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A SELF-CONSISTENT FIELD DENSITY-MATRIX FORMULATION AND
SYMMETRY REDUCTION OF THE SECULAR EQUATION IN THE
LCAO APPROXIMATION FOR α-RHOMBHOEDRAL BORON

Dissertation

Presented in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Rama Bai Chintakindi, B.Sc., D.I.I.Sc., M.Sc. (E.E.)

The Ohio State University
1962

Approved by

[Signatures]
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Chapter 1. Crystalline Forms and Structure of Boron

1.1 Introduction

The properties of elemental boron, such as its high melting point and low vapor pressure, its hardness, and its electrical, semiconductor, and optical properties make it likely that new and important applications for this material will be found in research, industry, and defense. Progress in understanding the properties of elemental boron has been slow because of the difficulty of preparing pure material in a definite crystalline state. Many early preparations were amorphous or contaminated with other elements, for example, from a substrate. However, three polymorphic crystalline forms of boron have now been definitely established by x-ray diffraction of single crystals. For two of these, tetragonal-I and simple or \( \alpha \) -rhombohedral boron, the detailed crystal structure including atomic positions and derived bond lengths are known. As a result it has been possible to obtain a qualitative understanding of the bonding in these two crystal forms. The identification of definite crystal forms has also made possible an improved understanding of the ranges of stability (or metastability) of the polymorphic forms, and of the methods by which they may be prepared. The time therefore seems opportune for a relatively complete and systematic
review of the existing status of our knowledge of the structure and physical properties of the polymorphic forms of crystalline boron. The only previous general publication in this area seems to be a brief review of the structure and polymorphism of crystalline boron by Hoard.¹

A dozen or more polymorphic forms have been claimed for crystalline boron, often on the basis of x-ray diffraction patterns on microcrystalline samples. As many as ten unit cells have been proposed. However, for only three of these forms, \( \alpha \)-rhombohedral,² \( \beta \)-rhombohedral,³ and tetragonal-I,⁴ has the space group and unit cell been unambiguously established from single crystal diffraction data. The structures of \( \alpha \)-rhombohedral and tetragonal-I boron are sufficiently simple so that the atomic positions have also been determined. Although atomic positions are not known for the complex \( \beta \)-rhombohedral structure the single crystal data do provide the principal interplanar spacings. Recently a fourth polymorph, tetragonal-II boron, has been proposed on the basis of quite convincing powder diffraction data.⁵

Hoard and Newkirk⁶ have given a critical analysis of the reported polymorphic forms of elementary boron, and have suggested that the remaining forms which have been claimed on the basis of diffraction data on microcrystalline aggregates are probably to be explained in one of the following ways: 1) the aggregate is a mixture of established polymorphs; 2) the aggregate may be a non-stoichiometric metal-boron compound having a structure influenced by the substrate; 3) the diffraction data may be of inadequate resolution (for example, obtained with short wave length radiation); or 4) the data may have been misinterpreted (for example, several preparations which were originally identified as
tetragonal by comparison with an early diffraction pattern of Laubengayer would appear to have been largely \( \beta \)-rhombohedral boron). In view of the careful and exhaustive discussion by Hoard and Newkirk no further attention will be given here to the doubtful polymorphic forms.

With regard to the thermodynamic stability of the established boron polymorphs, there is little doubt that \( \beta \)-rhombohedral boron is the stable form for a temperature range of several hundred degrees below the melting point of boron (1500-2000\(^\circ\)C, and possibly as low as 1000\(^\circ\)C). It is the form that is invariably obtained by crystallization of fused boron. The evidence also indicates that the structurally simple \( \alpha \)-rhombohedral form is the stable form at lower temperatures. It is the only form which has been obtained below 1000\(^\circ\)C, and the transition to the \( \beta \) form has been observed at 1500\(^\circ\)C (ref. 7). Hoard and Newkirk have made the plausible suggestion that tetragonal-I boron is a metastable monotrope which is not the stable thermodynamic form in any temperature range. Its formation by deposition of boron on various metals in the range 1100-1300\(^\circ\)C would in this case be a result of kinetic factors favoring it over the more complex \( \beta \)-rhombohedral form. Similar conclusions probably apply to tetragonal-II boron, which is about the same temperature range; fusion and recrystallization of this form yields \( \beta \)-rhombohedral boron.\(^5\) In order to reconcile the existence of stable tetragonal forms in this intermediate temperature range with the observed transformation of \( \alpha \) - to \( \beta \)-rhombohedral boron it would be necessary to assume that the latter is a metastable transition.
This chapter will be concluded with a more detailed discussion of the preparation and structure of each of the established polymorphs of boron.

1.2 Tetragonal-I Boron

The tetragonal-I polymorph of boron was the first for which the structure was definitely established, and is the most extensively studied. In spite of this it is very probably a metastable monotrope, as has been suggested by Hoard and Newkirk. However, this does not lessen the interest in this form and its possible usefulness in applications, as it is sufficiently stable to resist transformation to other forms up to at least 1500°C.

Tetragonal-I boron was first prepared by Laubengayer et al. by reduction of BBr₃ with hydrogen on a tantalum filament at 1300°C. Specimens from this original preparation have been used in the subsequent single-crystal x-ray diffraction studies of Hoard, Gellar and Hughes and Hoard, Hughes and Sands. For this reason it is worthwhile to describe the two observed crystal habits in some detail. The most common habit consisted of needles 0.1 to 0.25 mm in diameter which grew out from the filament along the thermal gradient. These crystals were always twinned. The second habit consisted of thin plates (0.05-mm thick) which appeared to be nearly perfect hexagons, and grew with their faces parallel to the thermal gradient.

The original powder diffraction data indicated that the needles were tetragonal D₄h/mmm, with the fourfold axis coincident with the needle axis. Although this conclusion has been sustained by further single-crystal work, it has now been concluded by Hoard and Newkirk
that the original powder pattern contained several strong lines not characteristic of tetragonal boron and probably due to inclusion of substrate. In particular, one line closely mimicked the strongest line in the powder pattern of $\beta$-rhombohedral boron, and this has probably led to the misidentification of $\beta$-rhombohedral as tetragonal boron by some investigators (for example, the sample used for heat capacity measurements by Johnston, et al.\textsuperscript{10}).

The first single-crystal investigations on tetragonal-I boron by Hoard, Geller, and Hughes\textsuperscript{4}, indicated the space group was $P4n2 (D_{2d}^8)$ or $P4nm (C_{4v}^4)$. The dimensions of the tetragonal unit cell and the density yield a value of 50 for the number of atoms per unit cell. It was concluded on the basis of $P4n2$ that two atoms occupied positions 2(b) and the remaining 48 occupied six sets of general positions 8(i). The parameters were such that these 48 atoms lay at the vertices of four nearly regular icosahedra of boron atoms "centered" at positions

\begin{align*}
  \frac{1}{4} \frac{1}{4} \frac{1}{4}, & \frac{3}{4} \frac{3}{4} \frac{1}{4}, \frac{1}{4} \frac{3}{4} \frac{3}{4}, \frac{3}{4} \frac{1}{4} \frac{3}{4}.
\end{align*}

Of the latter positions the first and fourth are of type 4(f) with site symmetry $C_2$, while the second and third are general positions 8(i) with site symmetry $C_1$.

Thus, in this preliminary structure the four icosahedra in the unit cell were not equivalent.

In a later more detailed investigation of the single crystals, both needles and plates, Hoard, Hughes, and Sands\textsuperscript{9} concluded the space group is the more symmetrical $P4_{2/}nm (D_{4h}^{12})$. A variation of about 1\% was noted in the dimensions of the tetragonal unit cell for different specimens: the best needle gave $a_0 = 8.740 \pm 0.045$, $c_0 = 5.068 \pm 0.010 \, \text{Å}$, while a platelet gave $a_0 = 8.771 \pm 0.013$, $c_0 = 5.088 \pm 0.015 \, \text{Å}$. 
The corresponding calculated densities assuming 50 atoms in the unit cell are 2.33 and 2.29 g/cm$^3$, respectively. The experimental density of one needle was 2.31 g/cm$^3$. The variation in cell parameters and atomic positions observed for different specimens probably indicates the presence of considerable concentrations of short-range defects in preparations of tetragonal boron.

The fact that the plate-like crystals grow as nearly regular hexagons is adequately explained by the axial ratio, $a_o/c_o$, of the tetragonal cell, which is very nearly $\sqrt{3}$. The plate faces are $\pm (100)$, planes and the lateral "hexagonal" faces appeared on first examination to be $\pm (010)$, $\pm (011)$, and $\pm (01\bar{1})$. The interfacial angles for the latter are very close to 120°. Closer examination showed that eight narrow faces of the form $\{11\bar{1}\}$ usually replaced (in pairs) the faces $\pm (011)$ and $\pm (01\bar{1})$. The $c$-axis lay along one of the face-diagonals of the hexagonal plate. There is now no doubt that the plate-like crystals have the same tetragonal cell and structure as the needles, although originally they were described as having an orthorhombic unit cell with four times the volume of the tetragonal cell.\(^8\)

The atomic positions as determined for space group $P4_2/nmm$ are essentially the same as those given earlier on the basis of $P4n2$. Two atoms occupy positions $2(b)$, $00\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$, with bisphenoidal site symmetry $42m (D_{2d})$. Two sets of 8 atoms each occupy positions $8(m)$, with positions as follows:

\[
\begin{align*}
&x x z; \bar{x} \bar{x} z; \frac{1}{2} + x, \frac{1}{2} + x, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} - z; \\
&\bar{x} x \bar{z}; x \bar{x} \bar{z}; \frac{1}{2} - x, \frac{1}{2} + z, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} + z.
\end{align*}
\]
For the first set $x = 0.1195$, $z = 0.3780$; for the second set $x = 0.2425$, $z = 0.5815$ (based on the data for the needle, which yielded many more reflections than the plate). Finally, two sets of 16 atoms each occupy the general positions 16(n):

$$x \quad y \quad z; \quad \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z; \quad \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z;$$

$$\bar{x} \quad \bar{y} \quad \bar{z}; \quad \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; \quad \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z;$$

$$\bar{y} \quad x \quad \bar{z}; \quad \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} + z; \quad \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z;$$

$$y \quad x \quad z; \quad \frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} - z; \quad \frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z;$$

The parameters for the first set are $x = 0.3253$, $y = 0.0883$, $z = 0.3985$; for the second set $x = 0.2272$, $y = 0.0805$, $z = 0.0865$. The atoms at general positions, 16(n), of course have no site symmetry ($C_1$), while those at 8(m) lie on a mirror plane, $m$ (symmetry $C_s$). The 48 atoms at positions 8(m) and 16(n) occupy the vertices of four nearly regular icosahedra of boron atoms, which may be regarded as centered at positions 4(e): $1/4 \ 1/4 \ 1/4; \ 3/4 \ 3/4 \ 1/4; \ 3/4 \ 1/4 \ 3/4; \ 1/4 \ 3/4 \ 3/4$. Thus, each icosahedron possesses the symmetry 2/m ($C_{2h}$) of the 4(e) positions; note that this implies a center of symmetry as well as a twofold axis and mirror plane for each icosahedron. The 12 atoms of each icosahedron thus fall into two sets of 2 equivalent atoms each, lying on the mirror plane of 2/m at 4(e), and two sets of 4 equivalent atoms lying at general positions. The four icosahedra within a unit cell are equivalent under the operations of the point group 42m ($D_{2d}$) at site 2(a), $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$. It is clear that the operations of 42m generate a set 8(m) from each of the sets of 2 equivalent atoms, and a set 16(n) from each of the sets of 4 equivalent atoms within a single icosahedron. Thus the 48 atoms in question may be classified either with regard to positions they occupy
in the unit cell, or with regard to equivalent positions in each of four equivalent icosahedra. This rather detailed analysis of the symmetry of tetragonal boron will be useful in connection with a discussion of electronic structure of tetragonal boron given in a later section.

The present chapter will be concluded with a description of the distances between neighboring boron atoms in tetragonal boron, which are presumed to represent boron-boron bonds. Within each icosahedron there are 30 "bonds," although as will be discussed later these are undoubtedly electron deficient. As a result of the 2/m symmetry these 30 bonds may be classified into nine distinct types. The lengths of these intra-icosahedral bonds are: 1.785(4), 1.786(4), 1.789(4), 1.800(4), 1.812(4), 1.813(2), 1.822(4), 1.837(2), and 1.846 Å(2). The number of times each is repeated is given in parentheses. These distances are based on needle data and are estimated accurate to about 0.01 Å; however, values for the plates differ by as much as 0.04 Å.

Ten of the boron atoms in each icosahedron appear to be also bonded to boron atoms in adjacent icosahedra. The lengths of these inter-icosahedral bonds, with the number of times each occurs per icosahedron indicated in parentheses are 1.658(4), 1.709(2), and 1.858 Å(4), from the needle data. The remaining two boron atoms in an icosahedron, related by a center of symmetry, are bonded to two boron atoms in the special positions 2(b); in the case of the icosahedron centered at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ these two boron atoms are at 0 0 $\frac{1}{2}$ and $\frac{1}{2} \frac{1}{2} 0$. Each of these non-icosahedral boron atoms forms four bonds of this kind to boron atoms in four distinct icosahedra. These bonds are equivalent
and have bisphenoidal (42m) symmetry. Their length, from needle data, is 1.601 Å, indicating they are the shortest bonds in the structure.

Finally, it may be noted that the tetragonal boron lattice contains four "holes" per unit cell at positions 4(c), with radii of 1.79 Å (measured to the nearest boron atoms), and two holes at 2(a) with radii of 2.15 Å. These holes appear capable of accommodating interstitial atoms, although there is no evidence as yet that interstitial impurities occur in tetragonal boron.

1.3 α-Rhombohedral Boron

α-Rhombohedral boron is structurally the simplest of the boron polymorphs, and is apparently the stable low-temperature form (below 1000-1200°C). It was first reported by McCarty et al. who prepared it by pyrolytic decomposition of $\text{BI}_3$ on tantalum, tungsten, and boron nitride surfaces at 800-1100°C. It has also been prepared by decomposition of boron hydrides, and by crystallization from boron-platinum melts at 800-1200°C (ref. 12). The deposit obtained by decomposition of $\text{BI}_3$ was predominantly black, but clear red crystals about 0.25 mm long could be isolated. Analysis showed 0.04% (by weight) of iodine and 0.003% carbon, but no other impurities in greater concentration than 0.001% were detected. The density is 2.46 g/cm$^3$, the highest for any known polymorph.

A detailed study of the x-ray diffraction data from such a single crystal has been carried out by Decker and Kasper. The results were supported by partial data from a second crystal, and the black glassy or microcrystalline deposit gave the same powder diffraction pattern as obtained from powdered red crystals. Three-dimensional precession data
from the single crystal showed that the structure is rhombohedral, with three possible space groups, R32, R3m, and R3m. Only centrosymmetric R3m (D3d) was considered, and was found adequate to account for all the data. The unit cell dimensions (from powder data) are: \( a_0 = 5.057 \pm 0.003 \, \text{Å} \); \( \alpha = 58.06 \pm 0.05^\circ \).

The atoms are at two sets of special positions, \( 6(h) \), as indicated in Table 1.

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The equivalent rhombohedral axes are designated by \( x_1, x_2, \) and \( x_3 \), and the numerical values are dimensionless ratios of the oblique projections on these axes to the parameter \( a_0 \). For convenience in a calculation of the energy bands of boron now in progress a special notation has been introduced for the atomic position. The three atoms in the first set related by rotation about the threefold axis are denoted by 1, 2, and 3, and the atoms obtained from these by inversion by \( \bar{1}, \bar{2}, \) and \( \bar{3} \). Similar but primed symbols are used for the second set of six atoms. It has
also seemed convenient to invert all the positions as originally given.\(^7\)
The 12 atoms within a single cell lie at the vertices of a nearly regular icosahedron: although slightly distorted the latter retains the symmetry of the point group \(R\overline{3}m\). The intra-icosahedral bonds correspond to the 30 edges of the icosahedron, and these may be classified into four types with the following lengths:

\[
\begin{align*}
    d(12) &= 1.73 \ \text{Å} \\
    d(13^\prime) &= 1.79 \ \text{Å} \\
    d(11^\prime) &= 1.79 \ \text{Å} \\
    d(13^\prime) &= 1.78 \ \text{Å}
\end{align*}
\]

The icosahedra (one per cell) are arranged in the crystal approximately in cubic close-packing (\(\alpha = 58^\circ\) as compared with \(60^\circ\) for close-packing of spheres). A given icosahedron is surrounded by six icosahedra in the same "layer," and three each in layers immediately above and below. The atoms in the unprimed set in the preceding table are separated by only 1.71 Å from corresponding atoms in the layer above or below, and are presumably bonded to them by normal two-center inter-icosahedral bonds. Each of the primed atoms is 2.03 Å distant from two equivalent atoms in two other icosahedra in the same layer. As the latter two atoms are separated by the same distance the three atoms form an equilateral triangle. Presumably this corresponds to a three-center or "\(\Delta\)" bond connecting three icosahedra. The entire structure is closely related to that of \(B_4C\), the essential difference being that in \(B_4C\) the \(\Delta\) bonds between boron icosahedra are replaced by \(C_3\) chains.\(^{13}\)

1.4 \(\beta\)-Rhombohedral Boron

\(\beta\)-Rhombohedral boron was the second polymorph of boron to be correctly identified (the first was the tetragonal-I form). In 1957 Sands and Hoard\(^3\) examined small single crystals taken from two samples
which were both prepared by crystallization from the melt, and were
stated to be of purity 99.4 and 99.5%. Oscillation, Weissenberg, and
precession photographs established that the lattice was rhombohedral,
of space group $R_3m$, $R32$, or $R3m$. Further studies of the statistical
distribution of intensities indicate the space group is the centro-
symmetric $R\bar{3}m$ ($D^5_{3d}$), characteristic also of $\beta$-rhombohedral boron\(^7\) and
boron carbide.\(^{13}\) The parameters reported by Sands and Hoard for
$\beta$-rhombohedral boron are $a = 10.12\ \text{Å}$ and $\alpha = 65^\circ 28'$. More recently
Hoard and Newkirk have reported on more extensive single crystal data
obtained on a similar sample by H. A. Weakleim and D. B. Sullenger which
give for the triply-primitive hexagonal unit cell the parameters
$A = 10.944\ \text{Å}$, $C = 23.811\ \text{Å}$. From these parameters, the reported density\(^3\)
of $2.35 \pm 0.01\ \text{g/cm}^3$, and the chemical atomic weight of 10.82, the
number of atoms in the primitive rhombohedral cell is calculated to be
$107.7 \pm 0.5$.

Although the extensive single crystal data on $\beta$-rhombohedral
boron give some promise that the atomic positions will eventually be
determined, the detailed structure is unknown. The studies now in
progress indicate that the icosahedral unit does not play the prominent
role in the $\beta$ form that it does in $\alpha$-rhombohedral and tetragonal-I
boron.\(^1\)

Hoard and Newkirk\(^6\) have computed the powder pattern to be
expected from $\beta$-rhombohedral boron, and have concluded that several
preparations of boron previously identified as tetragonal were in fact
$\beta$-rhombohedral (see section 1.1). It now appears that the
$\beta$-rhombohedral form is invariably obtained on crystallization from the
melt, and is the thermodynamically stable form down to 1500°C, and possibly much lower temperatures. The transition of \( \alpha \)- to \( \beta \)-rhombohedral boron has been observed at 1500°C. Hoard and Newkirk have suggested that the lattice types obtained below 1500°C may be determined in many cases by kinetic considerations which are unfavorable to the stable but complex \( \beta \)-rhombohedral structure. Such polymorphs, of which the two tetragonal forms are likely examples, may be monotropes which are thermodynamically unstable relative to the rhombohedral forms at all temperatures.

1.5 Tetragonal-II Boron

Tetragonal-I boron was the first polymorph of crystalline boron to be identified, and its structure is now definitely established. Recently Tally, LaPlaca, and Post^{5} have reported a microcrystalline preparation of boron which they identify as a new tetragonal form on the basis of the indexing of a large number of lines from a diffractometer tracing. Although this form must be regarded as somewhat tentative until single crystals have been prepared, the evidence seems sufficiently strong to designate it a distinct polymorph, tetragonal-II boron. The microcrystalline sample was prepared by reduction of \( \text{BBr}_3 \) vapor with \( \text{H}_2 \), and deposition of the boron on tungsten and rhenium filaments at 1540°C and atmospheric pressure. Chemical analysis indicated a purity in excess of 99%, with most of the impurity coming from the metal substrate. Spectroscopic analysis showed traces of aluminum (0.005%), and a total of 0.02% of several other elements.
The powder diffraction pattern indicates the unit cell to be tetragonal, pseudo-cubic, with parameters $a = 10.12 \pm 0.02$ and $c = 14.14 \pm 0.02 \AA$. The measured density of $2.364 \text{ g/cm}^3$ shows that the tetragonal cell contains approximately 192 atoms. These atoms may possibly be grouped in 16 icosahedra, but as single crystal data are not available the atomic positions are unknown.

On melting and recrystallization these samples transformed to $\beta$-rhombohedral boron, as is also observed on melting tetragonal-I boron. It is very likely that both tetragonal forms are thermodynamically unstable monotropes, as previously discussed.
Chapter 2. Bonding in Elemental Boron

2.1 Introduction

As has been discussed in detail in preceding chapter both poly-morphs of crystalline boron for which the structure has been established, \( \alpha \)-rhombohedral and tetragonal-I boron, contain as their most prominent structural feature nearly regular icosahedra of 12 boron atoms each. An accurate treatment of bonding, energy bands, etc., in the crystalline forms must clearly be based on a consideration of the entire structural configuration in the unit cell, including non-icosahedral boron atoms and inter- as well as intra-icosahedral bonding. However, it seems likely that some of the main features of bonding in these two forms of crystalline boron may emerge from a consideration of an isolated icosahedron of boron atoms, or to avoid excessive unsaturation, the essentially equivalent problem of an icosahedral \( \text{B}_{12}\text{H}_{12} \) molecule. No such molecule is known, although in decaborane, \( \text{B}_{10}\text{H}_{14} \), the boron framework corresponds to 10 of the 12 atoms in a slightly distorted icosahedron, with four hydrogen "bridges" in the missing part of the icosahedron, and an additional hydrogen bonded to each boron atom.\(^{14}\)

In a boron icosahedron each atom is surrounded more or less symmetrically by five boron atoms, in addition to the external atom such as hydrogen to which it may be bonded. It is clearly impossible to describe the bonding in this situation in terms of the ordinary theory of covalent bonds using hybridized orbitals based on the 2s and 2p
orbitals of boron (it is unlikely on energetic grounds that d orbitals play any significant role in the bonding). However, the molecular orbital theory is well adapted to the treatment of the bonding in the hypothetical $\text{B}_{12}\text{H}_{12}$ molecule (or, for that matter, other known boron hydrides), and a detailed molecular orbital treatment of $\text{B}_{12}\text{H}_{12}$ has been given by Longuet-Higgins and Roberts. Their theory will next be summarized, and will be followed by a discussion of its relation to bonding in crystalline boron.

2.2 Molecular Orbital Theory for a Boron Icosahedron

It will be useful as a start to consider the symmetry properties of a regular icosahedron as the icosahedral group is not as well known as the more familiar point groups, such as the crystallographic point groups. The icosahedron is one of the five possible regular solids, and has 12 vertices (representing 12 boron atoms in the present application), 20 equilateral triangular faces, and 30 edges. The icosahedron is closely related to the regular dodecahedron, which has 20 vertices and 12 regular pentagonal faces, and the point group characteristic of both figures is known as the icosahedral group. The rotational symmetry elements of the icosahedron consist of six equivalent fivefold axes between opposite pairs of vertices, ten equivalent threefold axes between the midpoints of opposite faces, and 15 equivalent twofold axes between the midpoints of opposite edges. When the identity operation, $E$, is added, and the possibility of clockwise and counterclockwise rotation is taken into account, the rotational point group of the
icosahedron is seen to consist of 60 symmetry operations divided into five classes as follows: $E$, $12 C_5$, $12 C_2$, $20 C_3$, and $15 C_2$.

From the principles of group theory it follows that the rotational group has five irreducible representations (symmetry species), and the sum of the squares of the dimensions (or degeneracies) of these representations must equal 60 (the order of the group). Furthermore, one representation is the one-dimensional identity representation. The only solution to these requirements using integers is $1^2 + 3^2 + 3^2 + 4^2 + 5^2 = 60$, from which it follows that the rotational group has as its irreducible representations the identity representation, $A$, two three-dimensional representations, $F_1$ and $F_2$, one four-dimensional representation, $G$, and one five-dimensional representation, $H$. The complete icosahedral point group is the direct product of the preceding rotational subgroup and the inversion group, which consists simply of the identity operation, $E$, and inversion operation, $I$.

Therefore, the icosahedral group contains, in addition to the five classes of operations given above, the additional five classes, $I$, $12 S_{10}$, $12 S_{3}$, $20 S_{6}$, and $15 \sigma$. Here $S_n$ represents an $n$-fold rotation-reflection operation, and $\sigma$ reflection in a plane. Finally, each irreducible representation of the rotational subgroup gives rise to two representations of the icosahedral or direct product group, both of the same dimensionality, but one symmetric ($g$) and the other antisymmetric ($u$) to inversion. The icosahedral point group therefore has the irreducible representations $A_g$ (identity representation), $A_u$, $F_{1g}$, $F_{1u}$, $F_{2g}$, $F_{2u}$, $G_g$, $G_u$, $H_g$, and $H_u$. The character table of the rotational
subgroup is given by Tisza,\textsuperscript{16} and of the complete group by Longuet-Higgins and Roberts. The figure in the last row and column of Tisza's table on page 69 of his paper should be 1, not 0, and the labeling of the last two columns in Longuet-Higgins and Roberts' Table 3a is interchanged. Tisza's notation for the representations has been followed here.

Longuet-Higgins and Roberts, as stated earlier, have treated the bonding in an isolated regular icosahedron of boron atoms, or in $B_{12}H_{12}$, by molecular orbital theory. The bonding of the boron atoms is assumed to involve only the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. Each of the 12 boron atoms in the icosahedron has four such orbitals, so that there are 48 boron orbitals to be considered in the molecular orbital problem. It is convenient to orient the $2p_z$ orbital of each boron along the fivefold axis passing through the boron atom (and also the center of the icosahedron), and the $2p_x$ and $2p_y$ orbitals will then have their axes in a plane perpendicular to the fivefold axis. The local point group symmetry at a boron atom is $C_{5v}$, and it is now easily seen that the $2s$ and $2p_z$ orbitals each transform according to the identity representation, $A_1$, and $2p_x$ and $2p_y$ together according to the doubly-degenerate representation, $E_1$, of $C_{5v}$. The $2s$ orbitals and the $2p_z$ orbitals each generate a twelve-dimensional reducible representation of the icosahedral group determined by the subgroup representation $A_1$, and similarly the $2p_x$ and $2p_y$ orbitals generate a 24-dimensional reducible representation determined by $E_1$.

