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SELF-CONSISTENT CALCULATIONS OF THE ELECTRONIC ENERGY BAND STRUCTURE OF Mg₂Si

by

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1. INTRODUCTION

1.1 Historical Sketch of Band Calculations

The fundamental concept underlying the band theory of solids is the independent particle model of a crystal (IPM) (e.g. see Kurtzelnigg, 1964) which pictures a single electron to be in the static average field of the remaining electrons and nuclei. The IPM provides a conceptually simple framework for qualitative and quantitative interpretation of the electronic properties of crystalline materials.

Pippard (1960) reviews experimental methods which may be used to study the electronic structure of metals in terms of the IPM.

The calculations of the IPM electronic energy levels or band structure involves two problems. The IPM potential must be determined and the IPM Schroedinger equation must be solved. In later sections both of these problems will be discussed in detail. The various methods which have been devised to solve the IPM Schroedinger equation, the calculation of the IPM potential, and descriptions and results of a number of band calculations are reviewed by Herman (1958) and Pincherle (1960).

The original methods for solving the IPM Schroedinger equation have been refined and generalized, but have not been essentially changed. The lack of high speed computational devices necessitated ad hoc calculations of the IPM potential in the early band calculations. The calculation of the band structure of aluminum by Heine (1955) is regarded as the first serious attempt to solve the IPM self-consistently.

Ideally a band structure should be a set of electronic energy levels corresponding to self-consistent solutions of an IPM Schroedinger equation.
derived from the many-electron Hamiltonian. The usual Hartree-Fock (HF) equations are an IPM of this ideal variety. However, self-consistent solutions of the HF equations are extremely difficult to obtain. The principal difficulty is in the treatment of the HF exchange operator. In practice the HF exchange operator is replaced by an approximation which can be treated simply and accurately. In the few cases where a serious attempt has been made to approximate the actual HF exchange operator (e.g. see Phillips, 1962) the effect has been to destroy agreement with experiment. This deficiency in the HF-IPM is attributed to the neglect of correlation or many-electron effects. Some questionable techniques have been used to "correct" IPM approximations for correlation (Pines, 1963, p. 85).

Despite the fact that the theoretical foundation for the IPM is not particularly strong, considerable success as measured by agreement with experiment has been obtained. Physical intuition must be given much of the credit. A notably successful IPM has been the augmented plane wave method (APW) which was invented by Slater (1937). The APW-IPM potential is composed of spherically symmetric potentials within spheres centered about the atomic nuclei and constant potentials outside the spheres. Loucks (1965) derived a relativistic version of the APW-IPM. The orthogonalized plane wave method (Herring, 1940), assuming the convergence of the OPW expansion, provides a more flexible representation of the wave-function than does APW as it places less restriction on the potential and lends itself well to iterative schemes. The OPW method formulated as a pseudopotential (Austin, 1962) has been applied extensively (e.g. see Harrison, 1963).
1.2 Purpose of This Work and Summary of Presentation

The primary objective of this work is to calculate from first principles the electronic energy levels for a non-relativistic IPM based on a well-defined model of the many-electron system. To accomplish this objective it is essential that the coulomb interaction be treated consistently at all phases of calculation.

In Section II.1 a model of the crystal is defined which is essentially the periodic extension of a finite crystal. The assumption is made throughout that nuclei are fixed at their equilibrium sites. The coulomb potential is expressed as an expansion in plane waves consistent with the periodicity of the model. Alternative equivalent expressions of the coulomb potential are obtained with the aid of identities. In this way the coulomb interaction is treated consistently in terms of the basic plane wave expansion.

Ideally the results for an IPM based on a realistic model of the crystal should be in substantial agreement with experiment. However, in previous attempts to calculate electronic energy levels for the Hartree-Fock IPM including the Hartree-Fock exchange operator, the results have been disastrous as measured by agreement with experiment. The contributing factor is generally believed to be the lack of screening of the exchange term in the Hartree-Fock model. This reflects an inadequacy on the part of the Hartree-Fock exchange operator to correlate the motion of the electrons. In Section II.2 several IPMs are proposed. The first is the usual Hartree-Fock IPM. Two other models are proposed which are based on well-defined models of the many-electron system, but which impose
limitations on the effectiveness of the Hartree-Fock exchange operator. The remaining terms of the Hartree-Fock operator are the same in all models.

In Section 11.3 the treatment of symmetry in crystal applications is presented in anticipation of the self-consistent formulation of a band calculation. The LCAO and OPW methods are defined and briefly discussed. The treatment of exchange for the models mentioned above is discussed.

In Section III.2 is presented the formulation of the self-consistent calculation of the electron energy bands for the semiconducting Mg$_2$Si.

The results for the Mg$_2$Si calculations are presented in Section III.3 and compared with experiment in Section III.4.

Finally, in Part IV the theory and calculations are discussed and evaluated.
II. MANY-ELECTRON THEORY

11.1 Basic Concepts and Techniques

11.1.1 The extended crystal model

An ideal crystal may be defined with respect to a lattice of points in space. Let \( \{ \mathbf{a}_i \} \), \( i = 1, 2, 3 \), be a set of linearly independent 'primitive' vectors. A lattice is the set of points \( \{ \mathbf{R}(m) \} \) where

\[
\mathbf{m} = (m_1, m_2, m_3) \quad \text{and} \quad \mathbf{R}(m) = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3 .
\]

The components of \( \mathbf{m} \) are natural numbers (+/- integers). The set of points \( \{ \mathbf{K}(m) \} \),

\[
\mathbf{K}(m) = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 ,
\]

where \( \{ \mathbf{b}_i = 2\pi \Omega^{-1} \sum_{j,k} \mathbf{a}_j \mathbf{a}_k \} \), \( i = 1, 2, 3 \), \( \Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \mathbf{a}_3 \) has the property that

\[
\mathbf{K}(m) \cdot \mathbf{R}(n) = 2\pi \mathbf{m} \cdot \mathbf{n} .
\]

The lattice formed by the set of points \( \mathbf{K}(m) \) is said to be reciprocal to the lattice formed by the set of points \( \mathbf{R}(m) \). The latter will be referred to as the lattice or space lattice and the former will be designated the reciprocal lattice. The three families of parallel planes,

\[
\mathbf{b}_i \cdot \mathbf{r} = 2\pi h, \quad i = 1, 2, 3 ,
\]

where \( h \) is a natural number partition the space such that the basic volume element or elementary cell is a parallelepiped of volume \( \Omega \).

A finite crystal is considered to occupy a parallelepiped in space whose edges are \( N_1 \mathbf{a}_1, N_2 \mathbf{a}_2 \) and \( N_3 \mathbf{a}_3 \). Consider \( \{ \mathbf{A}_i = N_i \mathbf{a}_i \} \), \( i = 1, 2, 3 \), to be
"Primitive" finite crystal vectors in the same sense that the \( \mathbf{a}_i \) above are primitive vectors. The finite crystal lattice is the set of points \( \{ \mathbf{R}_c(m) \} \),

\[
\mathbf{R}_c(m) = m_1 \mathbf{A}_1 + m_2 \mathbf{A}_2 + m_3 \mathbf{A}_3 .
\]

1.1.5

The vectors \( \mathbf{R}_c \) will be called finite crystal lattice vectors. The volume of the finite crystal is \( \Omega_1 = \mathbf{A}_1 \cdot \mathbf{A}_2 \cdot \mathbf{A}_3 \).

The finite crystal consists of nuclei and atoms which are confined within the finite crystal volume. The structure of the finite crystal is defined by specifying the equilibrium location and species of nuclei within a prototype elementary cell. Each elementary cell of the finite crystal contains nuclei of the same elements in the same relative positions as in every other cell. The nuclei are treated as point particles which are fixed at their equilibrium positions. The number of electrons in the finite crystal is such that the crystal as a whole is electrically neutral. Since the primitive vectors of simple compounds are of the order of \( 5 \times 10^{-8} \text{ cm} \) the primitive finite crystal lattice vectors must have \( N \), of the order \( 10^6 - 10^8 \) if the volume of the ideal crystal is to correspond to the typical real crystal.

The charge density\(^1\) of the finite ideal crystal is given by

\[
p(x) = \rho_n(x) + \rho_e(x)
\]

1.1.6a

where the nuclear charge density is

\[
\rho_n(x) = \sum_{m,s} Z_s \rho(x - \mathbf{R}(m,s))
\]

1.1.6b

---

\(^1\)All equations are written in atomic units (e.g. see Hartree, 1957)) except that energy units are in Rydbergs. One Rydberg equals one half atomic unit of energy. (1 Ry = .5 a.u. = 13.605 ev.)
and the electronic charge density is

$$\rho_e(x) = - \sum_i \rho(x - \mathbf{x}_i) \quad (1.1.6c)$$

The point vector $\mathbf{R}(m, s)$ specifies the location of a nucleus $s$ with charge $Z_s$ relative to the lattice point $\mathbf{R}(m)$. The point vector $\mathbf{X}_i$ specifies the position of an electron in the finite crystal.

$$\mathbf{R}(m, s) = \mathbf{R}(m) - \mathbf{R}_s \quad (1.1.7)$$

The electrostatic potential $\varphi(x)$ is related to the charge density by Poisson's equation,

$$-\nabla^2 \varphi(x) = 4\pi \rho(x) \quad (1.1.8)$$

In the absence of external sources the solution of Equation 1.1.8 that vanishes at large distances is

$$\varphi(x) = \sum_{m, s} \frac{2Z_s}{r_{m, s}} - \sum_i \frac{2}{r_i} \quad (1.1.9)$$

where $r_{m, s} = x - \mathbf{R}(m, s)$ and $r_i = x - \mathbf{x}_i$. The potential energy $V_e$ due to the interaction of electrons with the nuclear and electronic charges is

$$V_e = \int \varphi(x) \rho_e(x) \, dx \quad (1.1.10)$$

The many-electron Hamiltonian for the finite crystal is obtained by removing the divergent electron-electron self-energy terms from the potential energy and adding to this terms representing the kinetic energy of the electrons.

$$H_e = \sum_i -v_i^2 - \sum_{i, m, s} \frac{2Z_s}{r_{m, s}} + \sum_{i \neq j} \frac{1}{r_{ij}} \quad (1.1.11)$$
A factor of 1/2 has been included in the electron-electron interaction term so that these contributions to the energy are not counted twice.

The exclusion principle which was first postulated by Pauli (1925) requires that the many-electron wave function be antisymmetric with respect to the interchange of any two electron coordinate indices.

The Hartree-Fock equations constitute an IPM in which the many-electron wave function is approximated by a single anti-symmetrized product of linearly independent one-electron functions. The solution of the Hartree-Fock equations for the idealized finite crystal involves about $10^{20}$ simultaneous integro-differential equations which must be solved self-consistently. Except in the case of special geometries there does not appear to be any additional symmetry to exploit.

Since the problem as originally formulated is completely intractable, the obvious thing to do is to simplify the problem in such a way that the physical features which are considered most important are adequately represented by a further idealization of the problem. Probably, the two most obvious approaches are these. Firstly, the boundaries of the crystal may be extended indefinitely. In this way the periodicity which is characteristic of all crystals is manifested by the Hamiltonian. Secondly, the finite crystal may be decreased in size until it is just a big molecule. For example, let the crystal boundary vector be 8 lattice spacings instead of $10^8$ lattice spacings. Neither of these approaches is particularly satisfactory. Historically, the approach has been to postulate a periodic (Born-Von Karman, 1912) boundary condition on the Hartree-Fock one-electron functions. The one-electron functions are required to be invariant with respect to translations by finite crystal lattice vectors. The resulting
Hartree-Fock Hamiltonian subject to certain restrictions regarding wave functions which transform according to degenerate representations of the space group are invariant with respect to all transformations of the space group.

To require that the one-electron functions be periodic seems to be a very drastic condition. The obvious implication is that the finite crystal has been periodically extended. Of course, this has been recognized and is the basis for much of theory of the electron gas. However, it is not at all clear that the Hartree-Fock equations derived from the finite crystal model can be used interchangeably with those derived from the periodic extension of this model. In subsequent sections this problem will be investigated in detail from a point of view which considers a many-electron model as fundamental.

The periodically extended finite crystal or extended crystal model (ECM) is an infinite crystal. The ECM crystal is defined with respect to the finite crystal lattice (Equation 1,1.5). The prototype elementary cell or ECM cell is the finite crystal. Each ECM cell in the extended crystal is required to be identical in every respect to the prototype ECM cell. The nuclear charge distribution is periodic in space with periods \( a_i \), \( i=1,2,3 \), and the electron charge distribution is periodic in space with periods \( A_i \), \( i=1,2,3 \). The many-electron wave function is required to be periodic in space with periods \( A_i \), \( i=1,2,3 \). Expectation values of operators are averaged over an ECM cell.

The many-electron analogue to the Born-Von Karman boundary conditions would be the condition that the many-electron wave function be periodic in
the finite crystal lattice. If this approach were taken, the resulting Hartree-Fock 1PM equations would be identical to the Hartree-Fock 1PM which results when Born-Von Karman boundary conditions are imposed on the one-electron functions in the finite crystal Hartree-Fock equations. The ECM is formulated directly in terms of the charge densities because the many-electron Hamiltonian is to be formulated from periodic charge densities. In most situations the Hartree-Fock equations formulated from the ECM many-electron Hamiltonian and the finite crystal Hartree-Fock equations with Born-Von Karman boundary conditions are essentially the same and give identical results. However, in the case of exchange between plane waves, the ECM equations are well-defined and the other is not.

Since the ECM is periodically extended through all space, the model must ignore any surface effects which might occur in a finite crystal. However, the bulk properties should be quite well represented in the ECM.

In applications of the ECM it may be necessary to require the ECM period to be as small as possible. The finiteness of the ECM period will be emphasized in the theoretical discussion.

11.1.2 General symmetry considerations

By the crystal structure we mean the set of positions of nuclei of the several elements in the ECM. These positions are specified by point vectors relative to some arbitrary origin of coordinates. A linear transformation on the nuclear coordinates which transforms the crystal structure into itself is called a symmetry transformation. The set of all such symmetry transformations constitute the space group of the crystal.
All transformations which translate the lattice by a lattice vector transform the crystal structure into itself. The set of all transformation of the crystal structure by lattice vectors forms an Abelian subgroup of the space group of the crystal called the translation group.

In addition to the translation group the space group also may contain elements which correspond to rotations about special points in the lattice called symmetry points. The most general form that a symmetry transformation can have is shown in Equation 1.2.1

\[ g \vec{x} = \theta \vec{x} + R(m) + \vec{\tau} = \{\theta \mid R(m) + \vec{\tau}\} \vec{x} \quad 1.2.1 \]

where \( g \) represents an element of the space group which operates on the coordinate \( \vec{x} \). The lattice is translated by a lattice vector \( R(m) \) and a non-primitive vector \( \vec{\tau} \) and rotated about a symmetry point. The rotation \( \theta \) may be improper. The magnitude of the non-primitive vector is required to be less than the magnitude of any lattice vector.

The ECM is defined such that points in space which are related by a finite crystal lattice vector are physically equivalent. Therefore, only a subset of the translation group need be considered. This may be formulated mathematically in terms of the following definition.

The relation, congruent modulo the finite crystal lattice \( (\Xi_{fc}) \), is defined on the elements of the translation group as follows:

for each pair of transformations by a lattice vector \( R(m) \), \( R(m') \)

\[ R(m) \equiv_{fc} R(m') \text{ if and only if } R(m) = R(m') + R_c(n) \]

1 e.g. see Koster (1957).

2 The congruence relation defined here is analogous to the definition of the congruence relation on the set of integers, e.g. see (Johnson, 1953, p. 65).
for some vector $\mathbf{R}^n$ of the finite crystal lattice.

The relation $\Xi_{fc}$ is an equivalence relation. Therefore, the translation group is partitioned into equivalence sets by the relation $\Xi_{fc}$. The number of equivalence sets is finite and equal to $N_o$, the number of lattice points contained in one ECM cell. Since each transformation in an equivalence set transforms the lattice to a physically equivalent point in the extended crystal, only a representative element of each equivalence set need be considered in discussing the transformation properties of the ECM. In this sense we will refer to the translation group as a finite group with the understanding that each element is an infinite set of translations which are congruent modulo the finite crystal lattice.

The systematic treatment of symmetry by the theory of groups provides an invaluable aid in applications to the quantum mechanics of crystals.

The basic idea motivating the application of group theory to quantum mechanical problems may be stated simply in terms of the following results from quantum mechanics. Firstly, a time independent operator which commutes with the time independent Hamiltonian describing a quantum mechanical system is constant in time and is called a constant of the motion (Schiff, 1955, p. 138). Secondly, a set of mutually commuting operators (each operator commutes with every other operator in the set) possesses at least one eigenfunction which is simultaneously an eigenfunction for each operator in the set (Mandl, 1957, p. 79). Suppose there to be a set of operators which individually commute with the Hamiltonian of the system,
but not necessarily with one another, and form a group. The problem of obtaining a maximal set of commuting operators from the original set of operators is solved with the aid of the representation theory of groups. The ECM has been formulated in such a way that all groups which arise may be considered finite.

Let \( G = \{g\} \) be a finite group of order \( G^0 \). A set of linear transformations (matrices) on a vector space \( S \) which is homomorphic to \( G \) is called a representation of the group \( G \). The dimension of the vector space (the carrier space of the representation) is called the degree of the representation. Two representations \( \{U(g)\} \) and \( \{V(g)\} \) of \( G \) are said to be equivalent if there is a matrix \( M \) such that \( \{M U(g) M^{-1}\} = \{V(g)\} \).

A representation is said to be reducible if it leaves invariant a subspace \( S_1 \) contained in \( S \). The matrices of a reducible representation can be written in the form \( \begin{bmatrix} A & B \\ 0 & C \end{bmatrix} \) where \( A \) has the dimension of \( S_1 \). A matrix is fully reducible or decomposable if the representation leaves invariant two subspaces \( S_1 \) and \( S_2 \) where \( S = S_1 + S_2 \). In this case the matrices of the representation may be written in the form \( \begin{bmatrix} A & 0 \\ 0 & A_2 \end{bmatrix} \). All finite groups are decomposable. If a representation is not reducible it is said to be irreducible.

Suppose the operations of a group \( G \) to be defined on a coordinate \( r \). Consider a function \( f'_0(r) \). Let \( g f'_0(r) = f'_0(g^{-1} r) \). The set of functions \( g f'_0(r) \) formed in this way may be linearly dependent. Choose from the set a linearly independent set of functions to form a carrier space of dimension \( n = G^0 \). This space may be described by a row vector

\[
\begin{pmatrix} f'_0 \\ f'_1 \\ \vdots \\ f'_n \end{pmatrix}
\]

1.2.2
It follows from the construction of \( f' \) that

\[
g f' = f' D'(g) \tag{1.2.3}
\]

where \( D'(g) \) is an \( n \) by \( n \) matrix. The set of matrices constructed in this way form a representation of the group which in general will be reducible.

