{1}{3}}
\]

is the Coulombic potential of the crystal, arising from a superposition of the spherically symmetric free ion Coulombic potentials centered at appropriate lattice sites. The second term on the right, \( V_{x}(\mathbf{r}) \) defined by

\[
V_{x}(\mathbf{r}) = -6 \left( \frac{2}{3\pi} \right)^{\frac{1}{3}} \left[ \sum_{n,\nu} \rho^{\nu}_{PI}(\mathbf{r} - \mathbf{R}_{n,\nu}) \right]^{\frac{1}{3}}
\]

is the exchange potential, in the Slater approximation, of the SFI charge density.

In the APW approach of course, we do not consider \( V^{\nu}_{SPI}(\mathbf{r}) \) directly but the muffin tin approximation to \( V^{\nu}_{SPI}(\mathbf{r}) \) defined by Equations 49 and 50, with \( V^{\nu}_{SPI}(\mathbf{r}) \) taking the role of \( V_{CR}(\mathbf{r}) \). Let us first consider the contribution of \( V_{e}(\mathbf{r}) \) to the muffin tin potential.

Since \( V^{\nu}_{PI}(\mathbf{r}) \) is the Coulombic potential energy of a spherically symmetric ion of total charge \((-1)^{\nu-1}\). \( V^{\nu}_{PI}(\mathbf{r}) \) will approach \( 2(-1)^{\nu}/r \) for \( r \) greater than the ionic radius and,
consequently, the sum in Equation 73 will converge quite slowly. The evaluation of Equation 73 can be simplified, however, by introducing a potential \( U_\nu (r) \),

\[
U_\nu (r) = V^\nu_{\text{PI}}(r) - \frac{2(-1)^\nu}{r},
\]

which approaches zero more rapidly than \( \frac{1}{r} \) for \( r \) greater than the ionic radius since the asymptotic behavior of \( V^\nu_{\text{PI}}(r) \) is cancelled by the second term of Equation 75. \( V_e(r) \) can now be written as

\[
V_e(r) = \sum_{\nu} \frac{2(-1)^\nu}{|r - \mathbf{Q}_n,\nu|} + \sum_{\nu} U_\nu(r - \mathbf{Q}_n,\nu)
\]

The first term is simply the Ewald potential of a NaCl lattice of point charges and has been investigated in detail by Slater and DeCicco (1963). These authors show that the contribution of this term to the muffin tin potential inside a sphere of type \( \nu \) is

\[
E_\nu(r_\nu) = \frac{2(-1)^\nu}{r_\nu} - (-1)^\nu \frac{2\alpha_m}{\alpha}
\]

where \( \alpha_m = 1.747565 \) is the Madelung constant for a NaCl lattice and \( \alpha = 5.32a_o = 2.82 \, \text{Å} \) is the nearest neighbor distance of NaCl.

Since \( U_\nu (r) \) approaches zero more rapidly than \( \frac{1}{r} \) for \( r \) greater than the ionic radius, the sum in the second term of Equation 76 converges quite rapidly and the contribution of this term to the muffin tin potential can be evaluated numerically in a straightforward manner using the Löwdin
"a-summation" technique (Löwdin 1956, Loucks 1967).

When evaluating the contribution of the exchange interaction, $V_x(r)$, to the muffin tin potential inside a sphere of type $\nu$, we shall assume that

$$
\int \frac{d\Omega}{4\pi} \left[ \sum_{n,\nu} \rho_{FI}^{\nu'}(r_{\nu} - r_{n,\nu}) \right] \frac{1}{r_{\nu}^3} = \left[ \int \frac{d\Omega}{4\pi} \sum_{n,\nu} \rho_{FI}^{\nu'}(r_{\nu} - r_{n,\nu}) \right] \frac{1}{r_{\nu}^3}.
$$

That is, we assume that the spherical average of the exchange potential about any site is equal to the exchange potential of the spherically averaged charge density. This is a great numerical convenience since, using the Löwdin "a-summation" technique, the spherical average of a superposition of spherically symmetric quantities can be found quite easily. Further writing the crystalline charge density, $\rho$, as the sum of its spherical average about a given site, $\rho_o$, plus the deviation from this spherical average, $\Delta \rho$,

$$
\rho = \rho_o + \Delta \rho,
$$

we have, expanding $\rho$ about $\rho_o$

$$
\int \frac{d\Omega}{4\pi} \rho \frac{1}{r^3} = \int \frac{d\Omega}{4\pi} (\rho_o + \Delta \rho) \frac{1}{r^3} = \int \frac{d\Omega}{4\pi} \rho_o \frac{1}{r_o^3} (1 + \frac{1}{3} \frac{\Delta \rho}{\rho_o} + 0 \frac{(\Delta \rho)^2}{\rho_o^2}).
$$

But since, by definition, $\int d\Omega \Delta \rho = 0$ the above expression becomes

$$
\int \frac{d\Omega}{4\pi} \rho \frac{1}{r^3} = \int \frac{d\Omega}{4\pi} \rho_o \frac{1}{r_o^3} + 0 \frac{(\Delta \rho)^2}{\rho_o^2}.
$$
That is, the above approximation is correct to second order in deviations of the charge density from its spherical average.

Using Equations 76, 77 and 78, the muffin tin potential inside a sphere \( v \) approximating the SFI potential of Equation 72 is, then,

\[
V_v(r_v) = \frac{2(-1)^v}{r_v} - (-1)^v \frac{2a_m}{a} + \int \frac{d\Omega}{4\pi} \sum_{n_v} U_v(r_v - \mathbf{L}_{n_v})
\]

\[
- \frac{1}{j} \left[ \int \frac{d\Omega}{4\pi} \sum_{n_v} \rho^v_{FI}(r_v - \mathbf{L}_{n_v}) \right]^{\frac{1}{j}} \tag{82}
\]

The value of the muffin tin potential outside the spheres shall be discussed later.

At any stage of the self-consistent calculation other than the initial discussed above, the muffin tin potential is determined from the muffin tin charge density defined by Equations 70 and 71. The exchange potential of the muffin tin charge density is evaluated in a straightforward manner and, because of the muffin tin nature of the charge density, satisfies the conditions necessary for a muffin tin potential. In the following, then, we shall restrict our discussion to the electrostatic or Coulomb contributions to the muffin tin potential of the potential arising from a muffin tin charge density.

The muffin tin potential arising from the muffin tin charge density can be obtained most directly by visualizing the muffin tin charge density, including the nuclei, as a superposition of charge distributions as shown schematically in
Fig. 5. Fig. 5a represents the muffin tin charge density evaluated along the (100) or nearest neighbor direction. The points $Z_{\nu}$, $\nu = 1, 2$ represent the nuclei separated by a distance $a$ and centered inside the APW spheres of radius $R_{\nu}$. $\rho_{\nu}(r_{\nu})$ are the spherically symmetric electronic charge densities inside the spheres and $\rho_o$ is the constant electronic charge density outside the spheres. This distribution is now split into two distributions, one with a constant electronic charge density, $\rho_o$, as shown in Fig. 5b and the other as shown in Fig. 5c with electronic charge density $\rho'_\nu(r_{\nu})$ equal to the difference between the original electronic distribution and $\rho_o$. That is

$$\rho'_\nu(r_{\nu}) = \rho_{\nu}(r_{\nu}) - \rho_o. \quad (83)$$

Distribution $c$ can be thought of as a collection of neutral "atoms" of radius $R_{\nu}$ and non integer nuclear charge if we associate the nuclear charge with this particular distribution and in addition introduce point charges $q_{\nu}$ at the nuclear sites, as shown, which are chosen to insure the neutrality of these atoms. That is

$$Z_{\nu} - q_{\nu} = \int_{0}^{R_{\nu}} dr_{\nu} \frac{4}{\pi} r_{\nu}^2 \rho'_\nu(r_{\nu}) \quad (84)$$

In order to insure the neutrality of the entire original distribution, corresponding point charges of opposite sign are introduced into the uniform electronic charge distribution of Fig. 5b.
Fig. 5. Schematic of the technique by which the muffin-tin charge density is subdivided to determine the muffin-tin potential.
The potential of distribution c can now be found rather easily. Since the "atoms" are neutral and the charge density vanishes outside the spheres, the potential outside the spheres will vanish. Inside any one of the spheres, the potential due to all of the other neutral "atoms" is zero, and the potential, \( V'(r_v) \), is given by

\[
V'(r_v) = -\frac{2(Z_v-q_v)}{r_v} + U'(r_v)
\]

(85)

where \( U'(r_v) \) is the spherically symmetric potential of the electronic distribution \( \rho'(r_v) \) obtained from the solution of Poisson's equation,

\[
\nabla^2 U'(r_v) = -8\pi \rho'(r_v)
\]

(86)

subject to the boundary conditions of \( U'(0) \) finite and \( U'(R_v) = \frac{2(Z_v-q_v)}{R_v} \). The latter boundary condition insures that the potential of the neutral "atom" vanishes at the sphere boundary. Since the potential of distribution c satisfies the requirements of the muffin tin potential, it needs no further consideration.

The distribution of Fig. 5b represents a NaCl lattice of point charges imbedded in a uniform background of electronic charge \( \rho_0 \). The definitions of \( q_v \) (Equation 84) and of \( \rho'(r_v) \) (Equation 83) insure that this distribution is electrically neutral. That is

\[
q_1 + q_2 - \rho_0 \Omega_0 = 0
\]

(87)
where $\Omega_o$ is the volume of the unit cell. This distribution can be further divided into two face centered cubic lattices (the Na$^+$ and Cl$^-$ FCC sublattices) of point charges $q_v$ imbedded in uniform background electronic charge densities, $\rho_{ov}$, as shown in Figs. 5d and 5e. The $\rho_{ov}$ are chosen so that each of these distributions is electrically neutral. That is

$$\rho_{ov} = \frac{q_v}{q_1 + q_2} \rho_o = \frac{q_v}{\Omega_o}.$$ (88)

The potential of a FCC lattice of point charges imbedded in a uniform background of the opposite charge has been investigated in detail by Slater and DeCicco (1963) using Ewald techniques. They show that the spherical average of the potential about a charge site, $W_1(r)$, is given by

$$W_1(r) = -\frac{q_a}{a} \left[ \frac{1}{r/2a} + \frac{8\pi}{3} \left( \frac{r}{2a} \right)^2 - A \right]$$ (89)

where $q$ is the charge of the point charges in the lattice and $A = 4.584850$. In addition, the spherical average of the potential about the point $a = (a, 0, 0)$, $W_2(r)$, is

$$W_2(r) = \frac{q_a}{a} \left[ \frac{8\pi}{3} \left( \frac{r}{2a} \right)^2 - B \right]$$ (90)

where $B = 1.089730$ and $r$ is measured from the point $(a, 0, 0)$. We observe that in the Na$^+$ (or $q_1$) sublattice, for example, the point $(a, 0, 0)$ corresponds to a lattice site in the Cl$^-$ (or $q_2$) sublattice. Thus by superposition, the spherical average of the potential about a $q_1$ site, $U_1(r_1)$, arising from distribution $b$ (the sum of distributions d and e) is
Similarly, the spherically averaged potential about a q₂ site, $U_2(r_2)$ is given by

$$U_2(r_2) = -\frac{2q_2}{r_2} - \frac{2\pi}{3} \frac{(q_1 + q_2)}{a^3} r_2^2 + \frac{q_2 A + q_2 B}{a}.$$  \hspace{1cm} (92)

As in our usual convention, $r_1$ and $r_2$ are measured from the centers of type 1 and type 2 spheres respectively. Thus, inside a sphere of type $\nu$, the electrostatic contribution, $V_{\nu}(r_{\nu})$, to the muffin tin potential arising from the total muffin tin charge density of Fig. 5a is

$$V_{\nu}(r_{\nu}) = -\frac{2(Z - q_{\nu})}{r_{\nu}} + U_{1}(r_{\nu}) + U_{2}(r_{\nu})$$  \hspace{1cm} (93)

where $q_{\nu}$, $U_{1}(r_{\nu})$, $U_{2}(r_{\nu})$ and $U_{2}(r_{\nu})$ are given by Equations 84, 86, 91 and 92 respectively.