The reduction of these representations may be accomplished by means of the reciprocity theorem of Frobenius, or one may find directly
the characters of the reducible representations and use the orthogonality theorem for group characters. (The fourth and fifth figures in the first two rows of Longuet-Higgins and Roberts' Table Jb should be 2, not 0, but this error has not affected their results.) In this way one finds that the orbitals have the following reduced representations:

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Number</th>
<th>Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>12</td>
<td>( A_g + F_{1u} + F_{2u} + H_g )</td>
</tr>
<tr>
<td>2p_x</td>
<td>12</td>
<td>( A_g + F_{1u} + F_{2u} + H_g )</td>
</tr>
<tr>
<td>2p_y</td>
<td>24</td>
<td>( F_{1g} + F_{1u} + G_g + G_u + H_g + H_u )</td>
</tr>
</tbody>
</table>

There can be no interaction integrals in the secular equation between functions belonging to different representations (or to different "rows" of a representation of dimensions greater than one). Therefore, by an orthogonal transformation of the 48 atomic orbitals so as to obtain linear combinations belonging to individual irreducible representations, the original 48th degree secular equation can be factored in the following equations of lower degree.
### TABLE 3. Classification and Energy of Molecular Orbitals for a Boron Icosahedron

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Degeneracy</th>
<th>Degree</th>
<th>Type of Orbitals</th>
<th>Energy</th>
<th>Type of Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>2</td>
<td>$2s, 2p_z$</td>
<td>-4.45</td>
<td>Internal</td>
</tr>
<tr>
<td>$F_{lg}$</td>
<td>3</td>
<td>1</td>
<td>$2p_x', 2p_y$</td>
<td>-0.81</td>
<td>External</td>
</tr>
<tr>
<td>$F_{lu}$</td>
<td>3</td>
<td>3</td>
<td>$2s, 2p_z, 2p_x', 2p_y$</td>
<td>-2.13</td>
<td>Internal</td>
</tr>
<tr>
<td>$F_{2u}$</td>
<td>3</td>
<td>2</td>
<td>$2s, 2p_z$</td>
<td>0.30</td>
<td>External</td>
</tr>
<tr>
<td>$G_g$</td>
<td>4</td>
<td>1</td>
<td>$2p_x', 2p_y$</td>
<td>0.91</td>
<td>Internal</td>
</tr>
<tr>
<td>$G_u$</td>
<td>4</td>
<td>1</td>
<td>$2p_x', 2p_y$</td>
<td>0.60</td>
<td>Internal</td>
</tr>
<tr>
<td>$H_g$</td>
<td>5</td>
<td>3</td>
<td>$2s, 2p_z, 2p_x', 2p_y$</td>
<td>-1.21</td>
<td>Internal</td>
</tr>
<tr>
<td>$H_u$</td>
<td>5</td>
<td>1</td>
<td>$2p_x', 2p_y$</td>
<td>0.84</td>
<td>Internal</td>
</tr>
</tbody>
</table>

The degree indicates the number of distinct energies or eigenvalues associated with a given representation or symmetry. However, the number of individual molecular orbitals having a given energy will be equal to the degeneracy, so that the total number of molecular orbitals of a given symmetry is given by the product of the degree and the degeneracy.

The atomic orbitals from which the molecular orbitals are formed is given in the fourth column. The fifth column gives the energy parameter calculated by Longuet-Higgins and Roberts. The sign of their parameter has been changed to accord with the usual convention that the more stable a molecular orbital the lower its energy in an algebraic sense. The calculated energies are only approximate, as the resonance integrals were assumed to be proportional to the overlap integrals and
were not evaluated from first principles. The final column indicates: 1) whether the molecular orbital has its largest absolute values within or on the surface of the icosahedron, thus being a potential contributor to internal bonding of the boron icosahedron (although possibly also being of such high energy as to be antibonding); or 2) if the molecular orbital is primarily directed externally to the icosahedron, and therefore potentially a contributor to bonding between adjacent icosahedra in the crystal, or to the hydrogen atoms in B₁₂H₁₂. 

It can be seen from Table 3 that the internal orbitals of lowest energy are: A_g (1), -4.45; F_μ (3), -2.13; H_g (5), -1.21; and G_u (4), -0.53. These are assumed by Longuet-Higgins and Roberts to be internal bonding orbitals. From the degeneracies given in parentheses, there are 13 individual internally-bonding orbitals, capable of holding 26 electrons in pairs. The remaining internal orbitals have considerably higher energies and are assumed to be anti-bonding. In the crystal each of the internal bonding orbitals will give rise to a "band," and it would appear that if the crystal is to have the filled-band structure of an insulator or semiconductor, these bands must be occupied by 26 electrons from each icosahedron of boron atoms. As there are a total of 36 (or 3 x 12) valence electrons per icosahedron this leaves 10 electrons from each icosahedron available for forming bonds to adjacent icosahedra.

These qualitative results indicate that α-rhombohedral boron should have an electronic band structure characteristic of an insulator. In this crystal structure (described in detail in Section 1.3), with space group R̅3m, and point group D_{3d}, there is one icosahedron per unit
cell, oriented with its threefold axis parallel to the threefold rotation-inversion axis of the crystal. The centers of the icosahedra lie at the points of a slightly distorted face-centered cubic lattice, with the "cube" diagonal coinciding with the three-fold axis of R3m. Thus each icosahedron is surrounded by six others in the same layer (corresponding to the 1 1 1 layer of a cubic lattice), and by three in the layer above, and three in the layer below. From the geometry of the lattice it may be inferred that the central icosahedron forms 6 two-center bonds with icosahedra in the layer above or the layer below. On the other hand, symmetry requires that it participate in 6 three-center or \( \triangle \) bonds with icosahedra in the same layer. If it is assumed that each of the preceding bonds is an electron-pair bond, an icosahedron must contribute one electron to each of the 6 two-center bonds and \( \frac{2}{3} \) electrons to each of the 6 three-center bonds, or a total of 10 electrons to bonding with surrounding icosahedra. This leaves just the 26 electrons for internal bonding that are required for a filled-band structure by the theory of Longuet-Higgins and Roberts. These authors have given a similar explanation of the bonding in the closely related boron carbide lattice.

Longuet-Higgins and Roberts also applied their theory to the structure of tetragonal-I boron as first reported by Hoard, Geller, and Hughes, and concluded that the structure was inconsistent with a filled band structure and should be reconsidered. The structure has been thoroughly restudied using single-crystal diffraction data by Hoard, Hughes and Sands, with only minor changes in the cell parameters and
atomic positions, and a change to a slightly more symmetrical space group, $P4_{2}/nnm$. This structure, which must now be regarded as thoroughly established, at least in its essential features, has been described in detail in Chapter 1. Briefly, the structure is composed of 4 icosahedra, of 12 boron atoms each, centered at the positions $4(e), 1/4 1/4 1/4, 3/4 3/4 1/4, 3/4 1/4 3/4, 1/4 3/4 3/4$, of the tetragonal cell. Although distorted from strict icosahedral symmetry, each icosahedron possesses the relatively high symmetry $2/m (C_{2h})$. Two additional boron atoms occur at positions $2(b), 00\frac{1}{2} and \frac{1}{2}0$, with site symmetry $42m (D_{2d})$. From a consideration of interatomic distances it appears that 10 of the boron atoms in each icosahedron are bonded to a boron atom in an adjacent icosahedron, while the remaining two are bonded to atoms at the $2(b)$ boron positions. Conversely, each $2(b)$ boron atom is apparently bonded to a boron atom in each of the four icosahedra surrounding it.

The application of Longuet-Higgins and Roberts' theory proceeds as follows. If it is assumed that each intericosahedral bond is an electron-pair bond then 10 electrons from each icosahedron are required for the formation of these bonds. This leaves only 26 electrons to each icosahedron, the number required to fill the 13 stable molecular orbitals responsible for intraicosahedral bonding in Longuet-Higgins and Roberts' theory. The only electrons available for the formation of the 4 bonds about each boron at the $2(b)$ position are the 3 electrons contributed by that boron atom. This is clearly insufficient for formation of four bonds. Although these four bonds may well be somewhat electron deficient we assume as a basis for discussion that each is an electron-pair
bond. This requires the four surrounding icosahedra to contribute $5/4$ electrons each, or a total of 5 electrons, which with the 3 contributed by the central boron yields the necessary octet of electrons. Since each icosahedron contributes to two such bonds its total deficiency relative to a filled-shell structure is $2\frac{1}{2}$ electrons, and the overall deficiency for the four icosahedra in the unit cell is 10 electrons. This is the basis on which Longuet-Higgins and Roberts concluded that this structure was incompatible with their theory.

Hoard, Hughes, and Sands have pointed out that Longuet-Higgins and Roberts have ignored two factors: 1) the possibility of general conjugation of the system of inter- and intraicosahedral system of bonds; and 2) the effect of lowered symmetry of the icosahedra in the crystal. Although (1) is certainly possible it is impossible to treat it quantitatively without extensive calculations. Furthermore, such a transfer would not of itself remove the difficulty, as the electron deficiency and resulting partially filled bands would simply be distributed between the intra- and intericosahedral systems. It seems more likely that the apparent contradiction between the experimental structure and electrical properties and Longuet-Higgins and Roberts' bonding theory is to be found in the effect of lowered symmetry in the crystal. This question has been considered in some detail and the results will be presented in the next section.

2.3 Effect of Crystal Symmetry in Tetragonal-I and $\alpha$-Rhombohedral Boron

The essential reason Longuet-Higgins and Roberts' theory predicts unfilled bands in tetragonal-I boron is the high (up to fivefold)
degeneracy possible for the states of a regular icosahedron. When such states are perturbed by crystalline states having cubic or tetrahedral symmetry they must split in such a manner that no degeneracies higher than threefold remain. In crystals containing only one threefold or higher rotation axis, which includes the cases of $\alpha$-rhombohedral and tetragonal-I boron, no degeneracies higher than twofold are permitted. Finally, in crystals having no threefold or higher axes of rotation no symmetry-induced degeneracies occur (in this discussion we ignore the possibility of accidental degeneracy). It is therefore important to consider the specific effects of lowered symmetry for the particular crystal of interest.

In tetrahedral-I boron each icosahedron lies at positions 4(e) with symmetry $C_{2h}$, and the four icosahedra in a unit cell are equivalent under the operations of point group $D_{2d}$ centered at position 2(b) of space group $P_{2/nmm}$. The irreducible representations of the icosahedral point group, $I_h$, provide also representations of any subgroup of $I_h$, but the latter representations may be reducible in the subgroup. The reduction to irreducible representations in the subgroup is readily accomplished by means of the orthogonality theorem for group characters, using the tables of characters for $I_h$ and its subgroups. If there were only one icosahedron in the unit cell it would be natural to carry out this reduction for the subgroup $C_{2n}$ at position 4(e) characterizing an icosahedron in tetrahedral-I boron. However, to obtain the symmetry of the states characterizing the entire unit cell it is necessary to recombine at a later stage the states arising from the four icosahedra equivalent under point group $D_{2d}$ at position 2(b). It is therefore more
useful to choose the subgroup $C_s$ (or $m$), which is the subgroup of highest order containing elements common to both $I_h$ at 4(e) and $D_{2d}$ at 2(b). The resolution of the irreducible representations of $I_h$ into those of $C_s$ is shown in Table 4.

\begin{table}[h]
\centering
\caption{Resolution of the Irreducible Representations of $I_h$ into Representations of $C_s$}
\begin{tabular}{llll}
\hline
$I_h$ & $C_s$ & $I_h$ & $C_s$ \\
\hline
$A_g$ & $A'$ & $A_u$ & $A''$ \\
$F_{1g}$ & $A' + 2A''$ & $F_{1u}$ & $2A' + A''$ \\
$F_{2g}$ & $A' + 2A''$ & $F_{2u}$ & $2A' + A''$ \\
$G_g$ & $2A' + 2A''$ & $G_u$ & $2A' + 2A''$ \\
$H_g$ & $3A' + 2A''$ & $H_u$ & $2A' + 3A''$ \\
\hline
\end{tabular}
\end{table}

We require also the resolution of the irreducible representations of $D_{2d}$ into those of the common subgroup $C_s$, as given in Table 5.

\begin{table}[h]
\centering
\caption{Resolution of the Irreducible Representations of $D_{2d}$ into Representations of $C_s$}
\begin{tabular}{ll}
\hline
$D_{2d}$ & $C_s$ \\
\hline
$A_1$ & $A'$ \\
$A_2$ & $A''$ \\
$B_1$ & $A''$ \\
$B_2$ & $A'$ \\
$E$ & $A' + A''$ \\
\hline
\end{tabular}
\end{table}
The irreducible representations $A'$ and $A''$ of $C_s$ are both of dimension unity (non-degenerate), and are symmetric and antisymmetric, respectively, to the reflection in $C_s$. It is now clear that if an icosahedron at one of the 4(e) positions possesses a state of symmetry $A'$ under $C_s$, an equivalent state must be associated with each of the other three icosahedra at 4(e) positions, as all four icosahedra are equivalent (or can be interchanged) under the operations of $D_{2d}$ at 2(b). These four $A'$ states thus furnish the basis for a 4-dimensional reducible representation of $D_{2d}$. Exactly analogous statements apply to $A''$ states of individual icosahedra.

The resolution of these reducible representations into irreducible representations of $D_{2d}$ may be accomplished by means of the orthogonality theorem for group characters. The results are conveniently summarized by the reciprocity theorem of Frobenius, which states that the number of times an irreducible representation of a group (that is, $D_{2d}$) occurs in the reducible representation of the group furnished by an irreducible representation of a set of conjugate subgroups (for example, $A'$ of $C_s$) is equal to the number of times the latter irreducible representation occurs in the (generally) reducible representation of the subgroup provided by the given irreducible representation of the group. The latter set of numbers has been given in Table 5. Thus, the four-dimensional representation of $D_{2d}$ furnished by $A'$ of $C_s$ will contain $A_1$ of $D_{2d}$ just once, since the reduction of $A_1$ in $C_s$ contains $A'$ just once, but will not contain $A_2$, since the reduction of $A_2$ in $C_s$ does not contain
A'. In this way one finds that A' and A'' of C₅ furnish the reducible representations of D₂d shown in Table 6.

<table>
<thead>
<tr>
<th>C₅</th>
<th>D₂d</th>
</tr>
</thead>
<tbody>
<tr>
<td>A'</td>
<td>A₁ + B₂ + E</td>
</tr>
<tr>
<td>A''</td>
<td>A₂ + B₁ + E</td>
</tr>
</tbody>
</table>

By combining the results of Tables 4 and 6 one readily finds that each irreducible representation of Iₜ, or the corresponding states of four icosahedra at positions 4(e) having symmetry Iₜ prior to applying the crystal perturbations, will furnish states of the entire unit cell containing irreducible representations of D₂d as shown in Table 7.

Although we have used the point group, D₂d, associated with the space group P₄²/nmm, rather than the factor group of the translation group, in analyzing the symmetry of the states of the entire unit cell, this does not affect our results as the factor and point groups are known to be simply isomorphic and thus have the same irreducible representations. The highest or least stable intraicosahedral bonding orbital found by Longuet-Higgins and Roberts belongs to the irreducible representation G_u of Iₜ and is fourfold degenerate. The G_u states of the four icosahedra yield 8 non-degenerate and 4 doubly degenerate states of the entire unit cell as indicated in Table 7. In the crystal corresponding states
TABLE 7. Reducible Representations of the Unit Cell Group $D_{2d}$ of Tetragonal-I Boron (Space Group $D_{4h}^{12}$) Furnished by Irreducible Representations of the Icosahedral Group at Positions of Type $4(e)$

<table>
<thead>
<tr>
<th>$I_h$</th>
<th>$D_{2d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>$A_1 + B_2 + E$</td>
</tr>
<tr>
<td>$F_{1g}$</td>
<td>$A_1 + 2A_2 + 2B_1 + 2B_2 + 3E$</td>
</tr>
<tr>
<td>$F_{2g}$</td>
<td>$A_1 + 2A_2 + 2B_1 + B_2 + 3E$</td>
</tr>
<tr>
<td>$G_g$</td>
<td>$2A_1 + 2A_2 + 2B_1 + 2B_2 + 4E$</td>
</tr>
<tr>
<td>$H_g$</td>
<td>$3A_1 + 2A_2 + 2B_1 + 3B_2 + 5E$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>$A_2 + B_1 + E$</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>$2A_1 + A_2 + B_1 + 2B_2 + 3E$</td>
</tr>
<tr>
<td>$F_{2u}$</td>
<td>$2A_1 + A_2 + B_1 + 2B_2 + 3E$</td>
</tr>
<tr>
<td>$G_u$</td>
<td>$2A_1 + 2A_2 + 2B_1 + 2B_2 + 4E$</td>
</tr>
<tr>
<td>$H_u$</td>
<td>$2A_1 + 3A_2 + 3B_1 + 2B_2 + 5E$</td>
</tr>
</tbody>
</table>

from different unit cells will combine with varying factors to yield a band. In general, bands arising from different consecutive states in the unit cell will be separated by an energy gap, although they may overlap.

The difficulty with the application of Longuet-Higgins and Roberts' theory to tetrahedral-I boron lay in the fact that a deficiency of 10 electrons per unit cell is predicted relative to the number required to completely fill the band arising from the uppermost intra-icosahedral bonding state of symmetry $G_u$. However, with the splitting of this band into 12 sub-bands as predicted by the present analysis, there
is a good probability that one of the resulting energy gaps will lie immediately above the Fermi level (on the basis of a random ordering of the 12 sub-bands this probability is calculated to be .74). The structure would then be an insulator at ordinary temperatures. However, the gap introduced by crystal-field splitting between the valence and conduction bonds might be relatively small. The structure would then show a high temperature coefficient of conductivity, and would become an intrinsic semiconductor at elevated temperatures. Shaw, Hudson, and Danielson\textsuperscript{17} have found most single crystals of tetragonal-I boron to be insulators at room temperature, but intrinsic semiconductors at 800-1000\textdegree K (a smaller proportion of crystals were found to be extrinsic semiconductors, apparently at a result of donor impurities).

A similar analysis of the splitting of the icosahedral states in \textalpha-rhombohedral boron may be given. In this case there is only one icosahedron in the primitive rhombohedral unit cell, and the point group symmetry of the crystal is \textit{D}_{3d}. The irreducible representations of \textit{I}_{h} decompose in the subgroup \textit{D}_{3d} as shown in Table 8. Thus, in \textalpha-rhombohedral boron the uppermost intraicosahedral valence bond of symmetry \textit{G}_{u} will be split into three sub-bands. However, this will not significantly affect the conduction properties of the crystal, as the \textit{G}_{u} bond is completely filled according to Longuet-Higgins and Roberts' theory and the sub-bands will also be filled. \textalpha-rhombohedral boron is therefore expected to be an insulator or semiconductor.
TABLE 8. Resolution of the Irreducible Representations of the Icosahedral Group \( I_h \) into Representations of the Unit Cell Group \( D_{3d} \) of \( \alpha \)-rhombohedral Boron (Space Group \( D_{3d}^{2} \))

<table>
<thead>
<tr>
<th>( I_h )</th>
<th>( D_{3d} )</th>
<th>( I_h )</th>
<th>( D_{3d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>( A_{1g} )</td>
<td>( A_u )</td>
<td>( A_{1u} )</td>
</tr>
<tr>
<td>( F_{1g} )</td>
<td>( A_{2g} + E_g )</td>
<td>( F_{1u} )</td>
<td>( A_{2u} + E_u )</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>( A_{2g} + E_g )</td>
<td>( F_{2u} )</td>
<td>( A_{2u} + E_u )</td>
</tr>
<tr>
<td>( G_g )</td>
<td>( A_{1g} + A_{2g} + E_g )</td>
<td>( G_u )</td>
<td>( A_{1u} + A_{2u} + E_u )</td>
</tr>
<tr>
<td>( H_g )</td>
<td>( A_{1g} + 2E_g )</td>
<td>( H_u )</td>
<td>( A_{1u} + 2E_u )</td>
</tr>
</tbody>
</table>
PART II. CALCULATION OF ENERGY BANDS IN $\alpha$-RHOMBOHEDRAL BORON

Chapter 3. Survey of Energy Band Theory for Semiconductors

3.1 General Theory

In its simplest form the quantum theory of crystals is concerned with the motion of a single electron in the periodic field of the lattice, that is with "one-electron" states. The work of Bloch, Brillouin, and others has shown that the energy of such a state is a periodic function of the wave vector in reciprocal space, so that it is sufficient to consider wave vectors in the first Brillouin zone of the reciprocal lattice or the reduced zone scheme. In general, each basic solution of the wave equation in the unit cell of the crystal lattice, gives rise to a set of $N$ energy levels in a periodic lattice containing $N$ unit cells. This set of levels is called an "energy band" because the energy varies in a quasi-continuous manner as the wave vector ranges over the Brillouin zone, and there will in general exist finite upper and lower limits to the energy in a given band at particular values of the wave vector. The number of energy levels or density of states between $E$ and $E + dE$ for a given band is proportional to the volume of wave vector space between the "surfaces" $E$ and $dE$. When the energy bands for a given crystal are arranged in order of increasing energy some may overlap, but between others there may be forbidden regions or energy gaps.
If there are \( z \) electrons per unit cell, or \( Nz \) electrons in the crystal, then at the absolute zero of temperature the \( Nz \) one-electron states (assuming that "state" here implies a specification of the spin as well as the spatial wave function) of lowest energy will be occupied and those of higher energy will be vacant. As the temperature is raised electrons are excited to higher states in accordance with the Fermi-Dirac distribution of quantum statistics. The surface of constant energy separating the occupied and unoccupied levels in wave vector space is called the Fermi surface, and its energy is the free-energy of the electrons in the crystal (actually the free-energy or Fermi surface is sharply defined, but except at the absolute zero of temperature there will be a more or less gradual transition from completely occupied to completely unoccupied levels). In metals and other conductors, the highest occupied band at absolute zero is only partially filled, so that there is no energy gap between the highest occupied and the lowest unoccupied states. On the other hand, in insulators and semiconductors the highest occupied band is completely filled at absolute zero, and there exists a finite energy gap between the top of the occupied band and the bottom of the lowest unoccupied or vacant band. The partially occupied band in metals, or the first unoccupied band in semiconductors, is spoken of as the conduction band.

At sufficiently high temperatures all insulators become (in principle) intrinsic semiconductors as a result of thermal excitation of electrons into the conduction band. Both the negative electrons in the conduction band and the positive "holes" (unoccupied states) left in the occupied band act as charge carriers. The contribution of each type to
the conductivity is the product of its charge, its concentration, and its mobility. Of course, for an intrinsic semiconductor the concentrations of the two types of carriers are equal. The semiconductor is described as n-type if electrons make the greater contribution, and p-type if holes make the greater contribution to the conductivity. Of major importance in semiconductors is the Hall effect, in which a magnetic field transverse to the current generates a transverse electric field normal to both the current and the magnetic field. The product of the Hall coefficient and the conductivity is proportional to the mobility. Thus, the concentration and mobilities can be calculated from measurements of conductivity and the Hall coefficient. The sign of the Hall coefficient in intrinsic semiconductors indicates which type of carrier has the greater mobility.

For the theoretical prediction of conduction and related properties it is usually sufficient to have a knowledge of the structure of the energy bands or states in the neighborhood of the Fermi surface. In the case of semiconductors and insulators this means a knowledge of the energy gap separating the occupied and first unoccupied bands, and the functional dependence of energy on the wave vector at the top of the occupied levels and bottom of the conduction bands. The energy gap and the density of states at the band edges determine the concentration of charge carriers in an intrinsic semiconductor at a given temperature, in accordance with the familiar Boltzmann distribution formula (which is an adequate approximation of the Fermi-Dirac distribution unless the gap is very small or the temperature very high). On the other hand, the mobility of a carrier in a given state is in general a symmetric
second-order tensor whose components are proportional to the second
derivatives of the energy of the band at the point in wave vector space
withstanding to that state. The mobility tensor may be expressed as
the reciprocal of a tensor of effective mass, multiplied by a relaxation
time.

In addition to intrinsic semiconductors, there exist extrinsic
semiconductors containing impurity atoms or localized lattice defects.
The impurities may act as electron donors or acceptors. The case of
greatest importance is that in which the energies of the localized
impurity states fall within the energy gap between the occupied and
conduction bands. Impurity states with energies near the top of the gap
act as donors, since the electrons in these states are readily excited
into the conduction band. On the other hand, electrons from the occupied
band may easily be excited into acceptor impurity states with energies
near the bottom of the gap; the excited electron becomes localized in
the impurity state but the hole in the occupied band acts as a carrier.
Thus, these two types of impurity levels give rise to n- and p-type
semiconduction, respectively. Superimposed on this will be intrinsic
semiconduction due to thermal excitation across the energy gap; extrinsic
semiconduction will predominate at low temperatures and intrinsic at
high temperatures.

3.2 Application to Crystalline Boron

A survey of the energy band theory and its importance for semi-
conductors has been given in section 3.1. Energy band calculations may
yield information regarding the intrinsic energy gap, density of states,
electron mobility, etc. No such calculations appear to have been carried out for crystalline boron, undoubtedly because of the complex structures of the crystal. Until relatively recently tetragonal-I boron, with 50 atoms in the unit cell, was the only form for which the atomic positions were known in detail, and it is doubtful if present computational techniques are adequate for a structure of this complexity. However, in 1958 $\alpha$-rhombohedral boron was discovered and its structure soon completely established by x-ray diffraction methods, as discussed in section 1.3. This is by far the simplest known boron polymorph, with 12 atoms in the unit cell arranged at the vertices of a slightly distorted icosahedron. The lattice has the relatively high symmetry $R3m$, which will result in considerable factorization of the secular equation of the energy band theory at special points in the Brillouin zone. Thus it was considered practicable to undertake an investigation of the energy bands and density of states for $\alpha$-rhombohedral boron.

Two factors other than the relative simplicity of the structure further encouraged us in such a calculation. The first is the existence of a calculation by the tight-binding method for the closely related boron carbide ($B_4C$) lattice, which has also $R3m$ symmetry and an icosahedron of 12 boron atoms in each cell. A comparison of results for the two lattices should be of interest. The second factor is the molecular orbital theory for an isolated regular icosahedron of boron atoms given by Longuet-Higgins and Roberts, and reviewed in section 2.2. The energy levels for an isolated icosahedron should have a fairly definite relationship to the band structure for $\alpha$-rhombohedral boron at
the center of the Brillouin zone. However, in the crystal each level for an icosahedron will be broadened into a band by interactions with neighboring icosahedra of boron atoms. In addition the reduction from icosahedral symmetry, which cannot be maintained in a crystal, to the lower symmetry $R3m$ will produce splittings of the bands. This splitting has been discussed from a group theoretical viewpoint in section 2.3. A complete energy band calculation will take quantitative account of the lowered crystal symmetry and intericosahedral or lattice interactions, and will thus have much greater significance for $\alpha$-rhombohedral boron than the theory of Longuet-Higgins and Roberts.