Suppose \( M \) to be a matrix which decomposes \( D'(g) \) into a direct sum of irreducible representations, \( D^a(g) + D^b(g) \ldots \) which corresponds to a new vector space \( f = f' M^{-1} \). It is evident that the new vector space is a direct sum of invariant vector spaces, \( f = f^a + f^b \ldots \), corresponding to the irreducible representations \( D^a(g) \), \ldots . The original vector space \( f' \) is related to the new vector space \( f \) by

\[
f' = f M \tag{1.2.4}
\]

The \( m \)-th component of \( f' \) may be expressed in terms of \( f \) as

\[
f'_m = f M_m = \sum_{a,j} f^a_j M(a,j)_m \tag{1.2.5}
\]

where \( f^a_j \) is the \( j \)-th component of the invariant subspace \( f^a_j \) which corresponds to the irreducible representation \( a \). The row index of the matrix \( M \) has been labeled to correspond to the labeling of the components of \( f \). Equation 1.2.5 has been formulated such that the sum over the invariant subspaces may contain several terms corresponding to equivalent irreducible representations. It is clear that we may choose \( M \) such that the equivalent irreducible representations which occur are identical. Also, since the group is finite \( M \) may be chosen such that all irreducible representations which occur consist of unitary matrices. Therefore, Equation 1.2.5 may be expressed as
where \( f_{ij}^a(m) = \sum_{a'} f_{ij}^{a'} M(a',j)m \) is summed over all symmetry species \( a' \) equivalent to \( a \). It follows that any function \( f_o \) on which the operations of the group are defined can be decomposed according to the irreducible representations of the group as

\[
 f_o = \sum_{a,j} f_{ij}^a. \tag{1.2.7}
\]

The functions \( f_{ij}^a \) of Equation 1.2.7 are called symmetry-adapted functions.

The effect of an operation \( g \) of a group \( G \) on a symmetry-adapted function \( f_{ij}^a \) is by definition

\[
g f_{ij}^a = \sum_i f_{ij}^{a} D_{ij}^a(g) \tag{1.2.8a}
\]

Thus,

\[
g f_o = \sum_{a,j} \sum_i f_{ij}^{a} D_{ij}^a(g). \tag{1.2.8b}
\]

By multiplying Equation 1.2.8b by \( D_{pq}^b(g^{-1}) \) and summing the resulting expression over the elements of the group we obtain

\[
\sum_g D_{pq}^b(g^{-1}) f_o = \sum_{a,j} \sum_i f_{ij}^{a} \left[ \sum_g D_{pq}^b(g^{-1}) D_{ij}^a(g) \right]. \tag{1.2.8c}
\]

The bracketed term in the right member of Equation 1.2.8c is simplified by the orthogonality relation,

\[
\sum_g D_{pq}^b(g^{-1}) D_{ij}^a(g) = \left( G^o / n_a \right) \delta_{p,j} \delta_{i,q} \delta_{a,b} \tag{1.2.9}
\]

where if \( a = b \), the irreducible representation matrices must be identical.

The degree of the irreducible representation \( a \) is \( n_a \). Therefore,
The operator defined by Equation 1.2.10 appears to be a projection operator since it selects from the function \( f_0 \) that component which transforms according to the \( q \)-th column of the irreducible representation \( b \). An examination of the properties of \( P_{pq}^b \) reveals that in general it is not a projection operator in the accepted sense.

Consider the effect of an operation \( g \) of the group on \( P_{pq}^b \),

\[
g P_{pq}^b = \sum_j D_{jq}^b (g) P_{pq}^b.
\]

Therefore, by comparison with Equation 1.2.8b the operators \( P_{pq}^b \) with index \( p \) fixed produce functions which when used as a carrier space reproduce the irreducible representation from which the operators were derived. The row index \( p \) of \( P_{pq}^b \) may be chosen to correspond to any row of the representation matrices \( D_{pq}^b (g) \). The product of two operators \( P_{pq}^b \) is

\[
P_{pq}^b P_{rs}^c = P_{rq}^b \delta_{p,s} \delta_{c,b}.
\]

The operators

\[
P_{mn}^a \equiv P_{mm}^a = (n_a/G^0) \sum_g D_{mm}^a (g^{-1}) g
\]

have the property that

\[
P_{mn}^a P_{n}^b = P_{mn} \delta_{n,n} \delta_{a,b}.
\]

The symmetry decomposition of a function \( f_0 \) (Equation 1.2.7) can be expressed in terms of the operators \( P_{mn}^a \) as
\[ f_0 = \sum_{a,m} p^a_m f_0 \quad 1.2.15 \]

A direct proof of Equation 1.2.15 follows immediately from the orthogonality relation for the characters,\(^1\)

\[ (c_k/G^0) \sum_a \chi^*_{j_k} \chi^a_k = \delta_{j,k} \quad 1.2.16a \]

where \(c_k\) is the number of elements in class \(k\). Equation 1.2.16a specializes to the case where \(k\) is the class of the identity \(E\), is

\[ G^{0-1} \sum_a n_a \chi^*_{j} = \delta_{E,j} \quad 1.2.16b \]

Therefore,

\[ \sum_{a,m} p^a_m = G^{0-1} \sum_g \sum_{a,m} n_a D^a_{mm}(g^{-1}) \quad g = E \quad 1.2.16c \]

Other resolutions of the identity should be possible for the operators \(p^b_{pq}\). However, except for the trivial case which is equivalent to Equation 1.2.16c it is not clear how this can be done.

The adjoint \(T^+\) of a linear operator \(T\) is defined by

\[ (T f_1, f_2) = (f_1, T^+ f_2) = \int f_1^* T^+ f_2 \, d\tau \quad 1.2.17 \]

where \(f_1\) and \(f_2\) are arbitrary functions which lie in the vector space for which the operator \(T\) is defined. The adjoint of an operator \(p^a_m\) is

\[ p^a_{m'} = p^a_m \quad 1.2.18 \]

Therefore, the operators \(p^a_m\) have the properties of projection operators,

\[ \chi^a_j = \sum_m D^a_{mm}(g_j) \text{ where } g_j \text{ is an element of the group and of the class } j. \]
\[ p_m^a p_n^b = p_m^a \delta_{m,n} \delta_{a,b} \text{ and } p_m^{\pm a} = p_m^a. \]

Consider the matrix element,

\[ (p_{m'}^a f_1, H p_{m'}^b f_2) = (f_1, H p_m^{a} f_2) \delta_{m,n} \delta_{a,b}, \quad 1.2.19a \]

where \( H \) is some operator which is invariant with respect to operations by elements of the group. The corresponding equation for the projection operators is

\[ (p_m^a f_1, H p_n^b f_2) = (f_1, H p_m^a f_2) \delta_{m,n} \delta_{a,b}, \quad 1.2.19b \]

The projection operators \( p_m^a \) constitute a maximal set of commuting operators formed from the elements of the group. Thus, the problem which was originally stated has been solved. However, a new problem has been raised. Is it preferable to form symmetry-adapted functions with the projection operators \( p_m^a \) or with the operators \( p_m^{a_m} (m' \text{ fixed})? \) In either case the symmetry-adapted functions are eigenfunctions of the projection operators and the quantum mechanical problem is solved in this respect.

If the operators \( p_m^{a_m} \) are used to form symmetry-adapted functions, then the treatment of degenerate representations is simplified. Equation 1.2.19a shows that matrix elements of a symmetry invariant operator computed for different columns of the irreducible representation are identical. (They are zero if \( p_m^a f_1 \) or \( p_m^a f_2 \) is zero.) Also, the transformation properties of symmetry-adapted functions defined in this way are well-defined (Equation 1.2.11). The carrier space can always be spanned by linearly independent functions formed with \( p_m^{a_m}, p_m^{b_m}, \text{ etc.} \)

On the other hand if the projection operators \( p_m^a \) are used to form
symmetry-adapted functions, then it is evident that the carrier space can be spanned by the symmetry-adapted functions. However, in general the irreducible representations of the group obtained from these functions will not be the same as the irreducible representations from which the projection operators were defined (Equation 1.2.11). In self-consistent calculations (the solutions of the Schrödinger equation are used to construct the Schrödinger equation) it is essential that the transformation properties of the solutions be known. Thus, the projection operators do not seem to be suitable for symmetry-adapting the basis functions.

Suppose the eigenfunctions of a symmetry invariant Hamiltonian operator to be approximated by a linear combination of the component functions of a carrier space of the group. The component functions may be chosen to be symmetry-adapted functions, formed either with the operators $p_{m'm}^a$ with $m'$ fixed for each irreducible representation $a$ or with the projection operators $p_{m}^a$ constructed from the same irreducible representation. In general the component functions will not be the same. In the absence of accidental degeneracy the eigenfunctions which result from a Rayleigh-Ritz variational calculation will be identical (within a phase factor). Since the transformation properties of the individual components of the eigenfunctions which are expressed as linear combinations of the symmetry-adapted functions formed with operators $p_{m'm}^a$ are known, the eigenfunctions expressed as linear combinations of either set of symmetry-adapted functions must transform in the same way (within a phase factor). Therefore, the eigenfunctions of a symmetry invariant Hamiltonian operator are symmetry-adapted functions which when used to form a carrier space
reproduce the irreducible representations (within a phase factor) from which their symmetry-adapted component functions were derived. Either the operators $P^a_{m'm}$ or $P^a_m$ may be used to form symmetry-adapted component functions.

As an example of the projection operator formalism we consider the translation group of the ECM. This is a finite group in the sense discussed previously. Since the ECM translation group is an Abelian group, all irreducible representations are one-dimensional. A carrier space is formed from any function which is unchanged by a translation of a finite crystal lattice vector. The plane waves, $PW, k(m)$ are an example of a complete set of orthonormal functions each of which forms a carrier space for the ECM translation group.

$$PW, k(m) = \Omega_i^{-1/2} \exp(ik(m) \cdot r)$$

where $\Omega_i$ is the volume of an ECM cell and the $k(m)$ are vectors which are reciprocal to the finite crystal lattice,

$$k(m) = m_1B_1 + m_2B_2 + m_3B_3 .$$

The primitive finite crystal reciprocal lattice vectors $B_i$, $i=1,2,3$, are

$$B_i = 2\pi \Omega_i^{-1} \epsilon_{ijk} A_j A_k .$$

If the ECM periods $N_i$, $i=1,2,3$, are taken to be $N = N_1 = N_2 = N_3$, then

$$B_i = 2\pi (N_0)^{-1} \epsilon_{ijk} a_j a_k .$$

A projection operator formed from a plane wave representation of the ECM translation group has the form
\[ P(k(m)) = N_o^{-1} \sum_n \exp[ik(m) \cdot R(n)] T(n) \]  \hspace{1cm} 1.2.23

where \( N_o \) is the order of the ECM translation group and \( T(n) \) represents a translation operator which corresponds to a transformation by a lattice vector \( R(n) \).

From Equation 1.1.3 it follows that the projection operator

\[ P(k(m) + K(m')) = P(k(m)) \]  \hspace{1cm} 1.2.24

where \( K(m') \) is any reciprocal lattice vector (Equation 1.1.2). Thus, in the sense of Equation 2.2.24 a periodicity has been induced in the reciprocal lattice of the crystal by the spatial periodicity required in the ECM. The irreducible representations of the ECM translation group are completely specified by the \( N_o \) inequivalent (in the sense of Equation 1.2.24) \( k \)-vectors contained in the region of \( k \)-space surrounding the origin \( (k=0) \) and bounded by the polyhedron (the first Brillouin zone) formed by the envelope of the planes \( 1/2K(m)^2 = k \cdot K(m) \) in \( k \)-space which are nearest the origin. The inequivalent \( k \)-vectors contained in the first Brillouin zone are called reduced \( k \)-vectors.

The projection operator for the ECM translation group (Equation 1.2.23) can also be written as

\[ P(k(m)) = \exp(ik(m) \cdot r) P_B(k(m), r) \]  \hspace{1cm} 1.2.25a

where

\[ P_B(k(m), r) = N_o^{-1} \sum_n \exp[ik(m) \cdot (R(n) - r)] T(n) \]  \hspace{1cm} 1.2.25b

The operator \( P_B \) has the property that
Therefore, any translation symmetry-adapted function can be written in the Bloch (1929) form,

\[ \tilde{\psi}_k(m) = \exp(ik(m) \cdot r) \psi_k(m), r \]  

1.2.27

where \( u(k(m), r) \) displays the periodicity of the lattice.

Consider the transformation of a Bloch function by the transformation \( g = \{ \theta | \tau \} \),

\[ g \tilde{\psi}_k(m) = \exp(ik(m') \cdot r) \psi_k'(m), r \]  

1.2.28a

where

\[ k(m') = \theta k(m) \]  

1.2.28b

and

\[ \psi_k'(m), r = \exp(-ik(m') \cdot r) g u(k(m), r) \]  

1.2.28c

Thus, the transformed Bloch function is a Bloch function which transforms according to the irreducible representation \( k(m') \) of the translation group.

Suppose \( \tilde{\psi}_k(m) \) to be an eigenfunction of a space group invariant Hamiltonian. Then the set of functions \( g \tilde{\psi}_k(m) = \tilde{\psi}_k'(m') \) for all transformations \( g \) contained in the group will also be eigenfunctions of the Hamiltonian with the same eigenvalue. If all the representations \( \{ k(m') \} \) are inequivalent, the reduced \( k \)-vectors \( k(m') \) are called general points. If the representations \( \{ k(m') \} \) may be decomposed into sets of equivalent representations, the reduced \( k \)-vectors \( k(m') \) are called special points or symmetry points in \( k \)-space. The set of operators
which transform a representation $k(m)$ into equivalent representations $k(m')$ form a group called the group of the reduced $k$-vector $k(m)$. An efficient treatment of special symmetry in terms of the projection operator formalism is described in Appendix A.

11.1.3 The crystal potential

The first step toward obtaining the ECM many-electron Hamiltonian is the derivation of the potential due to the ECM charge distribution. The procedure which was used to derive the potential in the case of the finite crystal does not apply to the ECM because the ECM charge distribution is of infinite extent and periodic.

The ECM potential $\varphi$ will be required to satisfy the following conditions:

\begin{align}
(1) \quad -\nabla^2 \varphi &= 8\pi \rho(r) \\
(2) \quad \varphi(r) &= \varphi(r + R_c(m)) \\
(3) \quad \int_{\Omega} \varphi(r) \, dr &= 0 .
\end{align}

The first condition requires $\varphi$ to be a solution of Poisson's equation. The second condition requires $\varphi$ to be periodic with respect to transformation by a finite crystal lattice vector. The last condition requires the average value of the potential over an ECM cell to be zero. The three conditions completely specify the potential.

Consider the finite crystal lattice with primitive vectors $\{A_i\}$ ($i=1,2,3$) and reciprocal lattice primitive vectors $\{B_i\}$ ($i=1,2,3$). Let the charge distribution in each ECM cell consist of a single delta-function charge density and a neutralizing uniform charge density.
\[ \rho(r) = \sum_m \left[ \delta(r - r_1 - R_c(m)) - \Omega_1^{-1} \right] \]  

1.3.2a

The expansion of the charge density in terms of plane waves (Equations 11.1.2.20, 21, 22) is

\[ \delta(r) = \sum_{m \neq 0} \Omega_1^{-1} \exp i k(m) \cdot (r - r_1) \]  

1.3.2b

where \( r_1 \) is the position vector of the point charge relative to a lattice site.

A particular solution of Poisson's equation for the charge density given by Equation 1.3.2b is

\[ \varphi(r_1) = \sum_{m \neq 0} \frac{8\pi (\Omega_1 k(m)^2)^{-1}}{2} \exp i k(m) \cdot (r - r_1) \]  

1.3.3

This potential satisfies the conditions of Equations 1.3.1. The ECM potential may be obtained by superposing contributions in the form of Equation 1.3.3 due to the point charges and neutralizing uniform charge contained in an ECM elementary cell. The particular solution based on the charge density of Equation 1.3.2a is

\[ \varphi(r_1) = \sum_m 2 r_1^{-1} + V_{BG} \]  

1.3.4

where \( R_c(m) \) is a crystal lattice vector and \( r_1 = r - r_1 - R_c(m) \). The term \( V_{BG} \) represents the potential due to the neutralizing uniform charge.

It may be represented by

\[ V_{BG} = -\Omega_1^{-1} 2 \int r_2^{-1} \, dr_2. \]  

1.3.5

It is evident that this is just the negative of the average value over the unit cell of the first term in Equation 1.3.4. Thus, Equations 1.3.1 are also satisfied by the potential of Equation 1.3.4.
Since the crystal is neutral the contributions to the potential from
the background charge will cancel when the contributions from the
nuclear and electronic charges are superposed to form the ECM potential.
The background charge has been introduced in this discussion so that
expressions for the potential satisfying the conditions of Equation 1.3.1
might be obtained for either nuclear or electronic charges. In this way
certain difficulties in the treatment of Hartree-Fock LPMs are anticipated
and avoided.

11.1.4 Lattice sums

In Section 11.1.3 alternative expressions were obtained for the
potential due to a periodic array of point charges neutralized by a
uniform background charge. Equation 1.3.4 has the form of a lattice
sum. $
\phi(r) = \sum_{m} 2 \pi r m^{-1} + V_{BG} 
$

It is impossible to evaluate directly the potential at a point from
Equation 1.3.4 or the alternative expression,

$\phi(r) = \sum_{m} 8\pi (\Omega_1 k(m)^2)^{-1} \exp(i k(m) \cdot (r-r_1)) 
$

This problem was solved by Ewald (1921). Ewald was able to rewrite
Equation 1.3.3 as a convergent sum in real space plus a convergent
sum in reciprocal space. A simpler derivation due to Ewald and Shockley
(Kittel, 1963, p. 571) which emphasizes the physical content of the Ewald
method is presented carefully by Slater and DeCicco (1963).

The following approach is a generalization of the Ewald scheme.
Consider the identity
where \( f_{sr}(a,r) \) is a function of the parameter \( a \) and variable \( r \). The only requirement that is placed on \( f_{sr} \) is that the Fourier transform of \( f_{sr}(a,r)/r \) be well-behaved and that the plane wave expansion,

\[
\sum_m 2 f_{sr}(a,r_{1m}) r_{1m}^{-1} = \sum_m c(a,k(m)) \exp(i k(m) \cdot (r - r_1)),
\]

be convergent. The plane wave expansion coefficients are

\[
c(a,k) = \int \exp(-ixk) 2 f_{sr}(a,x) x^{-1} \, dx.
\]

By inserting Equation 1.3.3 for \( \Phi(r) \) and Equation 1.4.2 for the sum of \( f_{sr} \) in the bracketed term in Equation 1.4.1 we obtain an expression for \( \Phi(r) \) which has the form of an Ewald lattice sum,

\[
\Phi(r) = \sum_m 2 f_{sr}(a,r_{1m}) r_{1m}^{-1} + C(a,0)
\]

\[
+ \sum_{m \neq 0} c(a,k(m)) \exp i k(m) \cdot (r - r_1)
\]

where

\[
C(a,0) = \lim_{k \to 0} c(a,k)
\]

and

\[
C(a,k) = 8\pi (\Omega_1 k^2)^{-1} - c(a,k)
\]

The Ewald result is recovered if we choose

\[
f_{sr}(a,r) = 1 - \text{erf}(ar) = \text{erfc}(ar) = 2\pi^{-1/2} \int_0^\infty \exp(-t^2) \, dt.
\]
The usefulness of a particular form of Equation 1.4.5a depends on the application for which it is intended. The efficacy of the Ewald method for calculating a periodic potential at a point is not questioned. In Table 1 are listed the relevant parameters for two choices of simple analytic functions $f_{sr}$ for which the convergence of both series in Equation 1.4.5a is improved appreciably over that of the original series (Equation 1.3.3). Evidently, there are very few simple functions which have this desirable property.