The electrostatic contribution to the constant value of the muffin tin potential outside the spheres can now be found in a straightforward manner. We observe that the only non-vanishing contribution to this quantity arises from the charge distribution $b$ since the potential of distribution $c$ vanishes outside the spheres. Slater and DeCicco, in the solution of the Ewald problem which was used to obtain $U_{1}(r_{\nu})$, the potential of distribution $b$ inside the spheres, chose the zero of energy
such that the average value of the potential over the unit cell was zero.

That is, integrating over the unit cell, of volume $\Omega_o$,

$$0 = V_o(\Omega_o - \frac{4\pi}{3}(R_1^3 + R_2^3)) + \sum_v \int_0^R v dr_v 4\pi r_v^2 U_v(r_v)$$  \hspace{1cm} (94)

where $V_o$ is the average value of the potential of charge distribution $b$ outside the spheres and $U_v(r_v)$ is the potential inside the spheres given by Equations 91 and 92. Evaluating Equation 94, the electrostatic contribution to the muffin tin potential outside the spheres, $V_o$, is

$$V_o = \frac{1}{[\Omega_o - \frac{4\pi}{3}(R_1^3 + R_2^3)]} \left\{ 4\pi(q_1 R_1^2 + q_2 R_2^2) + \frac{8\pi^2}{15 a^3} (q_1 + q_2) (R_1^5 + R_2^5) - \frac{4\pi}{3} \left[ \frac{(q_1 A + q_2 B)}{a} R_1^3 + \frac{(q_2 A + q_2 B)}{a} R_2^3 \right] \right\}.$$ \hspace{1cm} (95)

When the exchange contributions are added to the potentials of Equations 93 and 95 the total muffin tin potential arising from the muffin tin charge density is determined.

There are, however, two points which should be kept in mind when using this formalism.

The first point is that the zero of energy will change from one stage of the self-consistent calculation to the next by an unknown amount. This is related to the fact that the potential is always arbitrary to an additive constant. In
this particular calculation this loss of zero of energy occurs when the Ewald technique is used to determine the potentials of charge distributions d and e (and thus b) of Fig. 5. In order to see why this occurs, let us assume that the "true" zero of energy is such that the average value of the potential of a NaCl lattice of unit charges (+1 on the Na sublattice and -1 on the Cl sublattice) is zero. If we now consider a collection of positive point charges of magnitude $q_1$ on a Na sublattice imbedded in a uniform negative background charge to insure neutrality, this collection will have some average potential, $V_1$ say, which will in general not be zero on the "true" energy scale defined above. Similarly if we have a collection of point charges $(-q_2)$, $q_2 \neq q_1$, placed at the points of the Cl sublattice and imbedded in a uniform background charge, the average value of the potential of this collection, $V_2$ say, will not be zero and since $q_1 - q_2 \neq 0$, $V_1 - V_2 \neq 0$. That is, the average value of the potential of the NaCl lattice composed of the point charges, $q_1$, on the Na sublattice and the point charges, $-q_2$, on the Cl sublattice with associated uniform background charges will not be zero on the chosen "true" scale. In the Ewald technique the zero of energy was chosen to correspond to this average value, i.e. chosen so that the average value of the Ewald potential is zero. Thus, since different charge distributions are in general considered at different stages of the self-consistent calculation, the indicated zero of energy will
be different at different stages of the calculation. This problem is unavoidable since infinite uniform charge densities are considered. The loss of the zero of energy is only an annoyance in our calculation since we are interested in differences in energies for a given set of bands. However caution should be used when applying the results of this type of calculation to calculations of the cohesive energies of a material for example.

The second and very important point is that the muffin tin potential derived from the muffin tin charge density is shifted relative to the muffin tin potential derived from the charge distribution used to obtain the muffin tin charge density. In fact the amount of shift outside the spheres is in general different from that inside the spheres.

In order to see why this occurs, let us denote by \( \rho_o(\overline{r}) \) the muffin tin charge density obtained from the charge density \( \rho(r) \) the crystalline charge density of both the electronic density and nuclear charges. That is, inside a sphere of type \( \nu \),

\[
\rho_o(\overline{r}_\nu) = \rho_o(r_\nu) = \int \frac{d\Omega_\nu}{4\pi} \rho(\overline{r}_\nu) \tag{96}
\]

and outside the spheres

\[
\rho_o(\overline{r}) = \rho_o = \int \frac{d^3r}{4\pi} \rho(\overline{r}) / (\Omega_o - \sum_\nu \frac{4\pi}{3} R^3_\nu) \tag{97}
\]

where the integration is over the region outside all of the spheres.
The difference between the muffin tin potential arising from \( \rho(r) \) and the muffin tin potential arising from \( \rho_o(r) \), \( \Delta V_v(r_v) \), is inside a sphere of type \( v \),

\[
\Delta V_v(r_v) = \int \frac{d\Omega_v}{4\pi} \int d^3r' \frac{[\Delta \rho(r')]}{|\mathbf{r}_v - \mathbf{r}'|} \tag{98}
\]

where the spatial integral extends over the entire crystal and

\[
\Delta \rho(r') = \rho(r') - \rho_o(r'). \tag{99}
\]

Using the addition theorem for spherical harmonics to expand \(|\mathbf{r}_v - \mathbf{r}'|^{-1}\) and performing the integral over \( \Omega_v \), Equation 98 becomes

\[
\Delta V_v(r_v) = \int \frac{d^3r'}{r_v} \frac{\Delta \rho(r')}{r_v} \tag{100}
\]

where \( r_v \) is the greater of \(|\mathbf{r}_v|\) and \(|\mathbf{r}'|\), both measured from the center of the sphere under consideration. Inside the sphere \( v \) under consideration the integral over \( \Omega_v' \) of \( \Delta \rho(r')/r_v \) vanishes, by definition of \( \Delta \rho(r') \), regardless of whether \( r_v = r' \) or \( r'_v \). Thus

\[
\Delta V_v(r_v) = \int_{\text{outside sphere}} d^3r' \frac{\Delta \rho(r')}{r_v} \tag{101}
\]

where the volume integral is over all of the crystal outside of the particular sphere under consideration. Note that although \( \Delta V_v(r_v) \) may depend on the particular sphere type under consideration, i.e. \( v \), it is independent of \( r_v \). That is, inside any of the spheres the difference between the muffin tin
potential derived from $\rho(r)$ and the muffin tin potential derived from $\rho_0(r)$ is a constant. Now outside the spheres, the difference between the two muffin tin potentials is by definition a constant which will not in general be the same constant as that given by Equation 10.

Thus, except for a constant shift, the radial dependence of the muffin tin potentials inside the spheres are the same whether we use the muffin tin or actual charge density. A relative shift of the potentials inside and outside the spheres is however induced in this approximation. Some difference in the potentials is, of course, expected when the actual charge density is approximated by the muffin tin charge density but the fact that the radial dependence of the potentials inside the spheres is unaltered indicates that this may be a rather good approximation. If, however, the relative shift of the potentials inside and outside the spheres is sufficiently large, as may be the case in semiconductors where the deviations of the actual density from its muffin tin approximation are sizeable, the entire approach may be of questionable validity. The magnitudes of these shifts are difficult to determine in practice since the actual charge density at any stage of the calculation is unknown (or more precisely uncalculated, since this is the rationale for introducing the muffin tin charge density). An order of magnitude estimate can however be made and the results indicate that this effect is probably not significant in NaCl.
The argument proceeds as follows: We note that the significant quantity in the calculation is \( \Delta \rho(r) \), the deviation of the actual density from its muffin tin approximation, a density which is overall neutral. We shall attempt to approximate this distribution by a reasonable collection of point charges. In NaCl, visualizing the lattice as a superposition of free ions, for example, we expect that \( \Delta \rho(r) \) will be sizeable only outside or near the APW sphere boundaries. Further, there will be a significant excess of electronic charge, \( \Delta \rho < 0 \), in the region between the ions probably along a next nearest neighbor or third nearest neighbor direction. Representing the excesses and deficiencies by point charges of the appropriate sign but of equal magnitude, the situation for a deficiency along next nearest neighbors is shown in Fig. 6a. The corners of the cube are at the sites of the cubic NaCl lattice. This particular arrangement can be thought of as a superposition of a CsCl (B.C.C.) lattice of the same cube edge and a NaCl lattice with the nearest neighbor distance one-half that of the original lattice as illustrated in Fig. 6b. If we imagine spheres of radius less than \( 1/2 \) the nearest neighbor distance, so that all the charge lies outside the spheres, the potential at the center of the spheres \( \Delta V_1 \), the shift inside the spheres given by Equation 101, is just the sum of the Madelung potentials of the CsCl and NaCl sublattices,

\[
\Delta V_1 = \frac{2a}{(a/2)} \left( a_1 - \frac{a^2}{3} \right)
\]  

(102)
Fig. 6. Arrangement of point charges used to estimate the relative shifts introduced by the muffin tin approximation. Part a shows the arrangement used in the calculation. Part b shows the division into a BCC and NaCl type lattice.
where \( a_1 = 1.748 \) is the Madelung constant of the NaCl lattice, 
\( a_2 = 1.763 \) is the Madelung constant of the CsCl lattice, and \( q \) is the absolute magnitude of the point charges. It is found later in this work that \( \rho_o \sim 3 \times 10^{-2} \) for NaCl, corresponding to about 0.5 electrons per unit cell outside the spheres. If we assume \( \Delta \rho(r) \sim \rho_o \) and associate an equal fraction of the volume outside the spheres with each of the 12 point charges per unit cell, we find \( q \sim 0.5/12 \sim 0.05 \) electrons. Evaluating Equation 102 with this value of \( q \) and with \( a = 5.32 \), the nearest neighbor distance of NaCl we find that the shift inside the spheres is \( \Delta V_i \sim 0.027 \) Ryd.

The value of \( \Delta V_o \), the shift in muffin tin potential outside the spheres, or equivalently the potential of \( \Delta \rho \) outside the spheres, can be determined by observing that the average value of the potential of \( \Delta \rho \), \( \overline{\Delta V} \), can be written

\[
\overline{\Delta V} = f\Delta V_i + (1-f)\Delta V_o
\]

where \( f \) is the fraction of the volume of the unit cell occupied by the spheres. For the particular distribution of charge considered here \( \overline{\Delta V} = 0 \) (for each potential due to positive charge there is a potential of opposite sign which cancel when the volume integral is performed). Thus, taking the radii of the spheres to be \( a/2 \), we find that the desired relative shift of the potentials, \( \Delta V_o - \Delta V_i \) is, in this approximation,

\[
\Delta V_o - \Delta V_i = \frac{-f}{1-f} \Delta V_i \sim 0.05 \text{ Ryd}.
\]
Although this relative shift is sizeable, it is, as we shall see, an order of magnitude less than both the difference between the "actual" crystalline potential and its muffin tin approximation and the probable error made when using the Slater exchange approximation in constructing the actual potential and should therefore be insignificant in the case of NaCl. In other materials where the deviation of the crystalline charge density from its muffin tin approximation is greater, this point should be investigated in more detail.
III. THE DETAILS AND RESULTS OF THE CALCULATION

A. Details of the Calculation

The general methods and techniques used in the calculation of the electronic energy band and charge density structure of NaCl were discussed in the preceding chapter. The particulars and the various results of the calculation shall be presented in this chapter. Since certain of the results obtained under different conditions (the energy bands obtained from different sets of APW radii for example) have features which are best discussed after all of the results are presented, this chapter shall be divided into two sections. Section A, the present section, shall be limited to a presentation of the details and numerical results of the calculation. Only those features which are necessary for an understanding of the conditions under which a particular set of numerical results were obtained shall be discussed. In Section B, the various results shall be discussed in detail and, when appropriate, compared with each other in detail.