A number of approximate methods for calculating the electronic band structure of crystals exist, of which the most important are: 1) the cellular method developed by Wigner and Seitz, and refined by Slater; 2) Herring's method of orthogonalized plane waves; 3) the method of augmented plane waves of Slater and Saffren; 4) the Bloch LCAO tight-binding approximation, or its refinement to orthogonalized atomic orbitals by Löwdin; and 5) the scattering matrix method of Korringa, or the equivalent variational method of Kohn and Rostoker. For a detailed discussion, with extensive references to the original literature, reference is made to recent reviews. 19-22

Of the preceding methods only the Block tight-binding approximation seems to be a practicable method for crystals with as many atoms in the unit cell and as complex a structure as occur in crystalline boron. Fortunately, it should also be a fairly accurate method for the essentially covalent boron crystal, at least for the filled bands. Possibly the method of orthogonalized plane waves can be applied to the conduction
band after treating the filled bands by the Bloch method. In this connection it is worth remarking that rather accurate energy band calculations by the method of orthogonalized plane waves have been carried out for the much simpler covalent diamond lattice, and the covalent semiconductor germanium (also a diamond-type lattice). Furthermore, Slater and Koster have shown that the Bloch method yields results for the diamond lattice in generally good agreement with the more accurate calculations of Herman. Slater and Koster also point out certain defects in an application of the Bloch method to diamond by Hall, in a discussion which has considerable relevancy to the boron problem if similar difficulties are to be avoided.
4.1 Introduction

In the calculation of the energy band structure of a crystal by the tight-binding method it is necessary to evaluate a number of two-center integrals involving atomic orbitals on pairs of atoms. As the orbitals fall off exponentially at larger distances it is only necessary in practice to consider pairs of atoms within some finite distance of one another, but it should be noted that these atoms need not lie in the same unit cell. Thus, we may classify such two-center integrals or interactions as intracellular if both atoms of the pair lie in the same unit cell, and intercellular if they lie in different cells. There is an element of arbitrariness in this classification as the choice of unit cell is not unique, but the two types of interaction enter somewhat differently into the formulation of the Bloch or tight-binding method and it is therefore convenient to consider them separately.

An essential ingredient for the evaluation of these two-center integrals is a knowledge of the interatomic distances and directions for the pairs of atoms involved. In view of the preceding discussion these distances and directions are conveniently classified as intra- and intercellular. In the present chapter all such distances and direction cosines required for the present calculation will be tabulated. For simplicity only the most important (smallest) intercellular distances will be considered.
4.2 Unit Cell and Atomic Coordinates

The crystallographic parameters and atomic coordinates in the unit cell are required for the calculation of the interatomic distances and directions. In addition, the parameters characterizing the Bravais lattice determine the form of the Brillouin zone, as discussed in a subsequent section. The results of the x-ray diffraction studies of the structure of single crystals of \( \alpha \)-rhombohedral boron by Decker and Kasper\(^7\) have been described briefly in section 1.3. The space group is \( \bar{R}_3m (D_{3d}^5) \), and the parameters characterizing the primitive rhombohedral unit cell are \( a_0 = 5.057 \pm 0.003 \ \text{\AA}, \alpha = 58.06 \pm 0.05^\circ (58^\circ 4' \)\). The three rhombohedral axes will be denoted by \( x_1, x_2, \) and \( x_3 \), as shown in Figure 1. The interaxial angle is \( \alpha \). The three primitive translation vectors of length \( a_0 \) lie along these axes but are not shown in the figure. The three axes, \( x_1, x_2, \) and \( x_3 \) make equal angles with the threefold \( (3) \) symmetry axis of the crystal which passes through the origin 0, and is perpendicular to the plane of the figure. A rotation by \( 120^\circ \) about this axis effects a cyclic permutation of the axes, \( x_1 \rightarrow x_2 \rightarrow x_3 \).

The space group \( \bar{R}_3m \) possesses also a center of inversion, which lies at the origin in the figure, and three planes of symmetry, each passing through the threefold axis and one of the axes \( x_1, x_2, \) or \( x_3 \). Reflection in a plane of symmetry interchanges two of the axes, for example, \( x_2 \) and \( x_3 \) if the plane contains \( x_1 \).

The 12 atoms per primitive unit cell lie at two sets of special positions of type \( 6(h) \). The projected rhombohedral coordinates, or values of \( x_1, x_2, x_3 \), are for the first set \( u \, v \, v, v \, u \, v, v \, v \, u, \bar{u} \, \bar{v} \, \bar{v}, \bar{v} \, \bar{u} \, \bar{v}, \) and \( \bar{v} \, \bar{v} \, \bar{u} \), with \( u = 0.3427, \, v = -0.0104 \). These coordinates are
given explicitly in the first six rows on the left of Table 9. These atoms will be denoted by 1, 2, 3, 1, 2, and 3, respectively, as illustrated in Figure 1. The coordinates of the second set of six atoms are denoted by similar primed symbols, with \( u' = 0.3677 \) and \( v' = -0.2206 \), and are given in the final six rows on the left of Table 9. Similarly, the second set of atoms is denoted by \( 1', 2', 3', 1', 2', \) and \( 3' \), as shown in Figure 1. The six atoms in each set are related by symmetry; thus rotation by 120° about the threefold axis effects the cyclic permutations \( 1 \rightarrow 2 \rightarrow 3 \) and \( 1' \rightarrow 2' \rightarrow 3' \), and inversion interchanges \( 1 \) and \( 1' \), \( 1' \) and \( 1' \), etc. It is evident from Figure 1 and Table 9 that the two sets of atoms lie at the vertices of a slightly distorted icosahedron.

As the icosahedral configuration plays a role in other boron structures, for example, tetragonal-I boron (section 1.2), boron carbide,\textsuperscript{18} and decaborane,\textsuperscript{27} it is natural to regard the \( \alpha \)-rhombohedral lattice as composed of icosahedra of boron atoms, with the centers of the icosahedra or the point 0 in Figure 1 lying at the points of the rhombohedral lattice. Each rhombohedron has the symmetry \( \overline{3}m \) or \( D_{3d} \) of the point group of the lattice, which is important in simplifying the calculation.

The choice of unit cell requires some discussion. It is desirable in the present calculations to use a primitive cell exhibiting the full symmetry of the point group; thus the primitive rhombohedral cell is preferable to an hexagonal cell. In the preceding discussion of atomic positions it has been implicitly assumed, following Decker and Kasper,\textsuperscript{7} that the center of an icosahedron lies at the point 1(a), 000. In fact it is the coordinates of the atoms of this icosahedron that are listed
TABLE 9. Rhombohedral and Cartesian Coordinates for Atoms in α-rhombohedral Boron

<table>
<thead>
<tr>
<th>Rhombohedral coordinates</th>
<th>Atom</th>
<th>Cartesian coordinates (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_1) (x_2) (x_3)</td>
<td></td>
<td>(x) (y) (z)</td>
</tr>
<tr>
<td>0.3427 (-0.0104) (-0.0104)</td>
<td>1</td>
<td>0 (1.000) (1.348)</td>
</tr>
<tr>
<td>(-0.0104) (0.3427) (-0.0104)</td>
<td>2</td>
<td>(0.866) (0.500) (1.348)</td>
</tr>
<tr>
<td>(-0.0104) (-0.0104) (0.3427)</td>
<td>3</td>
<td>(-0.866) (0.500) (1.348)</td>
</tr>
<tr>
<td>(-0.3427) (0.0104) (0.0104)</td>
<td>(\bar{1})</td>
<td>(0) (0.000) (-1.348)</td>
</tr>
<tr>
<td>(0.3427) (-0.0104) (0.0104)</td>
<td>(\bar{2})</td>
<td>(-0.866) (0.500) (-1.348)</td>
</tr>
<tr>
<td>(0.0104) (0.0104) (-0.3427)</td>
<td>(\bar{3})</td>
<td>(0.866) (0.500) (-1.348)</td>
</tr>
<tr>
<td>(0.3677) (-0.2206) (-0.2206)</td>
<td>(1')</td>
<td>(0) (1.666) (-0.308)</td>
</tr>
<tr>
<td>(-0.2206) (0.3677) (-0.2206)</td>
<td>(2')</td>
<td>(1.444) (-0.833) (-0.308)</td>
</tr>
<tr>
<td>(-0.2206) (-0.2206) (0.3677)</td>
<td>(3')</td>
<td>(-1.444) (-0.833) (-0.308)</td>
</tr>
<tr>
<td>(-0.3677) (0.2206) (0.2206)</td>
<td>(\bar{1}')</td>
<td>(0) (-1.666) (0.308)</td>
</tr>
<tr>
<td>(0.2206) (-0.3677) (0.2206)</td>
<td>(\bar{2}')</td>
<td>(-1.444) (0.833) (0.308)</td>
</tr>
<tr>
<td>(0.2206) (0.2206) (-0.3677)</td>
<td>(3')</td>
<td>(1.444) (0.833) (0.308)</td>
</tr>
</tbody>
</table>
FIGURE 1. Boron Icosahedron in α-Rhombohedral Boron Showing Notation for Atoms and Intericosahedral Distances.
in Table 1 and illustrated in Figure 1. The centers of other icosahedra then lie at the other vertices of the unit cell, 100, 010, 001, 110, 101, 011, and 111. However, this choice of unit cell is undesirable as the cell does not contain entirely any one icosahedron, but two atoms from each of six icosahedra. This is readily established by noting that if an atom is to lie in the rhombohedral cell its coordinates \( x_1, x_2, \) and \( x_3 \) must each lie in the range from 0 to +1. It follows from Table 9 that the cell contains no atoms of the icosahedra centered at 000 and 111, and only two atoms of each icosahedron centered at the other six equivalent vertices. For example, the atoms \( I \) and \( I' \) of the icosahedron at 100 lie within the cell.

This difficulty could be remedied by the simple expedient of taking the centers of the icosahedra at the body-centered positions \( 1(b), \frac{1}{2} \frac{1}{2} \frac{1}{2} \). The rhombohedral coordinates of the atoms in an icosahedron centered at this position are obtained by increasing each coordinate in Table 9 by \( \frac{1}{2} \). All the atoms of the body-centered icosahedron are seen to lie within the rhombohedral cell, and these are the only atoms within the cell. However, we have preferred an equally satisfactory alternative procedure in which the icosahedra remain centered at the positions 1 (a), 000, as in Table 9. This involves the use of the symmetrical unit cell for the rhombohedral (trigonal) lattice as described by Koster. The symmetrical unit cell for any Bravais lattice contains by definition those points of the three-dimensional manifold lying closer to a given lattice point than to any other lattice point. Since all point group operations leave distances invariant, the symmetrical cell so defined is clearly carried into itself under all operations of the point group of
the lattice. It is obvious from its definition that the symmetrical cell is primitive, and with its replicas obtained by the translations of the Bravais lattice fills all space. Such a cell is readily constructed for any given lattice point and lies within all planes bisecting perpendicularly lines drawn from the given lattice point to all other points of the infinite lattice. In practice a few such planes define the surface of the symmetrical cell. It will be noted that this is the precise analog of the procedure by which the first Brillouin zone is constructed in the reciprocal lattice; the latter is the symmetrical unit cell of the reciprocal lattice.

The symmetrical unit cell for the rhombohedral lattice will have qualitatively the form shown in Figure 16 of Koster. \( \alpha \)-rhombohedral boron, with \( \alpha = 58^\circ 4' \), corresponds to Koster's case (a). In fact, since \( \alpha \) has approximately the value 60\(^\circ\) characteristic of the face-centered cubic lattice, the symmetrical unit cell will appear approximately as in Figure 6 of Koster, with the \( \bar{3} \) axis passing through the points T and P in the figure. It is readily established from the coordinates in Table 1 that all 12 atoms of the icosahedron centered at 000 lie within the symmetrical unit cell also centered at this point. It is sufficient to show that atoms 1 and 1' lie at a smaller distance from the center, 000, than from any other lattice point having rhombohedral coordinates \( n_1 n_2 n_3 \), with \( n_1, n_2, \) and \( n_3 \) any positive or negative integers or zero (but excluding \( n_1 = n_2 = n_3 = 0 \)). As all other atoms may be generated by applying the point group operations to 1 and 1', and the symmetrical unit cell is invariant to such operations, the conclusion stated above follows.
For the computation of interatomic distances and direction cosines in the next sections it is convenient to introduce Cartesian coordinates. Mutually orthogonal x, y, and z axes are defined as follows. The origin of the Cartesian axes coincides with that of the rhombohedral axes. The z-axis is coincident with the threefold symmetry axis passing through point 0 in Figure 1, with its positive direction upward and perpendicular to the plane of the figure. The y-axis coincides with the intersection of the plane, containing the z and x_1 axes, and the plane through 0 perpendicular to the z axis, and is directed upward in the figure. The x-axis is perpendicular to the y and z axes and directed to the right in the figure. The linear transformation connecting the Cartesian and rhombohedral coordinates of an arbitrary point is as follows.

\[
x = \left(\frac{\sqrt{3}}{2}\right) (x_2 - x_3) a_o \sin \theta \quad (1a)
\]
\[
y = \frac{1}{2} (2 x_1 - x_2 - x_3) a_o \sin \theta \quad (1b)
\]
\[
z = (x_1 + x_2 + x_3) a_o \cos \theta \quad (1c)
\]

where \( \theta \), the angle made by each of the rhombohedral axes with the z or symmetry axis is determined by the relation

\[
\sin \theta = \left(2 / \sqrt{3}\right) \sin (\alpha/2) \quad (2)
\]

From \( \alpha = 58.06^\circ \) one calculates \( \theta = 34.08^\circ \). The rhombohedral coordinates are dimensionless ratios, but the Cartesian coordinates have the same units as the lattice parameter, \( a_o = 5.057 \AA \). The Cartesian coordinates of the atoms in the icosahedron centered at 000 are given on the right of Table 9.
We consider next the coordinates of atoms in neighboring cells or icosahedra. Hereafter, the symmetrical unit cells of the lattice, or the icosahedra contained therein, will be identified by the rhombohedral coordinates of the lattice point at the center of the cell. The central or 000 cell is surrounded by 12 neighboring cells with each of which it shares a face. The corresponding icosahedra, indicated by their hexagonal projections on the x, y-plane, are shown in Figures 2 and 3. The icosahedra 110, 101, 011, 110, 101, and 011 lie in the same lattice "layer" as the icosahedron 000, the lattice plane with Miller indices (111), as shown in Figure 2. The icosahedra 100, 010, and 001 lie in the layer above this, and 100, 010, and 001 in the layer below, as shown in Figure 3. As previously noted the icosahedra are arranged approximately in cubic close-packing. The rhombohedral and Cartesian coordinates of the centers of the 12 neighboring icosahedra are given in Table 10.

An atom in a given icosahedron will be identified by affixing the rhombohedral coordinates of its center to the atomic symbols defined for the central icosahedron in Table 9 and Figure 1. Thus the atom in the icosahedron 110 translationally equivalent to atoms 2 in the central icosahedron will be denoted by 2_{110}. If it is necessary to indicate explicitly the corresponding atom in the central icosahedron the notation 2_{000} will be used. In the present calculation the coordinates of only a few atoms in surrounding icosahedra are required. These are the atoms to which the central icosahedron is considered to be bonded by three-center and two-center bonds, as discussed briefly in section 1.3 and 2.2. The three-center or "Δ" intericosahedral bonds to icosahedra
FIGURE 2. Arrangement of Icosahedra in the (111) Lattice Plane of $\alpha$-Rhombohedral Boron Showing Notation for Icosahedral Centers or Lattice Points and for Atoms Participating in Three-center Intraicosahedral Bonds.
Figure 3. Arrangement of Icosahedra in Three Adjacent (111) Lattice Planes of $\alpha$-Rhombohedral Boron Showing Notation for Icosahedral Centers or Lattice Points and for Atoms Participating in Two-Center Intraicosahedral Bonds.
TABLE 10. Rhombohedral and Cartesian Coordinates for Centers of Icosahedra in $\alpha$-rhombohedral Boron

<table>
<thead>
<tr>
<th>Rhombohedral coordinates</th>
<th>Icosahedral Center</th>
<th>Cartesian coordinates (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$ $x_2$ $x_3$</td>
<td></td>
<td>$x$ $y$ $z$</td>
</tr>
<tr>
<td>1 0 0</td>
<td>100</td>
<td>0 2.834 4.189</td>
</tr>
<tr>
<td>0 1 0</td>
<td>010</td>
<td>2.454 -1.417 4.189</td>
</tr>
<tr>
<td>0 0 1</td>
<td>001</td>
<td>-2.454 -1.417 4.189</td>
</tr>
<tr>
<td>1 0 0</td>
<td>100</td>
<td>0 -2.834 -4.189</td>
</tr>
<tr>
<td>0 1 1</td>
<td>101</td>
<td>2.454 -4.250 0</td>
</tr>
<tr>
<td>0 0 1</td>
<td>001</td>
<td>2.454 1.417 -4.189</td>
</tr>
<tr>
<td>1 0 1</td>
<td>101</td>
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<td>0 1 1</td>
<td>011</td>
<td>4.907 0 0</td>
</tr>
<tr>
<td>1 1 1</td>
<td>110</td>
<td>2.454 -4.250 0</td>
</tr>
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<td>101</td>
<td>-2.454 -4.250 0</td>
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<td>-4.907 0 0</td>
</tr>
<tr>
<td>1 1 0</td>
<td>110</td>
<td>-2.454 4.250 0</td>
</tr>
</tbody>
</table>
in the same layer as the central icosahedron are indicated by the
dashed triangles in Figure 2. The coordinates of the outer atoms
involved in these bonds are given in Table 11. The two-center inter-
icosahedral bonds to icosahedra in the layer above and below. The
central icosahedron are indicated by the heavy lines in Figure 3. The
coordinates of the outer atoms at the outer termini of these bonds are given
in Table 12.

4.3 Interatomic Distances and Direction Cosines

As discussed in section 4.1 there are required for the evaluation
of the two-center quantum integrals the interatomic distances and
directions. Let the Cartesian coordinates of the i th and j th atoms
be \(x_i, y_i, z_i\), and \(x_j, y_j, z_j\), respectively. Then the interatomic
distance, \(r_{ij}\), and direction cosines \(\ell_{ij}\), \(m_{ij}\), and \(n_{ij}\), are obtained
from the elementary relations

\[
    r_{ij} = \left( (x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2 \right)^{\frac{1}{2}}, \quad (3)
\]

\[
    \ell_{ij} = \frac{(x_j - x_i)}{r_{ij}}, \quad (4a)
\]

\[
    m_{ij} = \frac{(y_j - y_i)}{r_{ij}}, \quad (4b)
\]

\[
    n_{ij} = \frac{(z_j - z_i)}{r_{ij}}, \quad (4c)
\]

The intraicosahedral distances and direction cosines for all
pairs of atoms within the same icosahedron, as computed from the
Cartesian coordinates in Table 9, are given in Table 13. Thus, the
vector from atom 1 to atom 3' in the central icosahedron (see Figure 1)
has a length \( r = 1.787 \) Å, and direction cosines \(\ell = 0.8077\), \(m = -0.0935\),
and \(n = -0.5821\). The distinct intraicosahedral distances are classified
<table>
<thead>
<tr>
<th>Rhombohedral coordinates</th>
<th>Atom</th>
<th>Cartesian coordinates (X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x1</td>
<td>x2</td>
<td>x3</td>
</tr>
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<td>-0.2206</td>
</tr>
<tr>
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</tr>
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<tr>
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<td>0.2206</td>
</tr>
<tr>
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<td>0.6323</td>
</tr>
<tr>
<td>-0.6323</td>
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</tr>
<tr>
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<td>-0.6323</td>
<td>0.7794</td>
</tr>
<tr>
<td>0.2206</td>
<td>-0.7794</td>
<td>0.6323</td>
</tr>
<tr>
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<td>-0.7794</td>
<td>0.2206</td>
</tr>
</tbody>
</table>
TABLE 12. Rhombohedral and Cartesian Coordinates of Atoms Participating in Two-Center Intercosahedral Bonds in $\alpha$-Rhombohedral Boron

<table>
<thead>
<tr>
<th>Rhombohedral coordinates</th>
<th>Atom</th>
<th>Cartesian coordinates (Å)</th>
</tr>
</thead>
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and listed with their multiplicities, or the number of times each is repeated, in Table 14. The distinct nearest-neighbor distances are shown also in Figure 1, and are the lengths of the principal icosahedral bonds.

The intericosahedral distances and direction cosines for the three-center intericosahedral bonds indicated by the dashed lines in Figure 2, as calculated from the Cartesian coordinates in Tables 9 and 11, are given in Table 15 (only the two "sides" of the three-center bond involving an atom in the central icosahedron or cell are required for the calculation by the Bloch tight-binding method).

The intericosahedral distances and direction cosines for the two-center intericosahedral bonds indicated by the heavy lines in Figure 3, as calculated from the Cartesian coordinates in Tables 9 and 12 are given in Table 16.
### Intraicosahedral Distances Multiplicity Description

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### Intericosahedral Distances Multiplicity Description

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TABLE 15. Bond Lengths and Direction Cosines for Three-Center Intericosahedral Bonds

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Same Value: 2.0204
TABLE 16. Bond Lengths and Direction Cosines for Two-Center Intericosahedral Bonds

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Chapter 5. Brillouin Zone and Symmetry of the Electron

Wave Functions for $\alpha$-Rhombohedral Boron

5.1 Reciprocal Lattice

In connection with the calculation of the electronic band structure of crystalline boron in the tight-binding approximation, a study has been made of the first Brillouin zone and of the symmetry properties of the wave functions at various positions in the zone. This is sufficient for the discussion of any band in the reduced zone scheme. Denote by $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ the three equivalent primitive translation vectors of the rhombohedral lattice, all of magnitude $a$, and making equal angles $\alpha$ with one another. The volume of the unit cell in the direct lattice is

$$v = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = a^3 (1 - \cos \alpha) (1 + 2 \cos \alpha)^{\frac{3}{2}}. \quad (5)$$

The base vectors of the reciprocal lattice are defined by

$$\vec{b}_1 = (1/v) \vec{a}_2 \times \vec{a}_3, \quad (6)$$

with $\vec{b}_2$ and $\vec{b}_3$ obtained by cyclic permutation of indices. These vectors all have equal magnitudes $b$, and make equal angles with one another, where

$$b = \sin \alpha / a (1 - \cos \alpha) (1 + 2 \cos \alpha)^{\frac{1}{2}}, \quad (7)$$

$$\cos \beta = -\cos \alpha / (1 + \cos \alpha). \quad (8)$$

$\vec{b}_1$ is perpendicular to the plane of $\vec{a}_2$ and $\vec{a}_3$, etc. It is clear that the reciprocal lattice also belongs to the rhombohedral or trigonal
system. The volume of the unit cell in the reciprocal lattice, and therefore also of each Brillouin zone, is

$$\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3 = \frac{1}{v},$$

(9)

where $v$ is given by Eq. (5). The general reciprocal lattice vector is

$$\mathbf{B}_{\text{hk}\ell} = h \mathbf{b}_1 + k \mathbf{b}_2 + \ell \mathbf{b}_3,$$

(10)

where the Miller indices, $h$, $k$, and $\ell$, assume all integral values (positive, negative, or zero). The magnitude of $|\mathbf{B}_{\text{hk}\ell}|$ is

$$|\mathbf{B}_{\text{hk}\ell}| = (Q_{\text{hk}\ell})^{\frac{1}{2}},$$

(11)

where $Q_{\text{hk}\ell}$ is a quadratic form in the Miller indices which for the rhombohedral lattice may be put in the form

$$Q_{\text{hk}\ell} = A \left[ (h^2 + k^2 + \ell^2) - (k\ell + \ell h + h k) \right] \left[ 1 - \tan^2 \left( \frac{\alpha}{2} \right) \right],$$

(12)

$$A = \cos^2 \left( \frac{\alpha}{2} \right) \left[ a^2 \sin \left( \frac{\alpha}{2} \sin \left( \frac{3\alpha}{2} \right) \right) \right].$$

(13)

Associated with each reciprocal lattice vector $\mathbf{B}_{\text{hk}\ell}$, is a set of parallel planes in the direct lattice, all perpendicular to $\mathbf{B}_{\text{hk}\ell}$, and with inter-planar spacing

$$d_{\text{hk}\ell} = \frac{1}{|\mathbf{B}_{\text{hk}\ell}|} = (Q_{\text{hk}\ell})^{-\frac{1}{2}}.$$ 

(14)

5.2 Irreducible Representations and the Brillouin Zone

The electronic wave functions in a perfect crystal must belong to the irreducible representations of the space group of the crystal. Each operation of the space group consists of an operation, (a proper or improper rotation), associated with the point group of the crystal,
followed by a translation, \( \mathbf{t} \). For a symmorphic space group, \( \mathbf{t} \) is of the form

\[
\mathbf{t} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2 + t_3 \mathbf{a}_3 ,
\]

(15)

where \( t_1, t_2, \) and \( t_3 \) are integers; more generally \( \mathbf{t} \) may contain fractional translations associated with glide-planes and screw-axes.

Let \( \mathbf{k} \) be an arbitrary wave vector in the reciprocal space defining a plane wave, \( \exp (2\pi i \mathbf{k} \cdot \mathbf{r}) \), in the direct lattice (or crystal). The group of the wave vector is defined as the subgroup of the space group consisting of all operations under which \( \mathbf{k} \) transforms as follows,

\[
\mathbf{k} \rightarrow \mathbf{k} + \mathbf{B}_{hk\ell} ,
\]

(16)

where \( \mathbf{B}_{hk\ell} \) is a reciprocal lattice vector defined by Eq. (10) (the case \( \mathbf{B}_{hk\ell} = 0, \mathbf{k} \rightarrow \mathbf{k} \), is included in Eq. (16). The rotational parts, \( \omega \), of the operations in the group of the wave vector form a subgroup of the crystallographic point group which will be called the point group of the wave vector. The irreducible representations of the 32 crystallographic point group and their subgroups are well known, and thus the irreducible representations of the point group of the wave vector are readily obtained. Let \( \Pi(\omega) \) be the matrix of a given irreducible representation of the point group of the wave vector for the operation \( \omega \). Then an irreducible representation of group of the wave vector is given by \( \Pi(\omega) \exp (2\pi i \mathbf{k} \cdot \mathbf{t}) \), this being the matrix corresponding to the operation \( (\omega, \mathbf{t}) \). It is clear that the wave vectors \( \mathbf{k} \) and \( \mathbf{B}_{hk\ell} \) yield the same irreducible representations when \( \mathbf{t} \) has the form Eq. (15). Thus, all irreducible representation of the group of the wave vector may be obtained by restricting \( \mathbf{k} \) to a zone of reciprocal space such that for
every \( k \) in the interior of the zone (not on the surface), and for every non-vanishing reciprocal lattice vector \( \mathbf{B}_{hk\ell} \), \( \mathbf{k} \to \mathbf{B}_{hk\ell} \), lies outside the zone. If, in addition, it is required that the zone have the symmetry of the point group of the lattice, so that every \( \mathbf{k} \) in the zone is transformed either into itself or another \( \mathbf{k} \) in the zone under all operations of the point group, then one obtains a Brillouin zone of the lattice. For every wave vector \( \mathbf{k} \) on the surface of the zone there will exist a wave vector \( \mathbf{k}' \) to the "opposite point" on the surface such that \( |\mathbf{k}'| = |\mathbf{k}| \), and \( \mathbf{k}' = \mathbf{k} - \mathbf{B}_{hk\ell} \), where \( \mathbf{B}_{hk\ell} \) is a particular reciprocal lattice vector. Squaring both sides of the last two equations and subtracting the first from the second yields the following equation for the faces of the Brillouin zones,

\[
\mathbf{k} \cdot \mathbf{B}_{hk\ell} = \frac{1}{2} |\mathbf{B}_{hk\ell}|^2
\]

or

\[
k_B = \frac{1}{2} |\mathbf{B}_{hk\ell}| = \frac{1}{2} (Q_{hk\ell})^{\frac{1}{2}},
\]

where \( k_B \) is the projection of \( \mathbf{k} \) on \( \mathbf{B}_{hk\ell} \). It follows that each face of the Brillouin zone is a plane perpendicular to and bisecting a reciprocal lattice vector \( \mathbf{B}_{hk\ell} \). The faces occur in opposite pairs corresponding to vectors \( \mathbf{B}_{hk\ell} \) and \( -\mathbf{B}_{hk\ell} = \mathbf{B}_{hk\ell} \). The first Brillouin zone is the region of reciprocal space interior to (closer to the origin than) all such pairs of faces, for all non-vanishing \( \mathbf{B}_{hk\ell} \), together with those faces bounding this region. In practice it is only necessary to consider a few such faces corresponding to low values of the Miller indices to establish the first Brillouin zone. The plane face bisecting the vector \( \mathbf{B}_{hk\ell} \) will be referred to as the \( hk\ell \) face of the zone.
5.3 Brillouin Zone for α-Rhombohedral Boron

The form of the first Brillouin zone for the rhombohedral lattice depends on the angle $\alpha$ between the axes. For $\alpha = 109^\circ28'$ (tetrahedral angle) the rhombohedral system becomes equivalent to body-centered cubic, while $\beta = 60^\circ$ and the reciprocal lattice is face-centered cubic. For $\alpha = \beta = 90^\circ$, both the direct and reciprocal lattices are simple cubic. Finally, for $\alpha = 60^\circ$, $\beta = 109^\circ28'$, the direct lattice becomes face-centered cubic and the reciprocal lattice body-centered cubic. For $\alpha > 90^\circ$ (direct lattice tending toward body-centered cubic), the first Brillouin zone is bounded by the faces $\overline{100}$, $\overline{100}$, $\overline{010}$, $\overline{001}$, $\overline{100}$, $\overline{110}$, $\overline{011}$, $\overline{011}$, $\overline{011}$, and $\overline{011}$. For $\alpha < 90^\circ$ (direct lattice tending toward face-centered cubic), the first zone is bounded by the faces $\overline{111}$, $\overline{111}$, $\overline{100}$, $\overline{100}$, $\overline{100}$, $\overline{001}$, $\overline{001}$, $\overline{100}$, $\overline{101}$, $\overline{101}$, $\overline{011}$, and $\overline{011}$.