Table 1. Generalized lattice sum parameters

<table>
<thead>
<tr>
<th>$f_{sr}(a,r)$</th>
<th>$\Omega_i C(a,k)$</th>
<th>$\Omega_i C(a,0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{erfc}(ar) = \frac{2}{\pi} \int_{ar}^{\infty} e^{-t^2} dt)</td>
<td>(\frac{8\pi}{k^2} \exp\left(-\frac{k^2}{4a^2}\right))</td>
<td>(-2\pi/a^2)</td>
</tr>
<tr>
<td>(\exp(-ar))</td>
<td>(8\pi a^2/k^2(a+k^2))</td>
<td>(-8\pi/a^2)</td>
</tr>
</tbody>
</table>

By construction the potential in the form of Equation 1.4.5a is independent of the parameter $a$. The two examples listed in Table 1 have the property that for small values of the parameter $a$ the potential approaches the form of the potential of Equation 1.3.4 and for large values of the parameter $a$ the potential approaches the form of the potential of Equation 1.3.3.
11.2 Many-Electron Equations

11.2.1 The ECM many-electron Hamiltonian

Since each elementary cell of the many-electron crystal lattice has been constructed in the same way, the properties of the system are completely described in terms of a single ECM cell. The potential energy contribution to the many-electron Hamiltonian for a single ECM cell consists of the potential energy due to the interaction of the electrons in single cell with all the other charges, electronic and nuclear, in the extended crystal.

The many-electron Hamiltonian for a single ECM cell is

\[ H_e = \sum_i K_i + \sum_i H_i + \frac{1}{2} \sum_{i \neq j} H_{ij} \]  \hspace{1cm} 2.1.1a

where \( K_i \) represents the kinetic energy contribution

\[ K_i = -\frac{2}{\varphi_i^2} \]  \hspace{1cm} 2.1.1b

of electron \( i \), \( H_i \) represents the potential energy due to the interaction of electron \( i \) with the nuclear charges,

\[ H_i = -\varphi_n (r_i) \]  \hspace{1cm} 2.1.1c

\[ \varphi_n (r) = \sum_{m,s} Z_s \varphi (r - R(m,s)) \]  \hspace{1cm} 2.1.1d

where \( \varphi (r) \) is a form of the potential given by Equation 1.4.5a corresponding to a unit charge at \( R(m,s) = R_s + R(m) \) where \( R_s \) specifies the position of atom \( s \) relative to a lattice vector \( R(m) \). The potential energy due to electron-electron interactions is

\[ H_{ij} = \varphi (r_{ij}) \]  \hspace{1cm} 2.1.1e
The factor $1/2$ in Equation 2.1.1a assures that electron-electron potential energy contributions are not counted twice.

In addition to the symmetry due to the indistinguishability of the electrons which was discussed in the case of the finite crystal many-electron Hamiltonian (Section 11.1.1) the ECM many-electron Hamiltonian is invariant with respect to translations by a finite crystal lattice vector of an individual electron coordinate. Since the nuclear constituents are taken to be fixed at their equilibrium positions the nuclear term is invariant with respect to translations by a lattice vector of an individual electron coordinate.

11.2.2 The symmetry-extended crystal model

Although an IPM based on the ECM many-electron formulation represents an appreciable simplification relative to an IPM based on the finite crystal many-electron formulation, self-consistent ECM-IPM calculations have been done only for simplified models. We adopt the view that in developing an IPM, the approximations should be made in the many-electron theory before going to an IPM rather than in the IPM itself. The procedure will be to rewrite the electron-electron interaction terms of the many-electron Hamiltonian. The dominant terms are retained. IPMs based on the model suggested in this section and the model suggested in Section 11.2.3 differ only in their exchange terms from the ECM Hartree-Fock IPM. In this way we hope to account for correlation effects which are attributed to the long range character of the coulomb interaction (Pines, 1963, p. 85).

Consider the plane wave representation of the ECM electronic charge
density
\[ \rho_e(r) = \sum_i \sum_m \Omega_i^{-1} \exp \{ i \mathbf{k}(m) \cdot (r - r_i) \} . \] 2.2.1

This may be rewritten as
\[ \rho_e(r) = \rho_e^s(r) + \rho_e^f(r) \] 2.2.2a

where
\[ \rho_e^s(r) = P_o \rho_e(r) \] 2.2.2b

and
\[ \rho_e^f(r) = (1 - P_o) \rho_e(r) . \] 2.2.2c

The operator \( P_o \) is the projection operator for the \( k=0 \) plane wave representation of the ECM translation group (Equation 1.2.24). The charge density \( \rho_e^s \) is invariant with respect to ECM translation group transformations. The effect of \( P_o \) on the original charge density is to distribute the charge throughout the crystal. Each cell of the crystal lattice is electrically neutral when the electronic charge density is represented by \( \rho_e^s \). The remaining charge density averages to zero over an ECM cell. For this reason it is called the fluctuation charge density. This term may be quite small for the charge distributions which are realized in a crystal near equilibrium.

In terms of the charge density partition of Equation 2.2.2 the ECM many-electron Hamiltonian is
\[ H_e = \sum_i K_i + \sum_i H_i + \frac{1}{2} \sum_{i \neq j} H_{ij}^s + \frac{1}{2} \sum_{i \neq j} H_{ij}^f \] 2.2.3

where
The projection operator is considered to operate on either of the electronic coordinates. \( H_{ij} \) is given by Equation 2.1.1e.

No restriction has been placed on the location of the electrons within an ECM cell. Presumably, the charge distribution for a given state of the system should be a consequence of the theory and not a condition to be imposed on the theory. The most that one can hope to obtain from a theory that neglects the fluctuation potential (Equation 2.2.5) contributions is an approximation to the ground state of the many-electron system. The effect of the projection operator on the coulomb repulsion term \( H_{ij} \) is greatly to reduce the contribution of this term near the point \( r_{ij} = 0 \) and in doing this force the electrons to be distributed uniformly throughout the crystal. In this sense a measure of spatial correlation has been forced upon electron distribution. Apparently, the cost of neglecting the fluctuation term is to remove the possibility of retaining important correlation effects. The many-electron model in which the fluctuation potential is neglected will be called the symmetry-extended crystal model (SECM).

In Section 11.1.4 expressions were obtained for the coulomb interaction potential which might be interpreted as a resolution into short range interactions and long-range interactions. However, these forms provide little insight into the significance of the symmetrized coulomb

\[
H_{ij}^s = P_0 H_{ij} \hspace{2cm} 2.2.4
\]

and

\[
H_{ij}^f = (1 - P_0) H_{ij} \hspace{2cm} 2.2.5
\]

\( H_{ij} \) is given by Equation 2.1.1e.
interactions or the fluctuation potential.

It is instructive to rewrite the plane wave expansion of the coulomb potential (Equation 1.3.3) in a form which may be related to the partition described above. An expression equivalent to Equation 1.3.3 is

$$\varrho(r) = \sum_{m}^{BZ} \frac{8\pi \exp[i(K(m') + k(m)) \cdot r]}{\Omega_{i}[K(m') + k(m)]^2}$$  \hspace{1cm} 2.2.6

where the sum on \( m \) includes only reduced \( k \)-vectors. The prime on this sum indicates that the term \( m'=0 \) is excluded if \( m=0 \). Equation 2.2.6 may be rewritten with the aid of the identity

$$\frac{1}{K + k} = \frac{1}{K^2} + \left[ \frac{K^2/(K + k)^2 - 1}{K^2} \right]$$  \hspace{1cm} 2.2.7

as

$$\varrho(r) = \varrho^s(r) + \varrho^l(r)$$  \hspace{1cm} 2.2.8

where

$$\varrho^s(r) = s(r) \varrho^s(r)$$  \hspace{1cm} 2.2.9

and

$$\varrho^l(r) = \sum_{m}^{BZ} \sum_{m'} c(m,m') \exp[i(K(m') + k(m)) \cdot r]$$  \hspace{1cm} 2.2.10

with

$$c(m,m') = \frac{8\pi}{\Omega_{i} \Omega_{l}} \frac{[K(m')^2 - 1]}{[K(m') + k(m)]^2}$$  \hspace{1cm} 2.2.11a

if \( m' \neq 0 \), and

$$c(m,0) = \frac{8\pi}{\Omega_{l}} k(m)^2$$  \hspace{1cm} 2.2.11b
In Equation 2.2.9 \( \varphi^S \) is the symmetrized form of the coulomb interaction

\[
\varphi^S(r) = \sum_{m \in \Omega} \frac{8\pi \exp(iK(m) \cdot r)}{\Omega |K(m)|^2} \tag{2.2.12}
\]

and

\[
S(r) = \frac{BZ}{\sum_{m} \exp(iK(m) \cdot r)} \tag{2.2.13}
\]

is a geometrical factor.

Due to the overriding influence of the geometrical factor \( S \) the first term in Equation 2.2.8 is of predominantly short-range character. The second term is dominated by the smaller \( k \)-vectors and is therefore long-range in character.

The effect of the projection operator \( P_0 \) on the first term of Equation 2.2.8 is to replace the geometrical factor by unity. The second term is removed completely by \( P_0 \). Thus, a model of a crystal based on a translational symmetrized electronic charge density (Equation 2.2.2b) completely ignores the long-range part of the coulomb interaction and seriously reduces the effectiveness of the short-range part of the coulomb interactions.

In Section 11.3.4 we find that Hartree-Fock single-particle approximations based on the ECM and SECM differ only in the exchange terms. Exchange contributions in the SECM are much less than those in the ECM. In fact the SECM single-particle equations are essentially Hartree equations.
11.2.3 The correlated-extended crystal model

Although it may be desirable to reduce the effectiveness of the coulomb interaction in the exchange term of a single-particle approximation, the reduction which occurs in the SECM is probably too extensive. The model suggested in this section is based on the coulomb identity of Equation 2.2.8.

The ECM many-electron Hamiltonian may be written with the aid of Equation 2.2.8 as

\[ H_e = \sum_i K_i + \sum_i H_i + \frac{1}{2} \sum_{i \neq j} H_{ij}^r + \frac{1}{2} \sum_{i \neq j} H_{ij}^s \]

where

\[ H_{ij}^s = \sum_{m \neq 0} \frac{8\pi \exp(iK(m) \cdot \mathbf{r}_{ij})}{\Omega_k K(m)^2} \]

and

\[ H_{ij}^r = \sum_{m \neq 0} \sum_{m'} \mathbf{C}(m, m') \exp(i [K(m') + K(m)] \cdot \mathbf{r}_{ij}) \]

where \( \mathbf{C} \) is given by Equations 2.2.11 and \( S \) is given by Equation 2.2.13.

The behavior of the short-range and long-range terms for an f.c.c lattice is indicated in Figure 1 and Figure 2, respectively. The interaction is represented in dimensionless form \( 1/2 a_0 \) and plotted as a function of \( r/a \) \( (r = r_{ij}) \) in the region near the origin. The parameter \( a \) is the lattice constant for the f.c.c lattice. Except for the violent fluctuations which occur near lattice sites the long-range term is very nearly the tail of the coulomb interaction. A typical lattice constant is about 10 a.u. Thus, the long-range term has a maximum of about .5 and
Fig. 1 Behavior of the screened coulomb potential near the origin
Fig. 2: Behavior of the coulomb tail near the origin.
behaves asymptotically as $1/r$.

The solution $\psi_e$ of the ECM many-electron Schrödinger equation,

$$H_e \psi_e = E \psi_e$$  \hspace{1cm}  (2.3.4)

may be written as

$$\psi_e = \exp(-1/2F) \psi_e'$$  \hspace{1cm}  (2.3.5)

where $F$ is an unspecified function of the electronic coordinates. An expression corresponding to Equation 2.3.4 for the function $\psi_e'$ is

$$H_e' \psi_e' = E \psi_e'$$  \hspace{1cm}  (2.3.6)

where

$$H_e' = H_e + \sum \left[ \frac{1}{2} \nabla_i \cdot F + \nabla_i \cdot F \cdot \nabla_i - \frac{1}{4} (\nabla_i \cdot F)^2 \right].$$  \hspace{1cm}  (2.3.7)

By choosing

$$F = \sum_{i \neq j}^{\text{BZ}} \sum_{m}^{\text{BZ}} \sum_{m' \neq 0}^{\text{BZ}} C(m,m') \exp(i[k(m') + k(m)] \cdot \mathbf{r}_{ij}) \left[ K(m') + k(m) \right]^2$$  \hspace{1cm}  (2.3.8)

the long-range terms corresponding to $m' \neq 0$ are eliminated from Equation 2.3.7. Equation 2.3.7 becomes

$$H_e' = \sum_{i} K_i + \sum_{i} H_i + \frac{1}{2} \sum_{i \neq j}^{\text{BZ}} H^{SR}_{ij} + \frac{1}{2} \sum_{i \neq j}^{\text{BZ}} H^{BZ}_{ij}$$  \hspace{1cm}  (2.3.9)

where

$$H^{BZ}_{ij} = \sum_{m \neq 0}^{\text{BZ}} \frac{8\pi \exp(i k(m) \cdot \mathbf{r}_{ij})}{\Omega |k(m)|^2}.$$  \hspace{1cm}  (2.3.10)
Except for the first few K-vector modules the terms of $F$ will be smaller term by term than the corresponding quantities in $H^{1r}$. The destructive interference of the phases which must occur in $H^{1r}$ may be slightly inhibited in $F$. Thus, $F$ can be expected to be a smooth function resembling $H^{1r}$.

Since the probability density

$$\psi_+ \psi_+ = \exp(-F) \psi_+ \psi_+$$  \hspace{1cm} 2.3.11

is decreased when the positions of any two of the particles coincide or nearly coincide $F$ may be interpreted as a two-particle correlation function.

The terms in Equation 2.3.9 involving gradients of $F$ must be small since the gradient operation introduces a vector in the numerator of $F$ which can be expected to abet the destructive interferences of the phases.

The behavior of the remaining long-range term (Equation 2.3.10) may be approximated by

$$H_{ij}^{BZ} \approx (r/\pi) Si(k_o r_{ij})/r_{ij}$$  \hspace{1cm} 2.3.12

where

$$Si(x) = \int_0^x \sin (t) dt$$  \hspace{1cm} 2.3.13

and $k_o$ is the radius of a sphere which approximates the Brillouin zone.

Near the origin the sine integral behaves\(^2\) as

\(^1\)Eg. see Bohm, 1953, p. 612.

\(^2\)Jahnke, 1945, p. 1.
\[ Si(x) \approx x - x^{3/18} + \ldots \]  

2.3.14

and asymptotically as

\[ Si(x) \approx 1/2\pi - \cos(x)/x. \]  

2.3.15

The parameter \( k_o \) is of the order of \( 2\pi/a \approx 1/2 \) for an f.c.c lattice. Therefore, \( H_{\text{BZ}} \) is a very slowly varying function near the origin and for \( k_or\gg 1 \) behaves as \( 1/r \).

The model of the many-electron crystal which is described by the Hamiltonian

\[ H_e = \sum_i K_i + \sum_i H_i + 1/2 \sum_{ij} H_{ij}^{\text{ex}} \]  

2.3.16

will be called the Correlated-Extended Crystal Model (CECM). As in the case of the SECM Hartree-Fock single-particle approximations based on the CECM differ from the ECM only in the exchange terms. However, in the CECM the dominant features of the coulomb interaction are retained.

11.2.4 Single-particle approximations

The approximation of the many-electron wave function of an anti-symmetrized product of one-electron functions \( \varphi_i \)

\[ \psi_e = P_A \prod_{i=1}^{N} \varphi_i(x_i) \]  

2.4.1

is the starting point for IPMs of fermion systems. The operator \( P_A \) is the anti-symmetrization operator on the coordinate indices of the \( N \)-electron system. The wave function represented by Equation 2.4.1 is a symmetry-adapted function corresponding to the anti-symmetric representation of the symmetric group of order \( N \). Thus, the Pauli exclusion principle is satisfied.
Equation 2.4.1 may be written as a determinant,
\[ \psi_\varepsilon = \det(\varphi_1(\mathbf{r}_1), \varphi_2(\mathbf{r}_1), \ldots, \varphi_N(\mathbf{r}_1)) , \]
where each row of the determinant is characterized by a particle coordinate index. From the properties of determinants it follows that the N one-electron functions must be linearly independent or the determinant is zero. Since the value of a determinant is unchanged by replacing a column of the determinant by the original column plus linear combinations of the remaining columns, there is no loss in generality in assuming the one-electron functions to be orthonormal.

The total energy of a system described by a Hamiltonian of the form
\[ H_\varepsilon = \sum_i K_i + \sum_i H_i + 1/2 \sum_{i \neq j} H_{ij} \]
with a wave function consisting of a single determinant of orthonormal one-particle functions is
\[ E_{\text{tot}} = (\psi_\varepsilon, H_\varepsilon \psi_\varepsilon) / (\psi_\varepsilon, \psi_\varepsilon) = (\psi_\varepsilon, H_\varepsilon \psi_\varepsilon) / N ! \]
or in terms of the single-particle operators is
\[ E_{\text{tot}} = \sum_i (\varphi_i(1), [K_i + H_1] \varphi_i(1)) + 1/2 \sum_{i \neq j} (\varphi_i(1) \varphi_j(2), \]
\[ H_{12} \varphi_i(1) \varphi_j(2)) - 1/2 \sum_{i \neq j} (\varphi_i(1) \varphi_j(2), H_{12} \varphi_i(2) \varphi_j(1)) . \]

Equations 2.4.4, 5 are written in a notation in which
\[ \langle f(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_M), g(\mathbf{r}_1, \ldots, \mathbf{r}_M) \rangle = \int \ldots \int f^{+}(\mathbf{r}_1, \ldots, \mathbf{r}_M) \]
\[ g(\mathbf{r}_1, \ldots, \mathbf{r}_M) \, d\mathbf{r}_1 \ldots d\mathbf{r}_M . \]
Integration is indicated only if a coordinate occurs twice. In the case
of the ECM the region of integration is an ECM cell.

Minimization of the total energy by varying the one-electron functions subject to the orthonormality constraint,

\[ (\varphi_i(1), \varphi_j(1)) = \delta_{ij}, \]

leads to single-particle equations for the one-electron functions:

\[ K_i \varphi_i(1) + H_i \varphi_i(1) + \sum_{j \neq i} (\varphi_j(2), H_{12} [\varphi_j(2) \varphi_i(1) - \varphi_j(1) \varphi_i(2)]) = \sum_j \lambda_{ij} \varphi_j(1). \]

The parameters \( \lambda_{ij} \) are the Lagrange multipliers which are used to impose the orthonormality constraint. If the operators \( K_i, H_i \), and \( H_{12} \) are Hermitean and \( H_{12} = H_{21} \), it follows that the Lagrange multipliers are Hermitean \( (\lambda_{ij}^+ = \lambda_{ji}^*) \). Therefore, the Lagrange multiplier matrix may be placed in diagonal form by a unitary similarity transformation. Thus, the single-particle equations can be written in the form

\[ K_i \varphi_i^+(1) + H_i \varphi_i^+(1) + \sum_j (\varphi_j^+(2), H_{12} [\varphi_j^+(2) \varphi_i^+(1) - \varphi_j^+(1) \varphi_i^+(2)]) = \varepsilon_i \varphi_i^+(1) \]

where \( \varepsilon_i \) is a diagonal element of the transformed Lagrange multiplier matrix. The one-particle functions \( \varphi_i^+ \) are related to the functions \( \varphi_i \) by \( \varphi_i^+ = \sum_j U_{ij} \varphi_j \), where \( U \) is the unitary matrix which diagonalizes the Lagrange multiplier matrix.