The reciprocal lattice vectors, \( \mathbf{K}_1 \), retained in Equation 47 and subsequent, related equations were chosen according to the method discussed by Loucks (1967, p. 38). In this method we observe first of all that the \( \mathbf{K}_1 \) always appear through the quantities \( \mathbf{k}_1 = \mathbf{k} + \mathbf{K}_1 \). Further, there will exist some radius in \( \mathbf{k} \)-space, \( R \) say, such that, for a given value of \( \mathbf{k} \), the series of Equation 47 will have converged adequately retaining
only those terms for which \( |k_1| < R \). In order to obtain a given degree of convergence, a different value of \( R \) and a different set of \( k_1 \) will in general be required for each value of \( k \) as \( k \) ranges throughout the 1/48th irreducible zone. The object of the method under discussion is to find the minimum value of \( R \), or equivalently the minimum set of \( K_1 \), which yields adequate convergence of the series for all values of \( k \). This is accomplished in practice by determining the set of \( k_1 \) with \( k \) taking on values appropriate to the points of high symmetry \( \Gamma, X, L, K, W \) and \( U \). The \( K_1 \) are allowed to range over all values. Of this entire set of \( K_1 \), a finite subset lies within a sphere of given radius centered at the origin of \( k \)-space. The \( K_1 \) retained in Equation 47, finite in number, are just those necessary to map out this subset of \( K_1 \). In principle the number of \( K_1 \) retained can be made arbitrarily large by increasing the radius of the sphere defining the subset of \( K_1 \). It is desirable of course to retain a large number of \( K_1 \) in order that the expansion in Equation 47 converges well to \( \psi_k (r) \) and that, consequently, the energy eigenvalues calculated be good approximations to the actual values. Observe that, since we are performing a variational calculation, the calculated eigenvalue will always be greater than the true eigenvalue. As we increase the number of reciprocal lattice vectors and thus obtain a trial wave function which is a better approximation to the true wave function, the calculated eigenvalues will
decrease in energy toward the true eigenvalues. However, because of time and space limitations the maximum number of reciprocal lattice vectors that can be reasonably used on the computing system available for the calculation is about 40. In the present calculation the number finally used was 36. These reciprocal lattice vectors, listed in Table 1 in order of increasing order of importance in the set of $k_\parallel$ discussed above, do yield results which are satisfactorily convergent. Increasing the number to 42, chosen in the same manner, lowered the eigenvalues at the symmetry points $\Gamma$, $X$, $L$ and $K$ by 0.005 Ryd typically whereas decreasing the number to 27 raised the eigenvalues by 0.015 Ryd typically. The relative positions of the eigenvalues were, however, changed by a factor of 5 to 10 less. We conclude, then, that, although the absolute positions of the bands are in error by at least 0.005 Ryd, the relative positions should be correct to about 0.001 Ryd. This, of course, disregards any errors associated with the approximations made in obtaining the particular potential being used.

Observe that since group theoretical techniques were not used in the selection of the reciprocal lattice vectors of the calculation (Miyakawa and Oyama 1965), the group theoretic symmetry labels often used to designate certain states of high symmetry cannot be determined easily. The symmetry designations shown on the bands determined in this calculation were assigned primarily on the basis of degeneracy and compatibility (Slater
Table 1. Reciprocal lattice vectors, \( \frac{1}{a} \) (n\#m), used in the APW expansions for all points in the Brillouin Zone. Bar above integer denotes negative.

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<td>((\bar{1})1(\bar{1}))</td>
<td>(002)</td>
<td>(1(\bar{3})1)</td>
<td>(220)</td>
</tr>
<tr>
<td>(0(\bar{2})0)</td>
<td>((\bar{2})0(\bar{2}))</td>
<td>(0(\bar{2})2)</td>
<td></td>
</tr>
<tr>
<td>(00(\bar{2}))</td>
<td>(0(\bar{2})2)</td>
<td>(1(\bar{1})3)</td>
<td></td>
</tr>
<tr>
<td>(1(\bar{1})(\bar{1}))</td>
<td>((\bar{2})2(\bar{0}))</td>
<td>(2(\bar{2})2)</td>
<td></td>
</tr>
<tr>
<td>(1(\bar{1})(\bar{1}))</td>
<td>((\bar{2})0(\bar{2}))</td>
<td>(2(\bar{2})2)</td>
<td></td>
</tr>
</tbody>
</table>

1965, App. 3-2) and by comparing the bands determined here with similar bands of other substances (primarily KCl (DeCicco 1967, Oyama and Miyakawa 1966), Ar (Mattheiss 1964), and Kr (Fowler 1963)). The notation employed is that of Bouckaert et al. (1936). It should be mentioned here that the labeling along the symmetry axis L-Q-W depends upon which ion is located at the origin of coordinates (Scop 1965). For labeling purposes only we have taken the convention corresponding to the chlorine ion being at the origin.

As a check on these assignments and to obtain information useful for later discussion, the charge densities associated with certain low lying states in the conduction band were
calculated. Observe that the expressions for the muffin tin charge densities derived in the appendix are still valid if we consider only one electron in a given state. The sums over \( k \) and \( \alpha \) are simply over one term. Also the normalization of the wave function can be altered formally so that there is one electron per unit cell rather than the numerically annoying \( \frac{1}{N} \approx 10^{-23} \) electrons per unit cell. In particular the electronic charge inside a sphere of type \( \nu \) can be written, using Equations A13 and A19 of the Appendix, as

\[
Q_\nu = \sum_k Q_\nu(k)
\]

where \( Q_\nu(\ell) \) is the amount of charge associated with the spherical harmonic of order \( \ell \) used in the expansion of the electronic wavefunction inside the sphere, given in Equation 53. The relative strengths of the \( Q_\nu(\ell) \) can then be taken as an indication of the orbital character of an electron in the sphere \( \nu \), although, strictly speaking, the orbital angular momentum is not a good quantum number in the solid. The calculated orbital character of states of high symmetry can then be compared with the theoretical orbital character tabulated by Bell (1954).

The \( Q_\nu(\ell) \) for \( \ell = 0, 1, 2 \) of a few low lying states of the conduction bands shown in Fig. 12 are tabulated in Table 2. The details of this particular set of bands are not essential to the discussion here and shall be discussed later. The orbital character in this table confirms our assigned symmetry labeling. For example, in Bell's tables, the triply degenerate point
Table 2. Total charge inside the APW spheres associated with a given value of L for some symmetry points in conduction band.

<table>
<thead>
<tr>
<th>Symmetry point</th>
<th>L = 0</th>
<th>L = 1</th>
<th>L = 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Cl</td>
<td>Na</td>
</tr>
<tr>
<td>( \Gamma_1 )</td>
<td>0.15</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>( X_1 )</td>
<td>0.20</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>( L_1 )</td>
<td>0.16</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>( \Gamma_25' )</td>
<td></td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>( \Gamma_{12} )</td>
<td></td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>( X_3 )</td>
<td></td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>( L_2 )</td>
<td>0.20</td>
<td></td>
<td>0.34</td>
</tr>
</tbody>
</table>

labeled as \( \Gamma_25' \), on the bands of Fig. 12 could be any of the points \( \Gamma_{15} \) (p-like), \( \Gamma_{15'} \) (g-like), \( \Gamma_{25} \) (f-like) or \( \Gamma_{25'} \) (d-like) if only the degeneracy were known. From Table 2 we see that the dominant term is d-like (L = 2) and the state must be \( \Gamma_{25'} \).

The values chosen for the sphere radii in any calculation employing the muffin tin potential approximation are in principle arbitrary except that the values chosen must be such that nearest neighbor spheres do not overlap. It is, however, desirable to choose these radii to be as large as possible, i.e. such that nearest neighbor spheres are in contact. In the first place, this additional requirement causes the volume in which the crystalline potential is approximated by a constant
to be minimized. Secondly, the portion of the wave function which is approximated by a sum of plane waves is reduced, leading to a more rapid convergence of the expansion in Equation 47. In the case of a monatomic metallic lattice this additional requirement alone is sufficient to fix the sphere radii. Since there is only one type of atom in this case, all sphere radii will be the same; since spheres are to be in contact along a nearest neighbor axis, the radius of each sphere must then be one-half the nearest neighbor distance.

In the case of NaCl, on the other hand, there are two dissimilar ionic types and some additional requirement must be employed to determine the radius appropriate to each of the ionic types. One such requirement which has been used (Scop 1965, Ern and Switendick 1965, Onodera et al. 1966) is to require that the muffin tin potential just inside the APW spheres be the same for the different spheres as shown schematically in Fig. 7a. The chief merit of this scheme is that the zero slope extrema or "flat" portions of the crystalline potential lie outside the spheres, in the region in which the potential will be approximated by a constant. With another choice of radii the variation of the crystalline potential outside the spheres would be increased with a resultant degradation of the muffin tin approximation. This particular choice of radii, then, optimizes the muffin tin approximation to a given crystalline potential. Using this method, the radii
Fig. 7. Illustration of the two criteria for determining the APW radii.
determined from the superimposed free ion potential used in the initial stages of the calculation (see later) are, for sodium, $R_1 = 1.30\text{Å}$ and, for chlorine, $R_2 = 1.51\text{Å}$. We shall refer to this radii set henceforth as the first radii set.

Although the above set of radii are quite reasonable if only the potential is considered, they have little relation to ones intuitive feeling for the "size" of an atom or ion which is derived more from the radial extent of the charge density than from the range of the potential. In X-ray diffraction analysis of the charge density of ionic crystals for example, the radii of the ions are taken to correspond to that point along the nearest neighbor axis for which the charge density is a minimum as shown in Fig. 7b. For NaCl, the experimental radii determined by this method are for sodium, $1.15 \pm 0.06\text{Å}$, and for chlorine, $1.67 \pm 0.06\text{Å}$ (Kurki-Suonio and Fontell 1964) which are considerably different than the values obtained above from the potential criterion. This suggests that a more reasonable choice for the radii to be used in the APW calculation are those determined from the criterion that the spherically averaged charge density just inside the APW spheres be the same for the different sphere types. Using this method, the radii determined from the superimposed free ion charge density are, for the sodium site, $R_1 = 1.12\text{Å}$ and, for the chlorine site, $R_2 = 1.67\text{Å}$. Note that $R_1 + R_2 = 2.79\text{Å}$ which is not equal to the nearest neighbor distance. The spheres are
thus not in contact. This occurs because the potentials and charge densities about a given site are calculated on a radial grid centered on that site. Along a nearest neighbor direction the points of the grid centered on a sodium site do not coincide with the points of the grid centered on the chlorine sphere. It is numerically convenient, however, to pick the APW radius of a given sphere to correspond to a grid point. The radius of a given sphere type is thus chosen to correspond to the grid point which most nearly satisfies a given criterion for determining a radii set.

Aside from the fact that these radii are quite close to those determined from X-ray work and therefore agree with the more common definition of ionic radii, there are other reasons why this particular set is preferable to the first set. Observe that with the second set of radii the low density, slowly varying portions of the charge density lie outside the APW spheres or, in other words, the amount of rapidly varying charge density which is contained within the spheres has been maximized. If, for example, the first set of radii, with a larger sodium sphere and smaller chlorine sphere, is used, the minimum in the charge density along the nearest neighbor axis is included in the sodium sphere and much of the rapidly varying charge at the outer edge of the chlorine site in off axis directions is included in the region outside the spheres. The second set of radii is, then, more consistent with the rationale of the APW method which is to obtain a technique in which the
rapidly varying portions of the wavefunctions are treated accurately. Furthermore this second set of radii would seem to be a better choice when performing a self consistent calculation when using the muffin tin charge density technique described in Sections C and D of Chapter II. This is the case since there is little hope of obtaining a muffin tin potential which is a good approximation to the true potential if the muffin tin charge density is not a good approximation to the true charge density. Since the second set of radii were chosen in such a manner that the muffin tin charge density obtained with this set of radii is a better approximation to the actual charge density than the muffin tin charge density obtained with another set, the potential obtained with this set of radii should be a better approximation to the actual potential than those obtained with another set of radii. For this reason, the self-consistent calculation was performed to completion only for the second set of radii.

The initial muffin tin potential was obtained by the superimposed free ion (SFI) method discussed in Section D of Chapter II, using Equation 82 in particular. The free ion charge densities used to obtain this potential were those obtained by Liberman et al. (1965) in the relativistic Hartree-Fock-Slater approximation. The two sets of APW radii used were determined by the methods just discussed. The spherical average of the crystalline potential about the sodium (ν = 1) site, the quantity used for the muffin tin potential inside the sodium
spheres, is shown in Fig. 8 as a function of distance from the sodium nucleus. Note that the radius is measured in units of the nearest neighbor distance \((a = 2.82\text{Å})\). A similar plot about the chlorine site is shown in Fig. 9. Also shown in these figures are the total SFI potentials given by Equation 72, the exchange contributions to these potentials evaluated along the (100), or nearest neighbor, direction and the (111), or third nearest neighbor, direction. As can be seen from these figures for radii up to about 0.4, the crystalline potential is approximated quite well by its spherical average. Beyond this point the non-spherically symmetric contributions to the cubic crystal potential become significant and the muffin tin potential approximation becomes somewhat poorer. At the edge of the chlorine sphere for the second set of radii, for example, the crystal potential differs from its spherical average by about 0.2 Ryd. Deviations at values of the radii corresponding to the first set of sphere radii are somewhat less, about 0.1 Ryd. These deviations are of the same order of magnitude as those obtained by DeCicco (1967) and will therefore have an insignificant effect upon the bands. It is important to note that the major contribution to the potential near the sphere radii and in the interstitial region is that of exchange. This will have a significant bearing upon later remarks.