The latter case is of interest in the present calculation, as the lattice parameters for rhombohedral boron are $a = 5.06 \text{Å}$ and $\alpha = 58^\circ4'$. Then from Eqs. (7) and (8), $b = 0.248 (\text{Å})^{-1}$ and $\beta = 110^\circ15'$. The first Brillouin zone is drawn in Figure 4 as it appears for $\alpha < 60^\circ$. The figure has been copied from Figure 22(i) of Jones with insertion of the vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ of the reciprocal lattice and explicit labeling of the faces. The "visible" faces of the polyhedron are labeled $hk\ell$, while faces on the "back" side of the polyhedron are indicated with dotted lines and labeled $(hk\ell)$.

For $\alpha = 60^\circ$ the polyhedron has cubic symmetry and the eight six-sided faces are regular hexagons while the remaining six faces are square. For $\alpha \neq 60^\circ$ these faces become irregular hexagons and rectangles, respectively, but the polyhedron retains $D_{3d}$ symmetry, which
FIGURE 4 Arrangement of Icosahedra in Three Adjacent (111) Lattice Planes of $\alpha$-Rhombohedral Boron Showing Notation for Icosahedral Centers or Lattice Points and for Atoms Participating in Two-center Intraicosahedral Bonds.
is the point group associated with the space group, \( D_{3d}^5 \) or \( R\bar{3}m \), reported for rhombohedral boron.\(^2\) The perpendicular "distance" of each type of face from the origin or center of the zone is given by \( k_B \) of Eq. (18). However, a quantity of greater physical interest is the corresponding kinetic energy of a free electron. For a free electron of mass \( m \) and momentum \( p = h k_B \) this is

\[
E_{hk\ell}^O = \frac{p^2}{2m} = \frac{h^2 k_B^2}{2m} = \frac{(h^2/8m)}{Q_{hk\ell}}, \tag{19}
\]

using Eq. (18). On inserting the values of the fundamental constants, this yields

\[
E_{hk\ell}^O \text{ (electron-volt)} = 37.60 \, Q_{hk\ell} \, (\AA)^{-2}. \tag{20}
\]

On inserting the values \( a = 5.06 \, \AA \) and \( \alpha = 58^\circ 4' \) for rhombohedral boron in Eqs. (12) and (13), and substituting Eqs. (12) in (20) the free-electron energy is expressible directly in terms of the Miller indices of a face,

\[
E_{hk\ell}^O \text{ (ev)} = 2.316 \, \left[ (h^2 + k^2 + \ell^2) - 0.6919 (k \ell + \ell h + h k) \right] \tag{21}
\]

The values of \( E_{hk\ell}^O \) for the (100), (110), and (111) faces of the first Brillouin zone of rhombohedral boron, as illustrated in Figure 4, are 2.316, 3.030, and 2.141 electron-volts, respectively. The values of the energies for the (100) and (111) faces would be equal for a face-centered cubic lattice (\( \alpha = 60^\circ \)).

5.4 Symmetry of Wave Functions

The symmetry properties of the wave functions at several special points in the Brillouin zone of Figure 4 will now be discussed. Such symmetry is important in facilitating the calculation of the band
energies. At the center of the zone, \( \vec{k} = 0 \), point group of the wave vector is the full point group, \( D_{3d} \), of the lattice. The wave functions derived from the 2s, 2p_x, 2p_y, and 2p_z orbitals of the 12 boron atoms per unit cell may be classified as follows under the irreducible representations of \( D_{3d} \):

\[
6A_g + 2A_{1u} + 2A_{2g} + 6A_{2u} + 8E_g + 8E_u
\]

That is, there will be 6 wave functions belonging to \( A_g \), 2 to \( A_{1u} \), etc. The secular determinant for the energies will factor into blocks (sub-determinants) of dimensions 6, 2, 2, 6, 8, and 8, on a side (the latter two blocks each occurring twice as the irreducible representation is degenerate. The linear combinations of the atomic orbitals transforming according to each irreducible representation are given in Table 17.

These symmetry orbitals are designated as \( S, P_x, P_y, \) and \( P_z \). There are 48 atomic orbitals per unit cell to be considered, consisting of the 2s, \( 2p_x, 2p_y, \) and \( 2p_z \) orbitals on each boron atom. To simplify the notation the principal quantum number, 2, is omitted, and \( x, y, \) and \( z \) have been written for \( p_x, p_y, \) and \( p_z \); the subscript indicates the atom on which the orbital is located. There are 24 additional symmetry orbitals related in the same way to the atomic orbitals on the "primed" atoms. The Cartesian \( x, y, \) and \( z \)-axes have the same orientation at each atom, with the \( z \)-axis parallel to the threefold axis, and the \( y \) and \( x \)-axes parallel and perpendicular, respectively, to the symmetry plane containing atoms 1 and 1'. The derivation of correct symmetry orbitals is of considerable importance; Yamazaki,\(^{18}\) in his similar calculation on rhombohedral boron carbide, has used degenerate symmetry orbitals which are not mutually orthogonal. In general, matrix elements will vanish
<table>
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<tr>
<th>Irreducible Representation</th>
<th>Symmetry Orbitals</th>
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| \(A_{1g}\)                | \[S_1 = (1/6)^{1/2}(s_1 + s_2 + s_3 + s_1^+ + s_2^+ + s_3^+)\]  
|                           | \[P_{y1} = (1/8)^{1/2}(x_2^*-x_3^*-x_2^+ x_3^+) + (1/24)^{1/2}(2y_1-y_2-y_1^+ y_2^+ y_3)\]  
|                           | \[P_{z1} = (1/6)^{1/2}(z_1 + z_2 + z_3 - z_1^+ - z_2^+ - z_3^+)\]  |
| \(A_{1u}\)                | \[P_{x2} = (1/24)^{1/2}(2x_1-x_2-x_3 + 2x_1^+ - x_2^+ + x_3^+) - (1/8)^{1/2}(y_2-y_3+y_2^+-y_3)\]  |
| \(A_{2g}\)                | \[P_{x1} = (1/24)^{1/2}(2x_1-x_2-x_3 - 2x_1^+ + x_2^+ + x_3^+) -(1/6)^{1/2}(y_2-y_3+y_2^+-y_3)\]  |
| \(A_{2u}\)                | \[S_2 = (1/6)^{1/2}(s_1 + s_2 + s_3 - s_1^+ - s_2^+ - s_3^+)\]  
|                           | \[P_{y2} = (1/8)^{1/2}(x_2^*-x_3^*-x_2^+ x_3^+) + (1/24)^{1/2}(2y_1-y_2-y_1^+ 2y_1^+ y_2^--y_3)\]  
|                           | \[P_{z2} = (1/6)^{1/2}(z_1 + z_2 + z_3 + z_4 + z_5 + z_6)\]  |
| \(E_g\) (row 1)           | \[S_3 = (1/12)^{1/2}(2s_1-s_2-s_3 + 2s_1^+ - s_2^+ - s_3^+)\]  
|                           | \[P_{x3} = (1/48)^{1/2}(4x_1 + x_2 + x_3 - 4x_1^+ - x_2^+ - x_3^+) + (1/4)(y_2-y_3-y_2^+-y_3)\]  
|                           | \[P_{y3} = -(1/4)(x_2^*-x_3^*-x_2^+ x_3^+) + (1/48)^{1/2}(4y_1+y_2+y_3+4y_1^+ y_2^--y_3)\]  
|                           | \[P_{z3} = (1/12)^{1/2}(2z_1-z_2-z_3 - 2z_1^+ + z_2^+ + z_3^+)\]  |
| \(E_g\) (row 2)           | \[S_4 = (1/2)(s_2 - s_3 + s_2^+ - s_3^+)\]  
|                           | \[P_{x4} = -(1/4)(x_2^*-x_3^*-x_2^+ x_3^+) -(3/16)^{1/2}(y_2^+ y_3+y_2^--y_3)\]  
|                           | \[P_{y4} = (3/16)^{1/2}(x_2^+ - x_3^--x_2^+ x_3^+) -(1/4)(y_2-y_3+y_2^+-y_3)\]  
|                           | \[P_{z4} = (1/2)(z_2 - z_3 - z_2^+ + z_3)\]  |
| \(E_u\) (row 1)           | \[S_5 = (1/12)^{1/2}(2s_1-s_2-s_3 - 2s_1^+ + s_2^+ + s_3^+)\]  
|                           | \[P_{x5} = (1/48)^{1/2}(4x_1 + x_2 + x_3 + 4x_1^+ + x_2^+ + x_3^+) + (1/4)(y_2-y_3+y_2^--y_3)\]  
|                           | \[P_{y5} = -(1/4)(x_2^*-x_3^*-x_2^+ x_3^+) + (1/48)^{1/2}(4y_1+y_2+y_3+4y_1^+ y_2^--y_3)\]  
|                           | \[P_{z5} = (1/12)^{1/2}(2z_1-z_2-z_3 + 2z_1^+ - z_2^+ - z_3^+)\]  |
| \(E_u\) (row 2)           | \[S_6 = (1/2)(s_2 - s_3 - s_2^+ + s_3^+)\]  
|                           | \[P_{x6} = -(1/4)(x_2^*-x_3^*-x_2^+ x_3^+) -(3/16)^{1/2}(y_2^+ y_3+y_2^--y_3)\]  
|                           | \[P_{y6} = (3/16)^{1/2}(x_2^+ - x_3^--x_2^+ x_3^+) -(1/4)(y_2-y_3+y_2^+-y_3)\]  
|                           | \[P_{z6} = (1/2)(z_2 - z_3 + z_2^+ - z_3)\]  |
between symmetry orbitals belonging to different rows of the same
degenerate representation only if the orbitals are orthogonal.

The classification of the wave functions and factoring of the
determinant will be the same at centers of the 111 and \( \overline{111} \) faces, where
they intersect the threefold axis. This follows from the fact that all
the operations of the point group \( D_{3d} \) carry \( \vec{k} \) into either itself or \( -\vec{k} \),
but for these special positions \( \vec{k} - (-\vec{k}) = 2\vec{k} = \overline{B} \) (111), so that Eq. (16)
is satisfied. However, at intermediate points along the threefold axis
the point group of the wave vector is reduced to \( C_{3v} \) and from the usual
correlation tables the wave functions will classify as follows under the
irreducible representation of \( C_{3v} \):

\[
12 \, A_1 + 4A_2 + 16E
\]  
(23)

At the intersections of perpendiculars from the origin or zone center to
the faces of type 100 and 110 (provided these intersections lie within
the zone surface) the point group of the wave vector will be \( C_{2h} \), with
classification:

\[
14 \, A_g + 10 \, A_u + 10 \, B_g + 14 \, B_u.
\]  
(24)

At points lying on the three symmetry planes passing through the three-
fold axis and the centers of faces of type 100 and 110, but excluding
the points previously discussed, the point group wave vector is \( C_s \), and
the classification is:

\[
28 \, A' + 20 \, A''
\]  
(25)

At points on the three twofold axes, and also at the intersections of
the 111 and \( \overline{111} \) faces with planes through the threefold axis and each
twofold axis in turn (these are not symmetry planes), but exclusive of
points previously discussed, the point group of the wave vector is \( C_2 \)
with classification:

\[ 24 \, A + 24 \, B. \]  \hspace{1cm} (26)

Wave functions at other points in the first Brillouin zone possess no point group symmetry other than the identity operation, and there will be no factorization of the secular equation other than that provided by translational symmetry, which insures in all cases that there will be no matrix elements between wave functions with different wave vectors.
Chapter 6. Secular Equation: Reduction of Matrix Elements to Standard Integrals

6.1 Bloch Tight-Binding Approximation

6.1.1 Atomic Positions and Atomic Orbitals

In the Bloch tight-binding or LCAO method the one-electron wave functions are assumed to be linear combinations of atomic orbitals centered at the atomic positions in the crystal. It will be desirable to introduce a general notation adapted to the description of the unit cells, atomic positions, and atomic orbitals (the specific values of the crystallographic parameters for \(\alpha\)-rhombohedral boron have been given in detail in Chapter 4 for use in connection with the calculations of the present section). The vector to the origin of the \(n_1n_2n_3\)th unit cell will be denoted by

\[
r_{n_1n_2n_3} = n_1 a_1 + n_2 a_2 + n_3 a_3
\]  

(27)

where \(a_1, a_2\), and \(a_3\) are the translation vectors of the lattice. We may assume that for the central or reference cell \(r_{000} = 0\). It should be noted that the unit cells do not necessarily have the conventional parallelepipedal form, but may have a form exhibiting the point group symmetry of the lattice. In the case of rhombohedral boron the origin of the reference cell is taken at the center of a boron icosahedron, as illustrated in Figure 1 of section 4.2. The rhombohedral axes are denoted by \(x_1\), \(x_2\), and \(x_3\), respectively. The translation vector \(a_i\) in Eq. (27) is directed along the axis \(x_i\) (\(i = 1, 2, 3\)). In rhombohedral...
boron the vectors, \( r_{n_1 n_2 n_3} \), to the origins of the 12 unit cells adjacent to or bounding the reference cell are obtained by assigning to the triplet of integers, \( n_1 n_2 n_3 \), in Eq. (27) the following values: (i) for the six cells in the same layer of the lattice, \( 101, 01\bar{1}, \bar{1}10, \bar{1}01, 0\bar{1}1, \) and \( \bar{1}\bar{1}0 \); (ii) for the six cells in adjacent layers of the lattice, \( 100, 010, 001, \bar{1}00, \bar{1}10, \) and \( 00\bar{1} \). The origins of these two groups of cells and the icosahedra of boron atoms centered at these two positions are illustrated in Figures 2 and 3 which are drawn to the same scale and may be superimposed. In these figures \( x \) and \( y \) are Cartesian axes, and the \( z \) or \( z \) axis is perpendicular to the plane of the paper; the figures are projections on the \( x, y \)-plane. The vectors \( a_1, a_2, \) and \( a_3 \) are directed from the origin of the reference cell, \( 000 \) in Figure 3, to the positions \( 100, 010, \) and \( 001 \), respectively. The symmetric or Wigner-Seitz type unit cell for rhombohedral boron is the volume bounded by the planes which are perpendicular bisectors of the 12 vectors, \( r_{n_1 n_2 n_3} \), described under categories (i) and (ii), as discussed in detail in section 4.2. The unit cell is a 12-sided figure having the point group symmetry, \( \overline{3}m \), of the lattice, and enclosing symmetrically a single (non-regular) icosahedron of boron atoms. This unit cell is primitive, and it and its replicas generated by the lattice translations of Eq. (27) fill completely the volume of the crystal.

The subscripts \( i \) and \( j \) will denote particular atoms in the unit cell. Thus, in the present calculation \( i \) may indicate any of the 12 boron atoms designated by 1, 2, 3, \( \bar{1}, \bar{2}, \bar{3}, 1', 2', 3', \bar{1}', \bar{2}', \) or \( \bar{3}' \) in
Figure 1 of section 4.2. The position vector of the \(i\)th atom in the reference cell relative to the origin of that cell will be designated by

\[
\mathbf{r}_i = x_{1i} \mathbf{a}_1 + x_{2i} \mathbf{a}_2 + x_{3i} \mathbf{a}_3, \tag{28}
\]

where \(x_{1i}, x_{2i},\) and \(x_{3i}\) are the rhombohedral atomic coordinates. These coordinates may be obtained from Table 9. The position vector of the translationally equivalent atom in the \(n_1n_2n_3\) th cell is then

\[
\mathbf{r}_{n_1n_2n_3} + \mathbf{r}_i.
\]

A particular atomic orbital of a given atom will be designated by subscripts \(a\) or \(b\). Thus \(u_{ia}(\mathbf{r} - \mathbf{r}_i)\) will denote the \(a\)th orbital of the \(i\)th atom in the reference cell. The translationally equivalent orbital on the \(i\)th atom in the \(n_1n_2n_3\) th unit cell will be denoted by \(u_{ia}(\mathbf{r} - \mathbf{r}_{n_1n_2n_3} - \mathbf{r}_i)\). It should be noted that these two orbitals are identical functions of their arguments; only the arguments differ. However, an orbital \(u_{ja}(\mathbf{r} - \mathbf{r}_j)\) on an atom not translationally equivalent to the \(i\)th atom may have a different orientation in space even though it is the same type of orbital.

6.12 Bloch Wave Function and the Secular Equation

Bloch wave functions are now formed as the following linear combinations of each set of translationally equivalent atomic orbitals,

\[
\psi_{ia}(\mathbf{r}, \mathbf{k}) = \sqrt{\frac{1}{N}} \sum_{n_1n_2n_3} u_{ia}(\mathbf{r} - \mathbf{r}_{n_1n_2n_3} - \mathbf{r}_i) \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_{n_1n_2n_3}). \tag{29}
\]

The summations extend over the \(N\) unit cells of the crystal. The behavior of the wave function under lattice translations is characterized by the
wave vector $k$; in particular, if the crystal is translated by the
vector $r_{m_1 m_2 m_3}$ we obtain from Eq. (29).

$$\psi_{ia}(r_{m_1 m_2 m_3} + r, k) = \psi_{ia}(r, k) \exp(2\pi i k \cdot r_{m_1 m_2 m_3}), \quad (30)$$

as required by Bloch's theorem. That is, the wave function of Eq. (29)
is an eigenfunction of the translation operator with eigenvalue
$\exp(2\pi i k \cdot r_{m_1 m_2 m_3})$. Note that all translations commute, so that it is
possible for a single function $\psi_{ia}(r, k)$ to be an eigenfunction of each
translation operator. However, as it stands it is not generally an
eigenfunction of the effective one-electron Hamiltonian operator, $H$.

Eigenfunctions of $H$ may be obtained in the form of linear combinations
of functions $\psi_{ia}(r, k)$ by the familiar variation method. Since the
translation operators commute with $H$, we know that it is possible to
find eigenfunctions of $H$ which remain eigenfunctions of the translation
operators. It is therefore sufficient to take linear combinations only
of functions $\psi_{ia}(r, k)$ having the same value of $k$ in finding the eigen-
fuctions of $H$. Matrix elements of $H$ between functions with different
values of $k$ vanish in any case, since from a group theoretical viewpoint
such functions belong to different irreducible representations of the
translation group, while $H$ belongs to the totally symmetric represen-
tation; by the same argument Bloch functions having different $k$ values
are orthogonal (these conclusions are valid regardless of the orthogo-
nality or non-orthogonality of the atomic orbitals). On applying the
variation method one obtains, for each value of $k$, a secular equation
of the form

$$\left| H_{ia, jb}(k) - S_{ia, jb}(k) E(k) \right| = 0, \quad (31)$$
with roots $E(k)$ equal to the band energies for the given $k$ (in Eq. (31) it has been assumed that the atomic orbitals form an orthonormal set).

The matrix elements of the operator $H$ in Eq. (31) have the form

$$H_{ia,jb}(k) = \int \psi^*_i(r,k)H\psi_j(r,k)dr.$$  

(32)

On substitution of Eq. (29) in Eq. (32), and use of the periodicity of the lattice to carry out one of the triple summations, there is obtained

$$H_{ia,jb}(k) = \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp(2\pi ik \cdot r_{n_1n_2n_3})$$

$$\times \int u^*_i(r-r_{i1})u_j(r-r_{n_1n_2n_3})H_{n_1n_2n_3}dr.$$  

(33)

In Eq. (33) $u_i(r-r_{i1})$ is the $i$th orbital of the $i$th atom in the reference cell (with origin at $r_{000} = 0$), and $u_j(r-r_{n_1n_2n_3})$ is the $j$th orbital of the $j$th atom in the $n_1n_2n_3$th cell. In principle the sum extends over the entire crystal, but in practice it is sufficient to include only a few cells near the reference cell.

The quantity $S_{ia,jb}(k)$ in Eq. (31) is the overlap integral between the Bloch wave functions $\psi_i(r,k)$ and $\psi_j(r,k)$, and is given by the expressions obtained by substituting the identity operator for the operator $H$ on the right-hand sides of Eqs. (32) and (33). In the remainder of this section we consider explicitly only the matrix elements $H_{ia,jb}(k)$, but those for $S_{ia,jb}(k)$ are obtainable from these by the substitution indicated. The introduction of the overlap integrals between Bloch functions of the same $k$ avoids the necessity for introducing the cumbersome orthogonalized atomic orbitals defined by Lowdin, and is entirely equivalent to his procedure.
6.2 Reduction of Intraicosahedral Two-Center Integrals to Standard Form

6.21 Matrix Formulation of Method of Slater and Koster

For \( n_1 = n_2 = n_3 = 0 \) the integrals in Eq. (33) reduce to integrals between orbitals on atoms in the same cell. The two-center integrals between all pairs of boron atoms in the same unit cell or icosahedron have been reduced to integrals of a standard form by a modification of the method of Slater and Koster. The integrals involved are those between 2s and 2p atomic orbitals on each boron atom, but the present method is adaptable to higher orbitals (d, f, etc.). Consider two boron atoms in the same cell, designated by indices i and j, separated by a distance \( r_{ij} \), and with direction cosines \( \ell, m, \) and \( n \) for the line drawn from the \( i \)th to the \( j \)th atom. Considered as an isolated pair of atoms this system has the symmetry of the continuous two-dimensional rotary-reflection group, and the integrals assume their simplest form if the atomic orbitals are chosen to transform according to the irreducible representations of this group. It is convenient to designate such orbitals by the notation used for diatomic molecules: \( s\sigma, p\sigma, p\pi, \) and \( p\pi' \). \( s\sigma \) orbitals are totally symmetric to rotations about the line of centers, so that the \( p \) orbital is directed along this line. We assume that the positive lobe of \( p\sigma_j \) is directed toward the \( j \)th atom. The \( p\pi \) and \( p\pi' \) orbitals are directed perpendicularly to the line of centers and to each other. Each is anti-symmetric to a \( 180^\circ \) rotation about the line of centers. It is further specified that the axes of the \( p\pi \) orbitals lie in a common plane with the threefold rotation axis of
the crystal. It is convenient to have collective symbols $\eta_i$ and $\eta_j$, for the orbitals at the $i$th and $j$th atoms, written as row matrices. Thus,

$$\eta_i = (s\sigma_i, p\sigma_i, p\pi_i, p\pi_i)^t,$$

$$\eta_j = (s\sigma_j, p\sigma_j, p\pi_j, p\pi_j)^t.$$  \hspace{1cm} (34a)

(34b)

The Hermitian conjugate of a matrix will be designated by an asterisk, and is obtained by taking the complex conjugate of all elements and transposing the matrix; for real orbitals or elements, as in the present discussion, the asterisks may be regarded as indicating simply the transposed matrix. All the two-center integrals between the $i$th and $j$th atoms, collected in a square matrix array, are now conveniently indicated by the symbol $(\eta_i^* \ H \eta_j)$. This matrix may be written more explicitly as

$$\begin{pmatrix}
(s\sigma\sigma) & (sp\sigma) & 0 & 0 \\
(sp\sigma) & (pp\sigma) & 0 & 0 \\
0 & 0 & (pp\pi) & 0 \\
0 & 0 & 0 & (pp\pi)
\end{pmatrix}$$

where

$$\begin{align*}
(s\sigma\sigma) &= \int (s\sigma_i) H (s\sigma_j) \ d \tau \hspace{1cm} (36a) \\
(sp\sigma) &= \int (s\sigma_i) H (p\sigma_j) \ d \tau \hspace{1cm} (36b) \\
&= \int (p\sigma_i) H (s\sigma_j) \ d \tau \hspace{1cm} (36b) \\
(pp\sigma) &= \int (p\sigma_i) H (p\sigma_j) \ d \tau \hspace{1cm} (36c) \\
(pp\pi) &= \int (p\pi_i) H (p\pi_j) \ d \tau \\
&= \int (p\pi_i) H (p\pi_j') \ d \tau. \hspace{1cm} (36d)
\end{align*}$$
H is the Hamiltonian operator, which is Hermitian and is assumed to be real. All other two-center integrals in Eq. 35 vanish with the present choice of orbitals, provided the operator, H, and in particular the potential term in this operator, has axial symmetry about the line of centers of the ith and jth atoms (it should be understood, however, that this is only an approximation and ignores the contribution of other atoms to the potential). The non-vanishing integrals of Eqs. (36a-d) will depend on the radial variation of the orbitals and the interatomic distance, r_{ij}, but for the present we do not need to consider these factors explicitly.