If the assumption is made that the one-electron functions in Equation 2.4.7 occur in pairs (paired spin states) of the form

\[ \varphi_i^+(\pm)(\mathbf{x}_i) = u_i(\mathbf{x}_i) \alpha \]

2.4.8a
where \( \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \) and \( \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \) are spin functions, then Equation 2.4.7 may be written as

\[
\mathcal{H}_{ij}(\alpha_{j}) + H_{j}u_{j}(\alpha_{j}) + \sum_{j} \left[ u_{j}(2)u_{j}(1) - 1/2u_{j}(1)u_{j}(2) \right] = \epsilon_{j}u_{j}(1).
\] 2.4.9

If the one-electron function probability density is regarded as the probability density of an electron (or quasi-electron) in the many-electron system, then the single-particle equations (Equation 2.4.7 or Equation 2.4.9) may be interpreted as the Schrödinger equation for a single particle moving in the averaged potential due to the electronic charge density and the nuclear potentials. This interpretation is supported by the fact that the integro-differential operator which acts on the one-electron function \( \mathcal{H}_{ij}^{\alpha_{j}} \) (or \( u_{j} \)) in the single-particle equations is Hermitean. Thus, the Lagrange multiplier in the diagonal form may be interpreted as the single-particle energy.

Single-particle equations derived from a single-determinant (or a small number of determinants) often are called Hartree-Fock equations. The operator defined by writing the left member of Equation 2.4.9 as

\[
H_{HF}^{ps}u_{j} = \epsilon_{j}u_{j}
\] 2.4.10

will be designated the paired spin Hartree-Fock operator. The \( \frac{N}{2} \) eigenfunctions of the paired spin Hartree-Fock operator which are used to form the Hartree-Fock operator are interpreted to represent occupied single-particle states. The Hartree-Fock approximation to the ground state
eigenfunction of the many-electron Hamiltonian (Equation 2.4.3) is formed from the N/2 occupied single-particle eigenfunctions of the paired spin Hartree-Fock operator for which the total energy (Equation 2.4.5) of the many-electron system is a minimum. The eigenfunctions of the ground state Hartree-Fock operator which correspond to unoccupied single-particle states represent excited states of the many-electron system in the sense of Koopmans' (1933) theorem.

From Equation 2.4.9 it is evident that the averaged potential due to electron-electron interactions in the Hartree-Fock operator is of a very special kind. The direct term,

\[ D u_i = 2 \sum_j \langle u_j(2), H, u_j(2) \rangle u_i, \quad 2.4.11 \]

is simply the electronic electrostatic average potential.

The exchange term,

\[ A u_i(1) = \sum_j \langle u_j(2), H, u_i(2) \rangle u_j(1), \quad 2.4.12 \]

represents a much more complicated type of average. Slater (1951) has shown that the exchange term tends to create a "hole" in the electronic charge density surrounding the electron represented by the wave function \( u_j \). Thus, the exchange term somehow acts to correlate the motion of the electrons.

Since, one-electron functions with opposite spins make no contribution to the exchange term, the paired spin form of the Hartree-Fock equation probably suffers a reduction in exchange correlation as compared with the Hartree-Fock Equation 2.4.7. However, the simplification afforded by the paired spin approximation necessitates its use in crystal
applications (at least for the present). In terms of the operators defined by Equations 2.4.11 and 2.4.12 the paired spin Hartree-Fock operator is

$$H_{HF}^{ps} = K_1 + H_1 + D - A.$$  \hspace{1cm} 2.4.13

11.3 Single-Particle Approximations in Crystal Applications

11.3.1 Symmetry considerations in the extended crystal model

The simplification afforded through the use of symmetry-adapted functions becomes available in crystal applications only if the Hartree-Fock operator is invariant with respect to the operations of the space group.

Consider the effect of a symmetry transformation $g$ on the ECM Hartree-Fock operator for paired spin states.\footnote{In this section symmetry transformations will be written as if they were symmorphic. This involves no loss in generality since the same techniques may be applied with non-symmorphic operators, except that in this case the meaning of the operator will depend on the context in which it is used.}

$$g H_{HF}^{ps}(1) \varphi(1) = H_{HF}^{ps}(g^{-1}_1 r_1) \varphi(g^{-1}_1 r_1)$$

The kinetic and nuclear terms are unaffected by the transformation. The direct and exchange terms the operators are represented by

$$W \varphi = \sum_j u_j(2), H_{12} P_W u_j(2) \varphi(1).$$  \hspace{1cm} 3.1.1

where in the case of the direct term $P_W = 2$ and in the case of the exchange term $P_W = P_{12}$, the two-particle permutation operator. By construction of the ECM symmetry transformations of the integration variables do not alter the value of a scalar product. Therefore,
The derivation of Equation 3.1.2 is independent of $P_W$.

If the one-electron functions in Equation 3.1.2 are Bloch functions, then from Equation 1.2.30a the transformed one-electron function is also a Bloch function. If $g$ represents a translation operator $T(m)$, then

$$I(m) \Psi(1) = W I(m) \Psi(1).$$

Thus, the requirement that the one-electron functions be Bloch functions is a sufficient condition for the invariance of the ECM Hartree-Fock operator with respect to the ECM translation group. One way to guarantee the invariance of $W$ to any space group transformation is first to require the $u$'s to be functions symmetry-adapted to the group. Under any operation $g$ of the space group the $u$'s transform according to some unitary representation of the group.

$$g u_i = \sum_j u_j D_{ji}(g)$$

Invariance of $W$ to the group is assured if for every $u_j$ which occurs in $W$, all the $u$'s appear that span the representation subspace containing $u_j$. From Equations 3.1.2, 4

$$g W \Psi = \sum_{j,m,n} (u_m(r_2), H_{12} P_w u_n(r_2) \Psi(g^{-1} r_1)) D_{jm}^\Psi(g) D_{nj}(g).$$

Therefore,

$$g W \Psi = W g \Psi,$$

and the Hartree-Fock operator is invariant with respect to operations of the space group.
If the Hartree-Fock operator is invariant to the space group, then its eigenfunctions can be chosen to be symmetry-adapted functions. These functions can be used to build the Hartree-Fock operator itself as is required for self-consistency. A recipe for constructing a space group invariant Hartree-Fock operator from the symmetry-adapted eigenfunctions of the Hartree-Fock operator is given in the following paragraphs.

Suppose \( \varphi_{k,j}^a \) to be a carrier space for a unitary irreducible representation \( a \) of the group of the \( k \)-vector \( G_k \). The components of \( \varphi_{k,j}^a \) are symmetry-adapted eigenfunctions (labeled by the index \( j \)) of the Hartree-Fock operator. By definition

\[
g \varphi_{k,j}^a = \varphi_{k,j}^a D_k^a(g)
\]

where \( D_k^a(g) \) is a unitary matrix representative of the operator \( g \) of \( G_k \). A left coset \( hG_k \) of the space group \( G \) is defined to be the set of operators \( \{hg\} \) where \( g \) is contained in \( G_k \) and \( h \) is contained in \( G \). The operator \( h \) is called the generator of the coset. It is easy to show that if cosets \( h_1 G_k \) and \( h_2 G_k \) possess a common element, then they are identical. Therefore, the space group \( G \) may be partitioned uniquely into cosets.

\[
G = G_k + h_1 G_k + \ldots \ldots
\]

A carrier space of the space group may be formed from \( \varphi_{k,j}^a \) according to the partition into cosets,

\[
\psi_{k,j}^a = (\varphi_{k,j}^a, h_1 \varphi_{k,j}^a, \ldots)
\]

Since,

\[
g h_i \varphi_{k,j}^a = h_i g^l \varphi_{k,j}^a D_k^a(g^l)
\]
where \( g \) is contained in \( G \), \( g' \) is contained in \( G' \), and \( h \) and \( h' \) are coset generators, the group \( G \) is represented in the carrier space \( \psi_{k,j}^a \) by unitary matrices.

The operator \( W \) may be written in terms of the carrier spaces \( \psi_{k,j}^a \) (considered to be a row matrix) as

\[
W \mathcal{O} = \sum_k \sum_i \sum_j (\psi_{k,j}^a, H_{12}^i, \psi_{k,j}^a) \mathcal{O}(1) \quad 3.1.10
\]

where the prime on the sum on reduced \( k \)-vectors means that only those inequivalent \( k \)-vectors are included for each index \( a \) and \( j \) which cannot be related by space group operations. A superscript \( T \) on \( \psi_{k,j}^a \) indicates that it is transposed (a column matrix).

From the transformation properties of the \( \psi_{k,j}^a \) and Equation 3.1.2 it is evident that \( W \) as expressed by Equation 3.1.8 is invariant with respect to space group operations.

Matrix elements between symmetry-adapted functions with the symmetry-invariant Hartree-Fock operator display the selectivity expressed by Equations 1.2.19. The symmetry selectivity is of great practical value, since only matrix elements between symmetry-adapted functions which transform according to the same irreducible representation need be considered.

An additional simplification is provided by the construction of the carrier space \( \psi_{k,j}^a \) (Equation 3.1.6). All components of \( \psi_{k,j}^a \) are eigenfunctions of the Hartree-Fock operator with the same eigenvalue.

Therefore, only one of the component functions need be calculated.

As an example of the utilization of symmetry in crystal applications consider the expansion of the electronic charge density in plane waves. The electronic charge density may be written in terms of the vector...
By construction the electronic charge density is invariant with respect to space group transformations. Since the electronic charge density is invariant with respect to transformations by translation group elements, it may be expanded in the complete set of translation invariant plane waves,

\[ \rho_e(r) = -\sum_K \rho_K \exp(iK \cdot r) . \]  

Since the electronic charge density is invariant with respect to general space group transformations, expansion coefficients \( \rho_K \) for K-vectors related by a point group transformation must be related to one another. A module of K-vectors consists of the set of K-vectors which can be transformed into one another by the rotational part of group operations. If the group is symmorphic, all expansion coefficients of the same module of K-vectors must be equal. In this case,

\[ \rho_e(r) = -\sum_{[K]} \rho_{[K]} \rho_e [K] \exp(iK \cdot r) . \]  

The symbol \([K]\) designates a module of K-vectors. In general,

\[ \rho_e(r) = -\sum_{[K]} \rho_{[K]} \rho \sum_{e[K]} \exp(iK \cdot r) \]  

where

\[ P_{\Gamma_1} = G^{\Gamma_1} \sum g \]  

is the projection operator for the identical irreducible representation.
of the ECM space group of order $G^0$.

The expansion coefficient $\rho[K]$ is given by

$$\rho[K] = \Omega^{-1}_0 \int \rho_{e}(r) \Gamma_1 \sum_{K \in [K]} \frac{\exp(iK \cdot r)}{N[K]} \, dr$$  \hspace{1cm} 3.1.14a

where $N[K]$ is the number of $K$-vectors contained in the $K$-vector module. The region of integration in Equation 3.1.14a consists of one primitive cell of the space lattice. An alternative expression for Equation 3.1.14a is

$$\rho[K] = \sum_{K} \sum_{a} \sum_{j} \left( \psi_{K,j}^{a} \right)^* (r) \tilde{\rho}[K] \psi_{K,j}^{a} (r)$$  \hspace{1cm} 3.1.14b

where

$$\tilde{\rho}[K] = \Omega^{-1}_0 \Gamma_1 \sum_{K \in [K]} \frac{\exp(iK \cdot r)}{N[K]}$$  \hspace{1cm} 3.1.14c

is a space group invariant operator. Therefore, the expansion coefficient may be expressed in terms of one component function $u_{K,j}^{a}$ of $\psi_{K,j}^{a}$ for each term in the sum.

$$\rho[K] = \sum_{K} \sum_{a} \sum_{j} (u_{K,j}^{a}, \tilde{\rho}[K] u_{K,j}^{a})$$  \hspace{1cm} 3.1.15

where $M_K$ is a multiplicity factor equal to the number of inequivalent reduced $K$-vectors which are related to $K$ by a space group operation and $d_a$ is the degree of degeneracy of the irreducible representation $a$.

The potential energy due to the electronic charge density is

$$\Phi_e = \sum_{[K]} \rho[K] \Gamma_1 \sum_{K \in [K]} \frac{\Phi_{[K]} \exp(iK \cdot r)}{K^2}$$  \hspace{1cm} 3.1.17

Methods similar to those used in the preceding treatment of the plane wave expansion of the electronic charge density may be applied to the
nuclear and direct terms of the paired spin Hartree-Fock operator. The plane wave expansion of the nuclear and direct paired-spin Hartree-Fock operators is

$$H_1 + D_1 = \sum_{K \neq 0} S(K) \Omega _0^{-1} \exp (iK \cdot r_1) + [K] \sum \rho [K] \sum \rho _1 [K] \sum \rho _2 \exp (iK \cdot r)$$

where $S(K)$ is the structure factor,

$$S(K) = \sum Z_s \exp (-iK \cdot R_s)$$

and $\rho [K]$ is given by Equation 3.1.16.

The direct term of the Hartree-Fock operator operating on a function of position $\tau$ is a multiplicative operator $D(\tau)$. The value of $D(\tau)$ is independent of the function on which it operates. Therefore, the direct term of the Hartree-Fock operator may be regarded as a space group invariant function of position. Consequently, the direct term may be written as

$$D(\tau) = 2 \sum \sum _{a} \sum _{j} \int \psi _{a, j}^a \chi (2) P_0 H_{12} \psi _{a, j}^a \chi (2) d\tau$$

where $P_0$ is the projection operator for the $k=0$ representation of the ECM translation group. Therefore, Hartree-Fock IPMs based on the ECM, SECM, and CECM many-electron models have identical direct terms in their respective Hartree-Fock operators.

11.3.2 Solution of the Schroedinger equation by expansion in a finite basis

Suppose that $\Omega$ represents a basis of linearly independent functions.

$$\Omega = (\varphi _1, \varphi _2, \ldots, \varphi _n)$$

In terms of this basis the solution of the Schroedinger equation
\[ H \psi = E \psi \quad 3.2.2 \]
is
\[ \psi = \varnothing \mathbf{C} \quad 3.2.3 \]
where \( \mathbf{C} \) is a coefficient vector which is chosen to satisfy Equation 3.2.2. The Rayleigh-Ritz procedure for determining \( \mathbf{C} \) requires the energy \( E \) to be extremal with respect to variation of the components of \( \mathbf{C} \). The resulting eigenvalue problem is
\[ H \mathbf{C} = E \mathbf{C} \quad 3.2.4 \]
where \( H \) is called the Hamiltonian matrix,
\[ H = J g^+ H g \quad 3.2.5 \]
and \( J \) is called the overlap matrix,
\[ J = \int g^+ g \quad 3.2.6 \]
In general the overlap matrix will not be simply a multiple of the identity matrix. Thus, Equation 3.2.4 is not in the standard form for an eigenvalue problem. Since, the basis \( \varnothing \) consists of linearly independent components, there is at least one transformation \( T \) on \( \varnothing \),
\[ \varnothing' = \varnothing T \quad 3.2.7 \]
for which the overlap matrix,
\[ J' = \int \varnothing'^+ \varnothing' = 1 \quad 3.2.8 \]
the identity matrix. In this case the eigenvalue problem, Equation 3.2.4 may be transformed into the equivalent problem.
Practical procedures for obtaining the orthonormality transformation matrices are discussed by Davis (Todd, 1962).

11.3.3 Linear combinations of atomic orbitals

An atomic orbital is a function of the form

\[ \phi_j(r) = R_j(r) Y_j(\theta, \phi) \]  

where \( R_j \) is spherically symmetric about the origin and \( Y_j \) is a spherical harmonic or a similar function which depends only on the spherical polar coordinates, \( \theta \) and \( \phi \). Although \( \phi_j \) is not required to be a solution of a free atom Hartree-Fock Hamiltonian, it must satisfy the boundary conditions for bound state free atom solutions.

A linear combination of atomic orbitals (LCAO) is a symmetry-adapted function formed from one atomic orbital centered about different nuclear sites. In the ECM an LCAO which transforms according to the ECM translation group irreducible representation \( \lambda \) and irreducible representation \( \nu \) of the group of the \( k \)-vector may be represented as a projection of an atomic orbital,

\[ \phi_{k, \lambda, j}(r) = P_a \phi_{\lambda, k} \phi_j(r - R_s), \]  

where \( \mathbf{R}_s \) is a point vector to a nuclear site.

Solutions of the ECM Hartree-Fock operator may be expanded in a basis of LCAO's formed from a set of atomic orbitals according to Equation 3.3.2. In general atomic orbitals centered about different nuclear sites will overlap appreciably. Thus, matrix elements between LCAO's of the same symmetry species with the Hartree-Fock operator expressed in terms of LCAO's will involve integrals with atomic orbitals centered about as many as four different nuclear sites. This is a practical difficulty. A difficulty in principle arises from the non-orthogonality of the LCAO basis functions. If the overlap between atomic orbitals is sufficiently large, the LCAO basis set tends to become overcomplete. The overcompleteness is manifested by a nearly singular or singular overlap matrix.

In certain physical situations it may be justifiable to expand some eigenfunctions in a basis of LCAO's formed from atomic orbitals which are so tightly bound to individual nuclei that orbitals centered about different sites in the crystal overlap negligibly. This is the motivation for the bare-ion model of the core electrons (Section III.2.1). To the extent that the overlap is negligible a solution of the Hartree-Fock Schroedinger equation for the 1PM in question can be constructed from a single LCAO. The atomic orbital from which the LCAO is formed is essentially independent of the \( \mathbf{k} \)-vector. In this case the representation of the paired-spin ECM Hartree-Fock operator is particularly simple.

\[
H_{HF}^{PS} = K + H_1 + 2 \sum \sum \int_0^2 \psi_j \phi_j^*(2) \psi_2 \phi_2^*(1) \frac{1}{2} \mathbf{r} \cdot \mathbf{r} \, d\mathbf{r}
\]
In Equation 3.3.3 $\phi_{j_s,n}$ is the j-th function centered about atomic site s relative to the lattice vector $R_n$. The plane wave expansion of the direct term $D$ of Equation 3.3.3 is

$$D = \sum_{K \neq 0} \frac{8\pi}{K^2} \rho_K \exp(iK \cdot r)$$  \hspace{1cm} 3.3.4

where

$$\rho_K = 2\Omega_o^{-1} \sum_{j_s} \exp(iK \cdot R_s) \int |\phi_{j_s}(x)|^2 \exp(-iK \cdot x) \, dx .$$  \hspace{1cm} 3.3.5

The region of integration in Equation 3.3.5 is all space.