The constant value of the muffin tin potential outside the spheres, \(V_o\), can in principle be determined by a numerical
Fig. 8. Potentials near the sodium site. The arrows labeled by 1 and 2 indicate the values of the sodium APW sphere radius for radii sets I and II respectively.
Fig. 9. Potentials near the chlorine site. The arrows labeled by 1 and 2 indicate the values of the chlorine APW sphere radius for radii sets I and II respectively.
averaging of the potential outside the spheres. This was, however, not done in the present calculation as preliminary calculations showed that any value of \( V_0 \) which could possibly be equal to the average potential outside would not produce a calculated optical band gap which would agree with the experimental gap. For example, the dependence upon \( V_0 \) of the top of the normally filled valence band, the bottom of the normally empty conduction band and their difference, the optical gap, \( E_g \), are shown in Fig. 10 for the SFI potential with the first set of radii. Comparing this figure with the SFI potentials shown in Figs. 8 and 9, we see that any value of \( V_0 \) which could possibly correspond to the average value of the crystalline potential outside the spheres, about -0.4 Ryd to -0.7 Ryd, would yield an optical gap which would be several electron volts too small. This indicates either that the SFI charge density is not a good approximation to the actual charge density or that some physical interaction, e.g. exchange, has been mistreated when obtaining the potential. At the time it was believed that the former was the case and further that the self-consistent calculation would produce a rearrangement of charge and a more correct optical gap. \( V_0 \) was therefore simply determined empirically by adjusting its value until the calculated optical gap agreed with the experimental value to within a few tenths of an electron volt. Specifically the value of \( V_0 = -0.134 \) for both sets of radii yielded band gaps of
Fig. 10. Variation of the bottom of the conduction band ($\Gamma_1$), the top of the valence band ($\Gamma_{15}$) and the energy gap with $V_0$. 
\( E_g = 8.6 \text{ eV} \) for the first radii set and \( E_g = 8.8 \text{ eV} \) for the second radii set which are to be compared with the experimental value of \( 8.6 \pm 0.1 \text{ eV} \) (Baldini and Bosacchi 1967, Teegarden and Baldini 1967). Henceforth the potentials and bands obtained by adjusting \( V_0 \) until the correct band gap is obtained shall be referred to as the "adjusted" potentials and bands.

The energy bands resulting from the adjusted SPI potential are shown in Figs. 11 and 12 for the first and second radii sets respectively. As is common practice, the bands are shown only for \( k \) along certain axes of high symmetry (see Fig. 2). As these bands will be discussed in Section B, let us for the moment note only that the set of three (six including spin degeneracy) narrow bands near the bottom of these figures are the uppermost normally filled valence bands. The complex of bands having a minimum at \( \Gamma_1 \) some 8.6 eV above these valence bands are the normally empty conduction bands.

In order to proceed with the self consistent calculation, the total muffin tin charge density of all of the occupied states in the above set of bands must be determined using the techniques and equations of Section C, Chapter II and Appendix A. The summation over the occupied states \( (k, \alpha) \) was performed in the manner discussed by Kleinman and Phillips (1959). In this technique, reciprocal space is divided into volumes having the same shape as the original Brillouin zone. The wave function of any state lying within one of these volumes is assumed to be identical with that of the state at the center
Energy bands of NaCl. These bands result from the SFI potential with $R(\text{Na}) = 1.30 \text{ Å}$ and $R(\text{Cl}) = 1.51 \text{ Å}$. The potential has been adjusted so that the calculated optical gap agrees with experiment.
Fig. 12. Energy bands of NaCl. These bands result from the SFI potential with $R(\text{Na}) = 1.12 \ \text{Å}$ and $R(\text{Cl}) = 1.67 \ \text{Å}$. The potential has been adjusted so that the calculated optical gap agrees with experiment.
of this volume. The first division of reciprocal space simply uses the original Brillouin zone about each reciprocal lattice point. The second division introduces sub-lattice points midway between the original reciprocal lattice points. The resulting lattice, including the original lattice points, has the same structure (body centered cubic in our case) as the original lattice but with the points separated by only one-half the original separation. A sub-zone with the same shape as the original Brillouin zone but with $\frac{1}{2^3}$ the volume is then associated with each of these lattice points. This process can be repeated indefinitely yielding an arbitrarily fine covering of reciprocal space. Since the reduced zone scheme is used, that is all occupied states are labeled by values of $k$ lying in the first Brillouin zone, only those points lying in the first Brillouin zone need be considered when using this technique. The weight assigned to each point is the fraction of the volume of the original zone occupied by the sub-zone about the point. The inequivalent points and the weights for the first three divisions of this technique as applied to the body centered reciprocal lattice of NaCl are shown in Table 3.

When this technique for performing the summation over occupied states is applied to NaCl, the calculated muffin tin charge density is found to have converged adequately in the second division. This is illustrated in Fig. 13 where the muffin tin charge density inside the chlorine sphere for the uppermost set of valence bands is shown for the first two
Table 3. Divisions of k-space used when performing the summation over k in expressions related the charge density

<table>
<thead>
<tr>
<th>Division</th>
<th>Points</th>
<th>Symmetry Designation</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(0,0,0)</td>
<td>Γ</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>(0,0,0)</td>
<td>Γ</td>
<td>1/8</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{8})</td>
<td>X</td>
<td>3/8</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2},\frac{1}{2},\frac{1}{2})</td>
<td>L</td>
<td>4/8</td>
</tr>
<tr>
<td>3</td>
<td>(0,0,0)</td>
<td>Γ</td>
<td>1/64</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2},0,0)</td>
<td>Δ</td>
<td>6/64</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2},0,0)</td>
<td>X</td>
<td>3/64</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2},\frac{1}{2},0)</td>
<td>Σ</td>
<td>12/64</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2},\frac{1}{2},0)</td>
<td>W</td>
<td>6/64</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{4},\frac{1}{4},\frac{1}{4})</td>
<td>Δ</td>
<td>8/64</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{4},\frac{1}{4},\frac{1}{4})</td>
<td>W</td>
<td>24/64</td>
</tr>
<tr>
<td></td>
<td>(\frac{1}{2},\frac{1}{2},\frac{1}{2})</td>
<td>L</td>
<td>4/64</td>
</tr>
</tbody>
</table>

divisions. The third division results are almost indistinguishable from the second division results and are not shown. The absolute value of difference between the second and third division results, magnified by a factor of ten, are however shown by the lower curve in this figure. As can be seen, the third division results differ from the second, by less than 1% of the total charge density. Further this difference is an order of magnitude less than the difference between the
calculated charge density and the charge density assumed in the preceding, initial step of the self consistent calculation. This is seen by comparing the calculated results with the radial charge density of the free chlorine ion 3P shell (the analogue of this band in the free ion), also shown in Fig. 13.

Using the above technique, the muffin tin charge densities resulting from the initial, adjusted SFI potential were found for the top four filled sets of bands, corresponding to the free ion Cl$^{-3}$P, Cl$^{-3}$S, Na$^{+2}$P and Na$^{+2}$S shells. The charge densities of the lower four sets of bands were assumed to be those of the corresponding Cl$^{-2}$P, Cl$^{-2}$S, Cl$^{-1}$S and Na$^{+1}$S free ion shells.

The muffin tin potential necessary for the next iteration was obtained using the methods discussed in Section D of Chapter II. However, in order to increase the rate of convergence of the self-consistent calculation, the muffin tin charge density used to derive this potential was the average of the charge density used to derive the preceding potential and the charge density resulting from the preceding potential.

The iterative cycle was performed three times using the second set of radii. At the end of the third cycle, the potential differed from that of the previous cycle by less than 0.01 Ryd which was the arbitrarily chosen criterion for self consistency. The final or self consistent charge densities inside the APW spheres are shown in Fig. 14 along with the
Fig. 13. Effect of successive k-space divisions upon radial charge density. Results are shown for the uppermost filled valence band. The dashed line at the bottom of the figure represents the difference (+ or -) between the second and third divisions, magnified by a factor of 10.
Comparison of SFI and SC radial change densities.
The crosses represent the initial SFI charge density and the solid line, the final, SC charge density.
spherical averages of the SFI charge densities used initially in the calculation in order to obtain the starting potential. The self consistent muffin tin potential and the initial SFI muffin tin potential inside the APW spheres are compared in Fig. 15. The self consistent energy bands are shown in Fig. 16. Let us for the moment note that the optical band gap of these self consistent bands is 6.0 eV, considerably smaller than the observed value of 8.6 eV. If we retain the self consistent potential inside the APW spheres and adjust the value of the potential outside the spheres until the calculated value of the optical gap agrees with the experimental value, in the manner in which the initial potential was obtained, the energy bands of Fig. 17 are obtained. The significance of this and the other results of the self consistent calculation shall be discussed in Section B.

The experimental quantity to which we can compare our calculated bands most directly is the optical absorption coefficient, \( \alpha(\omega) \), measured by Eby et al. (1959) and Teegarden and Baldini (1967). If there occur only vertical interband transitions, i.e. transitions for which the initial and final values of the wave vector \( \mathbf{k} \) are the same, the absorption coefficient is given by (Stern 1963, Phillips 1966)

\[
\alpha(\omega) = \frac{2m^2e^2}{mc} \cdot \frac{f(\omega)}{n(\omega)} \cdot N(E_f - E_1)
\]

\( n(\omega) \) is the index of refraction for light of frequency \( \omega \) and \( N(E_f - E_1) \) is an interband density of states at \( E_f - E_1 = h\omega \).
Fig. 15. Comparison of the initial and final muffin tin potentials
Fig. 16. The self consistent energy bands of NaCl
Fig. 17. The modified self consistent energy bands of NaCl. The potential outside the spheres has been adjusted so that the calculated and experimental values of the optical band gap are in agreement.
That is, \( N(E_f - E_i) \) is the number of possible transitions per unit volume from initial states \( i \), with energy \( E_i \), to final states \( f \), with energy \( E_f \) such that \( E_f - E_i \) lies within an energy increment \( dE \) centered at \( \hbar \omega \). The oscillator strength \( f(\omega) \) is the mean value of the individual transition oscillator strengths

\[
f_{fi} = \frac{2}{3m} \frac{|<f|P|i>|^2}{E_f - E_i}
\]

for transitions in a given energy increment. The theoretical evaluation of \( f(\omega) \), and thus \( \alpha(\omega) \), is quite difficult but, as has been emphasized by Phillips (1966), a great deal of information about \( \alpha(\omega) \) can be obtained by calculating \( N(E_f - E_i) \).

If we consider an energy band of index \( \alpha \), \( E_\alpha(k) \), to be a continuous function of \( k \) inside the Brillouin zone, the density of states can be written

\[
N(E_f - E_i) = \frac{2}{(2\pi)^3} \sum_{\alpha,\alpha'} \int \frac{dS_k}{|\nabla_k(E_\alpha(k) - E_{\alpha'}(k))|}
\]

where the integral is over a surface of constant energy \( E_\alpha(k) - E_{\alpha'}(k) = E_f - E_i \). As first emphasized by Van Hove (1953), \( N(E_f - E_i) \) will have critical points at those values of \( E_f - E_i \) for which \( |\nabla_k(E_\alpha(k) - E_{\alpha'}(k))| = 0 \). For example, if we consider transitions from a perfectly flat band, \( E_\alpha(k) = 0 \) to a parabolic band, \( E_\alpha(k) = E_o + k^2 \), the density of states is, evaluating the above expression,

\[
N(E) = \begin{cases} 
0 & \text{if } E \leq E_0 \\
\frac{1}{2\pi^2} (E - E_0)^{1/2} & \text{if } E > E_0 
\end{cases}
\]
The singularity in this case is the abrupt rise in or discontinuity in the slope of the density of states at $E = E_0$, the energy at which $|\nabla_{k}E_a(k)| = 0$.