The preceding choice of orbitals yields the simple form indicated in Eq. (35) for the two-center integrals between a given pair of atoms. However, the integrals in the secular equation must all be referred to a single set of orbitals on each atom. We now introduce a set of basic atomic orbitals for each atom, designated as s_i, p_{xi}, p_{yi}, and p_{zi} for the ith atom, and having the same orientation at each atom. That is, p_{xi}, p_{yi}, and p_{zi} are directed along the corresponding right-handed Cartesian axes of Figures 2 and 3 of section 4.2 (since the s orbital is spherically symmetric it is unnecessary to indicate a special orientation for it). We introduce also the collective symbols

\[ \chi_i^O = (s_i, p_{xi}, p_{yi}, p_{zi}) \]  \hspace{1cm} (37a)

\[ \chi_j^O = (s_j, p_{xj}, p_{yj}, p_{xj}) \]  \hspace{1cm} (37b)
It is readily shown that the following linear transformation connects the basic atomic orbitals with those of Eqs. (34a-b):

\[
\chi_i^O = \eta_i U_+,
\]

\[
\chi_j^O = \eta_j U_-,
\]

where \( U_+ \) and \( U_- \) are matrices dependent on the direction cosines of the line connecting the \( i \)th to the \( j \)th atom.

\[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \ell^+ & m^+ & n^+ \\
0 & \ell n(l-n^2)^{-\frac{1}{2}} & -mn(l-n^2)^{-\frac{1}{2}} & (1-n^2)^{\frac{1}{2}} \\
0 & m(l-n^2)^{-\frac{1}{2}} & -\ell(l-n^2)^{-\frac{1}{2}} & 0
\end{pmatrix}
\]

It now follows from Eqs. (38a-b) that all the two-center integrals between basic atomic orbitals at the \( i \)th and \( j \)th atoms may be represented in a square matrix array as

\[
\left( \begin{array}{c} \chi_i^O \\ H^* \\ \chi_j^O \end{array} \right) = U_+ \left( \begin{array}{c} \eta_i^* \\ H^* \\ \eta_j^* \end{array} \right) U_-.
\]

That is, these integrals may be obtained by premultiplying the matrix on the right-hand side of Eq. (35) by the transpose of \( U_+ \) and post-multiplying the result by \( U_- \). The integrals will then be expressed as linear combinations of the standard forms of Eqs. (36a-d), with coefficients depending on the direction cosines. The resulting matrix, \( \left( \chi_i^O \big| H \big| \chi_j^O \right) \), is shown in Table 18 as the central matrix of the three matrices preceding the equality sign. This result is equivalent to the formulae given by Slater and Koster, except for certain differences in sign resulting from a difference in the definition of \( \sigma_j^i \). Although the matrix formulation developed here has led to a verification of the
TABLE 18. REDUCTION OF TWO-CENTER INTEGRALS BETWEEN ATOMS 1 AND 2 TO STANDARD FORM.

From 1 to 2: \( t = +0.5000, m = -0.8661, n = 0, r = 1.733 \)

\[
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
(SS^0) & -t(SP^0) & -m(SP^0) & -n(SP^0) \\
(t(SP^0)) & -t^2(PP^0) + (1-t^2)(PP^\pi) & -tm(PP^0 + PP^\pi) & -tn(PP^0 + PP^\pi) \\
m(SP^0) & -tm(PP^0 + PP^\pi) & -m^2(PP^0) + (1-m^2)(PP^\pi) & -mn(PP^0) + PP^\pi \\
n(SP^0) & -tn(PP^0 + PP^\pi) & -mn(PP^0 + PP^\pi) & -n^2(PP^0) + (1-n^2)(PP^\pi) \\
\end{bmatrix}
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\
0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 0 & 1 \\
\end{bmatrix}
\]

\[
\begin{bmatrix}
(SS^0) & -0.5000(SP^0) & -0.8661(SP^0) & 0 \\
+0.5000(SP^0) & -0.2501(PP^0) -0.7501(PP^\pi) & -0.4330(PP^0) + 0.4330(PP^\pi) & 0 \\
-0.8661(SP^0) & +0.4330(PP^0) -0.4330(PP^\pi) + 0.7501(PP^0) + 0.2501(PP^\pi) & 0 \\
0 & 0 & 0 & PP^\pi \\
\end{bmatrix}
\]

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results of Slater and Koster, its principal importance is that it facilitates the further transformations of the orbitals which are desirable in symmetrical molecules or crystals, and which will now be considered.

6.22 Properties of Site Groups and Equivalent Orbitals

In a crystal with non-trivial symmetry the atoms in a unit cell will in general occur in sets which are equivalent under the factor group of the lattice. In many cases the factor group reduces to a point group; thus, for rhombohedral boron it is the point group $\tilde{D}_3$, or $D_{3d}$. In the latter structure there are two sets of equivalent boron atoms, each containing six atoms, as indicated by the primed and unprimed numerals of Figure 1 of section 4.2. Under the operations of the point group each set is carried into itself. However, if we fix our attention on a given atom, say $B_1$, we find there are two operations, the identity and a plane of reflection, which leave $B_1$ unmoved. These operations constitute a subgroup, $C_3$, of the point group. A subgroup of this type which leaves a given site invariant is also referred to as a site group. For each other atom of the equivalent set there exists a site group which is either the same or a conjugate subgroup. Although operations in a site group leave the associated site invariant, they will in general transform in a non-trivial manner functions associated with the site, such as the atomic orbitals of an atom at the site. It will be shown subsequently that there are significant simplifications in the form of the two-center integrals if the atomic orbitals of each atom are oriented so that they transform according to the irreducible representation of the
associated site group. However, we will first indicate how such atomic orbitals may be defined conveniently.

It will be observed that the basic atomic orbitals previously introduced at sites 1 and 1' are already oriented so that \( s_1, p_{y1}, \) and \( p_{z1} \) transform according to the totally symmetric irreducible representation \( A^1 \) of \( C_s \), while \( p_x^0 (i = 1 \text{ or } 1') \) transforms according to the antisymmetric irreducible representation \( A' \). We now define a set of equivalent atomic orbitals, as follows (cf. Eq. (37b)):

\[
\chi_j = (s_j, p_{xj}, p_{yj}, p_{zj}) \quad (41)
\]

\[
\chi_j = R_{1j} \chi_1^0 \quad (42)
\]

Here \( R_{1j} \) is an operation of the point group \( D_{3d} \) which carries the site 1 to site j. The index j ranges over the entire set of equivalent sites (the original site 1 may be included by permitting \( R_{1j} \) to be the identity operation, so that \( \chi_1 = \chi_1^0 \), there being no distinction between the equivalent atomic orbitals and basic atomic orbitals at site 1). The operations \( R_{1j} \) may be selected in any convenient manner. We make the following choices, indicating in parentheses the site into which 1 is carried by each operation (see the figures referred to previously):

\[
R_{1j} = \left[ \text{E(1), } C_3 (2), C_3^2 (3), I(1), I_C (2), I_C^2 (3) \right].
\]

\( (43) \)

Here \( E \) is the identity operation, \( I \) the inversion, and \( C_3 \) rotation by \( 2\pi/3 \) about the threefold axis. A set of equivalent atomic orbitals \( \chi_j^0 \) at the primed sites is defined in an exactly similar manner by operating on the basic atomic orbitals \( \chi_1^0 \) with the set of operations (42).
We will designate operations in the site group at 1 by $R_1$, $R_1'$, $R_1''$, etc. Then $R_j = R_1 R_j^{-1}$, $R_j' = R_1 R_j$, $R_j'' = R_1 R_j'' R_1^{-1}$, etc., are the equivalent operations in the conjugate, simply isomorphic, site group at the $j$th site. First, we note that operations of the type $R_j = R_1 R_j R_1^{-1}$ leave the $j$th site invariant and therefore belong by definition to the corresponding site group ($R_1^{-1}$ carries the $j$th site to site 1, $R_1$ leaves it at site 1, and $R_1$ then returns it to its original position). Second, if $R_1 R_1' = R_1$, it follows that

$$R_1' R_1'' = R_1 R_1' R_1 R_1 R_1 = R_1 R_1' R_1 R_1 = R_j,$$  

which establishes the isomorphism. Finally, the isomorphism is simple since $R_1 \neq R_1'$ is easily seen to imply $R_j \neq R_j'$, and conversely.

The atomic orbitals $\chi_1$ generate a representation of the site group at site 1 which is fully reduced, since we have chosen the atomic orbitals so that they transform according to the irreducible representation of the site group. That is, $R_1 \chi_1 = \chi_1 M$, $R_1' \chi_1 = \chi_1 M'$, etc., where $M$, $M'$, etc., are the square orthogonal matrices of the reduced representation. It will be recalled that $\chi_1$ represents a row matrix, so that a linear transformation may be represented by post-multiplication by a square matrix. We now find, using also Eq. (42), that

$$R_j \chi_j = R_1 R_j R_1 R_1 R_1 = R_1 R_1 R_1 R_1 R_1 = \chi_j M.$$

Similarly, $R_j' \chi_j = \chi_j M'$, etc. Thus, the atomic orbitals $\chi_j$ generate the same fully reduced representation of the site group at the $j$th site that $\chi_1$ generates at site 1, and the equivalent atomic orbitals $\chi_j$ therefore transform according to the irreducible representation of the $j$th site group.
6.23 Transformation to Equivalent Orbitals

It has now been established that the equivalent atomic orbitals $\chi_j$ defined by Eqs. (41-43) have the desired transformation properties. The next step is the transformation of the two-center integrals between basic atomic orbitals, $(\chi_1^O | H | \chi_j^O)$ of Eq. (40), to two-center integrals between equivalent atomic orbitals at the same sites. This is easily accomplished with our matrix formulation. We first note that the basic atomic orbitals at the jth site may be obtained by a simple translation of those at the first site,

$$\chi_j^O = T_{lj} \chi_1^O, \quad \chi_1^O = T_{lj}^{-1} \chi_j^O. \quad (46)$$

From Eqs. (42) and (46)

$$\chi_j = R_{lj} \chi_1^O = R_{lj} T_{lj}^{-1} \chi_j^O = \chi_j^O U_{lj}. \quad (47)$$

The operation $R_{lj} T_{lj}^{-1}$ clearly leaves the jth site invariant, and is therefore a rotation or rotary-reflection centered at the jth site. The linear transformation of $\chi_j^O$ corresponding to this operation is easily determined, and is represented by post-multiplication of $\chi_j^O$ by the orthogonal matrix $U_{lj}$ in Eq. (47). A similar relation connects $\chi_i^O$ and $\chi_1^O$. We now obtain for the matrix of two-center integrals between equivalent atomic orbitals at the ith and jth sites,

$$(\chi_i^* | H | \chi_j^O) = U_{1i}^* (\chi_i^O^* | H | \chi_j^O)U_{lj}. \quad (48)$$

The atomic orbitals $u_{ia}$ and $u_{jb}$ introduced in the general formulation of the Bloch method in section 6.1 are taken in the present treatment to be equivalent orbitals. Therefore, the matrix on the left of Eq. (48) is
a square matrix having as the element in the $a^{th}$ row and the $b^{th}$ column the integral

$$\int u_{ia}^* (r-r_i) |H| (r-r_j) \, dr,$$

which occurs in Eq. (33) in the terms for which $n_1 = n_2 = n_3 = 0$. This transformation is illustrated in Table 18. The central matrix preceding the equality sign is $(\chi_1^o | H | \chi_2^o)$, calculated from Eqs. (35), (39), and (40), as previously discussed. This is premultiplied by $U_{11}^*$ and post-multiplied by $U_{12}$ to obtain the matrix $(\chi_1^* | H | \chi_2)$ which follows the equality sign. It will be noted that for $j = 1$ in Eq. (47), $U_{1j}$ reduces to the unit matrix, since $\chi_1^o = \chi_1^o$.

6.24 Symmetry Relations between Matrices of Two-Center Integrals

The present discussion will be concluded by considering the relations that exist between matrices of integrals between equivalent atomic orbitals, such as $(\chi_1^* | H | \chi_j)$, for pairs of sites which can be carried into one another by operations of the point group. Let $R$ be an arbitrary operation of the point group, and assume that it carries the $i^{th}$ site to the $m^{th}$ site, and the $j^{th}$ site to the $n^{th}$ site. Assume, also, that the Hermitian operator $H$ belongs to the totally-symmetric irreducible representation of the point group, so that it is invariant to all operations of the point group, or $RH = H$. Since the operations $R$ are measure-preserving linear transformations (rotations, reflections) of the coordinate space, the numerical values of infinite integrals over the whole of this space are invariant to such operations. From the preceding considerations, and Eq. (42) we obtain
\[
(\chi_i^* | H | \chi_j) = (R \chi_i^* | R^0 H | R \chi_j)
\]
\[
= (R R_{li} \chi_i^* | R R_{lj} \chi_j)
\]
\[
= (R R_{li} R_{im}^{-1} \chi_i^* | H | R R_{lj} R_{ln}^{-1} \chi_j)
\]
\[
= (R_m \chi_m^* | H | R_n \chi_n),
\]
(50)

where \( R_m = R R_{li} R_{lm}^{-1} \) is clearly an operation in the \( m \)th site group and \( R_n = R R_{lj} R_{ln}^{-1} \) an operation in the \( n \)th site group. (If the \( i \)th site belongs to the primed set generated from site \( l' \), replace \( l \) by \( l' \) where it occurs in association with \( i \) or \( m \), and make a similar change if the \( j \)th site belongs to the primed set). We denote the representation matrices corresponding to \( R_m \) and \( R_n \) in their respective site groups by \( M \) and \( M' \), respectively. Then (cf. Eq. (45)),

\[
R_m \chi_m = \chi_m M, \quad R_n \chi_n = \chi_n M',
\]
(51)

so that Eq. (50) becomes

\[
(\chi_i^* | H | \chi_j) = \chi^* (\chi_m^* | H | \chi_n) M'.
\]
(52)

The site group representations generated by the equivalent atomic orbitals are fully reduced, so that \( M \) and \( M' \) are either diagonal matrices or composed of "blocks" on the diagonal. In the present example the site group, \( C_3 \), contains only two operations, the identity and reflection in a plane passing through the site and the threefold axis. The point group \( C_3 \) possesses only two irreducible representations, \( \Lambda' \) and \( \Lambda'' \), both one-dimensional, so that \( M \) and \( M' \) are diagonal. Furthermore, the orbitals \( s, p_xi, \) and \( p_{zi} \) transform according to the totally-symmetric representation \( \Lambda' \), so that the elements in the first, third, and fourth places on the diagonal are always 1. On the other hand \( p_{xi} \) belongs to
the irreducible representations $A''$, which is anti-symmetric to the reflection, so that the element in the second place on the diagonal of $M$ is $1$ if $R_m$ is the identity and $-1$ if $R_m$ is the reflection operation, and similarly for $M'$ and $R_n$. It can be shown, further, that the second diagonal elements of $M$ and $M'$ are either both $1$ or both $-1$, for all operations $R$ in the point group. Hereafter we will indicate the matrix of two-center integrals between equivalent atomic orbitals at the $i$th and $j$th sites by the symbol $(ij)$. It now follows from Eq. (52) that if the operation $R$ carries the $i$th and $j$th sites into the $m$th and $n$th sites respectively, then either $(ij) = (mn)$ or $(ij) = -(mn)$, where the matrix $(mn)$ is obtained by changing the signs of the off-diagonal elements in the second row and column of the matrix $(mn)$. It is easily determined by inspection which of these two relations is applicable in any given case. Thus, after the computation of one matrix of integrals, $(ij)$, a number of others may be obtained by the application of symmetry operations of the point group. Thus, $(12) = (23) = (31) = (\bar{1}\bar{2}) = (\bar{2}\bar{3}) = (\bar{1}\bar{3}) = (13) = (32) = (21) = (\bar{1}\bar{3}) = (\bar{3}\bar{2}) = (\bar{2}\bar{1})$.

Systematic application of the preceding results shows that all the matrices of integrals between atoms in the same icosahedron or unit cell may be obtained from the following matrices: $(12); (1'2'); (\bar{1}\bar{1}); (1\bar{2}); (1'1'); (1\bar{1}'); (1\bar{2}'); (1'1');$ and $(1'2')$. These matrices have been computed and are shown in Table 19, except for $(1'2')$, which has the same reduced form as Eq. (46) although the interatomic distance and therefore the numerical values of the integrals are different in these two cases. The computation of Eq. (46) is illustrated in Table 18. In these tables s and p orbitals have been denoted by $S$ and $P$ for
Table 19. **Reduction of Two-Center Integrals**

**Between Boron Atoms in the Same Icosahedron**

**To Standard Form**

**From 1 to 2:** \( t = 0.5000, m = -0.8661, n = 0, r = 1.733 \)

<table>
<thead>
<tr>
<th>SS(\sigma)</th>
<th>SP(\sigma)</th>
<th>-0.8661 SP(\sigma)</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5000 SP(\sigma)</td>
<td>-0.2501 PP(\sigma)+.7501 PP(\pi)</td>
<td>-0.4330 PP(\sigma)+.4330 PP(\pi)</td>
<td>0</td>
</tr>
<tr>
<td>-0.8661 SP(\sigma)</td>
<td>0.4330 PP(\sigma)-.4330 PP(\pi)</td>
<td>0.7501 PP(\sigma)+.2501 PP(\pi)</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>PP(\pi)</td>
</tr>
</tbody>
</table>

**From 1 to 1:** \( t = 0, m = -0.5959, n = -0.8031, r = 3.358 \)

<table>
<thead>
<tr>
<th>SS(\sigma)</th>
<th>0</th>
<th>-0.5959 SP(\sigma)</th>
<th>-0.8039 SP(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-PP(\pi)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-0.5959 SP(\sigma)</td>
<td>0</td>
<td>0.3550 PP(\sigma)-.6450 PP(\pi)</td>
<td>0.4786 (PP(\sigma)+PP(\pi))</td>
</tr>
<tr>
<td>-0.8039 SP(\sigma)</td>
<td>0</td>
<td>0.4786 (PP(\sigma)+PP(\pi))</td>
<td>0.6450 PP(\sigma)-.3550 PP(\pi)</td>
</tr>
</tbody>
</table>

**From 1 to 2': \( t = -0.3012, m = -1.739, n = -0.9376, r = 2.876 \)**

<table>
<thead>
<tr>
<th>SS(\sigma)</th>
<th>0.3012 SP(\sigma)</th>
<th>-1.739 SP(\sigma)</th>
<th>-0.9376 SP(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.3012 SP(\sigma)</td>
<td>-0.0908 PP(\sigma)+.4093 PP(\pi)</td>
<td>0.0524 PP(\sigma)-.8136 PP(\pi)</td>
<td>0.2824 (PP(\sigma)+PP(\pi))</td>
</tr>
<tr>
<td>-1.739 SP(\sigma)</td>
<td>-0.0524 PP(\sigma)+.8136 PP(\pi)</td>
<td>0.0303 PP(\sigma)+.5303 PP(\pi)</td>
<td>0.1630 (PP(\sigma)+PP(\pi))</td>
</tr>
<tr>
<td>-0.9376 SP(\sigma)</td>
<td>-0.2824 (PP(\sigma)+PP(\pi))</td>
<td>0.1630 (PP(\sigma)+PP(\pi))</td>
<td>0.8791 PP(\sigma)-.1209 PP(\pi)</td>
</tr>
</tbody>
</table>

**From 1 to 1': \( t = 0, m = 0.3732, n = -0.9277, r = 1.785 \)**

<table>
<thead>
<tr>
<th>SS(\sigma)</th>
<th>0</th>
<th>-0.3732 SP(\sigma)</th>
<th>0.9277 SP(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PP(\pi)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.3732 SP(\sigma)</td>
<td>0</td>
<td>-0.1394 PP(\sigma)+.8606 PP(\pi)</td>
<td>0.3462 (PP(\sigma)+PP(\pi))</td>
</tr>
<tr>
<td>-0.9277 SP(\sigma)</td>
<td>0</td>
<td>0.3462 (PP(\sigma)+PP(\pi))</td>
<td>-0.8606 PP(\sigma)+.1394 PP(\pi)</td>
</tr>
</tbody>
</table>
Table 19. (contd.)

FROM 1 to 1': \( t = 0, \ m = -0.9316, \ n = -0.3634, \ r = 2.863 \)

<table>
<thead>
<tr>
<th>SS( \sigma )</th>
<th>( \text{SP}( \sigma ) )</th>
<th>( \text{SP}( \sigma ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.9316</td>
<td>-0.3634</td>
</tr>
<tr>
<td>0</td>
<td>-PP( \pi )</td>
<td>0</td>
</tr>
<tr>
<td>-0.9316</td>
<td>0</td>
<td>0.8679 PP( \sigma ), 1.321 PP( \pi )</td>
</tr>
<tr>
<td>-0.3634</td>
<td>0</td>
<td>0.3385 (PP( \sigma )+ PP( \pi ))</td>
</tr>
</tbody>
</table>

FROM 1 to 2': \( t = 0.5044, \ m = -0.6408, \ n = -0.5787, \ r = 2.862 \)

<table>
<thead>
<tr>
<th>SS( \sigma )</th>
<th>( \text{SP}( \sigma ) )</th>
<th>( \text{SP}( \sigma ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.3027</td>
<td>-0.5044</td>
<td>-0.5787</td>
</tr>
<tr>
<td>0.1527 PP( \sigma )-6.527 PP( \pi )</td>
<td>-0.3819 PP( \sigma )+0.4841 PP( \pi )</td>
<td>-0.2919 (PP( \sigma )+ PP( \pi ))</td>
</tr>
<tr>
<td>-0.6408</td>
<td>0.1940 PP( \sigma )-6.720 PP( \pi )</td>
<td>0.4852 PP( \sigma )-0.0148 PP( \pi )</td>
</tr>
<tr>
<td>-0.5787</td>
<td>-0.1751 (PP( \sigma )+ PP( \pi ))</td>
<td>0.4415 (PP( \sigma )+ PP( \pi ))</td>
</tr>
</tbody>
</table>

FROM 1 to \( \bar{2}' \): \( t = -0.8077, \ m = -0.0935, \ n = -0.5821, \ r = 1.787 \)

<table>
<thead>
<tr>
<th>SS( \sigma )</th>
<th>( \text{SP}( \sigma ) )</th>
<th>( \text{SP}( \sigma ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4849</td>
<td>-0.8077</td>
<td>-0.5821</td>
</tr>
<tr>
<td>-0.3916 PP( \sigma )+1.084 PP( \pi )</td>
<td>0.5272 PP( \sigma )-3.388 PP( \pi )</td>
<td>0.4690 (PP( \sigma )+ PP( \pi ))</td>
</tr>
<tr>
<td>-0.0935</td>
<td>-0.0433 PP( \sigma )-0.8207 PP( \pi )</td>
<td>0.0698 PP( \sigma )+0.5611 PP( \pi )</td>
</tr>
<tr>
<td>-0.5821</td>
<td>-0.2815 PP( \sigma )</td>
<td>0.3790 (PP( \pi )+ PP( \sigma ))</td>
</tr>
</tbody>
</table>

FROM 1' to \( \bar{1}' \): \( t = 0, \ m = -0.9834, \ n = -0.1817, \ r = 3.390 \)

<table>
<thead>
<tr>
<th>SS( \sigma )</th>
<th>( \text{SP}( \sigma ) )</th>
<th>( \text{SP}( \sigma ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.9834</td>
<td>-0.1817</td>
</tr>
<tr>
<td>0</td>
<td>-PP( \pi )</td>
<td>0</td>
</tr>
<tr>
<td>-0.9834</td>
<td>0</td>
<td>0.9670 PP( \sigma )-0.0329 PP( \pi )</td>
</tr>
<tr>
<td>-0.1817</td>
<td>0</td>
<td>-0.1787 (PP( \sigma )+ PP( \pi ))</td>
</tr>
</tbody>
</table>

FROM 1' to \( \bar{2}' \): \( t = -0.8124, \ m = -0.4690, \ n = -0.3466, \ r = 1.777 \)

<table>
<thead>
<tr>
<th>SS( \sigma )</th>
<th>( \text{SP}( \sigma ) )</th>
<th>( \text{SP}( \sigma ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8124</td>
<td>0.8124</td>
<td>0.3466</td>
</tr>
<tr>
<td>-0.6600 PP( \sigma )+2.1600 PP( \pi )</td>
<td>0.3810 PP( \sigma )+4.8500 PP( \pi )</td>
<td>0.2816 (PP( \sigma )+ PP( \pi ))</td>
</tr>
<tr>
<td>-0.4690</td>
<td>-0.3810 PP( \sigma )+4.8500 PP( \pi )</td>
<td>0.2200 PP( \sigma )+7.2000 PP( \pi )</td>
</tr>
<tr>
<td>-0.3466</td>
<td>-0.2816 PP( \sigma )</td>
<td>-0.1626 (PP( \sigma )+ PP( \pi ))</td>
</tr>
</tbody>
</table>

FROM 1 to 1': \( t = 0, \ m = -0.9316, \ n = -0.3634, \ r = 2.863 \)
typographical reasons. It will be noted that a number of the matrices in Table 19 are either symmetric or partly symmetric and partly skew-symmetric. These symmetry properties have also been investigated by the preceding methods and are useful as a check on the calculations. For example, if there exists a symmetry operation which interchanges the $i$th and $j$th sites, then either $(ij) = (ji)$ or $(ij) = (ji)$. But $(ji) = (ij)^*$, since the operator $H$ is Hermitian, and therefore either $(ij) = (ij)^*$ or $(ij) = (ij)^*$. Examples of the second type are provided by $(12)$, $(12')$, $(1'2')$, and of the first type by $(11)$ and $(1'1')$. However, for the latter two matrices, and also for $(11')$ and $(1'1')$, all off-diagonal elements in the second row and column vanish identically, since application of Eq. (52) with $R$ the reflection of the site group yields $(ij) = (ij)$. Internal symmetry of matrices may lead to further equivalences. Thus, $(11') = (11') = (1'1) = (1'1)$, where the first and third equalities follow from the symmetry of the matrices, and the second equality from Eq. (50) with $R$ the inversion operation.

6.25 The Complete Matrix of Intraicosahedral Integrals in the Secular Equation

We are now in a position to give the reduced form of the complete $48 \times 48$ matrix of two-center integrals between the equivalent atomic orbitals in the same unit cell ($4$ orbitals on each of $12$ boron atoms). This is shown in partitioned form in Table 20, where each element represents one of the $4 \times 4$ matrices, $(mn)$, given in Table 19, or $(mn)^*$, or $(mn)$. If $(mn)^* = (mn)$ the notation $(mn)^*$ has been used. The matrices on the diagonal, $(ii) = (11)$, are all equal to the same $4 \times 4$ diagonal matrix, provided the operator $H$ is diagonal in the representation.
<table>
<thead>
<tr>
<th></th>
<th>1</th>
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<th>3</th>
<th>1'</th>
<th>2'</th>
<th>3'</th>
<th>1''</th>
<th>2''</th>
<th>3''</th>
</tr>
</thead>
<tbody>
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<td>(12)</td>
<td>(12')</td>
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<td>(12')</td>
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<tr>
<td>2</td>
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<td>(12')</td>
<td>(11')</td>
<td>(12')</td>
<td>(11')</td>
<td>(12')</td>
<td>(11')</td>
</tr>
</tbody>
</table>

TABLE 20. Complete Matrix of Reduced Two-Center Integrals between the 48 Equivalent Atomic Orbitals within the Same Unit Cell.
furnished by the orbitals of a single atom. In any case, the elements of the matrix (ll) are one-center integrals involving two atomic orbitals on the same atom. It is not necessary to indicate explicitly the matrices below the diagonal as the entire 48 x 48 matrix is symmetric, so that the transposes of the matrices above the diagonal occur in the symmetrically related positions below the diagonal. It will be observed that by the utilization of symmetry 1056 individual integrals above the diagonal have been obtained from the 144 integrals given in reduced form in Table 19. It should be noted that Table 20 gives either the matrix of H or the overlap matrix, depending on whether the operator H or the identity operator is inserted into the integrals of Eqs. (36a-d).