Consider the function,

$$V = \sum_{s,n} V_{sn} - V_o$$  \hspace{1cm} 3.3.6

where

$$V_{sn}(1) = -2Z^i_s / r_1^{sn} + 4 \sum_j \int |\phi_{j_s,n}(2)|^2 r_{12}^{-1} \, d\Sigma_2$$  \hspace{1cm} 3.3.7

and

$$V_o = \Omega_o^{-1} \sum_s \int V_s(x) \, dx .$$  \hspace{1cm} 3.3.8

The number $Z^i_s$ is given by

$$Z^i_s = 2 \sum_j \int |\phi_{j_s}(x)|^2 \, dx .$$  \hspace{1cm} 3.3.9

The plane wave expansion of $V$ is

$$V = \sum_{K \neq 0} V_K \exp(iK \cdot r)$$  \hspace{1cm} 3.3.10

where

$$V_K = 2\Omega_o^{-1} \sum_s \exp(iK \cdot R_s) \int [-Z^i_s / r_1 + 2 \sum_j |\phi_{j_s,n}(r_2)|^2 r_{12}^{-1} \exp(-iK \cdot r_1)] \, d\Sigma_1 .$$  \hspace{1cm} 3.3.11
With the aid of the identity,
\[
\frac{1}{r_{12}} = \frac{1}{2\pi} \int dq q^{-2} \exp(iq \cdot r_{12}) ,
\]
Equation 3.3.11 may be written as
\[
\psi_{K} = 8\pi \Omega_{0}^{-1} \sum_{s} \exp(iK \cdot \mathbf{R}_{s}) \left[-Z_{s} + 2 \sum_{j} |\phi_{js}(r_{2})|^{2} \exp(-iK \cdot r_{2}) dr_{2}\right].
\]
Therefore, the direct term and a compensating part of the nuclear term of Equation 3.3.3 can be represented by a superposition of atomic-like potentials, Equation 3.3.6.

11.3.4 Orthogonalized plane waves

The method of orthogonalized plane waves (Herring, 1940) is based on a partition of the one-electron functions into core electron functions and valence (or non-core) electron functions. The core functions are considered to have probability density predominantly in the region of an atomic site.

An orthogonalized plane wave (OPW) is defined by
\[
\text{OPW}_{k} = \text{PW}_{k} - \sum_{C} (\psi_{C}^{k}, \text{PW}_{k}) \psi_{C}^{k}
\]
where
\[
\text{PW}_{k} = \Omega_{1}^{-1/2} \exp(iK \cdot r)
\]
and $\psi_{C}^{k}$ is a symmetry-adapted core function which transforms according to the translation group irreducible representation $k$. The sum on core functions includes those occupied core functions for which the orthogonalization coefficient,
\[
(\psi_{C}^{k}, \text{PW}_{k}) = \Omega_{1}^{-1/2} \int \psi_{C}^{*} \exp(iK \cdot r) dr
\]
is not required to be zero by symmetry.

A symmetrized orthogonalized plane wave (SOPW) is defined by

$$\text{SOPW}_a(k) = \text{SPW}_a(k) - \sum \left( \phi_c, \text{SPW}_a(k) \right) \varphi_c^k$$

where

$$\text{SPW}_a(k) = P_a \text{PW}_k.$$  \hspace{1cm} 3.4.5

It is important to note that the projection operator $P_a$ is applied to a single plane wave in Equation 3.4.5. Implicit in the definition of SOPWs is the requirement that $a$ is an irreducible representation of the group of the associated $k$-vector.

In the OPW method the non-core functions are expanded in a linear combination of OPWs and SOPWs. The effect of the core terms in an OPW wave function is to orthogonalize the plane wave component of the OPW function to all core functions of the same translational symmetry. This orthogonalization would be the only effect if a complete set of plane waves were used in the expansion. However, in practice a truncated set of OPWs is used in the expansion.

Suppose that a truncated set of OPWs is an adequate basis set for the expansion of a normalized non-core function solution of a Schrödinger equation,

$$\psi_k^v = \sum_k \left( c_k \text{OPW}_k(k+k) \right)$$

The sum on $k$ in Equation 3.4.6 includes modules of $k+k$ vectors for which $(k+k)^2$ increases in magnitude up to the truncation point. The plane wave expansion of the non-core function is
\[ \psi_{K}^{V} = \sum_{K} A_{K}^{PW, K+K} \]  

The normalization integral for the non-core function is

\[ (\psi_{V}^{K}, \psi_{V}^{K}) = 1 \]

Three expressions for the normalization integral in terms of the expansion coefficients of Equations 3.4.6, 7 are

\[ 1 = \sum_{K} |C_{K}|^2 - \sum_{C} |C_{C}^{K}|^2 (\psi_{C}^{K, PW, K+K})^2 \]  

\[ 1 = \sum_{K} A_{K}^{*} C_{K} \]  

\[ 1 = \sum_{K} |A_{K}|^2 \]

where the sum of \( K \) in the first two Equations 3.4.9 is truncated in the same way that the OPW expansion (Equation 3.4.6) is truncated.

Suppose that the only role of the orthogonality coefficients in the OPW expansion is to remove core components from what is essentially a plane wave expansion of non-core functions. Thus, if a plane wave expansion provides an adequate description of the valence function, then no orthogonality contributions will occur. If this is the case, then as the number of modules of \( K+K \) vectors in the OPW expansion is increased the OPW expansion coefficients approach the plane wave expansion coefficients and the function,

\[ \psi_{V}^{K} = \sum_{K} C_{K}^{PW, K+K} \]

approaches the non-core function. Then, the negative definite orthogonality coefficient contributions to Equation 3.4.9a must approach zero.
Thus, the magnitude of the orthogonality coefficient contribution to the OPW normalization integral may be an indication of the convergence of the OPW expansion. However, this cannot be regarded as an absolute test. For example, if $\psi_{V}^{K}$ is a solution of the Schroedinger equation with an eigenvalue appreciably above the eigenvalues for the low-lying non-core solutions, then the OPW expansion will be dominated by the larger $k+K$-vector modules in the OPW expansion. Since, the orthogonality coefficients decrease with increasing $k+K$-vectors, the magnitude of the orthogonality coefficient contributions to the OPW normalization integral will be smaller for this reason alone. If the non-core function for a special point in the Brillouin zone is orthogonal to all core functions by symmetry, then the magnitude of the orthogonality coefficients is zero and no indication of convergence is provided. Thus, the magnitude of the orthogonality contributions to the normalization integral may provide a significant indication of the convergence of the expansion only for those low-lying non-core functions which interact (have non-zero orthogonality coefficients) with the core functions.

The OPW expansion coefficients are related to the plane wave expansion coefficients of a non-core function by

$$A_{K} = C_{K}^{i} - \sum_{C} \left( \psi_{C}^{K}, \psi_{V}^{k} \right) \left( \psi_{C}^{K}, PW_{K+K} \right)$$

3.4.11

where $C_{K}^{i} = C_{K}$ for $k+K$-vector modules below the truncation point and $C_{K}^{i} = 0$ otherwise. If the truncated plane wave expansion $\psi_{V}^{k}$ does not adequately describe the non-core function, the orthogonality terms will be finite. The orthogonality coefficient contributions to $A_{K}$ for $k+K$-vector modules below the truncation point may be interpreted as removing
the component of core space remaining in the approximate non-core 
function, $\psi_{K}^{K}$. It is clear that the orthogonality coefficient contribu­
tions for $k+K$-vector modules above the truncation point cannot be 
interpreted in this way. Since these terms involve relatively large 
$k+K$-vectors, the dominant behavior of the function

$$\psi_{K}^{K} = - \sum_{C} (\psi_{C}^{K}, \psi_{K}^{K}) \sum_{P} (\psi_{P}, \psi_{K+P})^{*} \psi_{K+P}$$ 3.4.12

is a rapid oscillation in the region of the atomic sites. Herring (1940) 
reasoned that the orthogonality terms might approximate the rapid varia­
tion near the atomic sites of the non-core functions. Since the rapidly 
varying part of the non-core functions cannot be expanded in a small 
number of plane waves, the convergence of a linear combination of OPWs 
might be significantly better than the corresponding plane wave expansion.

In the preceding paragraphs two conflicting points of view regarding 
the convergence of an expansion in OPW basis functions have been devel­
oped. Firstly, the orthogonality conditions are treated as if their only 
function is to impose the formal requirement that non-core functions be 
orthogonal to core functions. Secondly, the orthogonality conditions in 
addition to satisfying the formal demands are considered to add an 
essential component to the non-core functions which will significantly 
 improve the convergence of an OPW expansion. The fact that a large 
number of OPWs is needed in the expansion of non-core functions (e.g. 
see Kleinman, 1959) supports the first point of view. The first point 
of view is also supported by the fact that the OPW calculations for 
beryllium by Herring and Hill (1940) fail to account for the Knight 
shift in metallic beryllium despite the apparent rapid convergence of
the non-core function eigenvalues. Schneider, et al., (1964) have obtained good agreement with the experimental value of the beryllium Knight shift in a calculation in which the non-core functions were expanded in a basis set of OPWs augmented by a 2s tight-binding function. This point will be reconsidered in the discussion of the results of calculations for Mg$_2$Si.

The role of the core function in the convergence of OPW expansions of non-core functions is discussed by Heine (1957b). Heine emphasizes the importance of having core functions which satisfy the same crystal potential as the non-core functions. Consider the OPW matrix elements with the IPM Hamiltonian operator, $H_{IPM}$.

$$\langle \text{OPW}, \mathbf{k} + \mathbf{K}, H_{IPM} \rangle \langle \text{OPW}, \mathbf{k} + \mathbf{K}' \rangle = \langle \text{PW}, \mathbf{k} + \mathbf{K}, H_{IPM} \rangle \langle \text{PW}, \mathbf{k} + \mathbf{K}' \rangle$$

$$- \sum_{c} (\phi_{c}^{\mathbf{k}}, \text{PW}, \mathbf{k} + \mathbf{K}) \phi_{c}^{\mathbf{k}, \text{PW}, \mathbf{k} + \mathbf{K}'} (\phi_{c}^{\mathbf{k}}, \text{PW}, \mathbf{k} + \mathbf{K}') E_{c}^{k}$$

In Equation 3.4.13 the core functions are assumed to be solutions of the Schroedinger equation,

$$H_{IPM} \phi_{c}^{\mathbf{k}} = E_{c}^{k} \phi_{c}^{\mathbf{k}} .$$

The contributions from the orthogonality terms to the OPW matrix elements involving plane waves from the small $\mathbf{k} + \mathbf{K}$-vector modules is comparable to the contribution from the plane wave term. For the larger $\mathbf{k} + \mathbf{K}$-vector modules the kinetic energy contribution becomes prominent. The low-lying non-core functions and eigenvalues are found to be very sensitive to changes in the matrix elements which are not dominated by kinetic energy contributions. Thus, spurious contributions to these matrix
elements due to inappropriate core functions or core eigenvalues may have a disastrous effect on a calculation.

11.3.5 The exchange problem in the crystal

The space group invariant Hartree-Fock exchange operator is given by Equation 3.1.8 specialized to the case $P_{w} = P_{12}$.

$$A \varphi(1) = \sum_{K} \sum_{a} \int \psi_{k,j}^{a} \psi_{l,j}^{a+} H_{12} \varphi(2) d\mathbf{r}_{2}$$

The prime on the sum on reduced $k$-vectors means that only those $k$-vectors are included which cannot be related by group operations. Because of the symmetry properties of the exchange operator only matrix elements between functions of the same symmetry need be considered. In the case of IPM models based on the ECM and CECM many-electron models it is impossible to predict any reduction or selectivity between terms of the matrix element which involve functions of different symmetry. However, in the case of the SECM the coulomb interaction $H_{12}$ is invariant with respect to operations of the translation group acting on either coordinate separately. Therefore, the matrix elements of the exchange operator for the SECM IPM include only those terms which transform according to the same irreducible representation of the translation group. This is a reduction in the exchange contribution of the order $N_{o}^{-1}$ where $N_{o}$ is the order of the translation group. Thus, the SECM IPM is essentially the Hartree approximation in the crystal.

In the case of $k$-independent LCAOs the ECM exchange operator has a particularly simple form (Equation 3.3.3) and the direct evaluation of exchange matrix elements is feasible. However, in general the direct
evaluation of exchange matrix elements is limited by such practical
considerations as the calculation time and the size of the 'memory' of
the machine on which the calculations are performed. One way of
limiting the number of terms that need be considered in the ECM exchange
matrix elements is to limit the size of the ECM cell. The corresponding
cell in reciprocal space (the Brillouin zone) will contain the same
number of reduced \( \mathbf{k} \)-vectors as the ECM cell contains lattice vectors.
This may also be thought of as a sampling procedure. The ECM cell is
considered to be large, but exchange is computed for a sampling of
reduced \( \mathbf{k} \)-vectors corresponding to a small ECM cell.

In the ECM calculations which are described in Section III the
sampling of the Brillouin zone corresponds to an ECM cell bounded by the
finite crystal vectors

\[
\mathbf{A}_i = 2 \mathbf{a}_i \quad i=1,2,3
\]

where the \( \mathbf{a}_i \) are the primitive lattice vectors. In this case the
Brillouin zone contains 8 reduced \( \mathbf{k} \)-vectors. This appears to be an
extremely limited sample in which all \( \mathbf{k} \) reduced \( \mathbf{k} \)-vectors have special
symmetry. A partial justification for this sampling procedure is that
self-consistent charge density calculations are found to be nearly the
same when calculated for the sampling of \( \mathbf{k} \)-vectors described above and
when the sampling is extended to include 512 reduced \( \mathbf{k} \)-vectors.\(^1\)

This sampling procedure is also discussed by Phillips and Kleinman
(1962) in connection with self-consistent calculations on Si. They
report that the Hartree-Fock valence-valence exchange completely destroys

\(^{1}\)Goodman, B., Cincinnati, Ohio. Si results. Private communication. 1965.
agreement between their calculated value for the energy gap in Si and the experimental value. However, their results cannot be regarded as conclusive evidence for the failure of the Hartree-Fock IPM since they include the exact exchange for only one matrix element and approximate the remaining matrix elements by a free electron \( k \)-vector dependent model. Also, their treatment of so-called singular terms in the exchange matrix elements is wrong. These "singular" terms may be treated unambiguously by adhering rigorously to the plane wave expansion of the coulomb interaction (Equation 1.3.3) in all phases of calculation.
III. CALCULATION OF THE ENERGY BANDS FOR Mg\textsubscript{2}Si

III.1 Physical Properties of Mg\textsubscript{2}Si

The crystal structure of Mg\textsubscript{2}Si was first determined by Owen and Preston (1924). Their X-ray diffraction experiments showed that the Si atoms form a face-centered cubic lattice with lattice constant \( a = 6.391 \text{ Å} \) (1Å = 10\textsuperscript{-8} cm.). Relative to each Si atom are 8 Mg atoms located at the points \( 1/4(\pm 1, \pm 1, \pm 1) a \). The Mg atoms form a simple cubic lattice with lattice constant \( 1/2 a \). The position of the atoms in a unit cell is shown in Figure 3. The crystal structure just described is called the anti-flourite structure (Wyckoff, 1948, Vol. 1, Chap. IV, p. 2). The space group is \( Fm3m \) (\( O^5 \)) and the point group with respect to a Si center of symmetry is the full cubic group \( m3m \) (\( O^3 \)). Since the space lattice is face-centered cubic, the reciprocal lattice is body-centered cubic. The Brillouin zone for the body-centered cubic reciprocal lattice is shown in Figure 4. Reduced \( k \)-vectors of special symmetry are labeled according to the notation of Bouckaert (1936).

More recent investigations (Klemm, 1941, and Ageev, 1952) of the crystal structure of Mg\textsubscript{2}Si have shown the lattice constant to be \( a = 6.338 \text{ Å} \). Ageev and Guseva (Ageev, 1952) calculated the electron density distributions from their experimental data. A reproduction of their results is shown graphically in Figures 5, 6. In Figure 5 the electron density distribution is plotted from a Si site along the lines \((100)\), \((110)\) and \((111)\) and from a Mg site along the line \((001)\). In Figure 6 the electron density distribution is plotted in the \((110)\) plane. The atomic sites are labeled (A, B, etc.,) to correspond to Figure 3. The
Fig. 3 The position of Mg and Si atoms in the basic cube
Fig. 4  The Brillouin zone for the face-centered cubic space lattice
Fig. 5 Electron density distribution for Mg$_2$Si in the directions:
(a) (100), (b) (110), (c) (111), (d) (001)
Fig. 6 Electron density distribution in Mg$_2$Si in the (110) plane
electron density in the neighborhood of a Si site is observed to be nearly spherically symmetric about the Si site. The electron density about a Mg site exhibits a sizable distortion from spherical symmetry. An estimate of the ionicity of the atomic constituents was obtained by calculating the number of electrons near the Si and Mg sites from a spherical approximation to the Ageev and Guseva charge density. This admittedly rough estimate accounted for 10 of the 12 Mg electrons and all 14 of the Si electrons. From Ageev and Guseva's quotation \(0.2e/\text{Å}^3\) of the charge density in the region of the Si-Si bond it appears that at least one of the remaining electrons is involved in the Si-Si bond. Presumably, the one remaining electron is shared by the Si and Mg atoms in the Si-Mg bond. However, this should not be taken too seriously since Ageev and Guseva pointedly refuse to estimate the ionicity. They argue that the absence of a sharp boundary between the separate ions makes an estimate of the ionicity impossible. This is probably the most realistic assessment of the situation. Whitten (1965) estimates the Mg ionicity to be .66e. One can obtain this result by assuming that the 2 electrons in the Si-Mg bond are shared on a 1/3 - 2/3 basis (Lott, 1965). Although the extent of the ionic character of the Mg atom in Mg_2Si is not determined it is clear that a self-consistent calculation of the electronic energy levels must be sufficiently flexible to allow for charge transfer from a Mg to a Si atom and include the effects of the unscreened Mg nucleus.

Mg_2Si is a semiconductor. The energy gap has been determined both electrically and optically. The results from the various measurements of
The energy gap have been summarized and discussed by Stella (1964). The electrical gap is .77ev, the optical gap is about .67ev and the photoconductive gap is .655ev at 15°K.

The probable symmetries of the valence levels and low-lying conduction levels may be predicted for the points \( \Gamma \), \( X \), and \( L \) by considering the dominant terms which would occur in a LCAO calculation of these energy levels. For this purpose LCAOs formed from the 3s and 3p atomic orbitals will be considered. In the case of Mg symmetry-adapted LCAOs formed from \( s \) and \( p \)-type functions centered about Mg sites consist of symmetric \((\text{Mg}^+)\) and anti-symmetric \((\text{Mg}^-)\) combinations of the Mg orbitals centered about the two Mg sites in an elementary cell. In Table 2 are listed the symmetry species of the Mg and Si LCAOs for the points \( \Gamma \), \( X \), and \( L \).

**Table 2.** Symmetry species which occur in LCAOs formed from Mg and Si \( s \) and \( p \) orbitals at \( \Gamma \), \( X \), and \( L \).