These singularities should be reflected in the absorption coefficient, assuming $f(\omega)/n(\omega)$ is slowly varying over the energy range of interest, allowing a comparison of the density of states with the experimental absorption spectrum.

A technique for determining the density of states due to Gilat and Raubenheimer (1966) was used in the present calculation. In this method, a cubic mesh is constructed in $k$-space and both the magnitude and the gradient of the energy bands are calculated at these points. Within a small cube centered at each of the mesh points, the surfaces of constant energy are assumed to be planes normal to the gradient of the energy band at the center of the cube. Equation 103, with the surface integral restricted to the area of the constant energy plane lying within this cube, is then used to find the density of states in this cube. The total density of states is obtained from a sum over all such cubes. The only assumption in this technique is that any eigenvalue can be obtained by a linear interpolation within one of the cubes. The corresponding assumption in the usual histogram sampling technique is that the eigenvalues within a cube can be approximated by a constant. The difference in assumptions indicates clearly why the Gilat-Raubenheimer method is superior. For the calculations
performed here, the gradient at each point was determined by using an interpolation scheme involving neighboring points. The $x$-component of the energy gradient at the point $(k_x, k_y, k_z)$, for example, was determined from

$$\frac{d}{dk_x}E(k_x, k_y, k_z) = \frac{E(k_x+\Delta, k_y, k_z) - E(k_x-\Delta, k_y, k_z)}{2\Delta}$$

where $\Delta$ is the distance between points in the cubic $k$-space mesh. Given the magnitude and gradient of the energy bands at the points of the mesh, all formulae necessary for the calculation are given by Gilat and Raubenheimer (1966).

The densities of states calculated\(^1\) are shown in Figs. 18, 19, and 20. The density of states of Fig. 18 are those determined from the initial adjusted bands with the first set of radii (the bands of Fig. 11); those of Fig. 19, from the self-consistent bands (the bands of Fig. 16); and those of Fig. 20, from the bands obtained by using the self consistent potential inside the spheres and adjusting the potential outside the spheres (the bands of Fig. 17). Because of the similarity of the initial adjusted bands with the second set of radii (the bands of Fig. 12) to the adjusted self consistent bands, the density of states was not calculated for this case. It is adequately represented by Fig. 20.

---

\(^1\)The number of points of the cubic $k$-space mesh lying in or on the 1/48 irreducible zone was 110 in these calculations.
Fig. 18. The interband density of states corresponding to the bands of Fig. 11
Fig. 19. The interband density of states corresponding to the bands of Fig. 16
Fig. 20. The interband density of states corresponding to the bands of Fig. 17.
B. Results and Discussion

The most prominent feature of the calculation of the band structure of NaCl presented thus far is that a reasonable value of the band gap was not obtained without an empirical adjustment of the muffin tin potential outside the spheres. For the case where the form of the self-consistent potential was used inside the spheres, for example, it was necessary to increase the outer potential from -0.396 Ryd to -0.021 Ryd, a change of 0.375 Ryd, in order to bring the calculated value of the band gap, originally 6.0 eV into agreement with the experimented value of 8.6 eV. Some explanation of the origin of discrepancies of this magnitude must be given before any reasonable interpretation or indication of merit of the results can be given. What we intend to argue is that the problem is that of an improper treatment of exchange and that the technique of adjusting the potential outside the spheres leads to physically meaningful results.

We observe first of all that an effect of this magnitude is not caused by simple numerical inaccuracies such as round-off problems or lack of convergence but must be due to the neglect or mistreatment of some important physical phenomenon or interaction. Also the self consistent technique employed is not the problem since the band gaps obtained from the initial, unadjusted SFI potentials, prior to the use of the muffin tin charge density approximation, were too small. The most
suspect of the fundamental approximations made in the calculation are the neglect of polarization effects, the use of the muffin tin potential, and the use of the Slater exchange approximation.

The neglect of polarization effects would not seem to be the immediate difficulty. As emphasized by Fowler (1966), the value of the band gap obtained by a calculation in which the Hartree-Fock approximation is employed and further in which the electrons and holes are assumed to be in Bloch states, i.e. a calculation in which polarization is neglected, should always be greater than the observed value. In the present calculation, the calculated value is, of course, too small if the potential is not adjusted. Further, deviations of the muffin tin potential from the actual potential do not cause errors of the magnitude considered here. DeCicco (1967) has shown for KCl that the eigenvalues were changed by 0.01 Ryd or less when the deviations of the potential from its muffin tin approximation were included as a perturbation. As the deviations of the potentials in NaCl are the same order of magnitude, a few tenths of a Rydberg, as those in KCl, the bands of NaCl should be in error by about the same amount as in KCl because of the muffin tin approximation. This error is, however, an order of magnitude less than the difference between the calculated gap and the observed gap and we can therefore exclude the muffin tin approximation as the source of difficulty with the calculated band gap.
By process of elimination, then, we conclude that the reason that the calculated band gap is too small when the potential is unadjusted is that the exchange interaction has been treated improperly. That is the Slater exchange interaction has been used rather than the Hartree-Fock exchange interaction.

Support for this conjecture can be found in the literature where the results of calculations of the bands of other insulators indicate that whenever the Slater exchange approximation is used, the majority of cases, the calculated value of the band gap is too small. For example, the calculated bands gaps of KCl (DeCicco 1967), KI (Onodera et al. 1966), AgCl and AgBr (Scop 1965), Ar (Mattheiss 1964) and NaCl (Kunz 1967b) were all either too small or were fitted to the experimental value in the same manner as that of the present calculation. The common feature of all of the calculations was the use of the Slater exchange approximation. The NaCl calculation of Kunz was performed using the orthogonalized plane wave method in which the muffin tin potential approximation was not employed which supports the earlier remark that the muffin tin potential is not the reason for the discrepancy.

On the other hand, the optical band gap of KCl calculated by Oyama and Miyakawa (1966), not employing the Slater exchange approximation, was larger than the observed value. In this calculation, an effective potential was constructed using the
ground state wave functions obtained by Howland (1958) from the actual Hartree-Fock exchange interaction. Further Tolpygo and Tomasevich (1960) found that the bottom of the conduction band of NaCl was lowered several electron volts when the free ion Hartree-Fock exchange used in their calculation was replaced by the Slater exchange. These authors do not indicate the effect of this replacement upon the optical band gap, but, since the present calculation indicates that the conduction bands are considerably more sensitive to changes in the potential than the valence bands, we can assume that the band gap was decreased. In subsequent work, the Russians (see references cited in Chapter I) using the free ion Hartree-Fock exchange energy obtain values of the band gap which are several electron volts larger than the observed value.

Thus, although the number of calculations employing a close approximation to the Hartree-Fock exchange with which we can compare results is limited, it does appear that the use of the Slater exchange causes the calculated band gap to be too small and that a better approximation to the Hartree-Fock exchange would yield a larger band gap.

The importance of the exchange interaction in the present calculation can, further, be seen in Figs. 8 and 9 where the SFI potential and the exchange contribution to this potential are shown. In the region near the APW sphere edges and in the region outside the spheres, the major contribution to the
potential, 70 to 90 per cent of the total, is that of the exchange interaction. Thus the effect of altering the potential outside the spheres, an alteration to which the band gap is quite sensitive, is equivalent to altering the exchange interaction in this region. Further, Tolpygo and Tomasevich (1960) found in NaCl that the Slater exchange was larger in magnitude than the Hartree-Fock exchange. Since the Slater exchange potential is always negative, we would expect in the present calculation that a more reasonable approximation to the Hartree-Fock exchange, and thus a better calculated band gap, would be obtained by reducing the absolute magnitude of the exchange potential. This is effectively done in the present calculation by treating the potential outside the spheres as a parameter. When fitting the calculated gap to the observed gap, it was always necessary to decrease the absolute magnitude of the potential outside the sphere which is the same as decreasing the absolute value of the exchange in this region.

Thus, if we have in fact overestimated the exchange potential, the adjustment of the muffin tin potential should correct for this to a large extent with the net result that the bands obtained by the fitting process are a reasonable approximation to the actual bands of NaCl. This technique does not, of course, correct the exchange interaction inside the spheres, but the exchange in this region is to some degree less important due to the increased contributions of the nuclear and
electronic electrostatic potentials. It does seem more reasonable in future work to use the Kohn-Sham exchange approximation discussed in Section B, Chapter II rather than the full Slater exchange approximation employed here.

In light of the preceding remarks the discussion of the results necessarily cannot be of an absolute nature. The approach to the discussion will be to look for those qualitative and quantitative features which are relatively insensitive to the various parameters used in the calculation. However, even this limited approach leads to useful and significant results.

Let us first discuss the self-consistent calculation. The initial SFI, spherically averaged, and the final, self consistent charge densities, shown in Fig. 14 differ only slightly. The total charges inside the APW spheres of radii \( R(\text{Na}) = 1.12 \text{\AA} \) and \( R(\text{Cl}) = 1.67 \text{\AA} \), the set used in the self consistent calculation, were \( Q(\text{Na}) = 10.01 \) and \( Q(\text{Cl}) = 17.41 \) initially and \( Q(\text{Na}) = 9.99 \) and \( Q(\text{Cl}) = 17.49 \) finally. The net effect of the self-consistent calculation upon the charge density has been to transfer about 0.08 electrons from the region outside the APW spheres into the chlorine sphere, primarily into the long tail of the chlorine sphere distribution between \( r = 1.0 \text{ a.u.} \) and the sphere edge. This transfer of charge can be explained qualitatively by visualizing the potential about each site as that of the Madelung shifted free ion potentials. Since the potential of an electron about the chlorine site is lowered
relative to the free chlorine ion potential and to the potential near the sodium site by this Madelung shift, there will be a tendency for charge to build up about the chlorine site relative to a superposition of the free ion charge densities. The total amount of charge transferred is however small.

This small, if not negligible, transfer of charge is reflected in the potential. The initial and final potentials, compared in Fig. 15, differ inside the spheres by a nearly constant amount, about 0.3 Ryd near the nuclei and about 0.2 Ryd near the APW radii. This constant shift is not unexpected because of the replacement of the true charge density by the muffin tin charge density with the corresponding loss of the zero of energy when calculating the potential using the Ewald technique discussed in Section D of Chapter II. Allowing for this constant shift, then, the difference in potentials inside the spheres due to the rearrangement of charge is less than 0.1 Ryd.

If the final potential both inside and outside the spheres is shifted downwards in energy by about 0.2 Ryd, bringing the initial and final potentials inside the spheres into near agreement, the final potential outside the spheres is about -0.6 Ryd. This latter value for the final potential outside the spheres corresponds closely to the average value of the initial SFI potential outside the spheres, as judged qualitatively from Figs. 8 and 9, but is considerably less than the
empirical value of \( V_o = -0.134 \) used for the initial potential. Recall that this latter value was chosen so that the calculated value of the band gap of the initial potential agreed with the observed value. The primary effect of the self-consistent calculation upon the potential has thus been to negate the adjustment made in the initial potential. In retrospect, this is quite reasonable. As we have remarked, this adjustment in the initial potential was equivalent to an alteration of the Slater exchange potential. However, when constructing potentials in the self-consistent process at any step beyond the first, the full Slater exchange approximation was used. The self-consistent process then simply "corrected" the poor approximation to the exchange energy. Presumably, then, had a value of \( V_o \) closer to the average value of the SFI potential outside the spheres been chosen initially, the self-consistent process would have converged more rapidly.

Since the initial charge density and unadjusted SFI potential are quite similar to the final charge density and potential, we can conclude here that, given the Slater exchange approximation, the potential and charge density obtained from a superposition of free ions are a good approximation to the self-consistent potential and charge density. This has the important consequence that there is little advantage to be gained by the tedious self-consistent calculation. This will be true in particular until the potentials used in the
calculations are improved upon significantly by the inclusion of polarization effects for example.

In view of the fact that the optical gap obtained is too small, the quantitative significance of the bands obtained from the self-consistent potential is somewhat suspect. Qualitatively, however, all of the band structures obtained under various conditions are quite similar. We note, for example, that the order of the bands in each instance is the same. For this reason, we shall discuss those features of bands which are common to all first, and then indicate the significant differences.