6.3 Reduction of Intericosahedral Two-Center Integrals to Standard Form

6.3.1 Extension of Matrix Formulation to Intericosahedral Integrals

The next step in the calculation involves the introduction of integrals between atoms in different unit cells. The coefficients of these integrals in the secular equation depend on the wave vector, and they are essential to the calculation of the band structure at points other than the center of the Brillouin zone. In considering the transformation properties of the intracosahedral two-center integrals in the preceding section it was found useful to deal with all the integrals between orbitals on a given pair of atoms at once by a matrix formalism. This method will now be extended to Eq. (33) in which integrals between orbitals in different unit cells occur. Let the equivalent
atomic orbitals in the reference cell as defined in section 6.22 be represented by the row matrices

\[ \chi_{i,000} = (s_i, p_{xi}, p_{yi}, p_{zi}) \]  

there being one such row matrix for each atom in the reference cell (the method may, of course, be extended to include other than s and p orbitals). These equivalent atomic orbitals are transformed into one another under the operations of the point group of the lattice, and as a result the orientation of the \( p_x, p_y, \) and \( p_z \) orbitals is not necessarily the same at each atom. In a similar way the equivalent atomic orbitals in the \( n_1 n_2 n_3 \) th cell will be represented by row matrices \( \chi_{i,n_1 n_2 n_3} \) and defined as those obtained by applying the lattice translation \( r_{n_1 n_2 n_3} \) to the equivalent atomic orbitals in the reference cell. We may now represent all the integrals between orbitals on the \( i \)th atom in the reference cell and the \( j \)th atom in the \( n_1 n_2 n_3 \) th cell by the condensed notation

\[ (\chi_{i,000}^* | H | \chi_{j,n_1 n_2 n_3}) \]  

(54)

The asterisk indicates the complex conjugate of the transposed matrix, so that \( \chi_{i,000}^* \) is a column matrix of equivalent orbitals. As previously stated, the equivalent atomic orbitals represent in the present calculation the atomic orbitals \( u_{ia} \) and \( u_{jb} \) introduced in section 6.1. The expression (54) is therefore a square matrix, having as the element in the \( a \)th row and \( b \)th column the integrals occurring in Eq. (33).

\[ \int u_{ia}^* (r-r_i) H u_{jb} (r-r_{n_1 n_2 n_3}) \, dr, \]

(55)

for \( n_1 = n_2 = n_3 = 0 \) the matrix (54) reduces to the matrices \( (\chi_{i}^* H \chi_{j}) \) tabulated in section 6.2. In the present case the matrix (54) is of
dimension $4 \times 4$, as $u_{ia}$ and $u_{jb}$ each may be any one of the equivalent atomic orbitals, $s$, $p_x$, $p_y$, or $p_z$.

We now write the secular equation Eq. (31), in partitioned form,

$$\begin{vmatrix} H_{ij}(k) - S_{ij}E(k) \end{vmatrix} = 0,$$

where

$$H_{ij}(k) = \sum_{n_1} \sum_{n_2} \sum_{n_3} \left( \chi_{i,000}^* \mid H \mid \chi_{j,n_1n_2n_3} \right) \exp(2\pi ik \cdot r_{n_1n_2n_3})$$

is a $4 \times 4$ matrix with $H_{ia,jb}(k)$ of Eq. (33) as the element in the $a$th row and $b$th column, and $S_{ij}$ is obtained by replacing $H$ on the right-hand side of Eq. (57) by the identity operator. In a complex crystal it is more convenient to calculate the matrices (54) for the interaction of each atomic pair and then add these matrices with the appropriate exponential coefficients to obtain $H_{ij}(k)$, as in Eq. (57), than it is to compute each element $H_{ia,jb}(k)$ individually from Eq. (33).

6.32 Reduction of Two-Center Integrals to Standard Form

In section 6.2 it was shown how the two-center integrals in the matrix $(\chi_{i,000}^* \mid H \mid \chi_{j,000})$, denoted there by $(\chi_{i,0}^* \mid H \mid \chi_{j})$, could be reduced to linear combinations of integrals of standard types, denoted by $(ss\sigma)$, $(sp\sigma)$, $(pp\sigma)$, and $(pp\pi)$. The method is a modification of that of Slater and Koster in which the required transformations are facilitated by the matrix formalism. It was also shown that in a symmetrical crystal certain of the required matrices could be obtained from others by symmetry considerations. Thus, it was shown that associated with the 66 distinct pairs of atoms in the reference cell of rhombohedral boron there are only 9 distinct matrices $(\chi_{i,000}^* \mid H \mid \chi_{j,000})$. 
as listed in Table 19. The remaining matrices may be obtained from these by Hermitian conjugation or changing the signs of certain elements. These matrices occur in the partitioned matrix of Eq. (56) with coefficients unity, since \( r_{000} = 0 \) and \( \exp(2\pi i k \cdot r_{000}) = 1 \). The contribution of these matrices to the complete partitioned matrix is shown in Table 20 in an abbreviated notation in which \((ij)\) denotes \(\chi_{i,000}^* H_1 \chi_{j,000}\), \((ij)^*\) is the Hermitian conjugate of \((ij)\), and \((ij)\) is obtained by changing the signs of the off-diagonal elements in the second row and column of \((ij)\). The 4 x 4 unit matrix is denoted by \((11)\). The part of the partitioned matrix below the diagonal is obtained from the condition that the matrix be Hermitian, or \((ji) = (ij)^*\), for real matrices \((ji)\) is simply the transpose of \((ij)\).

In the present section we consider the most important of the matrices \(\chi_{i,000}^* H_1 \chi_{j,n_1 n_2 n_3}\) corresponding to interactions between atoms in the reference cell and atoms in adjacent cells. From a consideration of the distances between boron atoms in adjacent icosahedra it seems reasonably adequate to introduce only the interactions corresponding to the two- and three-center bonds represented by the heavy lines in Figures 3 and 2, respectively. The two-center bonds connect an icosahedron to the icosahedra in the layers above and below it, and the three-center bonds connect it to other icosahedra in the same layer of the lattice, which is an approximately cubic close-packed arrangement of boron icosahedra. The reduction of these matrices to matrices of standard integrals and the proof of the equivalence of certain matrices by symmetry considerations, proceeds in the same manner as indicated in the preceding report for the matrices \(\chi_{i,000}^* H_1 \chi_{j,000}\). It is found
that there is only one distinct matrix for the two-center interactions indicated in Figure 3, and the prototype of these matrices, \( \chi_{1,000}^* |H| \chi_{1,100}^* \) is given as the first matrix in Table 21. Similarly, for the three-center interactions in Figure 2 there is one distinct matrix, illustrated by the second matrix, \( \chi_{1',000}^* |H| \chi_{2',110}^* \), in Table 21. The transpose of the second matrix is also required; for example, \( \chi_{1',000}^* |H| \chi_{3',101}^* \) is the transpose of \( \chi_{1',000}^* |H| \chi_{2',110}^* \).

6.33 Complete Matrices of the Secular Equation

In Table 22 these matrices, with their exponential coefficients from Eq. (57), are arranged in the pattern in which they occur in the partitioned matrix of the secular equation. In this table \((ij)\) represents \( \chi_{1,000}^* |H| \chi_{j,n_1n_2n_3}^* \), and \((ij)^*\) the transpose of \((ij)\). The values of \(n_1, n_2,\) and \(n_3\) are indicated by the subscripts on the vector \(r\) in the coefficient \(\exp(2\pi ik \cdot r)\). In the present approximation the 4 x 4 null matrix is to be placed at all unfilled positions; this is indicated explicitly on the diagonal by \((0)\). The complete matrix of \(H\) the secular equation Eq. (56), is the sum of the partitioned matrices in Table 20 and Table 22. The complete overlap matrix is obtained similarly, but with the operator \(H\) replaced by the identity operator in the integrals of Eqs. (36a-d). The complete secular equation is then obtained by substituting these two matrices into the secular equation, Eq. (56).
TABLE 21. REDUCTION OF TYPICAL TWO-CENTER INTEGRALS BETWEEN ATOMS IN NEIGHBORING ICOSAHEDRA TO STANDARD FORM.

FROM $^{100}_{000}$ to $^{-100}_{000}$: $l = 0$, $m = .4872$, $n = .8733$, $r = 1.709$

\[
\begin{bmatrix}
SS\sigma & 0 & .4872 \ SP\sigma & .8733 \ SP\sigma \\
0 & -PP_{\pi} & 0 & 0 \\
.4872 \ SP\sigma & 0 & .2374 \ PP\sigma + .7626 \ PP_{\pi} & .4255 \ (PP\sigma + PP_{\pi}) \\
.8733 \ SP\sigma & 0 & .4255 \ (PP\sigma + PP_{\pi}) & .7626 \ PP\sigma + .2374 \ PP_{\pi}
\end{bmatrix}
\]

FROM $^{1'000}_{000}$ to $^{2'010}_{010}$: $l = -.5000$, $m = .8661$, $n = 0$, $r = 2.020$

\[
\begin{bmatrix}
SS\sigma & .5000 \ SP\sigma & .8661 \ SP\sigma & 0 \\
-.5000 \ SP\sigma & -.2501 \ PP\sigma + .7501 \ PP_{\pi} & -.4330 \ PP\sigma + .4330 \ PP_{\pi} & 0 \\
.8661 \ SP\sigma & .4330 \ PP\sigma + .4330 \ PP_{\pi} & .7501 \ PP\sigma + .2501 \ PP_{\pi} & 0 \\
0 & 0 & 0 & PP_{\pi}
\end{bmatrix}
\]
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The factors \( k \cdot r_{n_1 n_2 n_3} \) may be put in a more convenient form for calculation. Let the wave vector be expressed in terms of the reciprocal lattice vectors as

\[
k = k_1 b_1 + k_2 b_2 + k_3 b_3.
\]  

(58)

Then, from Eq. (56) and the relations \( a_i \cdot b_j = \delta_{ij} \),

\[
k \cdot r_{n_1 n_2 n_3} = n_1 k_1 + n_2 k_2 + n_3 k_3.
\]  

(59)

The cases occurring in Table 22 are as follows (note that \( r_{n_1 n_2 n_3} = - r_{n_1 n_2 n_3} \)): \( k \cdot r_{100} = k_1; k \cdot r_{010} = k_2; k \cdot r_{001} = k_3; k \cdot r_{110} = k_1 - k_2; k \cdot r_{101} = k_3 - k_1; \) and \( k \cdot r_{011} = k_2 - k_3 \). In the present approximation the matrix elements and therefore also the roots of the secular equation depend on the wave vector \( k \) only through the exponential factors in Table 22. Although these factors are complex, the matrix is Hermitian and thus has real roots.
Chapter 7. Atomic Wave Functions for Boron

7.1 Introduction

In preceding chapters the calculation of the energy bands of boron, particularly the formulation of the secular equation, has been carried as far as possible on the basis of the geometry and symmetry of the crystal. To proceed further the one- and two-center integrals entering into the equations must be evaluated, and if this is to be accomplished on a fundamental rather than an empirical basis it is necessary to consider in some detail the wave functions and potentials for the boron atom. Herman\textsuperscript{21} has pointed out that a calculation of the present type can be considered quantitatively reliable only if the necessary integrals are evaluated from first principles, and there have been only a few investigations in this category. Two practicable possibilities for the choice of atomic orbitals are Slater-type orbitals and self-consistent field wave functions. The former have the advantage that the required two-center integrals are available,\textsuperscript{31-33} but Hartree or Hartree-Fock wave functions have a better physical basis. Even if Slater orbitals are utilized for practical reasons, it seems desirable to compare them with available self-consistent field functions so as to obtain optimum values of the screening constants entering into the Slater orbitals. For this reason a thorough study and comparison has been made of the self-consistent field and Slater orbitals for the boron
atom, including two methods of orthogonalizing the Slater 1s and 2s
orbitals.

7.2 Hartree Self-Consistent Field
Wave Functions

7.21 Radial Functions and Normalization

The Hartree method is based on a spherically symmetrical (central)
average potential, so that the radial and angular coordinates are
separable in the wave equation. Thus, a given atomic orbital may be put
in the form

\[ \psi_i(r, \theta, \phi) = R_i(r) Y_i(\theta, \phi), \]  \hspace{1cm} (60)

where \( Y_i(\theta, \phi) \) is the normalized spherical harmonic associated with the
ith atomic orbital and \( R_i(r) \) is the corresponding radial function. The
following two normalization conditions apply by definition,

\[ \int \int \int \psi_i^2(r, \theta, \phi) r^2 \sin \theta \, d\phi \, d\theta \, dr = 1, \]  \hspace{1cm} (61)

\[ \int \int \psi_i^2(r, \theta, \phi) \sin \theta \, d\phi \, d\theta = 1, \]  \hspace{1cm} (62)

and therefore the normalization of the radial function is

\[ \int_0^{\infty} R_i^2(r) \, r^2 \, dr = 1. \]  \hspace{1cm} (63)

The Hartree equations assume their most convenient form in terms
of the modified radial functions,

\[ f_i(r) = r \, R_i(r). \]  \hspace{1cm} (64)

If atomic units are used, as will be the case throughout this report,
then the Hartree equations have the form

\[ \frac{d^2 f_i}{dr^2} + \left[ E_i - 2 \, V_i(r) - \ell_i (\ell_i + 1)/r^2 \right] f_i(r) = 0. \]  \hspace{1cm} (65)
$V_1(r)$ is the Hartree potential, $E_1$ the energy eigenvalue, and $\ell_1$ the azimuthal quantum number corresponding to $Y_1(\theta, \phi)$, all for the given atomic orbital. The complete specification of $Y_1(\theta, \phi)$ requires in addition the value of the projection or magnetic quantum number, $m_{\ell_1}$.

From Eqs. (63) and (64), the normalization condition for $f_1(r)$ is

$$\int_0^\infty f_1^2(r) \, dr = 1.$$  (66)

From Eqs. (60), (62), and (64), the probability that an electron in the $i$th atomic orbital lies between $r$ and $r + dr$ is

$$dr \int \int \mathcal{Y}_1^2(r, \theta, \phi) r^2 \sin \theta \, d\phi \, d\theta = R_1^2(r) r^2 \, dr = f_1^2(r) \, dr,$$  (67)

which is consistent with Eq. (66). This probability is required for the computations of the Hartree potentials which follow.

### 7.22 Hartree Functions for Boron

Hartree self-consistent field wave functions for the ground-state configuration, $1s^2$, $2s^2$, $2p$, of the boron atom have been calculated by F. W. Brown, J. H. Bartlett, Jr., and C. G. Dunn.\(^\text{35}\) The Hartree equations (65) have been solved for the three lowest energy radial functions, $f_1$, $f_2$, $f_3$ for the configuration referred to above (as will be seen, the electron configuration affects the Hartree potentials). These functions are tabulated in Table 1 of the paper by Brown et al. From their angular dependence it is also appropriate to refer to these atomic orbitals as $1s$, $2s$, and $2p$ atomic orbitals, respectively (s may be regarded as
symbolizing the spherically symmetric harmonic $Y_{00}$, and $p$ one of the three harmonics $Y_{10}$ or $Y_{1,\pm 1}$, where the first index is the azimuthal quantum number $\ell$, and the second the magnetic quantum number $m_{\ell}$). As the latter notation conveys more physical meaning it will frequently be used here, 1s, 2s, or 2p being attached as subscripts to the quantities associated with these orbitals.

7.23 Contributions of Individual Electrons to the Self-Consistent Field Potentials

The purpose of the present calculation is the reconstruction of the Hartree potentials from the radial functions, and in particular the contributions of individual electrons to these potentials. The Hartree potentials were of course required by Brown et al. for their calculation, but these authors did not tabulate the potentials. The potential of the neutral atom has been calculated by A. J. Freeman, but not the individual Hartree potentials.

The potential of unit negative charge (that is, the electron charge in atomic units) at radial distance $r$, arising from its interaction with a continuous spherically symmetric distribution of unit negative charge, with $f_1^2(r')$ dr' the fraction of charge between $r'$ and $r' + dr'$, is given by

$$v_i(r) = \frac{(1/r) \int_0^r f_1^2(r') \, dr' + \int_r^\infty \left[f_1^2(r')/r\right] \, dr'}. \quad (68)$$

The first expression on the right-hand side of the above equation is the potential arising from the charge lying within the radius $r$, and is the same as though all this charge resided on the nucleus, from a familiar result of potential theory. The potential due to all charge more distant
than $r$ is constant within the spherical cavity, from another well-known theorem, and may therefore be replaced by the potential at $r = 0$, which accounts for the second integral in the preceding equation.

The probability density functions, $f_{1s}^2$, $f_{2s}^2$, and $f_{2p}^2$, which occur in the integrands in Eq. (68) are compared with the corresponding density functions for the boron atoms obtained by other methods in section 7.51. The integrals required in Eq. (68) were evaluated by means of Simpson's rule, using the accurate tabulated values of the radial functions. The intervals were chosen so as to reduce the inherent error in Simpson's rule to $0.1\%$ or less. At $r = 15$ the first integral on the right-hand side of Eq. (68) was found to satisfy the normalization condition, Eq. (66), with errors of $-0.03$, $-0.15$, and $0.11\%$, for the $1s$, $2s$, and $2p$ functions, respectively. Thus, the numerical integrations are as accurate as is justified by the wave functions of Brown et al.

The potentials $v_{1s}$, $v_{2s}$, and $v_{2p}$ calculated from Eq. (68) are tabulated as functions of $r$ in Table 23, and plotted in Figure 5 (all potentials are expressed in the atomic unit of energy, $e^2/a_0 = 27.21$ electron-volts, and distances in the atomic unit $a_0 = 0.5292$ Angstrom, which is the radius of the innermost Bohr orbit of the hydrogen atom). These are the potentials of an electron at $r$ arising from the mean charge distribution of a single $1s$, $2s$, or $2p$ electron, respectively.

7.24 Equivalent Nuclear Charge or Screening Parameter

It is informative to calculate the equivalent negative charge on the nucleus required to produce the potentials $v_{1s}$, $v_{2s}$, and $v_{2p}$ at $r$. 
TABLE 23. Contribution of a Single Electron in the 1s, 2s, or 2p Subshell of the Boron Atom to the Atomic Potential (Atomic Units)

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FIGURE 5 CONTRIBUTION OF A SINGLE ELECTRON IN THE 1s, 2s, OR 2p SUBSHELL OF THE BORON ATOM TO THE ATOMIC POTENTIAL.
These charges are denoted by $z_{1s}$, $z_{2s}$, and $z_{2p}$, respectively, and are calculated from the simple relation

$$z_1(r) = -r v_1(r).$$

They may be regarded as a generalization of the usual concept of a screening "constant," as they are defined for individual atomic orbitals, and are functions of $r$. They will therefore be designated as "screening parameters." The physical significance of the two terms on the right-hand side of Eq. (68), as discussed following that equation, indicates that the term "screening" is somewhat of a misnomer in this connection as only the first term represents "screening" of the nucleus by charge within a sphere of radius $r$. The second term on the right-hand side of Eq. (68) actually exceeds the first for $r$ less than 0.242, 1.737, and 2.044, for the $1s$, $2s$, and $2p$ atomic orbitals, respectively. Of course, both terms represent electron-electron repulsion, and counteract to some degree the electron-nuclear attraction. For large values of $r$ the screening concept is entirely appropriate, as virtually all of the charge in the atomic orbital is then included within the sphere of radius $r$.

The first integral in Eq. (68) then tends to unity, and the second to zero; also, from Eq. (69), $z_1(r) \rightarrow -1$ for $r \rightarrow \infty$. Screening parameters, $z_{1s}$, $z_{2s}$, and $z_{2p}$ are compared with the corresponding parameters for the boron atom obtained by other methods in section 7.52.

7.25 Neutral Atom Potential and Effective Nuclear Charge

We consider next the potential of an electron (unit negative charge) at $r$ arising from the mean charge distribution for the neutral atom. In this calculation the electron is to be regarded as an added
test charge, and not as one of the atomic electrons. The mean charge
distribution of the atom is affected by the electron configuration, or
assignment to the atomic orbitals, and we specify the normal 1s²2s²2p
configuration of boron. The part of the potential due to the atomic
nucleus is
\[ V_n = - \frac{Z}{r} \]
(70)
where \( Z \) is the atomic number (\( Z = 5 \) for boron). On adding the contribu­
tions of the electron charge we obtain the potential of the neutral atom,
\[ V_{at} = V_n + 2v_{1s} + 2v_{2s} + v_{2p} \]
(71)

We may also calculate the effective nuclear charge, \( Z_{at} \), which
would produce the potential at \( r \) (in the absence of the atomic electrons)
which is calculated for the neutral atom. On using Eqs. (69), (70), and
(71), we obtain
\[ Z_{at} = -r V_{at} = Z + 2z_{1s} + 2z_{2s} + z_{2p} \]
(72)
This may conveniently be written as
\[ Z_{at} = Z - s \]
(73)
where \( s \) is the total screening parameter for the neutral atom,
\[ s = -(2z_{1s} + 2z_{2s} + z_{2p}) \]
(74)
s is a generalization of the familiar atomic screening constant, as \( s \)
varies with \( r \) (the negative sign has been introduced in Eq. (74) to make
this correspondence closer).

7.26 Hartree Self-Consistent Field Potentials
and Effective Nuclear Charges

We are now in a position to consider the Hartree potentials, \( V_i \),
which enter into the Hartree self-consistent field wave equations,
Eq. (65) The Hartree potential for an electron in a given atomic orbital is obtained by subtracting from the potential of the neutral atom, or \( V_{\text{at}} \) of Eq. (71) the self-potential of the given electron as given by \( \nu_1 \) of Eq. (68). From a physical point of view this may be regarded as a removal of the self-charge of the given electron as represented by the radial distribution \( f^2_1(r) \), leaving the so-called Fermi hole (strictly, the term "Fermi hole" is more appropriate to the Hartree-Fock theory in which exchange terms are included, in which case the "hole" is introduced in a less ad hoc manner). Thus, in the self-consistent field method (with or without exchange) the interaction of an electron with the charge distribution assigned to itself is excluded. For the \( 1s^22s^22p \) configuration of boron we obtain in this way the three potentials,

\[
V_{1s} = V_{\text{at}} - \nu_{1s} = V_n + \nu_{1s} + 2\nu_{2s} + \nu_{2p}, \tag{75a}
\]

\[
V_{2s} = V_{\text{at}} - \nu_{2s} = V_n + 2\nu_{1s} + \nu_{2s} + \nu_{2p}, \tag{75b}
\]

\[
V_{2p} = V_{\text{at}} - \nu_{2p} = V_n + 2\nu_{1s} + 2\nu_{2s}, \tag{75c}
\]

Values of these potentials as well as \( V_{\text{at}} \) and \( V_n \) are tabulated in Table 24.

It will be noted that the Hartree potentials necessarily lie above \( V_n \) and below \( V_{\text{at}} \). The "self-consistent" aspect of the Hartree method is a consequence of the fact that the Hartree potentials depend on the wave functions through Eq. (68), while the latter in turn are eigenfunctions of an operator depending upon the potentials, as in Eq. (65).

Effective nuclear charges for electrons in individual atomic orbitals may be calculated from the Hartree potentials, just as \( Z_a \) was calculated from \( V_{\text{at}} \). From Eqs. (69), (70), (71), (72), and (75),
### TABLE 24. Nuclear Potential $V_n$, Atomic Potential $V_{at}$ and Effective Potentials $V_{1s}$, $V_{2s}$, and $V_{2p}$ for an Electron in Individual Subshells of Boron Atom

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\[ Z_{ls} = -r V_{ls} = Z_{at} - z_{ls}, \quad (76a) \]
\[ Z_{2s} = -r V_{2s} = Z_{at} - z_{2s}, \quad (76b) \]
\[ Z_{2p} = -r V_{2p} = Z_{at} - z_{2p}, \quad (76c) \]

Values of \( Z \) at \( Z_{ls} \), \( Z_{2s} \), and \( Z_{2p} \) are given in Table 25 and plotted in Figure 6. They necessarily lie between \( Z_{at} \) and \( Z \). All these effective nuclear charges approach \( Z \) for \( r \to 0 \). For \( r \to \infty \), \( Z_{at} \to 0 \) while \( Z_{ls} \), \( Z_{2s} \), and \( Z_{2p} \) all approach unity (corresponding to the fact that removal of one electron leaves a singly-charged positive ion).

7.27 Hartree Functions with Configuration Interaction for Boron

Configuration interaction can be introduced into the Hartree method without exchange in essentially the same manner as discussed in section 7.3 for the Hartree-Fock method with exchange. The Hartree calculation of Brown et al. for the lowest, or \( 1s^2 2s^2 2p \), configuration of the boron atom has been corrected for the most important configurational interaction, that with the configuration \( 1s^2 2p^3 \), by Tsiunaitis and Iutsis. The procedure followed was that of Iutsis and Kavertskaia. The radial wave functions of Brown et al. were used as initial approximations. The final radial wave functions obtained do not differ very much from those of Brown et al. in which configuration interaction is neglected. They will not be considered further here, because as will be discussed in section 7.3 the interaction of these two configurations was subsequently treated in a more accurate mixed Hartree-Fock and Hartree method with partial exchange by Glembotskii, Kibartas, and Iutsis. The theoretical energy calculated by Tsiunaitis and Iutsis for the
TABLE 25. Effective Nuclear Charge for Atomic Potential, $Z_{at}$, and for an Electron in Individual Subshells of the Boron Atom, $Z_{1s}$, $Z_{2s}$ and $Z_{2p}$

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Effective nuclear charge

Figure 6: Effective nuclear charge for atomic potential \( Z_{at} \) and for an electron in individual subshells of the boron atom \( Z_{2s}, Z_{2p} \) and \( Z_{1s} \).
The 1s\(^2\)2s\(^2\)2p configuration was lowered by 0.025 as a result of the configuration interaction, yielding a final value of -24.551 atomic units. The experimental or spectroscopic value is -24.665. These authors treated in a similar way the next lowest configuration, 1s\(^2\)2s\(^2\)3s, but the results are of no particular interest here. This configuration has an energy only a little higher than that of the configuration 1s\(^2\)2s\(^2\)2p, but cannot interact with it because of its different parity.