<table>
<thead>
<tr>
<th>LCAO</th>
<th>( \Gamma )</th>
<th>( X )</th>
<th>( L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si ( s )</td>
<td>( \Gamma_1 )</td>
<td>( X_3 )</td>
<td>( L )</td>
</tr>
<tr>
<td>Si ( p )</td>
<td>( \Gamma_{15} )</td>
<td>( X_4, X_5 )</td>
<td>( L_2, L_3 )</td>
</tr>
<tr>
<td>Mg( + ) ( s )</td>
<td>( \Gamma_1 )</td>
<td>( X_3 )</td>
<td>( L_1 )</td>
</tr>
<tr>
<td>Mg( - ) ( s )</td>
<td>( \Gamma_2 )</td>
<td>( X_4 )</td>
<td>( L_2 )</td>
</tr>
<tr>
<td>Mg( + ) ( p )</td>
<td>( \Gamma_{15} )</td>
<td>( X_2, X_5 )</td>
<td>( L_2, L_3 )</td>
</tr>
<tr>
<td>Mg( - ) ( p )</td>
<td>( \Gamma_{25} )</td>
<td>( X_1, X_5 )</td>
<td>( L_3, L_1 )</td>
</tr>
</tbody>
</table>
Since Mg$_2$Si is a semiconductor the valence levels at $\Gamma$ must be $\Gamma_1$ and $\Gamma_{15}$. From the charge density results we expect the dominant LCAOs to be formed from Si functions. It is likely that the low-lying conduction levels at $\Gamma$ will be $\Gamma_1$ and $\Gamma_2$, since the mixing between the Si and Mg functions is not likely to be large and the Mg $p$-functions almost certainly must lie above the Mg $s$-functions as in the free atom. Thus, the probable order of the valence levels and low-lying conduction levels at $\Gamma$ is $\Gamma_1$, $\Gamma_{15}$, $\Gamma_2$, $\Gamma_1$. By compatibility with the $\Gamma$ valence assignment the valence levels at $X$ must be $X_1$, $X_4$, $X_5$, and the valence levels at $L$ must be $L_1$, $L_2$, $L_3$. At $L$ the mixing between the Mg L$_2$, LCAO and the Si L$_2$, LCAO may be quite strong, suggesting that the L$_2$ valence level will lie appreciably below the L$_3$ valence level. For this reason it is difficult to predict the symmetry of the low-lying conduction level at $L$. Within this scheme there are three choices, L$_1$, L$_3$, L$_2$, with L$_1$ as the most likely choice. At $X$ the Si X$_4$, LCAO mixes with the Mg LCAO of this symmetry. Thus, the low-lying conduction level at $X$ must be X$_3$.

Whitten (1964) finds that the conduction band minimum occurs in the (1,0,0) direction.

111.2 Formulation of the Calculation

111.2.1 The bare-ion model for the core electrons

The calculations will be formulated specifically for the IPM based on the Hartree-Fock approximation to the ECM. The formulation of the calculations based on the SECM or CECM many-electron models will be treated as a specialization of the ECM calculations.

In self-consistent calculations the Hartree-Fock operator itself is
not known. A zeroth-order approximation to the Hartree-Fock operator is made. The solutions of this problem are obtained and then used to form an improved Hartree-Fock operator. It is essential that the formulation of the calculation be flexible enough so that a self-consistent iterative procedure is practical.

In the region about a nuclear site the coulombic attraction of the nuclear charge will be the dominant factor governing the distribution of electron probability density. The wave function (core function) for an electron (core electron) whose probability density lies predominantly in the vicinity of a nuclear site should closely resemble the corresponding free atom or free ion wave function in this region. Thus, the wave function in the crystal should be well-described by a single LCAO or a linear combination of a small number of LCAOs formed from the low-lying atomic wave functions (orbitals). Core LCAO's are defined to be single LCAOs formed from those atomic orbitals (core orbitals) which when centered about different nuclear sites in the crystal overlap negligibly with one another.

In the bare-ion model for the core electrons a first approximation is obtained for the core functions and eigenvalues. In this model all effects due to occupied non-core (valence) orbitals are neglected. The dominant effects of the valence electrons are included self-consistently in the next stage of calculation.

The Hartree-Fock operator for the bare-ion model is formed from core LCAOs. In Section 11.3.3 an expression (Equation 11.3.3.3) was given for the Hartree-Fock operator formed from functions having the properties of
core LCAOs. The bare-ion Hartree-Fock operator is
\[ H_{HF}^{\text{core}} = -\varepsilon^2 + V_{\text{core}} - A_{\text{core}} \]
where
\[ V_{\text{core}} = \sum_{s,n} V_{sn} + H_{\text{ion}} - V_0. \]

In \( V_{\text{core}} \) are included the direct potential due to the core electrons and the entire nuclear potential. Each \( V_{sn} \) (Equation 11.3.3.7) contains the potential due to the \( Z_s^i \) core electrons associated with nuclear site \( s \) plus the potential due to \( Z_s^i \) nuclear charges at the same site. The potential due to the remaining nuclear charges (\( Z_s^{\text{ion}} = Z_s^i - Z_s^0 \)) is
\[ H_{\text{ion}} = \sum_{K \neq 0} V_{\text{ion}}^{\text{ion}} \exp(iK \cdot r) \]
where
\[ V_{\text{ion}}^{\text{ion}} = \sum_{s} Z_s^{\text{ion}} \frac{\exp(-iK \cdot R_s)}{\Omega_K^2}. \]

The core exchange operator is
\[ A_{\text{core}} = \sum_{j,s,n} \varrho_{j,s,n}^* (2) H_{12} \varrho_{j,s,n} (2) \int_{R_n} \varrho_{j,s,n} (2) \, dx \]
where \( \varrho_{j,s,n} \) is a core orbital with index \( j \) centered at nuclear site \( s \) in the elementary cell associated with lattice vector \( R_n \). \( V_0 \) is the ECM average of the atomic-like potential,
\[ V_0 = \Omega_0^{-1} \sum_s V_s (\infty) \, dx. \]

In \( \text{Mg}_2\text{Si} \) the closed shells orbitals corresponding to doubly ionized Mg and 4-times ionized Si are regarded as defining the cores. Thus,
$Z_{\text{ion}}^{\text{Mg}} = 2$ and $Z_{\text{ion}}^{\text{Si}} = 4$ in Equation 2.1.2b.

In the vicinity of a nuclear site $s$ the dominant behavior of the ion term is

$$H_{\text{ion}} \approx -2Z_{s}^{\text{ion}}/r_{s}^{S} + V_{s}^{\text{shift}} \quad 2.1.5$$

where $V_{s}^{\text{shift}}$ is the Madelung shift associated with atom $s$. The Madelung shifts for the Mg and Si atoms corresponding to doubly ionized Mg and 4-times ionized Si are 2.4038Ry and 3.598Ry, respectively. The shifts quoted above were calculated from tables prepared by Slater and DeCicco (1963).

In the vicinity of a nuclear site the bare-ion Hartree-Fock operator is essentially a free ion Hartree-Fock operator. The eigenfunctions are single LCAOs formed from the free ion atomic orbitals. The eigenvalues are shifted from their atomic values by the respective Madelung shifts and the constant shift $V_{o}$.

Equation 2.1.5 is an approximation to the ionic term which is strictly valid only at the nuclear site. A numerical investigation of the behavior of this term indicates that core eigenvalues calculated in this approximation will be within .2Ry of the exact value. An attempt was made to incorporate the ionic correction into the free ion atomic calculation exactly. The ionic potential was written as an Ewald sum (Equation 11.1.4.5). The Ewald parameter was chosen to emphasize the plane wave series and the heavily screened lattice sum terms from the neighboring sites were neglected. The method failed because the results were dependent on the Ewald parameter. However, it was evident from this calculation that the effect of the ionic potential on the behavior of core functions is
negligible and that the eigenvalues are shifted by nearly a constant (the 2p and 2s eigenvalues were shifted slightly more than the 1s eigenvalues). In view of the fact that Equation 2.1.5 is an approximation, the sensitivity of the non-core eigenvalues to small shifts of the core eigenvalues will be considered in the non-core calculation. In Section III.3 we find that the non-core eigenvalues are more sensitive to shifts in the Mg core levels than we would like.

The valence electron contributions to the ECM Hartree-Fock operator are

$$H_{\text{HF}}^{\text{val}} = v^{\text{val}} + A^{\text{val}}.$$  \hspace{1cm} (2.1.6)

The effect of the valence terms on the core functions and eigenvalues in the ECM Hartree-Fock operator should be comparable to the corresponding effect in the free atom. To estimate the magnitude of the effect the neutral atom core eigenvalues for Mg and Si (Clementi, 1965) were compared with the core eigenvalues for doubly ionized Mg and 4-times ionized Si. The removal of the valence electrons from the neutral atoms lowered the core eigenvalues by a nearly constant amount. Since the Mg ions in the crystal do not seem to be screened very well by the valence electrons, the Mg bare-ion core levels should stay nearly the same and the Si bare-ion core levels should be raised by about 1 Ry. It has been necessary to neglect the valence exchange ($A^{\text{val}}$) with core functions. The principal error made in neglecting this term is a small negative shift of the Si core levels.

The basic assumption on which self-consistent calculations based on the bare-ion model zeroth-order approximation depend is that the valence
screening potential $V^{\text{val}}$ can be expanded in a limited number (100-500) of plane waves. Valence screening corrections to the bare-ion core solutions are obtained through expansions of $V^{\text{val}}$ in plane waves. It is possible that the core corrections are slightly underestimated. However, this may be partially compensated by the neglect of valence exchange with core functions.

## 1.2.2 A self-consistent procedure

The starting point for self-consistent calculations in the crystal is the bare-ion model for the core electrons. The zeroth-order Hamiltonian operator for the crystal is the bare-ion Hartree-Fock operator (Equation 2.1.1).

All eigenfunctions (core and non-core) are approximated by linear combinations of a set of basis functions consisting of symmetry-adapted bare-ion core functions augmented by a limited number of SOPWs. The SOPWs consist of symmetrized combinations of plane waves orthogonalized to the bare-ion core functions.

The first step in the self-consistent procedure is to calculate the eigenfunctions and eigenvalues of the bare-ion Schrödinger equation for a representative sampling of the points in the Brillouin zone. An improved Hartree-Fock operator is formed in the following way. The plane wave expansion coefficients of the charge density are calculated from the new eigenfunctions for the occupied states. The expansion of the charge density is limited to 100-500 plane waves. The direct term of the Hartree-Fock operator is calculated from the charge density. At each stage the direct term of the improved Hartree-Fock operator is taken to be
the average of the direct term in the preceding operator with the direct term calculated from the charge density. The exchange operator of the improved Hartree-Fock operator is formed from the eigenfunctions for occupied states. No averaging is done. This process is then repeated. At each stage of iteration improved eigenfunctions and eigenvalues are calculated from the Hartree-Fock operator obtained in the previous stage of iteration. An improved Hartree-Fock operator is then calculated from the new eigenfunctions. The process is discontinued when the changes in the Hartree-Fock operator cause negligible changes in the eigenvalues and direct potential. About five iterations are normally required.

In Section 111.2.3 the calculational procedure is discussed in detail.

111.2.3 Evaluation of matrix elements

The Hartree-Fock operator for the crystal is written in terms of core and valence contributions (Equations 2.1.16) as

\[ H_{\text{HF}}^{\text{ps}} = H_{\text{HF}}^{\text{core}} + H_{\text{HF}}^{\text{val}}. \]  \[ 2.3.1 \]

The basis set consists of bare-ion core functions and SOPWs (Equation 11.3.3.4). The bare-ion core functions are symmetry-adapted eigenfunctions of \( H_{\text{HF}}^{\text{core}} \),

\[ H_{\text{HF}}^{\text{core}} \Psi_c = E_c \Psi_c. \]  \[ 2.3.2 \]

This property is utilized in forming the matrix elements.

Contributions due to valence exchange with core functions is neglected. The error made by neglecting valence-core exchange is
discussed in Section 111.3.

The core-core matrix elements have the form

\[
(\psi_c, H_{\text{core}}^\text{HF} \psi_{c'}) = E_c \delta_{c,c'} \tag{2.3.3a}
\]

and

\[
(\psi_c, H_{\text{core}}^\text{val} \psi_{c'}) \approx (\psi_c, V_{\text{val}} \psi_{c'}) \tag{2.3.3b}
\]

The core-valence matrix elements are

\[
(\psi_c, H_{\text{val}}^\text{core} \text{SPW;} a, k) = E_c (\psi_c, \text{SPW;} a, k) = 0 \tag{2.3.4a}
\]

and

\[
(\psi_c, H_{\text{val}}^\text{val} \text{SPW;} a, k) \approx (\psi_c, V_{\text{val}} \text{SPW;} a, k) \tag{2.3.4b}
\]

The valence-valence matrix elements are

\[
(\text{SPW;} a, k, H_{\text{val}}^\text{val} \text{SPW;} a, k') = (\text{SPW;} a, k, H_{\text{val}}^\text{val} \text{SPW;} a, k')
- \sum_c (\psi_c, \text{SPW;} a, k)\ast (\psi_c, \text{SPW;} a, k') E_c \tag{2.3.5a}
\]

and

\[
(\text{SPW;} a, k, H_{\text{val}}^\text{val} \text{SPW;} a, k') \approx (\text{SPW;} a, k, V_{\text{val}} \text{SPW;} a, k')
+ (\text{SPW;} a, k, V_{\text{val}} \text{SPW;} a, k') \tag{2.3.5b}
\]

The terms involving the valence screening potential \( V_{\text{val}} \) are evaluated by expanding \( V_{\text{val}} \) in plane waves. Since, the space group for the anti-flourite structure is symmorphic,
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\[ V^{\text{val}} = \sum_{[K]} V^{\text{val}}_{[K]} N_{[K]} F([K]) \]  \hspace{2cm} 2.3.6a

where

\[ F([K]) = \sum_{K \in [K]} \frac{\exp(iK \cdot r)}{N_{[K]}} \]  \hspace{2cm} 2.3.6b

and \( N_{[K]} \) is the number of reciprocal lattice vectors in the module \([K]\).

Let,

\[ \rho_{c,c'}^{[K]} = (\psi_c, F([K]) \psi_{c'}) , \]  \hspace{2cm} 2.3.7a

\[ \rho_{c;a,k}^{[K]} = (\psi_c, F([K]) \text{SPW}_a,k) , \]  \hspace{2cm} 2.3.7b

and

\[ \rho_{a,k;a,k'}^{[K]} = (\text{SPW}_a,k, F([K]) \text{SPW}_a,k') . \]  \hspace{2cm} 2.3.7c

In terms of the definitions (Equations 2.3.7) of the charge density matrices the contributions to the matrix elements due to the valence screening potential are

\[ (\psi_c, V^{\text{val}} \psi_{c'}) = \sum_{[K]} N_{[K]} V^{\text{val}}_{[K]} \rho_{c,c'}^{[K]} , \]  \hspace{2cm} 2.3.8a

\[ (\psi_c, V^{\text{val}} \text{SPW}_a,k) = \sum_{[K]} N_{[K]} V^{\text{val}}_{[K]} \left[ \rho_{c;a,k}^{[K]} - \sum_{c'} \rho_{c;a,k}^{[K]} \rho_{c,c'}^{[K]} \right] , \]  \hspace{2cm} 2.3.8b

and
The orthogonality coefficients are a special case of the charge density matrix (Equation 2.3.7b),

\[(\psi_c', \text{SPW}^a, k) = \rho_{c; a, k} \cdot 2.3.9\]

Consider the first term in the right member of Equation 2.3.5a. This may be written with the aid of Equation 2.1.1 as

\[(\text{SPW}^a, k, \text{H}_{\text{HF}} \text{SPW}^a, k') = (\text{SPW}^a, k, - V^2 \text{SPW}^a, k') 2.3.10\]

\[+ (\text{SPW}^a, k, V^\text{core} \text{SPW}^a, k') - (\text{SPW}^a, k, A^\text{core} \text{SPW}^a, k')\]

where for this purpose we choose to represent \(V^\text{core}\) as a plane wave expansion

\[V^\text{core} = \sum_{[K]} N_{[K]} V_{[K]} F([K]) \cdot 2.3.11\]

The kinetic energy term is

\[(\text{SPW}^a, k, - V^2 \text{SPW}^a, k') = k^2 \rho_{a, k; a, k'} \cdot 2.3.12a\]

The contribution due to the direct and nuclear potentials is

\[(\text{SPW}^a, k, V^\text{core} \text{SPW}^a, k') = \sum_{[K]} N_{[K]} V_{[K]} \rho_{a, k; a, k'} \cdot 2.3.12b\]
The method used to evaluate the core-valence exchange matrix elements is described in the appendix (Section VI.2.3). Since the core functions are not expected to change appreciably in the iteration procedure, the core-valence exchange matrix elements are included in the Hamiltonian matrix, but are not altered in the self-consistent scheme.

Consider the second term in the right member of Equation 2.3.5b. The valence exchange operator is

\[ A_{\text{val}} = \sum_{\nu j}^\psi \langle \psi \mid H_{12} \mid \phi \rangle \langle \phi \mid \psi \rangle \, d\vec{r}_2. \tag{2.3.13} \]

The valence functions are formed from linear combinations of SOPVs. These are approximated by a linear combination of SPWs. This approximation should be quite good, since the core orthogonalization contribution to the valence functions is observed to be small.

Let

\[ \varphi_\nu = (\text{SPW}; a, k+K_1, \text{SPW}; a, k+K_2, \ldots) \tag{2.3.14} \]

be a row matrix whose components are the SPWs which occur in the SPW expansion of the valence function \( \psi_\nu \). Then,

\[ \psi_\nu = \varphi_\nu b_\nu \tag{2.3.15} \]

where \( b_\nu \) is a column matrix whose components are the SPW expansion coefficients. In this notation the valence-valence exchange matrix elements are expressed as

\[ (\text{SPW}; a, k, A_{\text{val}} \text{SPW}; a, k') = \sum_\nu b_\nu^* A_{a, k; a, k'}^\nu b_\nu \tag{2.3.16a} \]

where \( A_{a, k; a, k'}^\nu \) is a valence-valence exchange supermatrix element.
A typical integral which occurs in calculating the supermatrix elements is

\[
A^V_{a, k; a, k'} = (SPW; a, k, \theta^V_{(2)} H_{12} P_{12} \theta^V_{(2)} SPW; a, k') .
\]

where if the denominator is zero the integral is zero. A zero denominator in Equation 2.3.17 corresponds to the \( \underline{k}=0 \) term in the plane wave expansion of the ECM coulomb potential (Equation 11.1.3-3). Thus, the integrals which occur in the valence-valence exchange matrix elements are very simple. However, there is an immense number of them even when the sampling of the Brillouin zone is limited to the principal symmetry points, \( \Gamma, X, \) and \( L \).

The calculations have been performed on an IBM 7074 digital computer. The Iowa State University version of this machine has a direct access (core) storage capacity of 20,000 words of 10 digits each. In addition there are 6 tape units available for programmer use. There are available two Fortran compilers and a basic language (Autocoder) compiler. The Autocoder language provides an extremely flexible symbolic language. For this reason the key programs for this calculation have been written in Autocoder. In the following paragraphs the calculations will be described with reference to machine procedures and capabilities.

The bare-ion calculations have been programmed in Fortran. Self-consistent solutions of the Hartree-Fock atomic problem have been obtained in terms of a finite basis of analytic functions. The radial
functions are expanded in a basis of Slater functions, SF(a,n),

\[ R_j(r) = \sum_{a,n} C(a,n) \text{SF}(a,n) \]  \hspace{1cm} 2.3.18a

where

\[ \text{SF}(a,n) = r^n \exp(-ar) \]  \hspace{1cm} 2.3.18b

The angular functions are expressed as cubic harmonics. The explicit form which is chosen for the atomic orbitals is

\[ u_j = R_j (4\pi)^{-1/2} \]  \hspace{1cm} 2.3.18c

for s functions and

\[ u_{ji} = R_{ji} (3/4\pi)^{1/2} (x_i/r), \quad i=1,2,3 \]  \hspace{1cm} 2.3.18d

for p functions.