The lowest set of three bands (six including spin degeneracy) shown in Figs. 11, 12, 16 and 17 are the uppermost normally filled valence bands corresponding to the free chlorine ion 3P shell. The total width of this set of bands is 1.1 eV for those determined from the adjusted potentials and 1.5 eV for those from the self-consistent potential. The difference in total widths for these two cases can be explained by noting the similarity between the muffin tin potential and the Kronig-Penny square well model of a lattice (Kittel 1956). In this model as the barrier height between the wells is increased, the bands become more narrow. Similarly, as the value of the muffin tin potential between the spheres is decreased (equivalent to increasing the square well barrier) the P-bands under consideration become more narrow. Both of these widths are in
agreement with those of NaCl found by Kunz (1967a) using the
tightbinding method. Kunz found widths of 0.8 eV or 1.6 eV
depending on the extent to which the overlap of the atomic
orbitals centered at different sites was treated. The overall
shape of these valence bands is quite similar to the corre­
sponding bands of KCl and KI found by DeCicco (1967) and
Onodera et al. (1966) respectively who also used a muffin tin
potential, but differ somewhat from those of NaCl found by
Kunz (1967a) and from those of various other alkali halides
obtained by the tightbinding method (Kunz 1966, Kunz and Van
Sciver 1966, Howland 1958, Kucher and Tolpygo 1961). In par­
ticular the maximum of the valence band is found at the center
of the Brillouin zone when the muffin tin potential is used
and, generally, along the (110) axis when the tightbinding
method is used. Kunz (1967a) does not calculate the bands
along the (110) axis for NaCl, but does find that the energy
at L is greater than at Γ. Whether the muffin tin results are
more correct than the tightbinding results is an open ques­
tion. On one hand, the destruction of the local cubic symme­
try of the crystal potential by the muffin tin approximation
is always suspect and should have some effect on the shape
of the bands although DeCicco (1967) finds this to be a small
effect typically 0.01 Ryd. On the other hand, the tightbind­
ing method has serious convergence problems because the
atomic orbitals used in the tightbinding Bloch sum are not a
complete set of states for the crystal. For example, when
Howland (1958) included $K^+3S$, $K^+3P$, and $Cl^-3S$ atomic orbitals
in addition to the $Cl^-3P$ orbitals, the width of the uppermost
valence bands of KCl decreased by a factor of two with a corres­
donning alteration in the shape of the bands. Further, the
difference between the energy band maximum and the energy at $\Gamma$
was decreased when the number of orbitals was increased. If
additional orbitals were included, e.g. excited states, this
difference might become even smaller resulting in closer agree­
ment of the tightbinding and muffin tin techniques. Regardless
of this, however, the energy of the maximum along the (110)
axis or of the point L is typically only a few hundredths of a
Rydberg greater than energy at the center of the zone in the
tightbinding calculations and is probably within the inherent
error of either technique. Within these limits, the present
calculation and the others are in substantial agreement.

The complex of bands above the normally filled valence
bands and with minimum at $\Gamma_1$ are the normally empty conduction
bands. In each of the four band structures presented in Figs.
11, 12, 16 and 17, the conduction band structure may be thought
of in terms of two different bands, or sets of bands, differing
in orbital character. The first band originating from $\Gamma_1$
at the center of the zone and of overall width of about 2 eV is
an s-like band corresponding to a mixture of the free sodium
ion $3S$ state and the free chlorine ion $4S$ state. Referring to
Table 2, we see that there is a strong mixing of states of other orbital, primarily d states, so that referring to this band as s-like is not strictly correct. For purposes of discussion we shall however continue to do so. As an example of the character of an electron in this band, the spherically averaged radial charge density inside the APW spheres of an electron in the state $\Gamma_1$ is shown in Fig. 21. The wave function has been normalized to one electron per unit cell. The nodal characteristics of the free ion 3S function in the sodium sphere and 4S function in the chlorine sphere is easily seen in this figure. Oyama and Miyakawa (1966) have calculated the corresponding quantities for KCl and find similar results but, of course, with the K$^+4$S state in place of the Na$^+3$S state. They find further that inside spheres of radii equal to one-half the nearest neighbor distance, that the ratio of charge inside the chlorine sphere to the charge inside the potassium is about 1.6. The corresponding ratio in NaCl, from Table 2, is 2.2. That these two are different is reasonable in view of the fact that the volume of the sodium sphere in NaCl is less than the volume of the potassium sphere in KCl. However it does appear that the character of the lowest conduction band in NaCl is determined primarily by the chlorine ion in the sense that the charge of an electron in this band is associated more with the chlorine site than the sodium site.

Above the s-like band is a set of five bands originating at the triply degenerate point $\Gamma_{25}$, and at the doubly
Fig. 21. Radial charge density of an electron in the state $\Gamma$. The results are normalized to one electron per unit cell
degenerate point $\Gamma_{12}$ at the center of the zone and of overall width of about 6 eV. Referring to Table 2, these bands at the points $\Gamma_{25}$, and $\Gamma_{12}$ are d-like and are associated with the chlorine ion. Again at other points near the edge of the zone these bands may take on orbital character other than the d-type (Bell 1954). For example, at the point $L_2$, the state is a mixture of sodium s and chlorine p. At $X_3$, the lowest point of these d-bands along the principle $\Gamma-L$, $\Gamma-X$, $\Gamma-K$ symmetry axes, however the character is chlorine d-like. Because of the dominance of the chlorine d orbital, we shall refer to this set of bands as the chlorine d bands.

Qualitatively, then, the four band structures presented in Figs. 11, 12, 16 and 17 are similar and consist of a filled Cl3P valence band and an s-like conduction band followed by a d-like conduction band. Quantitatively, however, there are significant differences between these bands.

Let us first compare the self-consistent bands of Fig. 16 with the bands of Fig. 17, those obtained by retaining the self-consistent potential inside the spheres and adjusting the potential outside until the observed band gap was obtained. We are thus studying the effect of the potential outside the spheres upon the band structure. As observed earlier, the valence bands have become more narrow and have shifted slightly upwards in energy as a result of increasing the potential outside the spheres. The alteration of valence bands is, however, considerably smaller than that of the conduction bands. To
lowest order, the conduction bands, especially the s-band, have simply been translated upwards in energy by a few tenths of a Rydberg, the amount required to bring the calculated gap into agreement with the experimental gap. To next order, significant quantitative alterations of the bands have occurred. We note, for example that the $\Gamma_{12}$ to $\Gamma_{25'}$ separation has decreased from 0.19 Ryd to 0.11 Ryd and the $\Gamma_{25'}$ to $X_3$ separation has decreased from 0.21 Ryd to 0.16 Ryd as a result of increasing the potential outside the spheres. That is, the width of the d-bands decreased just as the width of the lower lying p-like decreased. Also the spacing between the points $X_3$ and $X_1$ has increased. In general, although the relative spacing of the conduction bands may have changed by as much as 0.5 Ryd, the ordering of all of the bands has remained unchanged. The primary result of the increase of potential outside the spheres has been to increase the separation between the s-like conduction band and the p-valence band, and in turn, the separation of the d-like conduction band and the s-like conduction band.

If the "adjusted self-consistent" bands are compared with the SFI bands of Fig. 12, the bands from the adjusted SFI potential with the second set of radii, we see that these two sets of bands are the same to within about 0.01 Ryd, aside from an overall constant shift in energy. This was to be expected as a result of the self-consistent calculation. Recall
that aside from a constant shift the initial SFI potential and the final self-consistent potential inside the spheres were nearly equal. The empirical adjustment outside the spheres causes the two potentials to be nearly the same throughout the unit cell. The two calculated band structures should then be similar.

If the band structure of Fig. 12 is now compared with the band structure of Fig. 11, those obtained from the adjusted SFI potential with the first set of radii, the results of using different radii sets can be compared. Again we see that the band structures are quite similar, except that the s-band for the set with the first set of radii is narrower along the Γ-X axis and broader along the Γ-L axis than those with the second set of radii and that the d-bands are more energetic by a few hundredths of a Ryd. The net result of making the radii more equal has been to increase the separation of the d and s conduction bands. The increase of energy of the d-band can be explained by recalling that the wave function (or charge density) of an electron in this particular band is greatest inside the chlorine site and outside the spheres. The amount of charge inside the sodium spheres is quite small. Thus when the radius of the chlorine ion is reduced, the situation when going from Fig. 12 to Fig. 11, the average potential which an electron near the chlorine site senses is increased and its energy will increase. It should be pointed out that many of these changes
in bands when different radii are used are, fundamentally, related to the model potential used. That is, had it not been necessary to correct for the exchange by adjusting the potential outside the spheres, the change in potential when crossing the sphere boundary would have been less abrupt and the shifts in the d-bands, for example, when the radii are changed would have been smaller. Regardless of this, however, we see that quantitative changes in the band structures of the order of 0.05 Ryd can occur simply by changing the radii when using this model potential. This should also be true in other calculations employing this model potential, e.g. those of Onodera et al. (1966) and Scop (1965).

There are only two calculations of any of the conduction band structure of NaCl known to the author with which the results of this calculation can be compared. The first is that of the Russians (Tolpygo and Tomasevich 1960, Evseev and Tolpygo 1963, Evseev 1964) who investigated only the s-like band in any detail, employing techniques similar to the tight-binding method. They found an overall width of about 4 eV for this band which is considerably larger than the value of about 2 eV found in the present calculation. They assume in their calculation that the first conduction band can be determined solely from a combination of two s-type wave functions corresponding to the Na^3S and Cl^4S functions. Near the edges of the Brillouin zone, this assumption is invalid due to the mixing
of higher orbital types. Had they used states of higher orbital symmetry in addition to the s-functions in their calculation, the band width presumably would have been smaller. On the other hand near the center of the zone, i.e. near \( \Gamma_1 \), their assumption should be reasonable and the results of their calculation agree with those of the present calculation as judged by the effective band masses calculated. The Russians find an effective band mass \( m^* = 0.624 \), defined by
\[
E = E_{\Gamma_1} + \frac{k^2}{m^*},
\]
which agrees well with \( m^* = 0.63 \) found in the present calculation from the bands determined from the adjusted potentials.

The second calculation is that of Kunz (1967b) who calculated the energy eigenvalues of NaCl at the symmetry points \( \Gamma \) and \( X \) using the orthogonalized plane wave method. The results of Kunz' calculation clearly disagree in certain details with the present calculation. In particular he finds the ordering of the eigenvalues of the conduction bands at \( \Gamma \) to be \( \Gamma_1, \Gamma_2, \ldots \) \( \Gamma_2', \Gamma_{12} \) and at \( X \) to be \( \chi_3, \chi_1, \chi_4, \chi_5 \), whereas, in the present calculation, the ordering is \( \chi_1, \chi_2, \chi_3, \chi_4, \chi_5, \chi_0, \chi_2, \chi_3 \), respectively. The essential differences are that he finds the f-like state \( \Gamma_2 \) to be lower than the d-like state \( \Gamma_{12} \) and that the order of the s-d-like states \( \chi_1 \) and \( \chi_3 \) is the opposite of that in the present calculation. Kunz does not give many details of his calculation and consequently it is difficult to determine just why his results are different.
As we shall see, there is some experimental evidence that the ordering of the $X_1$ and $X_3$ states determined here is correct.

The optical absorption spectrum of NaCl at $T = 10^0\text{K}$ (Teegarden and Baldini 1967) is shown in Fig. 22 along with the reflectivities at normal incidence at $T = 55^0\text{K}$ (Baldini and Bosacchi 1968) and $T = 150^0\text{K}$ (Hartman et al. 1957). These are the quantities with which the results of the calculation, the density of states in particular, shall be compared. The reflectivity at normal incidence is given by (Stern 1963)

$$R(\omega) = \frac{(1-n(\omega))^2 + k^2(\omega)}{(1+n(\omega))^2 + k^2(\omega)}$$

where $n(\omega)$ and $k(\omega)$ are the real and imaginary parts, respectively, of the complex index of refraction. $R(\omega)$ is thus not directly proportional to the absorption coefficient, $\alpha(\omega) = 2k\omega/c$, and thus not directly proportional to the density of states. However as the absorption becomes large ($k(\omega)\to\infty$), the reflectivity also becomes large ($R(\omega)\to1$) and we expect a correspondence between the peaks of the absorption and reflection spectra. As seen in Fig. 22, these spectra are qualitatively quite similar in form. We shall therefore use the reflectivity as a qualitative extension of the dates beyond 11 eV, the end of existing absorption data.