7.3 Hartree-Fock Self-Consistent Field Wave Functions Including Configurational Interaction

7.31 Introduction

As is well known the self-consistent field equations of Hartree are obtained when the energy of a many electron system is minimized in accordance with the variation theorem using the correct Hamiltonian for the system but an approximate wave function of the simple product type (cf. Slater, Chapter 9). This wave function does not satisfy the antisymmetry principle, and a major improvement was proposed by Fock (and independently by Slater) in which the minimization procedure is carried out using an antisymmetrized Slater-type determinantal wave function (antisymmetrized linear combination of the product-type functions obtained by permuting the electrons). This leads to a system of integro-differential equations for the individual electron orbitals differing from the corresponding Hartree equations through the addition of exchange terms in the potential, and called the Fock or Hartree-Fock equations. An extensive review of the Hartree-Fock method and its applications has been given by Hartree. A brief review including recent developments is given by Slater (Chapter 17).
An important feature of the Hartree-Fock equations as applied to an atom with a closed-shell electron configuration is that the exchange terms yield a spherically symmetrical potential in the equation for each orbital. Thus the problem of finding the orbitals reduces to a central-field problem (although still with the requirement of self-consistency), without the necessity for the spherical averaging introduced artificially into the Hartree equations. However, for non-closed shell configurations spherical averaging is required even in the Hartree-Fock method to obtain a central-field problem. Methods of accomplishing this have been developed by Brown and Hartree and Hartree. Another complication for non-closed shells is that it is not always possible to diagonalize the matrix of Lagrangian multipliers entering into the Hartree-Fock equations by an unitary transformation of the one-electron orbitals, as it is for closed shells. Still another complicating feature of the general case of a non-closed shell configuration is the necessity for considering several multiplets having different L and S in the Russell-Saunders coupling scheme. Each of these multiplets requires a separate solution of the Hartree-Fock equations, with (in general) different potentials, energies, and one-electron orbitals. However, if there is only a single electron outside closed shells or subshells only a single multiplet exists; this is the case for the lowest configuration of the boron atom, 1s$^2$2s$^2$2p, which is of interest here.

Configurational interaction (or mixing, or superposition) was introduced into the Hartree-Fock method by Hartree, Hartree, and Swirles. Their procedure is simply an adaptation to the Hartree-Fock method of the familiar linear variation method in which the
coefficients in a linear combination of basis functions are varied to minimize the energy. However, in the case of configurational interaction the "basis functions" which are combined linearly are each an antisymmetrized determinantal wave function for a single multiplet of a single configuration. It should be noted that each of these determinants is in turn a linear combination of simple product-type or Hartree-like functions, but with coefficients determined by the requirement of antisymmetry and not subject to variation as are the coefficients for each configurational determinant taken in its entirety. The only configurations which can interact are those having the same parity, or same value for the sum of the azimuthal quantum numbers over all electrons. Further, for these configurations only those multiplets can interact having the same values for the total orbital and spin angular momentum quantum numbers, $L$ and $S$. Hartree, Hartree, and Swirles developed two procedures for the superposition of configurations (as they prefer to call it). The simpler procedure is to first solve the Hartree-Fock equations separately for each configuration to obtain the one-electron radial wave functions for each configuration. These one-electron functions, and the determinantal wave functions constructed from them for each configuration, are then regarded as fixed in the application of the variation theorem to the linear superposition of the configurational wave functions; only coefficients of the interacting determinantal wave functions are varied. The second procedure is more accurate but also more difficult. The energy is minimized simultaneously with respect to arbitrary variations of the radial one-electron wave functions for each configuration (subject to normalization and mutual orthogonality of
these functions within a configuration) and variation of the coefficients in the linear combination of configurational wave functions (subject to normalization of the overall wave function). This procedure leads to generalized Hartree-Fock equations for each configuration involving the coefficients of configurational mixing, plus additional equations to be satisfied by the latter coefficients containing configurational energy and interaction integrals. The procedure is to first estimate the mixing coefficients, then solve the generalized Hartree-Fock equations for each configuration, evaluate the configurational integrals, and solve for the mixing coefficients. This process is continued until a sufficiently self-consistent set of coefficients is obtained. The second method becomes extremely difficult for more than two configurations, but is practical for the latter case. When applying the second method to the interaction of the lowest configuration, such as the \(1s^2 2s^2 2p\) configuration of boron, with a higher energy configuration, such as the \(1s^2 2p^3\) configuration of boron, which mixes with it to only a small extent the wave function for the higher energy configuration should be regarded as a correction function which when combined with the wave function of the principal or low energy configuration improves the accuracy of the latter. The one-electron radial functions in this "correction function" may differ considerably from the functions best representing the higher energy configuration.

A simplified version of the second procedure above for the two-configurational case with a principal and a subsidiary or perturbing configuration has been developed by Iutsis et al. This simplification consists of solving the ordinary Hartree-Fock equations for the principal
configuration, and the Hartree equations supplemented by configurational terms for those radial wave functions of the perturbing configuration whose Hartree-Fock equations contain such terms. The configurational wave functions obtained in this way are then combined linearly so as to minimize the energy. This procedure has been applied to the interaction of the lowest (or principal) configuration of the neutral boron atom, \(1s^2 2s^2 2p\), with the perturbing configuration \(1s^2 2p^3\) by Glembotskii, Kibartas, and Iutsis,\(^\text{40}\) as discussed in the next section. The extension of the method to the many-configuration case has also been considered.\(^\text{52,53}\)

7.32 Hartree-Fock Radial Functions with Configuration Interaction for Boron

As mentioned briefly at the end of the preceding section the two-configuration Fock self-consistent field method of Iutsis,\(^\text{51,52}\) has been applied to the neutral boron atom by Glembotskii, Kibartas, and Iutsis.\(^\text{40}\) The ordinary Fock equations for the principal ground-state configuration, \(1s^2 2s^2 2p\), expressed in atomic units,\(^\text{34}\) have the form

\[
\frac{d^2}{dr^2} P_{1s,1s}(r) - \left( \frac{2Z - 2Y_o(1s,1s;r) - 4Y_o(2s,2s;r) - 2Y_o(2p,2p;r)}{r} - \epsilon_{1s,1s} \right) P_{1s,1s}(r) + \left( \frac{2Y_o(1s,2s;r)}{r} - \epsilon_{1s,2s} \right) P_{2s,2s}(r) + \frac{Y_o(1s,2p;r)}{3r} P_{2p,2p}(r) = 0, \quad (77a)
\]

\[
\frac{d^2}{dr^2} P_{2s,2s}(r) - \left( \frac{2Z - 4Y_o(1s,1s;r) - 2Y_o(2s,2s;r) - 2Y_o(2p,2p;r)}{r} - \epsilon_{2s,2s} \right) P_{2s,2s}(r) = 0. \quad (77b)
\]
\[ + \left[ \frac{2Y_0(1s,2s;r)}{r} - \epsilon_{1s,2s} \right] P(1s;r) + \frac{Y_1(2s,2p;r)}{3r} P(2p;r) = 0, \quad (77b) \]

\[ \left[ \frac{d^2}{dr^2} + \frac{2Z - 4Y_0(1s,1s;r) - 4Y_0(2s,2s;r)}{r} - \frac{2}{r^2} - \epsilon_{2p,2p} \right] P(2p;r) \]

\[ \frac{2Y_1(1s,2p;r)}{3r} P(1s;r) + \frac{2Y_1(2s,2p;r)}{3r} P(2s;r) = 0. \quad (77c) \]

Here \( P(n \ell ; r) \) is the modified radial function of principal quantum number \( n \) and azimuthal quantum number \( \ell \) for the principal configuration. It is defined in the same way as the modified radial function \( f_1(r) = f_{n \ell} (r) \) used in section 7.21 in discussing the Hartree wave functions of boron calculated by Brown et al.\textsuperscript{35} and is normalized according to the relation

\[ \int_0^\infty P^2(n \ell ; r) \, dr = 1. \quad (78) \]

The function \( P(2s;r) \) was orthogonalized to \( P(1s;r) \) by the method of Schmidt after each solution of Eqs. (77); radial functions having different values of \( \ell \), or angular parts, are not required to be orthogonal.

The calculation of the effect of the perturbing configuration, \( 1s^22p^3 \), is made subject to two approximations. The function \( P(1s;r) \) is assumed to be the same for the perturbing as for the principal configuration. The \( 2p \) radial function for the perturbing configuration, denoted by \( P_2(2p;r) \) to distinguish it from the corresponding function
for the principal configuration, is calculated from a generalized
Hartree-type equation in which the Hartree-Fock exchange terms are
omitted, but a term occurs representing the interaction of the two con­
figurations. This equation is
\[ \frac{d^2}{dr^2} + 2Z - 4Y_o(1s,1s;r) - 4Y_o(2p,2p;r) - \frac{2}{r^2} - \epsilon_{(2p,2p)} \]
\[ = \frac{4 \sqrt{2} Y_1(2s,2p;r)_{12}}{9a_{12} r} P_1(2s;r) N(2p,2p)_{12} = 0. \]  
(79)

It should be noted that \( P_2(2p;r) \) is not required to be orthogonal to
\( P(2p;r) \), and in fact the configuration interaction term in Eq. (79)
depends on the integral
\[ N(2p,2p)_{12} = \int_0^\infty P(2p;r) P_2(2p;r) \, dr. \]  
(80)

In the preceding equation \( Z = 5 \) is the atomic number of boron,
and \( Z/r \) is the potential due to the nucleus. The factor 2 appearing in
all potential terms in these equations arises from the transformation to
atomic units and the modified radial functions, \( P(n\ell ;r) \). \( Y_k(n\ell ,n' \ell ';r) \)
is defined by
\[ Y_k(n \ell ,n' \ell ';r) = \frac{1}{r^k} \int_0^r P(n\ell ;r')P(n' \ell ';r')(r')^k \, dr'. \]  
(81)

Thus
\[ Y_o(n \ell ,n \ell ;r) = \int_0^r P^2(n\ell ;r') \, dr' + \int_r^\infty P^2(n\ell ;r')(r/r') \, dr', \]  
(82)
is equal to the negative of the equivalent nuclear charge, $z_{n\ell}$, for an electron in the orbital $n\ell$, as defined by Eq. (69). Furthermore, $Y_0(n\ell,n\ell;r)/r$ is identical with the Hartree potential, $v_{n\ell}(r)$, defined by Eq. (68), arising from a single electron (unit charge in atomic units) with a spherically symmetric distribution having a fraction of charge $r^2(n\ell;r')$ between $r'$ and $r' + dr'$. Comparison of Eqs. (77) and (78) with the Hartree equations for boron provided by Eqs. (65), (70), and (75), shows that the first set of square brackets in each of Eqs. (77) and (78) contains simply the Hartree operators. The Hartree orbital energy, $E_{n\ell}$, is equivalent to the negative of the diagonal Lagrangian multiplier $\xi_{n\ell,n\ell'}$ of Eqs. (77); thus $E_{n\ell}$ is negative and $\xi_{n\ell,n\ell'}$ positive for a system of bound electrons.

In addition to the Hartree operators containing the coulombic part of the potential in which a given orbital electron moves, the Hartree-Fock equations, (77), contain exchange terms depending on the integrals $Y_0(n\ell,n'\ell';r)$ and $Y_{12}(n\ell,n'\ell';r)$. The integral $Y_{12}(2s,2p;r')$ in Eq. (79) is obtained by placing $P(n\ell;r') = P(2s;r')$, $P(n'\ell;r') = P_2(2p;r')$, and $k = l$, in Eq. (81). The exchange terms may also contain off-diagonal Lagrangian multipliers, $\xi_{n\ell,n'\ell'}$. For a closed-shell configuration the off-diagonal multipliers can be removed by an unitary transformation, but this is not always the case for a non-closed shell configuration such as $1s^22s^22p$. However, the off-diagonal multipliers are often small, and in the solution of Eqs. (77) $\xi_{1s,2s}$ was set equal to zero.40
Slater had discussed the representation of the exchange terms in the Hartree-Fock equation for \( P(n\ell;r) \) as the electrostatic potential at \( r \) arising from a distribution of charge in the neighborhood of \( r \) representing the self-charge of an electron in the \( n\ell \) orbital. This self-charge, and the corresponding self-potential, are subtracted in the Hartree-Fock equation, leading to the concept of the Fermi hole. Of course, as discussed in section 7.26, a rather crude subtraction of self-charge is made even in the Hartree method through the subtraction of \( v_{nl} \) from the neutral atom potential, \( V_{at} \), as in Eqs. (75). The exchange terms may be regarded as corrections to the representation of the self-potential in the Hartree method. However, it should be noted that even the Hartree-Fock equations are only an approximation, and allow for inter-electronic correlation in only an averaged fashion.

One method of taking more detailed account of inter-electronic correlation is through the use of wave functions which are explicit functions of the distances between electrons. Configuration interaction accomplishes somewhat the same purpose through introducing greater flexibility into the wave function.

### 7.33 Hartree-Fock Energies, Wave Functions, and Electron Densities

The calculation of the Hartree or Hartree-Fock energy requires the evaluation of matrix elements of the Hamiltonian for the system. It is convenient to divide the Hamiltonian into one-electron parts (involving kinetic energy, centrifugal, and nuclear attraction terms for each electron), and the Coulomb repulsion terms for each electron pair. The first will give rise to the one-electron integrals, \( I(n\ell) \), and the
second to the Coulomb integrals, $F_k(n \ell, n' \ell')$, and exchange integrals, $G_k(n \ell, n' \ell')$, defined below. The definition of these integrals given by Hartree and used by Glembotskii et al. leads to energies in the atomic unit $e^2/a$, where $e$ is the charge on the electron and $a$ the radius of the first Bohr orbit of a hydrogenic atom with infinite nuclear mass. This energy will be called the Hartree energy unit, and is equal to $4 \pi^2 m e^4/h^2$, where $h$ is Planck's constant and $m$ the rest-mass of the electron. Another commonly used energy unit is the Rydberg, $R_y(\infty) = 2 \pi^2 m e^4/h^2$, which is half of Hartree's unit, and equal to the ionization energy of the electron in the lowest state of an hydrogenic atom with infinite nuclear mass. It should be noted that $R_y(\infty)$ is determined by direct extrapolation of spectroscopic data and is known with greater accuracy than the constants $m, e, \text{and } h$; the best present value is $R_y(\infty) = 109737.323 \pm 0.010 \text{ cm}^{-1}$.

The integrals of Hartree, and numerical values of Glembotskii et al. will be multiplied here by a factor of 2 to convert them to Rydberg units. However, it should be noted that the Lagrangian multipliers, $\xi n \ell, n \ell'$, as defined by Hartree and given by Glembotskii et al. give the orbital or ionization energies in Rydbergs as they stand. This rather confusing feature is a result of Hartree's use of an Hamiltonian for computing the matrix elements which is half the Hamiltonian in his Hartree-Fock equations. Slater defines all these quantities consistently in Rydberg units. Finally, it should be noted that a Rydberg unit $R_y(M) = 2 \pi^2 \mu e^4/h^2$, corresponding to the actual nuclear mass $M$ of a given atom is frequently used in tabulations of spectroscopic term values, because it is experimentally determinable, whereas $R_y(\infty)$ is obtained by extrapolation to $M = \infty$. In the expression for $R_y(M)$,
\( m = (m + M) / m M \) is the reduced mass of the electron in a hydrogenic atom with nuclear mass \( M \).

With the modification just discussed, the necessary matrix elements are the one-electron energy integrals

\[
I(n \ell) = - \int_0^\infty P(n \ell ; r) \left[ \frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2} \right] P(n \ell ; r) dr ,
\]

(82)

the two-electron Coulomb-type integrals,

\[
F_k(n \ell, n' \ell') = \int_0^\infty P^2(n \ell ; r)(2/r)Y_k(n \ell, n' \ell ; r) dr ,
\]

(83)

and exchange-type integrals,

\[
G_k(n \ell, n' \ell') = \int_0^\infty P(n \ell ; r)P(n' \ell ; r)(2/r)Y_k(n \ell, n' \ell ; r) dr .
\]

(84)

The integrals \( Y_k(n \ell, n' \ell ; r) \) are defined by Eq. (81). Note that all these integrals are unchanged by interchange of the quantum numbers \( n \) and \( n' \ell' \). In terms of these integrals the total energy in the Hartree method is given by

\[
\sum_{i=1} I(n_i \ell_i) + \sum_{i,j} F_0(n_i \ell_i, n_j \ell_j) ,
\]

(85)

in the approximation in which all potentials are computed from spherically averaged charge distribution. The first sum extends over all electrons and the second over all distinct pairs of electrons in the atom.

The general formula for the Hartree-Fock energy for the case of non-closed shell configurations and non-spherical charge distributions
is complex, and therefore only the method of averaged configuration energies of Slater \(^\text{44}\) will be considered, and only those terms required for s and p electrons. In general, a given configuration gives rise to several multiplets having different quantum numbers for total orbital and spin angular momentum, \(L\) and \(S\), respectively. In the approximation in which spin-orbital coupling is neglected, and in the absence of external fields, the \((2L+1)(2S+1)\) states corresponding to a given multiplet have the same energy. Slater averages the multiplet energies for a given configuration, as computed by the Hartree-Fock method, with a weight \((2L+1)(2S+1)\) for each configuration. The average energy of the configuration is then given by

\[
E_{av} = \sum_{i} I(n_i \ell_i) + \sum_{i,j} Q(n_i \ell_i, n_j \ell_j). \tag{86}
\]

Here \(I(n_i \ell_i)\) is the one-electron energy for the \(i\)th electron of Eq. (82), and \(Q(n_i \ell_i, n_j \ell_j)\) is the average repulsion energy for the \(i,j\)-th pair of electrons. For an equivalent pair of s electrons, with \(n = n_i = n_j\),

\[
Q(ns,ns) = F_o(ns,ns), \tag{87}
\]

and for an equivalent pair of p electrons,

\[
Q(np,np) = F_o(np,np) - (2/25)F_2(np,np). \tag{88}
\]

For a non-equivalent pair of s electrons, with \(n = n_i \neq n_j = n'\),

\[
Q(ns,n's) = F_o(ns,n's) - (1/2)G_o(ns,n's), \tag{89}
\]

and for a non-equivalent pair of p electrons,

\[
Q(np,n'p) = F_o(np,n'p) - (1/6)G_o(np,n'p) - (1/15)G_2(np,n'p). \tag{90}
\]
Finally, for an s and a p electron, with \( n = n_i \) and \( n' = n_j \), where \( n \) may or may not be equal to \( n' \),

\[
Q(ns,n'p) = F_0(ns,n'p) - (1/6)Q_1(ns,n'p). \tag{91}
\]

Although the preceding formulas make possible the calculation of average configuration energies from the integrals \( I(n l) \), \( F_k(n l,n' l') \), and \( Q_k(n l,n' l') \) of Eqs. (82-84), the integrals \( I(n l) \), are not obtained directly in the Hartree-Fock method. The related quantities which are obtained directly and which are tabulated for boron by Glembotskii et al.\(^{40}\) are the diagonal Lagrangian multipliers, \( \epsilon_{n l,n l} \).

As is well known these have the significance of ionization energies, so that \( \epsilon_{n l,n l} \) is the energy required to remove an electron with quantum numbers \( n \) to an infinite distance from the atom (assuming the wave functions and distributions of the remaining electrons are unchanged).

Thus,

\[
-\epsilon_{n l,n l} = I(n l_i) + \sum_j Q(n l_i,n j l_j), \tag{92}
\]

where the sum extends over all other electrons in the atom. There is a similar expression for the ionization energy of each electron in the atom, and it is important to note that these refer not to successive ionization of the electrons, but in each case to the ionization of only the single electron in question. On taking the sum of all such ionization energies the electron-pair repulsion energies are counted twice, or from Eq. (92)

\[
-\sum_i \epsilon_{n l_i,n l_i} = \sum_i I(n l_i) + 2 \sum_{i,j} Q(n l_i,n j l_j), \tag{93}
\]
where the double sum extends only over distinct pairs, i and j. Comparison of Eqs. (86) and (93) shows that the average configuration energy is expressed in terms of the ionization energies by

$$E_{av} = - \sum \epsilon_{n_i \ell_i, n_i \ell_i} - \sum Q(n_i \ell_i, n_j \ell_j).$$

That is, the (average) configuration is more stable than the sum of its ionization energies would indicate by an amount equal to the total electron-pair repulsion energy.

The values of the ionization energies and radial integrals obtained from the solution of the two-configuration Hartree-Fock equations (77) and (79), for the boron atom are given in Table 26. All quantities have been expressed in Rydberg energy units, $R_y(\infty)$, as previously discussed, except the non-orthogonality integral, Eq. (80), which is a pure number. Subscripts 1 and 2 attached to the radial integrals indicate that the correspondingly ordered orbitals are solutions of Eqs. (77) for the principal 1s^22s^22p configuration, or Eq. (79) for the perturbing configuration, respectively. If both orbitals refer to the principal configuration the subscripts are omitted. A similar statement applies to the ionization energies.

The electron-pair repulsion energies for the configuration 1s^22s^22p may now be obtained from Table 26 and Eqs. (87), (89), and (91), and are:

$$Q(1s,1s) = F_0(1s,1s) = 5.8650,$$

$$Q(2s,2s) = F_0(2s,2s) = 0.9204,$$

$$Q(1s,2s) = F_0(1s,2s) - (1/2)G_0(1s,2s) = 1.2585.$$
TABLE 26. Values of the Ionization Energies (Lagrangian Multipliers) and Radial Integrals for the Ground State of the Boron Atom in the Two-Configuration Approximation

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Ionization Energy (eV)</th>
<th>Radial Integral (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1s,1s)</td>
<td>15.386</td>
<td>(2p,2p) = 0.6182</td>
</tr>
<tr>
<td>(2s,2s)</td>
<td>0.9903</td>
<td>(2s,2p) = 0.9903</td>
</tr>
<tr>
<td>(2p,2p)</td>
<td>0.6182</td>
<td>(2p,2p) = 0.6182</td>
</tr>
<tr>
<td>(2s,2s)</td>
<td>0.9903</td>
<td>(2s,2s) = 0.9903</td>
</tr>
<tr>
<td>(1s,2s)</td>
<td>1.2970</td>
<td>(1s,2p) = 1.2970</td>
</tr>
<tr>
<td>(1s,2p)</td>
<td>1.1988</td>
<td>(2p,2p) = 1.1988</td>
</tr>
<tr>
<td>(2s,2p)</td>
<td>0.8740</td>
<td>(2s,2p) = 0.8740</td>
</tr>
<tr>
<td>(1s,2p)</td>
<td>1.1988</td>
<td>(1s,2p) = 1.1988</td>
</tr>
</tbody>
</table>

\[Q(1s,2p) = F_0(1s,2p) - (1/6)G_1(1s,2p) = 1.1845\] \hspace{1cm} (95d)

\[Q(2s,2p) = F_0(2s,2p) - (1/6)G_1(2s,2p) = 0.7831\] \hspace{1cm} (95e)

The total electron-pair repulsion energy as obtained by summing over all distinct pairs of electrons for the given configuration is

\[
\sum_{i,j} Q(n_i l_i, n_j l_j) = Q(1s,1s) + Q(2s,2s) + 4Q(1s,2s) + 2Q(1s,2p) + 2Q(2s,2p) = 15.7546.
\] \hspace{1cm} (96)

The sum of the ionization energies for the electrons in the configuration \(1s^22s^22p\) is also obtained from Table 26,

\[
\sum_i \ell n_i l_i, n_i l_i = 2 \ell 1s,1s + 2 \ell 2s,2s + \ell 2p,2p = 33.3708
\] \hspace{1cm} (97)
The energy of the principal configuration is now obtained from Eqs. (94), (96), and (97),

\[ E_{11} = -33.3708 - 15.7546 = -49.1254 \]  

(98)

As the configuration \( 1s^2 2s^2 2p \) yields only a single multiplet, \( 2p^0 \), no averaging over multiplets is necessary in this case. Of course, spin-orbit interaction is ignored.

The energy \( E_{11} \) of Eq. (98) equals the diagonal matrix element of the complete Hamiltonian, \( H \), for the atom,

\[ E_{11} = \int \Phi_1^* H \Phi_1 \, d\tau. \]  

(99a)

For the two-configuration method the matrix elements

\[ E_{22} = \int \Phi_2^* H \Phi_2 \, d\tau, \]  

(99b)

and

\[ E_{12} = \int \Phi_1^* H \Phi_2 \, d\tau, \]  

(99c)

are also required. Here \( \Phi_1 \) and \( \Phi_2 \) are the antisymmetrized determinantal wave functions for the configurations \( 1s^2 2s^2 2p \) and \( 1s^2 2p^3 \), respectively. \( \Phi_1 \) is constructed from the solutions of Eqs. (77), and \( \Phi_2 \) from the solution of Eq. (79). The \( 1s \) radial function is taken to be the same in both configurations, as an approximation. The computation of the remaining matrix elements from the quantities given in Table 26 will not be given in detail. The complete set of matrix elements is

\[ E_{11} = -49.1254 \]  

(100a)

\[ E_{22} = -48.006 \]  

(100b)

\[ E_{12} = 0.278 \]  

(100c)

The final ground state wave function in the two-configuration approximation is

\[ \Phi = (1 + a_{12}^2)^{-3/2} (\Phi_1 + a_{12} \Phi_2), \]  

(101)
where $a_{12}^2$ is the same parameter as appears in the configuration interaction term of the generalized Hartree-Fock equation, (79). The normalization of $|\Phi\rangle$ follows from Eq. (101) and the orthonormality of $|\Phi_1\rangle$ and $|\Phi_2\rangle$. According to the variation theorem the energy of the ground state configuration is to be obtained by adjusting $a_{12}^2$ to minimize the energy or average value of the Hamiltonian

$$E = \langle \Phi | H | \Phi \rangle.$$

(102)

As is well known this leads to the secular equation

$$\begin{vmatrix}
(E_{11} - E) & E_{12} \\
E_{12} & (E_{22} - E)
\end{vmatrix} = 0,$$

(103)

where $E_{11}$, $E_{22}$, and $E_{12}$ are defined by Eqs. (99). The algebraically lowest root of Eq. (103) is the energy of the ground state in the two-configuration approximation. On inserting the numerical values from Eqs. (100), this theoretical Hartree-Fock energy is found to be

$$E = -49.190 \text{ Ry} \ (\infty).$$

(104)

An experimental (spectroscopic) value may be obtained in the following way. The successive ionization energies for the removal of the five electrons of the boron atom are $5666930$, $202895$, $305931.5$, $2091960$, and $2744063 \text{ cm}^{-1}$. Taking the negative of the sum of these ionization energies yields $-5411779.5 \text{ cm}^{-1}$ as the energy of the ground state, $1s^22s^22p^2 (^2P_3/2)$ of the boron atom, relative to the completely ionized atom which is taken as the state of zero energy for the quantum mechanical calculations. The other component $^2P_1/2$, of the ground-state multiplet lies $16 \text{ cm}^{-1}$ above this and thus has an energy of
-5411763.5 cm\(^{-1}\). As the Hartree-Fock calculation takes no account of this small splitting resulting from spin-orbit coupling it is appropriate to take a weighted average of the energies for the two components, with weights \(2J+1\), or 2 and 4 in the present case, as suggested by Slater.\(^{41}\) This yields an average value of -5411768.8 cm\(^{-1}\) for the energy of the \(2^3P^0\) multiplet. Expressed in Rydberg units, \(R_y(\infty) = 109737.323\) cm\(^{-1}\), this becomes

\[
E_{\text{exp}} = -49.3157 R_y(\infty) .
\]

(105)

The theoretical energy lies above the experimental energy, as it must from the variation theorem. The error of 0.25 percent is relatively small for this type of calculation.