The programs have been checked by repeating calculations by Clementi (1965) for several cases. Excellent agreement with Clementi's results was obtained. Several of the integrals which occur in the atomic calculation are described in the appendix (Section VI.2.2).

Real matrix elements are obtained by choosing the origin of coordinates at a Si site and by choosing the bare-ion core orbitals \( \varrho_{js} \) as the following combinations of the atomic orbitals \( u_{js} \),

\[ \varrho_{jSi} = y_j u_{jSi} \]  \hspace{1cm} 2.3.19a

\[ \varrho_{jMg(\pm)} = 2^{-1/2} y_j [u_{jMg} (r-R_{Mg}) + u_{jMg} (r\pm R_{Mg})] \]  \hspace{1cm} 2.3.19b
and

\[ y_j = 2^{-1/2} \gamma_j \begin{pmatrix} u_j^{\text{Mg}}(r - R_{\text{Mg}}) - u_j^{\text{Mg}}(r + R_{\text{Mg}}) \end{pmatrix}. \]  

The factor \( y_j \) is a phase factor which is taken to be \((1, i)\) if the atomic orbital \( u_j \) is an \((s, p)\) function. The point vector \( R_{\text{Mg}} = (1, 1, 1)a/4 \).

Symmetry-adapted bare-ion core functions are obtained by the projection operator technique described in the appendix (Section VI.1). The translational symmetry-adapted bare-ion core functions are

\[ \varphi_{j,s}^k = N^{-1/2} \sum_n \exp(i \cdot R_n) \varphi_{j,s}^n \]  

where \( \varphi_{j,s}^n \) is a bare-ion core orbital (Equations 2.3.19) formed from atomic orbitals centered in the elementary cell associated with the lattice vector \( R_n \). A bare-ion core function symmetry-adapted to the group of the \( k \)-vector is formed from a linear combination of the translational symmetry-adapted bare-ion core functions. Let

\[ \varphi_k = (\varphi_{1sSi}^k, \varphi_{2sSi}^k, \ldots, \varphi_{1sMg(+)i}^k, \ldots) \]  

be a row matrix whose components are translation symmetry-adapted bare-ion core functions. Then, a bare-ion core function which transforms according to the irreducible representation a of the group of the \( k \)-vector can be expressed as

\[ \varphi_{ms}^{ka} = \varphi_k C_{m}^{ka} \]  

where \( C_{m}^{ka} \) is a column matrix whose components are chosen such that \( \varphi_{ms}^{ka} \)
is normalized and has the prescribed transformation properties. Previously, the single index $c$ has been used to describe a symmetry-adapted bare-ion core function,

$$\psi_c = q^{ka}_m,$$  \hspace{1cm} 2.3.22b

where it is to be understood that the single index $c$ represents the complex of indices on $q^{ka}_m$ in Equation 2.3.23.

From the definition of the core-core charge density matrix (Equation 2.3.7a) and Equations 2.3.22 it follows that

$$\rho_{c,c'}^{[K]} = c^{ka+}_m q^{ka}_m ([K]) c^{ka'}_m.$$  \hspace{1cm} 2.3.23a

where

$$Q^{ka}_m ([K]) = \int g^{k+}_m g^{k}_m F([K]) \, dr.$$  \hspace{1cm} 2.3.23b

A typical element in the matrix $Q^{ka}_m ([K])$ is

$$Q^{ka}_{js, st} ([K]) = N^{-1}_o \sum_{n,n'} \exp[i \cdot (r_n - r_n')] \int \varrho_{js,n} \varrho_{it,n} F([K]) \, dr,$$  \hspace{1cm} 2.3.24a

where since overlap between bare-ion core orbitals on different centers is negligible this may be written as

$$Q^{ka}_{js, st} ([K]) = N^{-1}_o \int \varrho_{js,n} \varrho_{is,n} F([K]) \delta_{s,t}.$$  \hspace{1cm} 2.3.24b

The sum of the products of bare-ion core orbitals in Equation 2.3.24b is a translation symmetry-adapted function for $\Gamma$. Since $F([K])$ is a space group invariant function only those parts of the sum of products of
bare-ion core orbitals which transform according to the identical representation of the space group produce non-zero contributions to the integral. Therefore, all $Q$-matrix elements involving products of $s$ and $p$ atomic orbitals or products of $p_x$ and $p_y$, etc., atomic orbitals are zero. The non-zero $Q$-matrix elements are finally reduced to Fourier transforms of the atomic orbitals,

$$Q^a_{js,j's} ([K]) = q_s^{(K)} \int u^*_{js} u_{j's} \exp(iK \cdot \mathbf{r}) \, d\mathbf{r},$$  \hspace{2cm} 2.3.25

where $q_s^{(K)}$ is a phase factor and the $u$'s are either $s$ or $p$ functions. The Fourier transform integrals are discussed in the appendix (Section VI.2.1). The phase factors $q_s^{(K)}$ are listed in Table 3. Any $K$-vector in the module $[K]$ may be chosen for the calculation of the Fourier transform or the phase factor.

Table 3. Phase factors in $Q$-matrix elements

<table>
<thead>
<tr>
<th>Product functions (s or p)</th>
<th>$q_s^{(K)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si - Si</td>
<td>1</td>
</tr>
<tr>
<td>Mg(+) - Mg(+)</td>
<td>$\cos(K \cdot \mathbf{R}_{\text{Mg}})$</td>
</tr>
<tr>
<td>Mg(-) - Mg(-)</td>
<td>$\cos(K \cdot \mathbf{R}_{\text{Mg}})$</td>
</tr>
<tr>
<td>Mg(+) - Mg(-)</td>
<td>$-\sin(K \cdot \mathbf{R}_{\text{Mg}})$</td>
</tr>
<tr>
<td>Mg(-) - Mg(+)</td>
<td>$\sin(K \cdot \mathbf{R}_{\text{Mg}})$</td>
</tr>
</tbody>
</table>

The core-valence charge density matrix (Equation 2.3.7b) may be written with the aid of Equations 2.3.22 as
\[
\rho_{c; a, k'}^{[K]} = \frac{c^{k_a^+}}{m} (\psi^{k^+}, F([K]) SPW; a, k') \quad 2.3.26a
\]

Since a SPW is a linear combination of plane waves,

\[
SPW; a, k' = \sum_{k} b_{k'} PW, k + k' \quad 2.3.27
\]

Equation 2.3.26a may be expressed as

\[
\rho_{c; a, k'}^{[K]} = \frac{c^{k_a^+}}{m} \sum_{k'} b_{k'} (\psi^{k^+}, F([K]) PW, k + k') \quad 2.3.26b
\]

where \( k' = k + K' \) for some \( K' \) in the sum of plane waves.

Consider a term in the column vector \((\psi^{k^+}, F([K]) PW, k + k')\),

\[
(\psi^{k^+}, F([K]) PW, k + k') = \sum_{K \in [K]} (\psi_{js}^{k}, PW, k') \quad 2.3.28
\]

where \( k'' = k + K + K' \). The scalar product in the right member of Equation 2.3.28 may be written as

\[
(\psi_{js}^{k}, PW, k') = (N_0 \Omega) \frac{1}{2} \sum_{n} \exp(-ik \cdot R_n) \int u_{js}^*(k) \exp(ik'' \cdot r) \, dr
\]

or since \( \Omega_1 = N_0 \Omega \) as

\[
(\psi_{js}^{k}, PW, k') = \Omega^2_1 \int u_{js}^*(k) \exp(ik'' \cdot r) \, dr \quad 2.3.29
\]

Equation 2.3.29 is just an OPW orthogonality coefficient. The OPW orthogonality coefficient expressed as the Fourier transform of an atomic orbital is

\[
(\psi_{js}^{k}, PW, k') = \Omega^1_0 \int u_{js}^*(x) \exp(ik'' \cdot x) \, dx \quad 2.3.30
\]
where $f_{\vec{k''}/\vec{s}}$ is a phase factor which does depend explicitly on the vector $\vec{k''}$. The phase factors which occur in OPW orthogonality coefficients are listed in Table 4. The Fourier transform integrals which occur in Equation 2.3.30 are discussed in the appendix (Section VI.2.1). The core-valence charge density matrix elements are obtained by accumulating the sums of OPW orthogonality coefficients according to Equation 2.3.28 and Equation 2.3.26a.

Table 4. OPW orthogonalization coefficient phase factors

<table>
<thead>
<tr>
<th>Bare-ion Core Orbital</th>
<th>$f_{\vec{k''}/\vec{s}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si $s$</td>
<td>1</td>
</tr>
<tr>
<td>Si $p$</td>
<td>1</td>
</tr>
<tr>
<td>Mg(+) $s$</td>
<td>$\cos(\vec{k''} \cdot \vec{R}_{Mg})$</td>
</tr>
<tr>
<td>Mg(+) $p$</td>
<td>$\cos(\vec{k''} \cdot \vec{R}_{Mg})$</td>
</tr>
<tr>
<td>Mg(-) $s$</td>
<td>$\sin(\vec{k''} \cdot \vec{R}_{Mg})$</td>
</tr>
<tr>
<td>Mg(-) $p$</td>
<td>$\sin(\vec{k''} \cdot \vec{R}_{Mg})$</td>
</tr>
</tbody>
</table>

Although a symmetry reduction is possible in Equation 2.3.26a the calculation of the core-valence charge density matrix elements was performed as described above. At the stage in the program where these quantities were calculated it did not seem advisable to take advantage of this possibility. At all other points in the calculations where it was realized that symmetry could be used to reduce the number of terms that had to be handled, this symmetry reduction was incorporated into the calculation.
For example, in the calculation of the valence-valence charge density matrices (Equation 2.3.7a) the fact that a symmetrized plane wave is defined as

\[ \text{SPW}_{a,k} = P_a \text{PW}_{k} \]

is used to express the valence-valence charge density matrix elements as

\[ (\text{SPW}_{a,k}, F([K]) \text{SPW}_{a,k'}) = (\text{PW}_{k}, F([K]) \text{SPW}_{a,k'}). \]

This procedure was also used to reduce the number of terms in the valence-valence exchange matrix elements. The integrals in Equation 2.3.31 have the form

\[ (\text{PW}_{k}, \text{PW}_{k'}) = \delta_{k,k'} . \]

Thus, the problem of calculating the valence-valence charge density matrices is reduced to accumulating a set of Kronecker delta functions.

The charge density matrices are used to calculate the Fourier coefficients of the charge density at each stage in the iteration procedure. Let

\[ \varphi_{ka}^{\text{ka}} = (\psi_c, \psi_{c'}, \ldots, \text{SOPW}_{a,k_1}, \text{SOPW}_{a,k_2}, \ldots) \]

be a row matrix whose components are the symmetry-adapted basis functions. A solution of the ECM Hartree-Fock problem may be expressed as

\[ \psi_1 = \varphi_{ka}^{\text{ka}} b_1 \]
where \( b_i \) is a column matrix whose components are the coefficients of the basis functions as determined by a Rayleigh-Ritz variational calculation. If \( \psi_i \) is an eigenfunction corresponding to an occupied single-particle state, then the contribution to the charge density is

\[
\psi_i^* \psi_i = b_i^+ \rho_{-ka} b_i
\] 

2.3.35

where

\[
\rho_{-ka} = \rho_{ka+} \rho_{-ka}
\] 

2.3.36

is the charge density matrix for the symmetry species designated by \( ka \).

The contributions to the charge density of the crystal must also include contributions from eigenfunctions \( \psi_i' \) which are related to \( \psi_i \) by a space group transformation. A recipe for calculating the Fourier coefficients of the charge density in the crystal from symmetry-adapted eigenfunctions is given in Section 11.3.1. By specializing Equation 11.3.1.15 to the case of a symmorphic space group we obtain the result

\[
\rho^{[ka]} = \sum_{[K]} \rho^{[ka]}([K]) F([K])
\] 

2.3.37

where \( \rho^{[ka]} \) is the symmetry-invariant charge density associated with symmetry species \( ka \) and

\[
\rho^{[ka]}([K]) = \mathcal{M}_k a \left( \rho_{ka+}, F([K]) \rho_{-ka} \right)
\] 

\( \Omega \)

In Equation 2.3.38 \( \mathcal{M}_k \) equals the number of inequivalent \( k \)-vectors which
are related to \( k \) by space group transformations and \( d_a \) equals the degeneracy of the irreducible representation \( a \).

The main calculation consists of two preparatory stages and a final stage. The programs for these calculations have been written in Autocoder. In preparation for the final stage of calculations the charge density matrices are calculated and assembled on a tape. The valence-valence exchange supermatrix elements are calculated and assembled on a tape. For an ECM calculation with full valence-valence exchange the preparation time is about 15 hours on the IBM 7074. This calculation time could have been reduced substantially had there been an additional 20,000 words of direct access storage available.

In the final stage of calculation the matrix elements for each symmetry species are assembled from the appropriate charge density matrices and valence-valence exchange supermatrix elements. The resulting eigenvalue problem is treated as described in Section 11.3.2. The contributions to the potential from the charge density due to the occupied eigenfunctions are calculated and accumulated. This process is repeated for the selected sampling of symmetry species. Then, an improved direct potential is calculated and the entire procedure is repeated. About 5 minutes is required for each iteration.

All tape operations which occur in the assembly section of the iteration procedure are buffered. This means that information which is needed in a subsequent step in the calculation is being read into storage at the same time that the matrix elements are being assembled. In this way calculation time is substantially reduced.
III.3 Results From the Mg$_2$Si Calculations

SECM: The results from the SECM calculations are indicated in Figure 7. In the SECM exchange contributions are negligible. The matrix elements are calculated in the manner described in Section III.2.3 except that exchange contributions are omitted in all phases of calculation. The iteration procedure was terminated when the eigenvalues and Fourier coefficients of the potential were observed for successive iterations to change by less than .002 Ry. Both the ECM and SECM calculations were based on a division of charge into valence electrons and ions. Each ion $s$ with nuclear charge $Z_s$ included $Z'^s_s$ core electrons, $Z^s_s$ nuclear charges and $Z^{ion}_s = Z_s - Z'^s_s$ residual nuclear charges. In the SECM calculations the only approximation of any consequence consisted of replacing the potential of all the residual nuclear charges by a coulomb potential and a Madelung shift near any one nuclear site (Equation 2.1.5).

The sensitivity of the valence and low-lying conduction levels to small shifts of the bare-ion core energies was studied. For shifts of all the core energies of .1 Ry, the valence levels were changed by less than .01 Ry. The conduction level which was most responsive to the core shifts was the low-lying $X_3$ level. A shift of .1 Ry. for the core levels produced a shift in the $X_3$ level of .05 Ry. This sensitivity can be understood as follows. The core energies enter the valence calculation (Equation 2.3.5a) as a factor on the product of two SOPW orthogonalization coefficients. If the core energy is low, the SOPW orthogonalization is small. The largest contribution to the matrix elements is generally from terms involving the highest core eigenvalues since the product of
Fig. 7 Energy bands for Mg$_2$Si based on the SECM
SOPW orthogonalization coefficients is then relatively large. Thus, a small change in the eigenvalue may produce a significant change in the matrix element. However, to estimate the relative contributions to the matrix elements one must compare s functions with s functions and p functions with p functions. The effect on the matrix elements due to a small change in a ls core eigenvalue is roughly the same as the corresponding change in a 2p core eigenvalue. The SPWs in X_3 are orthogonalized to Mg^2^ s functions (Table 2). Since the highest s core eigenvalue corresponds to a Mg 2s function, it is not surprising that X_3 is sensitive to small shifts in the core eigenvalues. Now, the SPWs in the X_4^ valence function are also orthogonalized to Mg s functions. It is necessary to look a little deeper to understand why the X_4^ valence level is not equally sensitive to core shifts. The difference is that the X_4^ SPWs are orthogonalized to Mg^- s functions (Table 2). An examination of the orthogonalization coefficient phase factors (Table 4) reveals that the phase factors for the leading terms in the SOPW expansions for X_3 and X_4^ are 1,1,0 and 1,0,1, respectively. This must account for the X_3 level changing by .05 Ry. while the X_4^ level only changed by .01 Ry. when the core levels were shifted by .1 Ry. The change in the Si 2p eigenvalue almost certainly is a minor effect on the X_4^ level.

In the first SECM calculation the Fourier coefficients of the valence charge density were obtained for an 8 point sampling of the Brillouin zone. Essentially the same results were obtained for the \Gamma, X and L levels and the self-consistent direct potential when the
calculations was extended to include a sample of 64 points in the Brillouin zone. In the 64 point sample several points of very low symmetry were included in the sample. We conclude that at least for the direct potential an 8 point sampling of the Brillouin zone provides an adequate description of the charge density.

ECM: In Figure 8 the results of the ECM calculations are indicated. The sampling of the Brillouin zone was restricted to the 8 points equivalent to $\Gamma$, $X$ and $L$. The matrix elements were calculated exactly as described in Section III.3.

The shape of the low-lying conduction levels is qualitatively the same as the corresponding SECM levels. However, the valence bands are substantially different in the ECM calculation than in the SECM. The top of the valence band predicted by the ECM is at $L$. Also, the $X_4$, and $X_5$ valence levels have been interchanged. Since these results are somewhat disconcerting we will reconsider the approximations which were made in forming the ECM matrix elements. It seems unlikely that a more detailed sample of the Brillouin zone will change the results.

We first consider the Madelung shift approximation. Several of the levels are extremely sensitive to small shifts of the core levels. If all core levels are shifted by 0.05 Ry., the low-lying valence band $(L_1-\Gamma_1-X_1)$ is raised by 0.07 Ry. and the $X_3$ conduction level is lowered by 0.05 Ry. Smaller shifts are observed in the other levels.

The strange appearance of the valence band is caused by the valence exchange contributions to the matrix elements. If valence exchange is
Fig. 8 Energy bands for Mg$_2$Si based on the ECM
removed, the shape of the bands is qualitatively the same as the SECM bands, but the conduction band drops into the valence band. If, as suggested by the work of Phillips and Kleinman (1962) on Si, the valence exchange contributions are reduced by a factor of the order $1/3$, the shape of the bands is much the same as the SECM bands, but the $X_3$ conduction level lies 0.07 Ry. below the top of the valence band.

In forming the matrix elements three approximations were made which involved the interaction of the valence exchange operator with core functions. It was hoped that the main effect of the approximations would be to neglect a small shift of the core eigenvalues.

From the fact that most of the valence charge density is concentrated near Si sites, it appears likely that the core levels which are most affected by the valence exchange are the Si core levels. An estimate of the shift in the Si core levels was obtained by calculating the exchange contribution to the core eigenvalues in the $\text{Si}^{+4}$ ion. This turned out to be a uniform shift of about 0.8 Ry. Such a shift on the Si core levels produced almost no change in the shape or position of the bands. Si core shifts are much less critical than Mg core shifts as discussed on page 93.