The dominant feature of these data is the sharp doublet at about 8 eV. This has long been attributed to the formation of exciton states associated with the interband $\Gamma_{15}$ to $\Gamma_1$
Fig. 22. Absorption and reflection spectra of NaCl (a) is the reflection spectrum at normal incidence at $T = 150^\circ K$ (Hartman et al. 1957), (b) the reflection spectrum at $T = 55^\circ K$ (Baldini and Bosacchi 1965) and (c) the absorption spectrum at $T = 10^\circ K$ (Teegarden and Baldini 1967)
transitions. The occurrence of two peaks is readily explained by the fact that the hole band at $\Gamma_{15}$ is split into two bands, one singly degenerate and the other doubly degenerate, by the spin orbit interaction which has been neglected in the present calculation. These exciton lines will of course not be reflected in the interband density of states.

For energies greater than those of these exciton peaks, the spectra have the relatively unstructured form characteristic of interband transitions. The broad shoulder at 8.6 eV is generally assumed to be due to the onset of interband transitions (Taft and Philipp 1957). This was of course assumed to be the case when fitting the calculated band gap. It should be mentioned that this assignment may be in error by a few tenths of an electron volt. In the heavier alkali halides, RbI especially, additional, weak exciton lines corresponding to the $n = 2$ states of the Wannier model have been detected in the leading edge of this shoulder (Teegarden and Baldini 1967, Baldini and Bosacchi 1968). These lines have not been clearly resolved in NaCl but may be resolved in future higher resolution, lower temperature experiments in which case the above value for the onset of interband transitions will be too small. In any event, the above assignment will not be in error by more than a few tenths of an electron volt. Beyond the onset of interband transitions, the only pronounced features are the broad peaks or shoulders at 10.2, 11.3 and 12.4 eV. This lack
of structure causes the comparison of our results to the data to be rather difficult.

Let us now consider the density of states shown in Fig. 18.

This is the density of states of the bands of Fig. 11, obtained from the adjusted SFI potential with the first set of radii. In this case there exists a very pronounced structure with strong peaks at 10.7, 11.3 and 11.9 eV. The first peak is associated with transitions from points near \( X_5 \), in the valence band to the relatively flat band structure along the \( A \) axis (\( \Gamma-X \)) near \( X_1 \) in the first conduction band. The second peak, similarly, is associated with \( X_4 \), to \( X_1 \) transitions enhanced by \( L_3 \), to \( L_1 \) transitions on the low energy side. The third peak is due to transitions from the uppermost valence band along the \( \Sigma \) axis (\( \Gamma-K \)) to the lowest conduction band near the symmetry point \( K \), i.e. \( \Sigma_4-\Sigma_1 \) transitions. It should be mentioned that there is a broad plateau in the lowest conduction band at an off symmetry point near \( W \) in the Brillouin zone. This plateau gives rise to a large interband density of states enhancing the second and third peaks. For energies greater than 12 eV, the density of states becomes more complex because of the complex band structure near \( K \) and because of the onset of transitions to the \( d \)-band, \( X_5-X_2 \). A few of the more significant transitions are indicated on the figure.

Since we are considering transitions from \( p \)-like states in the valence band to \( s \) and \( d \) like states in the conduction
bands, transitions associated with the first three peaks in this density of states are electric-dipole allowed. It is very tempting then to associate these strong peaks with the corresponding peaks in the optical data. That is, to assign the calculated $X_5^-X_1^+$ transitions at 10.7 eV to the observed peak at 10.2 eV, the $L_3^-L_1$ and $X_4^-X_1^+$ transitions at 11.3 eV to the peak at 11.3 eV, and the $\Sigma_4^-\Sigma_1$ transitions at 11.9 eV to the peak at 12.4 eV. If this is done the agreement is rather good. However within these tolerances an equally reasonable assignment can be made by again assigning the $X_5^-X_1^+$ transitions to the first peak, but by assigning both the $X_4^-X_1^+$, $L_3^-L_1$ and $\Sigma_4^-\Sigma_1$ peaks to the broad peak at 11.3 eV. The third experimental peak at 12.4 eV is then accounted for by the large density of states between 12.5 and 13.0 eV arising from $X_5^-X_3^+$, $\Sigma_3^-\Sigma_1$ and $\Sigma_1^-\Sigma_1$ transitions among others. However, because of the sensitivity of the bands, and thus the density of states, to the parameters used in the calculation both of these sets of assignments are doubtful.

Let us consider the density of states shown in Fig. 20. The associated bands are those of Fig. 17, obtained from the adjusted self consistent potential, which are quite similar to those of Fig. 12, obtained from the adjusted SFI potential with the second set of radii. We are thus studying the effect of the APW radii upon the density of states. The density of states in this case increases much more uniformly than in the preceding and a definite peak structure is barely resolvable.
This is the case because the separation of the d- and s-like bands is smaller in this case than in the former and also because small alterations in the shapes of the bands have occurred. The \(X_5^-X_1\) peak has shifted upwards in energy to 11.2 eV and the \(X_4^-X_1\) peak to 11.8 eV where it is barely resolvable from the \(\Sigma_4^-\Sigma_1\) transitions among others as shown in the figure. The \(L_2^-L_1\) transitions have decreased in energy and now enhance the \(X_5^-X_1\) peak rather than the \(X_4^-X_1\) peak as in the previous situation. Because of the lack of definite structure and the general shift upwards in energy of the transitions to \(X_1\), the task of assigning transitions to peaks in the dates is considerably worsened. Simply on the order of their occurrence, we might assign the \(L_2^-L_1\) transitions to the first experimental peak, \(X_5^-X_1\) to the second, and the complex near 12 eV to the third.

Let us now consider the density of states shown in Fig. 19, that of the self consistent bands of Fig. 11. There is of course little to recommend this particular set of bands and density of states since the optical gap is too small, but by comparing this situation with that just preceding an indication of the effect of adjusting the potential outside the spheres upon the density of states can be obtained. First, the separation of the \(L_2^-L_1\) and \(X_5^-X_1\) peaks has increased. Also the \(X_4^-X_1\) peak is more energetic than and is now resolvable from the \(\Sigma_4^-\Sigma_1, L_2^-L_1, X_5^-X_3\) complex. Both of the peaks associated
with transitions to $X_\perp$ have broadened considerably, reflecting the less flat nature of the bands along the $\Delta$ axis near $X_\perp$. Assignments of transitions to experimental peaks will not be attempted in this case. We note however that if the energy scale were shifted by 2.5 eV corresponding to a rigid translation of the conduction bands upwards in energy, the assignment would be the same as in the case of the adjusted self consistent bands.

In summary, then, because of the sensitivity of the bands to the parameters used in the calculation, the transitions responsible for the structure in the optical data cannot be definitely assigned. However, primarily because of the presence of pronounced structure, the density of states of Fig. 18 would seem to yield the best agreement with experiment of the three sets of densities of states calculated. As noted earlier, this particular density of states has peaks at 10.7, 11.3, and 11.9 eV which are to be compared with the experimental peaks at 10.2, 11.3, and 12.4 eV. Although the agreement is reasonable, there are sizeable differences between the calculated and experimental peaks. We note in particular that the energy of the first peak in the density of states curve occurs at a somewhat greater energy than the first shoulder in the optical data. It is not inconceivable, however, that with a slightly different choice of parameters, radii in particular, the agreement would have been considerably better. To
illustrate this point let us once again compare the densities of states and consider the influence of the APW sphere radii upon the positions of the transition peaks. As we progress from the situation of Fig. 20 to that of Fig. 18, the sodium sphere radius is increased and the chlorine sphere radius is decreased. As a result of this alteration of the radii, the position of the peak associated with the $X'_2$-$X'_1$ transitions has lowered in energy from 11.2 to 10.7 eV. If the change in the radii were to continue, i.e. a further increase of the sodium radius and decrease of the chlorine radius, the position of this peak would probably continue to decrease in energy bringing it into closer agreement with the experimental value. Similarly the energies of the $X'_4$-$X'_1$ transitions would decrease by about the same amount as the $X'_2$-$X'_1$ transitions. Further, the $\Sigma'_4$-$\Sigma'_1$ transitions, as evidenced by Figs. 20 and 18, would remained fixed at about 11.9 eV. The $X'_2$-$X'_3$ transitions (to the d band) would continue to increase in energy as would the relatively weak $L'_2$-$L'_1$ and $L'_2$-$L'_1$ transitions.

The net result of all of these alterations could then be strong peaks or shoulders at 10.2 eV ($X'_5$-$X'_1$ transitions), 10.8 eV ($X'_4$-$X'_1$ transitions), 11.9 eV ($\Sigma'_4$-$\Sigma'_1$ transitions) and 13.0 eV ($X'_5$-$X'_3$ transitions), with the relatively weak $L'_3$-$L'_1$ and $L'_2$-$L'_1$ transitions possibly enhancing one or two of these peaks. The precise figures are of course speculative but seem to represent a reasonable extrapolation of Figs. 20 and 18.
Comparing these figures with the data of Fig. 22, we see that the agreement in this case would be quite good.

A linear extrapolation of the radii associated with to Figs. 20 and 18 indicate that the APW radii appropriate to the speculative situation just discussed would be about $R_1 \sim R_2 \sim 1.4\AA$, values which are not too unreasonable. Whether or not this approach is valid is another question. Within the framework of a model potential it is valid. We simply adjust the parameters until agreement with experiment is obtained. Physically, the necessary changes in the potential can be attributed to alterations of the exchange interaction.

Regardless of this, however, it does seem reasonable to conclude on the basis of the work here that the transitions from the p-like valence band to the s-like conduction band are responsible for the absorption in the energy range 8.5 to 12 eV. Further, the onset of transitions to the d-band, $X_5^-, X_3^-$, should occur only beyond 12 eV. Also in the range of 10 to 12 eV, most of the detailed structure is due to the transitions $X_5^-, X_1^-, X_4^-, X_1^-, L_3^-, L_1^-$ and those $\Sigma_4-\Sigma_1$ transitions near the symmetry point $K$.

Let us now compare the conduction band structure of NaCl with those of the potassium halides. The conduction bands of KCl, for example, calculated by DeCicco (1967) are shown in Fig. 23 along with the NaCl bands obtained from the adjusted SPI potential with the second set of radii. For ease of
Fig. 23. Comparison of the conduction bands of NaCl and KCl. (a) shows the conduction bands of NaCl and (b) shows those of KCl (DeCicco 1967)
comparison the energy is measured from the bottom of the bands, the point $\Gamma_1$, in both cases. The conduction band structures of KCl calculated by Oyama and Miyakawa (1966) and of KI calculated by Onodera et al. (1966) are quite similar to those of DeCicco especially with regard to the discussion presented below. We see that, as in the case of NaCl, there is an s-like band at $\Gamma_1$ and a set of d-like bands at $\Gamma_{12}$ and $\Gamma_{25'}$. The d-bands however are much lower in energy in KCl than in NaCl and in fact overlap the s band along the $\Gamma$-X axis and form a second parabolic minimum at $X_2$.

That the d-bands in KCl are lower than those in NaCl is quite reasonable in view of the fact that the separation of the 4S and 3D levels in atomic potassium is less than the separation of the 3S and 3D levels in atomic sodium. Further since the 5S-4D separation in atomic rubidium is somewhat smaller than the corresponding separation in potassium, we can generalize and conclude that the conduction band structure in the rubidium halides will be much like that of the potassium halides except that the d-bands will be somewhat lower in energy.

If we now compare the absorption spectra of the sodium halides on one hand and the potassium and rubidium halides on the other we see that there is a noticeable difference in the spectra of these materials. This difference is readily apparent in Fig. 24 where the absorption spectra of NaCl and KCl are
Fig. 24. Comparison of the absorption spectra of NaCl and KCl (Teegarden and Baldini 1967)
shown. In the case of NaCl as we have seen the absorption is relatively unstructured for several electron volts after the onset of $\Gamma_{15}$ to $\Gamma_1$ interband transitions. On the other hand, about one electron volt after the onset of interband transitions, there appears a second set of exciton peaks in the case of KCl. This second set of peaks occurs in all of the other potassium and rubidium halides, actually splitting into three distinct peaks for the bromides and iodides, but does not appear in the spectrum of the sodium halides. Baldini and Bosacchi (1968), elaborating on a suggestion by Onodera et al. (1966), have proposed that this second structure in the potassium and rubidium halides is due to the formation of excitons from electron states near the second relative parabolic minimum in the conduction band structure of these materials at the point $X_3$ and from hole states near the parabolic minima in the p-type valence bands at $X$. This proposal seems quite reasonable on empirical grounds. That is, excitons are known to be formed from electron states near parabolic minima in the conduction bands, e.g. those associated with the $\Gamma_1$ minimum in the alkali halides. Further, optical transitions between the hole (p type) and electron (d type) states are allowed.

From the experimental viewpoint this is also reasonable. We see from DeCicco's KCl bands that the point $X_3$ lies about 0.1 Ryd or about 1.4 eV above the $\Gamma_1$ point. The $X_3$ excitons should then be about 1.4 eV above the $\Gamma_1$ excitons which is the
observed magnitude in KCl. Also since the d-bands are lower
in the Rb halides than in the K halides, the X excitons should
be lower in energy in the Rb halides than in the K halides.
Again this is observed.

The critical test of any model proposed for this general
exciton structure is that it must somehow account for the fact
that this exciton structure does not appear in the sodium
halides. In particular if this second parabolic relative mini­
mum occurred at \( X_3 \) in the sodium halides, there is no clear
reason why this exciton structure should not be detected in the
sodium as well as the potassium and rubidium halides. As we
have seen however in the present calculation the point \( X_3 \) is
always above the point \( X_1 \) in NaCl. Thus, even if exciton
states were formed at \( X_3 \) in NaCl, they would be degenerate with
the large number of conduction states in the neighborhood of
\( X_1 \) in the first conduction band. We can conclude then that the
conduction band structure calculated here is in good agreement
with the proposal of Baldini and Bosacchi.
IV. SUMMARY

On the basis of this investigation into the electronic properties of NaCl, it may be concluded that significant improvements upon the approximations made in constructing the one-electron potential must be obtained before any advantage or enhanced accuracy is to be gained by a formally self consistent calculation in the alkali halides. Given the Slater exchange approximation, it was found that the self consistent or final charge density of NaCl is adequately approximated by the charge density obtained by a superposition of the closed shell, free ion charge densities of the constituent sodium and chlorine ions. That is, the energy band structure obtained from the final or self consistent charge density and the energy band structure of the initial superimposed free ion charge density differed from each other by much less than their mutual disagreement with experiment, as judged by a comparison of the optical band gap with the experimental band gap. Further, the results indicate that the Slater exchange approximation may have overestimated the effect of exchange to a considerable degree, especially in the region outside the APW spheres. The empirical adjustments in the potential necessary to bring the calculated results into near agreement with experimental results could be explained by an assumed reduction in the exchange potential. It is therefore suggested that in future work, the Kohn-Sham or reduced Slater exchange interaction
might be used as a better approximation to the exchange interaction. This point should, however, be investigated in greater detail. It should also be pointed out that, at such a time when formal self consistency becomes the major limitation to the accuracy of a band calculation in the alkali halides, the self consistent technique used in this calculation and other calculations at the present time should be investigated in greater detail. That is, as has been pointed out, the replacement of the crystalline charge density by its muffin tin approximation introduced a constant shift of the potential outside the spheres relative to the potential inside the spheres. This approximation is necessary at the present time in order to make the self consistent calculation manageable from a practical viewpoint. This relative shift has been estimated to be small in the present calculation, but in just those situations where self consistency may be of greatest concern, that is in situations where the crystalline charge density differs considerably from that obtained from a superposition of free ions, the error introduced by this approximation may be significant.

With respect to NaCl in particular, this calculation shows that the conduction band structure consists of a set of d-like bands more energetic than and overlapping little with an s-like band which is the lowest conduction band. By a comparison of the calculated interband densities of states with
the experimental and absorption spectra of NaCl, it can be concluded that the structure in the absorption spectra from about 8.5 eV to 12 eV is due to the transitions from the uppermost filled valence band to the lowest, or s-like, conduction band. The onset of transitions to the more energetic d-bands should occur only beyond 12 eV. It is further proposed that the structure is the spectra at 10.2, 10.8, 11.9, and 13.0 eV is due to the transitions $X_5^- - X_1^-$, $X_4^- - X_1^-$, $\Sigma_4^- - \Sigma_1^-$ and $X_5^- - X_3^-$ respectively with some of this structure possibly enhanced by transitions near L.

Finally the general qualitative structure of the bands, in particular near X, lends support to the recent proposals that the excitonic structure appearing after the onset of interband transitions in the alkali halides other than the sodium halides is due to the formation of exciton states near X. In the potassium and rubidium halides the d-band overlaps the s-band near X and forms a second relative parabolic minimum. It is proposed that the higher exciton states are formed near this minimum. The non-appearance of these exciton states in the sodium halides is explained by the results of this calculation which show that this second, d-band minimum does not appear in NaCl and presumably, the other sodium halides.
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VII. APPENDIX

The normalization condition is

\[ l = N \sqrt{\frac{d^3 r}{\Omega_o}} \sum_{ij} C_i C_j e^{ik j \cdot r} \]  

(A.1)

which using Equations 47, 55 and 56 may be written

\[ l = \frac{1}{\Omega_o} \sum_{ij} C_i C_j e^{ik j \cdot r} \]

(A.2)

The integral over the outer region (I), \( I_o(k, \alpha) \) is given by

\[ I_o(k, \alpha) = \int \frac{d^3 r}{\Omega_o} \sum_{ij} C_i C_j e^{ik j \cdot r} \]

\[ = \sum_{ij} \int \frac{d^3 r}{\Omega_o} \sum_{v} C_i C_j e^{ik j \cdot r} \]

\[ - \sum_{v} \int \frac{d^3 r}{\Omega_o} \sum_{ij} C_i C_j e^{ik j \cdot r} \]

\[ = \sum_{ij} C_i C_j \left\{ \delta_{ij} - \sum_{v} \frac{4\pi e^{ik j \cdot \hat{r}_v} j \Omega(k_{ij} \cdot \hat{r}_v)}{k_{ij}} \right\} \]  

(A.3)

The integral over the vth sphere, \( I_v(k, \alpha) \) is given by
\[ I_{\nu}(k,\alpha) = \sum_{ij} C_i C_j \sum_{lm} A_{\nu m}^i(v, k_i, E) A_{\nu m}^j(v, k_j, E) \]

\[ = \int_0^R \int \frac{r^2}{r^2} R^\nu(r, E) R^\nu(r, E) \, dr \, d\nu \, d\nu \]

where the orthogonality of the spherical harmonics has been used in the angular integration. The integrand \( I_{\nu}(k,\alpha, r, \nu) \) is defined for later convenience.

Now \( R^\nu(r, E) \) satisfies Equation 54. If we take two such equations, one with energy \( E_1 \), the other with energy \( E_2 \), multiply these equations by \( R^\nu(r, E_1) \) and \( R^\nu(r, E_2) \) respectively, and subtract the two equations we obtain

\[ \frac{R^\nu(r, E_1)}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} R^\nu(r, E_1) \right) + \frac{R^\nu(r, E_2)}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} R^\nu(r, E_2) \right) \]

\[ = R^\nu(r, E_1) R^\nu(r, E_2) (E_1 - E_2) \]

Integrating with respect to \( r \) and simplifying we obtain

\[ \int_0^R \frac{d}{dr} \left( r^2 R^\nu(r, E_1) R^\nu(r, E_2) \right) \]

\[ = \frac{1}{E_1 - E_2} \left[ r^2 R^\nu(r, E_1) \frac{d}{dr} R^\nu(r, E_2) - r^2 R^\nu(r, E_2) \frac{d}{dr} R^\nu(r, E_1) \right] \]

Taking the limit as \( E_1 \rightarrow E_2 = E \), we obtain

\[ \int_0^R \frac{d}{dr} \left[ R^\nu(r, E) \right]^2 = - \left( R^\nu(R^\nu, E) \right)^2 \frac{d}{dr} \left[ \frac{d}{dr} \ln R^\nu(r, E) \right] \]

\[ (A.7) \]
Using the form of $A_{\mathbf{m}}(\nu, \mathbf{k}_i, E)$ given in Equation 55 and the

\[ \sum_{m=-2}^{2} Y_{m}^{*} (\mathbf{k}_i) Y_{m} (\mathbf{k}_j) = \frac{2\mathbf{R}+1}{4\pi} P_{\mathbf{R}} \left( \frac{\mathbf{k}_i \cdot \mathbf{k}_j}{\mathbf{k}_i \mathbf{k}_j} \right) \]  

(A.8)

we have

\[ I_{\nu} (\mathbf{k}, \alpha) = -4\pi R_{\nu}^{2} \sum_{ij} \mathbf{C}_{i} \mathbf{C}_{j} e^{\frac{i\mathbf{k}_i \cdot \mathbf{R}_{\nu}}{\mathbf{k}_i}} \]

\[ \chi \left( \frac{2\mathbf{R}+1}{4\pi} J_{\alpha} (k_{i} R_{\nu}) J_{\alpha} (k_{j} R_{\nu}) P_{\mathbf{R}} \left( \frac{\mathbf{k}_i \cdot \mathbf{k}_j}{\mathbf{k}_i \mathbf{k}_j} \right) \right) \]

\[ \chi = \frac{\partial}{\partial E_{\alpha}} \left[ \frac{d}{dr_{\nu}} \ln R_{\nu}^{\nu} (r_{\nu}, E_{\alpha}) \right]_{r_{\nu}=R_{\nu}} \]  

(A.9)

The normalization equation then is

\[ l = \sum_{ij} \mathbf{C}_{i} \mathbf{C}_{j} \left\{ \delta_{ij} - \sum_{\nu} \frac{4\pi R_{\nu}^{2}}{\Omega_{0}} e^{\frac{i\mathbf{k}_i \cdot \mathbf{R}_{\nu}}{\mathbf{k}_i}} \right\} \left( \frac{J_{\alpha} (k_{i} R_{\nu})}{\mathbf{k}_i} \right) \]

\[ \chi \left( \frac{2\mathbf{R}+1}{4\pi} J_{\alpha} (k_{i} R_{\nu}) J_{\alpha} (k_{j} R_{\nu}) P_{\mathbf{R}} \left( \frac{\mathbf{k}_i \cdot \mathbf{k}_j}{\mathbf{k}_i \mathbf{k}_j} \right) \right) \]

\[ \chi = \frac{\partial}{\partial E_{\alpha}} \left[ \frac{d}{dr_{\nu}} \ln R_{\nu}^{\nu} (r_{\nu}, E_{\alpha}) \right]_{r_{\nu}=R_{\nu}} \]  

(A.10)

The muffin tin charge density outside the spheres, $\rho_{o}$, is

given by

\[ \rho_{o} = \int \frac{d^{3} r}{2} \sum_{\mathbf{k}_{\alpha}} \psi_{\mathbf{k}_{\alpha}}^{*} (\mathbf{r}) \psi_{\mathbf{k}_{\alpha}} (\mathbf{r}) \left/ \left\{ \Omega_{0} - \frac{4\pi}{3} R_{1}^{3} - \frac{4\pi}{3} R_{2}^{3} \right\} \right. \]

\[ = \frac{2}{N} \sum_{\mathbf{k}_{\alpha}} I_{o} (\mathbf{k}, \alpha) \left/ \left\{ \Omega_{0} - \frac{4\pi}{3} R_{1}^{3} - \frac{4\pi}{3} R_{2}^{3} \right\} \right. \]  

(A.11)

where $I_{o} (\mathbf{k}, \alpha)$ is given by Equation A.3 with the $\mathbf{C}_{i}$'s properly normalized. Similarly the muffin tin charge density inside the $\nu$th sphere, $\rho_{\nu} (r_{\nu})$ is given by
\[ \rho_v(r_v) = \int \frac{d\Omega}{4\pi} 2 \sum_{k\alpha} \psi^*_\alpha(x_v) \psi_\alpha(x_v) \]
\[ = \frac{2}{4\pi} \frac{1}{N} \sum_{k\alpha} I_v(k,\alpha, r_v) \quad \text{(A.12)} \]

where \( I_v(k,\alpha, r_v) \) is the integrand defined in Equation A.4.

The total charge in the \( v \)th sphere \( Q_v \) is
\[ Q_v = 4\pi \int_0^R dr_v r_v^2 \rho_v(r_v) \]
\[ = \frac{2}{4\pi} \frac{1}{N} \sum_{k\alpha} I_v(k,\alpha). \quad \text{(A.13)} \]

where \( I_v(k,\alpha) \) is given by Equation A.9.