The neglect of valence exchange in those terms of the valence-valence matrix elements which involve core functions may be of serious consequence. The approximation in which valence eigenfunctions in the valence exchange operator are expanded in SPWs is observed to be a good one, at least as measured by the contribution of the core parts of the SOPWs to the normalization. In the ECM calculation of valence exchange the SPW approximation to a valence function was formed by correcting the
SOPW expansion coefficients for the core contributions in the SOPW expansion. These corrections were observed to be small. However, in valence exchange matrix elements with individual SOPWs it is not evident that the terms which involve core functions will be negligible. The dominant part of the matrix element is the term which we have included (Equation 2.3.5b). However, the core terms may reduce this by as much as 10 or even 20 percent. To obtain an estimate of this effect all the valence exchange contributions were reduced by 20 percent. This reduction was enough to raise the $\Gamma_{15}$ level to the top of the valence band. Although the $X_{51}$ and $X_{41}$ levels were not interchanged they have been pulled together. The results of this experiment are indicated in Figure 9. It appears likely that an improved treatment of valence exchange would remove the disturbing features of the ECM Hartree-Fock bands. However, this is virtually impossible within the present formulation, since the terms which have been omitted involve an immense number of difficult integrals.

CECM: In view of the sensitivity of the ECM Hartree-Fock calculations to the core energies a calculation based on the CECM Hartree-Fock IPM did not seem advisable. Although the valence exchange contributions would be reduced in this model, it appears to be essential to calculate the core functions and eigenvalues accurately. The complicated form of the CECM coulomb interaction (Equation 11.2.3.2) in the core exchange operator makes an accurate calculation prohibitive.
Fig. 9 Energy bands for Mg$_2$Si based on a modified ECM
III.4 Comparison with Experiments

On the basis of piezoresistance measurements of n-type $\text{Hg}_2\text{Si}$ Whitten (1954) predicted that the minimum in the conduction band is in the (100) directions. Both the SECM and ECH bands are in complete agreement with this prediction.

Experimental determinations of the energy gap have been discussed by Stella (1964). The experiments predict gaps ranging from .60 ev to .77 ev at 15°K. These energies are obtained from various processes all believed to be due to an indirect (phonon assisted) transition. Reflectivity measurements by Scouler\(^1\) indicated that the direct gap occurs at 2.1 ev.

The SECM calculations yield an indirect gap corresponding to a transition from $\Gamma_{15}$ to $X_3$. However, the SECM gap is 1.40 ev which differs by about a factor 2 from the experimental results. The SECM direct gap at $\Gamma$ and $L$ is about 2.6 ev and at $X$ is 2.5 ev. A core shift of .1 Ry, brings the $X_3$ level down by .05 Ry, without changing the top of the valence band appreciably. This change puts the direct and indirect gaps in approximate agreement with experiment, but the direct gap occurs at $X$ between the $X_2$ and $X_3$ levels. However, such a shift can not be justified except by treating the potential due to the distant ions or the core electrons in the bare-ion model exactly instead of approximating the effect by a Madelung shift.

In Table 5 are listed a selected sample of optical transition

---

energies based on the SECM calculations. In the first column of energies the unmodified SECM results are presented. In the second and third columns all the core energies have been shifted by .1 Ry. and .15 Ry., respectively.

Table 5. Optical transition energies for MgSi based on the SECM

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energies (core shift=0)</th>
<th>Energies (core shift=.1)</th>
<th>Energies (core shift .15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{15} - \Gamma_1$</td>
<td>2.84</td>
<td>2.38</td>
<td>2.113</td>
</tr>
<tr>
<td>$\Gamma_{15} - \Gamma_{25'}$</td>
<td>6.07</td>
<td>6.04</td>
<td>6.04</td>
</tr>
<tr>
<td>$X_{51} - X_3$</td>
<td>2.50</td>
<td>1.97</td>
<td>1.36</td>
</tr>
<tr>
<td>$X_{51} - X_1$</td>
<td>6.54</td>
<td>6.54</td>
<td>6.48</td>
</tr>
<tr>
<td>$L_{31} - L_1$</td>
<td>2.72</td>
<td>2.28</td>
<td>2.03</td>
</tr>
<tr>
<td>$L_{31} - L_3$</td>
<td>6.94</td>
<td>6.94</td>
<td>6.96</td>
</tr>
<tr>
<td>$\Gamma_{15} - X_3$</td>
<td>1.40</td>
<td>.89</td>
<td>.60</td>
</tr>
</tbody>
</table>

In view of the inadequate treatment of the valence exchange matrix elements no further discussion of the ECM results will be made. Qualitatively, the features of ECM Hartree-Fock bands are in agreement with experiment, but the detailed features of the bands are probably wrong.
IV. DISCUSSION AND CONCLUSIONS

In making the Hartree-Fock approximation to the many-electron problem for a crystal it is hoped that the essential features of the many-electron system are retained. In Section 1.1 it was suggested that this might not be the case. Since all IPMs are in some sense based on the Hartree-Fock IPM, it is important that both the capabilities and limitations of the Hartree-Fock IPM be understood. For this reason we have attempted to calculate the Hartree-Fock electron energy bands for Mg$_2$Si as accurately and with as few approximations as practical considerations allowed.

In the usual formulations of band calculations the crystal potential including an approximation for the exchange operator consists of spherically symmetric potentials centered about the nuclear sites. From these results it is impossible to determine the limitations of the Hartree-Fock IPM since it is not at all clear with what accuracy exchange effects have been approximated. On the basis of his calculations on Si and Ge, Herman$^{1}$ claims that it may be essential to retain the $\lambda$-dependence$^{2}$ of the Hartree-Fock exchange operator in the IPM if band calculations are to provide detailed agreement with experiment.

To our knowledge the only calculations which have attempted to include a realistic Hartree-Fock exchange operator are those of Phillips

$^{1}$Herman, F., unpublished paper presented at the "March" meeting of the American Physical Society, Kansas City, Missouri, 1965.

$^{2}$The term "$\lambda$-dependence" refers to the fact that the form of the Hartree-Fock exchange operator depends on the function on which it operates.
and Kleinman (1962) on Si. However, for the reasons indicated in Section II.3.5 we are unable to accept their results as conclusive evidence for the failure of the Hartree-Fock IPM. In Section III.3 we have attributed the unsatisfactory appearance of the ECM Hartree-Fock bands in our results as being largely due to the neglect of orthogonalization terms in the valence exchange contributions to the valence-valence matrix elements. This approximation was also made by Phillips and Kleinman. However, as was noted in Section III.3 it is hopeless, at least at present, to take these neglected quantities accurately into account. Certainly before an attempt in this direction is made, alternative formulations of the problem should be considered.

An alternative formulation of the problem along lines similar to those described in Section III.2 might be as follows. The basis set we have used consisted of bare-ion functions augmented by SOPWs. An alternative basis set which should provide an equally good description of the valence and core functions can be formed from the bare-ion core functions augmented by SPWs. As in the case of the SOPW formulation it is essential that the valence functions be adequately represented by the SPW basis set. The SOPW results indicate that this is likely to be the case with a practicable number of SPWs. Although the difficult valence exchange matrix elements involving core functions are not eliminated in this formulation the number of them which occur is substantially reduced.

The ECM is in no sense a radical departure from the traditional Hartree-Fock formulation of an IPW. For most purposes it is equivalent
to the usual formulation of the problem. Only when the basis set involves plane waves does the problem which is solved by the ECM arise. This has come to be called the problem of $V_{\infty \infty \infty}$, where $V_{\infty \infty \infty}$ represents the $k=0$ coefficient in a Fourier expansion of the potential. Historically, this problem has two aspects.

First, in the early calculations of bands in crystals with plane waves or OPWs (e.g. see Herman, 1964), no attempt was made to do the calculation self-consistently. A potential was formed from a superposition of the atomic potentials for the constituent atoms in the crystal. Then, the OPWs were formed for the valence calculation from the core atomic functions and plane waves, and the core atomic eigenvalues were used in calculating the matrix elements. However, in general the atomic potentials overlap appreciably. The potential near any nucleus is shifted by the tails of potentials arising from neighboring atoms. Consequently, the zero of the core energy is shifted. This shift has been called $V_{\infty \infty \infty}$. A variation on this aspect of the problem arises when attempts are made to recalculate the crystal potential from the OPW expansion of the valence eigenfunctions. In this case the representation of the potential as a superposition of atomic potentials breaks down. The nuclear charges are not as effectively screened by the valence electrons as is the case in atoms. This aspect of $V_{\infty \infty \infty}$ is treated in our calculations by approximating the potential due to distant ions on core electrons by a Madelung shift.

The second aspect of the problem of $V_{\infty \infty \infty}$ entered our calculations in the treatment of valence exchange matrix elements with plane waves.
If the traditional formulation of the Hartree-Fock IPM is used, some matrix elements diverge. In the ECM the coulomb interaction has been treated consistently and unambiguously at all phases of calculation.

A band calculation has been performed by Lee (1964) on \( \text{Mg}_2\text{Si} \) and \( \text{Mg}_2\text{Ge} \). In his calculation Lee superposed the pseudopotentials of Mg and Si and of Mg and Ge obtained from independent calculations on the elemental solids, in the hope that this simple approach might lead to reasonable bands for the compounds. The shape of the valence bands calculated by Lee is about the same as the shape obtained in the SECM calculations. However, the conduction bands bear little resemblance to the SECM bands. In view of the ad hoc scheme on which Lee's calculation is based it appears unlikely that his results can be correct. We conclude that either the calculations are in error or the formulation of the potential is not valid.
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VI. APPENDICES

VI.1 Appendix A. Factorization of Projection Operators

Melvin (1956) discusses at length methods for finding factored projection operators for finite point groups. The basic idea is most easily expressed by an example.

Projection operators were defined by Equation 11.1.2.13,

\[ P_m^a = (n_a/G^0) \sum_g D_m^a(g^{-1}) g, \]

where \( D_m^a \) is a diagonal element of the \( n_a \) by \( n_a \) matrix representative \( D^a \) of the irreducible representation \( a \). The sum of \( g \) includes all \( G^0 \) elements of the group. The number of terms in this sum may be large. In this case it is not convenient to use the projection operators in the form of Equation 11.1.2.13. By factoring the projection operator the number of terms that must be handled is reduced.

Consider the group of the \( k \)-vector for a point on \( \Delta \). The characters of the small representation of \( \Delta \) are given in Table 6. The notation and language is that of Bouckaert (1936).

In forming the factored projection operators we seek to express all projection operators in terms of a minimal number of operators of the group. Each order of degeneracy must be handled separately. We first seek a factor which distinguishes the one and two-dimensional irreducible representations. Such a factor must be \((E+C_{4x}^2)\) for the one-dimensional representations and \((E-C_{4x}^2)\) for the two dimensional representations. We next seek a factor which distinguishes the \( \Delta_1 \) from the \( \Delta_2 \) irreducible
representations. Such a factor is \((E \pm C_{4x})\) for the \(\Delta_1\) and \((E - C_{4x})\) for the \(\Delta_2\) irreducible representations. In this way we can immediately write down the following projection operators for the one-dimensional irreducible representations:

\[
P_{\Delta_1} = (E + C_4^2) (E + C_{4x}^1) (E \pm J_{C_{4y}}^2),
\]

\[
P_{\Delta_2} = (E + C_4^2) (E - C_{4x}^1) (E \pm J_{C_{4y}}^2),
\]

\[
P_{\Delta_2'} = (E + C_4^2) (E - C_{4x}^1) (E - J_{C_{4y}}^2),
\]

\[
P_{\Delta_1'} = (E + C_4^2) (E + C_{4x}^1) (E - J_{C_{4y}}^2).
\]

<table>
<thead>
<tr>
<th>Irreducible Representation</th>
<th>(E)</th>
<th>(C_4^2)</th>
<th>(C_{4x}^2)</th>
<th>(J_{C_{4y}}^2)</th>
<th>(J_{C_{4z}}^2)</th>
<th>(J_{C_{2x}}^2)</th>
<th>(J_{C_{2x}'}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\Delta_2)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(\Delta_2')</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\Delta_1')</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\Delta_5)</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

To obtain the projection operators for the two-dimensional representation a matrix representation of the group is needed. Since the procedures are the same as in the one-dimensional case we will not describe this in detail. However, it is evident that a judicious choice
of the degenerate representations may simplify the projection operators.

Thus, a recipe for obtaining factored projection operators is as follows. First, find factors which distinguish the various orders of degeneracy from one another by an inspection of the character table for the group. Then, find factors that distinguish the various irreducible representations of the same order of degeneracy. The last step requires detailed knowledge of the irreducible representations of the group.

VI.2 Appendix B. Integrals and Integral Approximations

VI.2.1 Fourier transform integrals of Slater functions

The two types of Fourier transform integrals which occur in the Mg$_2$Si calculations are

\[ FT(k, a, n, s) = \int \exp(ik \cdot r) r^{2n} \exp(-ar) \, dr \quad 2.1.1a \]

and

\[ FT(k, a, n, p_i) = -i \int \exp(ik \cdot r) r^{2n} \exp(-ar) x_i \, dr \quad 2.1.1b \]

The Fourier transform of the \( p \)-function is related to the Fourier transform of the \( s \)-function by

\[ FT(k, a, n, p_i) = -\frac{\partial}{\partial k_i} FT(k, a, n, s) \quad 2.1.2 \]

The Fourier transform of the \( s \)-function is

\[ FT(k, a, n, s) = \frac{(2n+1)!}{(a^2 + k^2)^{2n+2}} \sum_{s=0}^{n} \frac{2n+2}{(2s+1)} a^{2n-2s+1}(-k^2)^s \quad 2.1.3 \]
VI.2.2 Single-center coulomb integrals

Since the angular integrations in the atomic calculations can be done exactly the matrix elements are reduced to integrals over the radial functions. In the procedure which was developed for the atomic calculations only two types of integrals occur.

The first is a single-center overlap integral,

\[ O_l(a,m) = \int_0^\infty \exp(-\alpha r) r^m dr, \]

where \( m \) is an integer. Thus,

\[ O_l(a,m) = \frac{m!}{a^{m+1}}. \]

The second type of integral is a coulomb integral of the form

\[ C_l(a,b;m_1,m_2,m) = \int_0^\infty \exp(-\alpha r_1) r_1^{m_1-m} \int_0^{\infty} \exp(-\beta r_2) r_2^{m_2-m} \cdot \]

\[ \cdot (r_1^{2m+1} - r_2^{2m+1}) dr_2 dr_1, \]

where \( m_1 \) and \( m_2 \) must be greater than or equal to \( m \). This integral was performed in a straight-forward manner. Then, the following recursion relation was developed to facilitate machine computation:

\[ C_l(a,b;m_1,m_2,m) = - (m_1-m)! \left[ C(m_2,m,0) + CUR(m_2+m_1, b/(a+b)) \right], \]

where

\[ CUR(m_2+m_1, b/(a+b)) = \frac{b^{m_2+m_1} (a+b)^{m_1+m_1-m}}{b^{m_2+m_1} (a+b)^{m_1+m_1-m}}. \]
\[
\text{CUR}(s, y) = \frac{(m_1^2 + m_y - s + 1) \gamma \left[ C(m_2, m_y, m_2 + m - s + 1) + \text{CUR}(s - 1, y) \right]}{(m_2 + m - s + 1)}
\]

and

\[
C(m_1, m_2, m_2 + m - s + 1) = \frac{(m_2 + m - s)! - (m_2 - m)! (m_2 + m + 1 - s)!}{(n_2 - m - s)!}
\]

VI.2.3 Core exchange with plane waves

The core exchange operator is given by Equation 11. Matrix elements of the core exchange operator with plane waves have the form,

\[
(PW_{k, l}^k, A_{\text{core}} t^k_{l'}) = \Omega^{-1} \sum_j j^\lambda \exp(-i k \cdot r_j) \bar{\varphi}_{j}^\lambda (2) H_{12} \cdot
\]

\[
\cdot \int \exp(i k^1 \cdot r_2) \varphi_{js} (1) \bar{\varphi}_{js} (1) \bar{\varphi}_{js} (2) H_{12} \exp(i k^1 \cdot r_2) \varphi_{js} (1) dr_1 dr_2
\]

Since the core functions \( \varphi_{js} \) are tightly bound we may replace \( H_{12} \) by \( 2/r_{12} \).

Let,

\[
F(k) = \int \exp(i k \cdot r) \varphi (r) dr
\]

where we have dropped the subscript on js from the core function \( \varphi_{js} \).

Then, with the aid of the identity,

\[
\frac{1}{r_{12}} = \frac{2}{(2\pi)^2} \int dx \ x^{-2} \exp(i x \cdot r_{12}),
\]

and Equation 2.3.2 a typical form of Equation 2.3.1 may be written as.
We were unable to evaluate this integral with the Fs as Fourier transforms of Slater functions. The Fourier transform of the core functions was approximated by a linear combination of Gaussians,

\[ F(k) \sim \sum m (r_m)^{1/2} Q_m(k^2) \exp(-b_m k^2) \left( \frac{1}{k} \right) , \]

where \( Q_m(k^2) \) is a polynomial in \( k^2 \). Since \( F \) may be either an s or p-function, both possibilities are included in the bracketed factor in Equation 2.3.4. The Fourier transforms were approximated by a least squares technique in which both exponents and coefficients were varied until no further decrease in the average least squares deviations occurred. Although it was especially difficult to approximate the high Fourier coefficients of the Fourier transform for the more tightly bound core functions, it was felt that a good approximation had been obtained for all core functions.

In terms of Equation 2.3.4

\[ I = \sum_{m,s,m'} \frac{2}{(2\pi)^2} \int d\Omega \times^{-2} \exp(-b_m(k-k')^2 - b_{m'}(k'\cdot\Omega)^2) \]

\[ \cdot Q_m((k-k')^2) Q_{m'}((k'\cdot\Omega)^2) \left( \frac{1}{3(k-k') \cdot (k'\cdot\Omega)} \right) . \]

This may be rewritten as
\[ I = \sum_{m,m'} Q_m \left( -\frac{\partial}{\partial b_m} \right) Q_{m'} \left( -\frac{\partial}{\partial b_{m'}} \right) \exp \left( -b_m k^2 - b_{m'} k'^2 \right). \]

\[ (3(k \cdot k') - 1/2[\frac{\partial}{\partial b_m} + \frac{\partial}{\partial b_{m'}}]) i^1 \]

where

\[ I^1 = \frac{2}{\pi} \int dK \exp (-bK^2) \]

\[ b = b_m + b_{m'} \quad \text{and} \quad K = b_m k + b_{m'} k'. \]

Equation 2.3.5b becomes after several transformations,

\[ I^1 = 4(\pi/b)^{1/2} \int_0^1 \exp (K^2 t^2 / b) \, dt. \]

\[ I^1 = 4(\pi/b)^{1/2} \text{F}_1 (1/2; 3/2; K^2 / b). \]

Since this integral is evaluated a large number of times in the course of a calculation of core exchange matrix elements with plane waves, it was necessary to develop high speed methods for determining its value. By tabulating the function and interpolating the value of the function by a central difference technique we were able to reduce the calculation time to a maximum of .5 ms per integral. Fortunately, we were able to compare our calculated values to a table of the function prepared by Lohmander (1958). The calculated points compared to 8 digits and the interpolated points to 4 digits.
Since the derivatives in Equation 2.3.5a make the equations much more complicated, the least squares fitting procedure was biased to keep the power of the polynomial terms in Equation 2.3.4 as small as possible.
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