The configurational mixing parameter \(a_{12}\) of Eq. (101) is obtained from the condition that \(\Phi\) must be an eigenfunction of \(H\) corresponding to the lowest eigenvalue \(E\) of Eq. (103). Equivalently the column matrix \((1, a_{12})\) must be an eigenvector of the matrix appearing in Eq. (103), which leads to

\[
a_{12} = (E - E_{11}) / E_{12} .
\]

(106)

Substitution of the values from Eqs. (100) and (104) yields

\[
a_{12} = -0.238 .
\]

(107)

From Eqs. (101) and (107) the ground-state wave function is therefore

\[
\Phi = 0.9728 \Phi_1 - 0.2315 \Phi_2 ,
\]

(108)

where \(\Phi_1\) is the wave function for the principal configuration, \(1s^22s^22p\), and \(\Phi_2\) that for the perturbing configuration, \(1s^22p^3\).
Assuming orthogonality of the wave functions for the two configurations, the corrected total electron probability density is

\[
W(r) = \left[ \frac{1}{1 + a_{12}^2} \right] W_1(r) + \left[ \frac{a_{12}^2}{1 + a_{12}^2} \right] W_2(r), \quad (109)
\]

where \(W_1(r)\) and \(W_2(r)\) are the corresponding densities for the principal and perturbing configurations, respectively,

\[
W_1(r) = 2P^2(ls;r) + 2P^2(2s;r) + P^2(2p;r), \quad (110)
\]

and

\[
W_2(r) = 2P^2(ls;r) + 3P^2(2p;r). \quad (111)
\]

The neutral atom potential, \(V_{at}\), in the coulombic or Hartree approximations, and the effective nuclear charge, \(Z_{at}\), as defined in section 7.25, depend linearly on \(W(r)\) and combine with the same squared weights,

\[
Z_{at}(r) = \left[ \frac{1}{1 + a_{12}^2} \right] Z_1(r) + \left[ \frac{a_{12}^2}{1 + a_{12}^2} \right] Z_2(r). \quad (112)
\]

From Eq. (72), on noting that \(Y_o(n\ell,n\ell;r) = -z_{n\ell}\),

\[
Z_1(r) = Z - 2Y_o(ls,ls;r) - 2Y_o(2s,2s;r) - Y_o(2p,2p;r), \quad (113)
\]

and

\[
Z_2(r) = Z - 2Y_o(ls,ls;r) - 3Y_o(2p,2p;r), \quad (114)
\]

Glembotskii et al.\(^{40}\) denote \(2Z_{at}(r)\) by \(T(r)\).

7.4 Slater Type Wave Functions

7.41 Non-Orthogonalized Radial Functions

In the preceding sections the Hartree and Hartree-Fock self-consistent field radial wave functions for the boron atom have been discussed. Although these are the most accurate wave functions available, they have the practical disadvantage that they are known only as numerical functions of their arguments. This is not a serious
disadvantage and necessary integrals can be evaluated by numerical integration for a system consisting of a single atom possessing spherical symmetry or for which such symmetry has been introduced by a suitable averaging process. The integration over angle variables, involving products of spherical harmonics, can then be carried out analytically, leaving only the radial integrals in one dimension to be evaluated numerically. As soon as spherical symmetry and the resulting separation of variables is lost numerical integrations become enormously more difficult as the integrals become multidimensional. It is largely for this reason that in treating systems of several atoms it is almost essential to use simplified analytic wave functions for which the required integrals can be evaluated analytically in terms of known functions. The most important functions of this type are now usually called the Slater functions, as he gave general rules for determining the parameters in the functions, although similar functions were first used by Zener and Eckart. All the comprehensive tabulations of one- and two-center quantum integrals are based on Slater-type orbitals. Slater suggested the radial part of the atomic orbital for an electron of principal quantum number be taken proportional to $r^{n^*-1} e^{-\zeta r}$, where $\zeta = (Z - s)/n^*$. This function is a solution of the central-field problem with the potential (all quantities including $r$ are in atomic units).

$$V(r) = - (Z - s)/r + \ell^*(\ell^* + 1)/2r^2,$$  \hspace{1cm} (115)

with $\ell^* = n^* - 1$. It is clear that $Z - s$ is an effective nuclear charge. The quantity, $s$, by which the true nuclear charge, $Z$, must be decreased to obtain the effective nuclear charge for a given orbital is
known as the shielding or screening constant. Comparison with Eqs. (76) will show that $s$ is equivalent to the equivalent nuclear charge or screening parameter defined by Eq. (69) in connection with the Hartree method, except that the latter parameter is a function of $r$ whereas $s$ is a constant for a given orbital. As defined here, $s$ is not equivalent to the $s$ of Eqs. (73) and (74) which yields the neutral atom potential rather than the effective potential for an electron in a given orbital.

We consider next the significance of $n^*$ and $\ell^*$. The radial wave functions for an hydrogenic atom contain the exponential factor $e^{-Zr/n}$, where $n$ is the principal quantum number. Comparison with the Slater function shows that $n^*$ is an effective value of $n$. The general form of the rotational kinetic energy term in the central-field problem is $\ell(\ell + 1)/2r^2$ where the azimuthal quantum number assumes the values $\ell = 0, 1, 2, \ldots, n - 1$. However, from Eq. (115), the Slater orbital is the solution equivalent to the hydrogenic atom wave function for $\ell = \ell_{\text{max}} = n - 1$, as $\ell^* = n^* - 1$. That is, all the Slater functions for given $n$ (or $n^*$) have the radial dependence appropriate to the maximum allowable value of $\ell$. This introduces a difficulty as the Slater orbitals corresponding to the same $\ell$, but successive values of $n$ are not orthogonal (for example, the 1s, 2s, 3s, etc., functions are not orthogonal). Two possible procedures for orthogonalizing Slater functions having the same value of $\ell$ will be considered subsequently.

Orthogonality of Slater functions for the same $n$, but different values of $\ell$ and/or the magnetic quantum number $m$, is assured by the angular part of the wave functions for the central-field problem, which are simply the spherical harmonics.
The values recommended by Slater\(^\text{57}\) are \(n^* = 1, 2, 3, 3.7, 4.0,\) and \(4.2,\) for \(n = 1, 2, 3, 4, 5,\) and \(6,\) respectively. Slater's rules for determining \(s\) are somewhat complicated and reference should be made to the original sources.\(^4^1,\text{57}\) The general form of the real normalized Slater orbitals is

\[
(2\pi)^{n^*+\frac{1}{2}} \left[ \sqrt{(2n^* + 1)} \right]^{-\frac{1}{2}} r^{n^* - 1} e^{-\zeta r} S_{\ell,m}(\theta, \phi),
\]

where \(\zeta = (Z - s)/n^*.\) Here \(S_{\ell,m}(\theta, \phi)\) is a real normalized spherical harmonic.\(^6^1\) For \(m = 0,\)

\[
S_{\ell,0}(\theta, \phi) = \left[ (2\ell + 1) / 4\pi \right]^{\frac{1}{2}} P\ell(\cos \theta),
\]

with \(P\ell(\cos \theta)\) the Legendre polynomial. For \(m \neq 0,\)

\[
S_{\ell,|m|}(\theta, \phi) = \left[ \frac{(2\ell + 1)}{2\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!} \right]^{\frac{1}{2}} P\ell^{|m|}(\cos \theta) \cos |m| \phi,
\]

\[
S_{\ell,-|m|}(\theta, \phi) = \left[ \frac{(2\ell + 1)}{2\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!} \right]^{\frac{1}{2}} P\ell^{|m|}(\cos \theta) \sin |m| \phi,
\]

with \(P\ell^{|m|}(\cos \theta)\) the associated Legendre function.

For the ground state configuration of boron only the functions for \(n = 1\) and \(2\) are required. Then \(n^* = n,\) and the explicit forms of the real normalized Slater orbitals are

\[
\begin{align*}
(1s) & = (2\pi)^{3/11} e^{-\zeta r}, & (118a) \\
(2s) & = (2\pi)^{5/3\pi} r e^{-\zeta r}, & (118b) \\
(2p\sigma) & = (2\pi)^{5/3\pi} r e^{-\zeta 3^{\frac{1}{2}} \cos \theta}, & (118c)
\end{align*}
\]
\[(2p\pi) = (\zeta_3^5/\pi)^{\frac{1}{2}} r e^{-\zeta_3 r} \sin\theta \cos\phi, \quad (118d)\]

\[(2p\pi') = (\zeta_3^5/\pi)^{\frac{1}{2}} r e^{-\zeta_3 r} \sin\theta \sin\phi. \quad (118e)\]

The notation for the orbitals is that used previously in sections 6.2 and 6.3, except that the principal quantum number was suppressed there. According to Slater's rules the values of the screening constant \(s\) are 0.30 for an 1s electron and 2.40 for a 2s or 2p electron in the ground state configuration, 1s\(^2\)2s\(^2\)2p, of boron. Therefore the values of \(\zeta = (Z - s)/n\) occurring in Eqs. (118) are \(\zeta_1 = 4.70\) and \(\zeta_2 = \zeta_3 = 1.30\).

Although \(\zeta_2 = \zeta_3\) in the Slater functions, the possibility of different values of \(\zeta\) for the 2s and 2p functions has been considered by Roothaan\(^{52}\) and Tubis\(^{63}\) (see also the discussion by Slater\(^{41}\)). Roothaan began with the functions of Eq. (118), and first orthogonalized the 2s orbital to the 1s orbital by the Schmidt method as considered explicitly in section 7.42. That is, his final 2s orbital was a linear combination of the functions of Eqs. (118a) and (118b). Tubis' procedure was identical except his 2s orbital was orthogonalized by adding to the function (118b) the function obtained from (118a) by replacing \(\zeta_1\) by \(\zeta_1'\). Both authors considered a number of configurations and multiplets for light atoms, taking the total wave function for the atom as the appropriate linear combination of antisymmetrized Slater determinants. The best wave function for the assumed form of the orbitals was found by applying the variation theorem and minimizing the total energy through variation of the parameters \(\zeta_1, \zeta_2, \) and \(\zeta_3\) (and also \(\zeta_1'\) in the case of Tubis). For the 1s\(^2\)2s\(^2\)2p \((^2P^0)\) state of boron,
Roothaan found in this way the best values, \( \zeta_1 = 4.6794, \zeta_2 = 1.3382, \)
and \( \zeta_3 = 1.2105. \) Tubis' values are \( \zeta_1 = 4.70, \zeta_2 = 1.30, \zeta_3 = 1.21, \)
and \( \zeta_1' = 4.30. \) The exact agreement of Slater's recommended values with
Tubis' results for \( \zeta_1 \) and \( \zeta_2 \) is fortuitous, particularly since in
Slater's procedure Roothaan's orthogonalization of the 2s function,
with \( \zeta_1' = \zeta_1' \), would normally be used. However, Slater's values of \( \zeta_1 \)
and \( \zeta_2 \) only differ by 0.44 and -2.9 percent, respectively, from
Roothaan's values. On the other hand both Roothaan and Tubis find
\( \zeta_3 = 1.21 \) which is 6.9 percent below Slater's value, and strongly
indicates that \( \zeta \) has a lower value for the 2p than for the 2s orbital.

7.42 Orthogonalization of Slater-Type
2s Orbital

As pointed out in the preceding section the Slater 1s and 2s
orbitals of Eqs. (118a) and (118b) are not orthogonal. In rectifying
this deficiency the plausible assumption is made that the lower energy
orbital, 1s, is to remain unchanged and the higher energy 2s orbital is
to be modified to make it orthogonal to the 1s orbital. This is in
conformity with the viewpoint in the variation theorem in which each
orbital minimizes the energy subject to the restriction that it be
orthogonal to all orbitals of lower energy. It is of course desirable
that the method of orthogonalization of the 2s orbital retain the
simplicity of the Slater-type orbitals.

Tubis,\(^63\) following the lead of Morse, et al.,\(^64\) has orthogonal-
ized the 2s orbital by forming a linear combination of the orbital of
Eq. (118b) with an orbital similar to the 1s orbital of Eq. (118a), but
with \( \zeta_1' \) replaced by \( \zeta_1' \). His normalized and orthogonalized 2s orbital is thus

\[
(2s') = (\zeta_2^5/3\pi N)^\frac{1}{2} \left[ A e^{-\zeta_1' r} - r e^{-\zeta_2 r} \right],
\]

where

\[
A = 3(\zeta_1' + \zeta_1^1)^3 / (\zeta_1 + \zeta_2)^4,
\]

\[
N = 1 - \left[ 16A\zeta_2^5 / (\zeta_1' + \zeta_2)^4 \right] + (A^2\zeta_2^5 / 3\zeta_1^4) .
\]

Tubis then determined by the variation theorem the best values for \( \zeta_1', \zeta_1', \zeta_2, \) and \( \zeta_3 \) as discussed in the preceding section. For the ground state \( ls^22s^22p \) configuration of boron he found \( \zeta_1 = 4.70, \zeta_1' = 4.30, \zeta_2 = 1.30, \) and \( \zeta_3 = 1.21. \) Thus, Tubis found that the best value of \( \zeta_1' \) is only about 8.5 percent less than \( \zeta_1 \) for the boron atom (he obtained very similar results for carbon, nitrogen, and oxygen atoms, also). This suggests the simplification adopted by Roothaan of setting \( \zeta_1' = \zeta_1 \), thus reducing the number of parameters by one.

Roothaan's normalized and orthogonalized 2s orbital is therefore

\[
(2s') = (\zeta_2^5 / 3\pi N)^\frac{1}{2} \left[ A e^{-\zeta_1' r} - r e^{-\zeta_2 r} \right]
\]

with

\[
A = 24\zeta_1^3 / (\zeta_1 + \zeta_2)^4,
\]

\[
N = 1 - \left[ 192 \zeta_1^3\zeta_2^5 / (\zeta_1 + \zeta_2)^8 \right].
\]

An alternative way of writing Roothaan's function is

\[
(2s') = N' \left[ \beta(1s) - (2s) \right],
\]

\[(122, 123, 124, 125)\]
where (1s) and (2s) are given by Eqs. (118a) and (118b), respectively, and
\[
\psi = 8(3)^{1/2} \zeta_1^{3/2} \zeta_2^{5/2} / (\zeta_1 + \zeta_2)^{3/4},
\]
\[
N' = (1 - \beta^2)^{-1/2}.
\]
It will be noted that Roothaan's 2s orbital is exactly the same as that obtained by using the standard method of Schmidt to orthogonalize it to the 1s orbital. Both Tubis' and Roothaan's procedures are equivalent to assuming that Slater's original 2s orbital, Eq. (118b), yields correctly the radial variation of the outer part of the 2s wave function, but that the inner part has a quite different variation which is essentially that of the 1s orbital (with the amplitude reduced to accord with the probability of the 2s electron being in the inner region, but the radial scale unchanged). That is, their 2s electron behaves as a 1s electron when it is in the region of the 1s electron. This is simply an assumption in Roothaan's treatment, but emerges naturally from the variation calculation of Tubis.

A quite different approach to the orthogonalization of the 2s orbital is adopted by Kopineck, who assumes that \( \zeta_1' = \zeta_2 \) in Eq. (119). His normalized and orthogonalized 2s orbital is therefore
\[
(2s') = (\zeta_2^5 / 3\pi N)^{1/2} (A - r) e^{-\zeta_2r},
\]
where
\[
A = 3/(\zeta_1 + \zeta_2),
\]
\[
N = 1 - A \zeta_2 + (A^2 \zeta_2^2 / 3).
\]
An alternative notation used by Kopineck, and similar to the second way of writing Roothaan's function, is

\[(2s') = N' \left[ \beta(1s') - (2s) \right],\]  

(131)

where \((2s)\) is given by Eq. (118b), \((1s')\) is obtained by substituting \(\zeta_2\) for \(\zeta_1\) in Eq. (118a), and

\[\beta = (3)^{1/2} \zeta_2 / (\zeta_1 + \zeta_2),\]  

(132)

\[N' = (\zeta_1 + \zeta_2) / (\zeta_1^2 + \zeta_2^2 - \zeta_1 \zeta_2)^{1/2}.\]  

(133)

Kopineck's orthogonalized 2s orbital is made plausible by its resemblance to the functional form of the 2s orbital for a hydrogenic atom. For an atom of nuclear charge \(Z\) with a single electron the exact wave functions or orbitals (neglecting spin and relativity effects), through principal quantum number \(n = 2\), are

\[(1s) = (\zeta_1^3 / \pi)^{1/2} e^{-\zeta_1 r},\]  

(134a)

\[(2s) = (\zeta_2^5 / \pi)^{1/2} \left[ (1/\zeta_2) - r \right] e^{-\zeta_2 r},\]  

(134b)

\[\left(2p_\sigma^-\right) = \left(2p_\sigma^+\right) = (\zeta_3 / \pi)^{1/2} r e^{-2r} \cos \theta,\]  

(134c)

\[\left(2p_\sigma^0\right) = (\zeta_2^5 / \pi)^{1/2} r e^{-\zeta_2 r} \sin \theta \cos \phi,\]  

(134d)

\[\left(2p_\sigma^1\right) = (\zeta_2^5 / \pi)^{1/2} r e^{-\zeta_2 r} \sin \theta \sin \phi,\]  

(134e)

where \(\zeta_n = (Z/n)\). These equations are to be compared with Eqs. (118).

It is seen that in the hydrogenic atom \(\zeta_2 = \zeta_3 = (\zeta_1 / 2)\). Except for the special values to be assigned to \(\zeta_n\), the hydrogenic 1s and 2p
functions are identical with the Slater-type functions. However, the hydrogenic 2s function of Eq. (134b), which is of course orthogonal to the corresponding 1s function, has a functional form similar to that of Kopineck's orthogonalized 2s function of Eq. (128). In fact, the substitution of the hydrogenic value $X^2 = X^2$ in Eqs. (128-130) yields Eq. (134b). On the other hand, the values of the $\zeta_n$'s obtained in the variation treatments of Tubis and Roothaan, as well as the more accurate Hartree and Hartree-Fock self-consistent field treatments which are also based on the variation theorem, but do not restrict the orbitals to simple analytic functions, show that boron and other light atoms are far from hydrogenic. It will be shown in the next section that Roothaan's orthogonalized 2s orbitals agree better with the most accurate available Hartree-Fock 2s orbital than does the 2s orbital of Kopineck. In spite of this Kopineck's procedure has an important advantage from the computational viewpoint, as his 2s orbital involves only a single exponential term while Tubis' and Roothaan's function involve two such terms. If the approximation $\zeta_2 = \zeta_3$ is made, then the 2p Slater orbitals and Kopineck's 2s orbital all have the same exponential term appearing as a simple factor. This considerably simplifies the evaluation of the quantum integrals involving 2s and 2p electrons, which play the principal role in bonding of atoms in the first row of the periodic table.
7.5 Comparison of Hartree, Hartree-Fock, and Slater-Type Orbitals for the Boron Atom

7.5.1 Radial Probability Density

The Hartree, Hartree-Fock, and Slater-type atomic orbitals for the ground state configuration, 1s^2 2s^2 2p, of the neutral boron atom have been discussed in sections 7.2, 7.3, and 7.4, respectively. In the present section the 1s, 2s, and 2p orbitals and some related quantities as obtained by these three methods will be compared, with the aim of determining how well the simple analytical functions of Slater approximate the more accurate functions. It appears to be virtually a necessity in the further stages of the present calculation to use Slater orbitals, so that use may be made of the available tables of integrals involving these orbitals.

The comparison of the orbitals themselves may be made in terms of either the amplitude of the wave function or its square, which represents the probability density for the electron. The latter has the advantage of an immediate physical significance, and also a close relation to the atomic potentials. The square of the modified radial function denoted by \( f^2_n \) or \( f^2_{n\ell} \) in section 7.2, and \( P(n\ell; r) \) in section 7.3, has been chosen for comparison where \( f_{n\ell} \) is defined by Eq. (64) and normalized according to Eq. (66). From Eq. (67), \( f_{n\ell}^2(r) \, dr \) is the probability an electron with principal quantum number \( n \) and azimuthal quantum number \( \ell \) is at a distance \( r \) to \( r + dr \) from the nucleus. The dependence of the Hartree potentials on \( f_{n\ell}^2(r) \) or \( P_{n\ell}^2(r) \) is shown by Eqs. (68) and (82).
The values of the modified radial functions $f_{n\ell}^{2}(r)$ are given in Tables 27, 28, and 29, and are plotted in Figures 7, 8, and 9, for the $1s$, $2s$, and $2p$ electrons, respectively, of the $1s^{2}2s^{2}2p$ configuration of boron. The unit for $r$ is the radius of the first Bohr orbit for the hydrogen atom, $a_o = 0.5292$ Angstrom. In each case the Hartree and one or more Hartree-Fock and Slater-type orbitals are shown. The values of the Hartree orbitals are taken from Brown et al., and of the Hartree-Fock orbitals from Glembotskii et al. The Slater-type orbitals are calculated from the analytic functions, and the screening constant $\xi = (Z - s)/n$ is given in each case. Unless otherwise stated these are the values recommended for boron by Slater. The symbols $a$, $b$, $b'$, $c$, and $d$ are used consistently in all the figures and tables, as indicated by the legends on the figures.

Figure 7 shows that the Hartree, Hartree-Fock, and Slater-type $1s$ orbitals are in very close agreement. This is to be expected as the $1s$ electrons are nearly hydrogenic. For the $2s$ orbitals in Figure 8 it is useful to distinguish the outer and inner parts which are separated by a node in $f_{n\ell}^{2}(r)$. As discussed in section 7.4 the inner part is largely determined by the requirement of orthogonality to the $1s$ orbital, while the outer part is of predominant importance in bond formation. Two Slater-type $2s$ orbitals are shown, with orthogonalization by the methods of Kopineck and Roothaan as discussed in section 7.4. From Figure 8 it is evident that both the outer and inner parts of the Hartree-Fock and Slater-Roothaan $2s$ orbitals are in excellent agreement. The Hartree $2s$ orbital is displaced to slightly larger radial distances and has a somewhat higher inner maximum. The Slater-Kopineck $2s$ orbital deviates
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### TABLE 28. Probability Density or Square of Normalized Wave Function for the 2s Orbital of the Boron Atom

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TABLE 29. Probability Density or Square of Normalized Wave Function for the 2p Orbital Boron Atom

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FIGURE 7 PROBABILITY DENSITY, OR SQUARE OF NORMALIZED WAVE FUNCTION, FOR THE 1S ORBITAL OF THE BORON ATOM
FIGURE 8  PROBABILITY DENSITY, OR SQUARE OF NORMALIZED WAVE FUNCTION, FOR THE 2S ORBITAL OF THE BORON ATOM
FIGURE 9  PROBABILITY DENSITY, OR SQUARE OF NORMALIZED WAVE FUNCTION, FOR THE 2P ORBITAL OF THE BORON ATOM
considerably from the others, with a much smaller inner maximum and the outer part displaced to larger values of \( r \). It is clear that Roothaan's orthogonalization procedure is superior to that of Kopineck.

In Figure 9 two Hartree-Fock 2p orbitals are shown, and identified in a somewhat oversimplified fashion as belonging to the configurations \( 1s^22s^22p \) and \( 1s^22p^3 \). The correct interpretation of these functions is given in section 7.3. The orbital labelled \( 1s^22s^22p \) is calculated for the ground state or principal configuration. The other orbital is not actually the 2p orbital for the \( 1s^22p^3 \) configuration, but a correction function to be added with a particular weight to the 2p orbital for the \( 1s^22s^22p \) configuration to take account of its interaction with the \( 1s^22p^3 \) configuration. As shown by Eqs. (107) and (109-111) the weighted average radial density function for the 2p electron in this two-configuration Hartree-Fock treatment is

\[
\left[ \frac{1}{1 + 3\alpha_{12}} \right] \left[ f_{2p}^2(r;1s^22s^22p) + 3\alpha_{12} f_{2p}^2(r;1s^22p^3) \right] \\
= 0.855 f_{2p}^2(r;1s^22s^22p) + 0.145 f_{2p}^2(r;1s^22p^3), \quad (135)
\]

and thus lies about 15 percent of the way from the first to the second value of \( f_{2p}^2(r) \) in the figure. However, it was considered more informative to plot the two separate \( f_{2p}^2(r) \) functions than the weighted average. Figure 9 shows that the Hartree 2p orbital has a much broader and lower maximum than the weighted average Hartree-Fock 2p function. On the other hand the Slater-type 2p orbitals with \( \zeta = 1.30 \) and 1.21 are in fairly good agreement with the Hartree-Fock orbital. The value \( \zeta = 1.30 \) recommended by Slater gives better agreement with the unperturbed
Hartree-Fock 2p function for the 1s²2s²2p configuration, but the value £ = 1.21 found by Roothaan and Tubis in their variation treatments is in about as good agreement with the weighted average Hartree-Fock function.

7.52 Equivalent Nuclear Charges or Screening Parameters

The potentials in which the individual electrons move and the total atomic potential are of major interest in any treatment of atomic structure. The former potentials will be considered in this section and the latter in the next section. The potential to which an electron in a given orbital is subject is the sum of the nuclear potential, \( V_n = -Z/r \), and the potentials arising from the other electrons. In the Hartree approximation in which the electrons are treated as static charge distributions the potential at \( r \) due to an electron in the \( i \)th (or \( n'f \)th) orbital is given by \( v_i(r) \) of Eq. (68). These Hartree-like potentials may be computed for any assigned orbitals, such as Slater-type orbitals or even Hartree-Fock orbitals. The Hartree-like part of the Hartree-Fock potentials is included within the square brackets in Eqs. (77), and omits the exchange potentials which give a more accurate representation of the Fermi hole or self-charge of the electron.

Because the potentials are relatively rapidly varying functions of \( r \), it is preferable to tabulate or plot equivalent nuclear charges, \( z_i(r) \) of Eq. (69), for each orbital. This is the negative charge at the nucleus which would produce the same potential, \( v_i(r) \), at \( r \) as the static charge distribution of an electron in the \( i \)th orbital. Thus, for the 1s²2s²2p configuration the total potential of the neutral atom at \( r \)
is given in terms of $Z$ and the $z_1(r)$'s by Eq. (72) and the Hartree-like potential for the $i$th electron is obtained from Eq. (76). Thus the $z_1(r)$'s may be regarded as generalized screening parameters dependent on $r$.

The equivalent nuclear charges or screening parameters, $z_1(r)$, have been computed from Eqs. (68) and (69) and the values of the radial probability densities $f_1^2(r)$. For the Hartree and Hartree-Fock orbitals all values of the latter given in the original papers were utilized and the integrals in Eq. (68) were evaluated numerically using Simpson's rule. The second-order correction to Simpson's rule was evaluated in selected cases and shown to be negligible compared to the uncertainties in the tabulated values. It was necessary to re-evaluate the potentials in this way because they are not reproduced in the papers of Brown et al.\textsuperscript{35} and Glembotskii et al.\textsuperscript{40} For the Slater-type orbitals the integrals in Eq. (68) were evaluated analytically. The equivalent nuclear charges, $z_1(r)$, for an electron in $1s$, $2s$, and $2p$ orbitals of the $1s^22s^22p$ configuration of boron are given in Tables 30, 31, and 32, and plotted in Figures 10, 11, and 12, respectively. They vary from 0 at $r = 0$ to -1 at $r = \infty$. The differences in the values of $z_1(r)$ as calculated from the Hartree, Hartree-Fock, and Slater-type orbitals will not be elaborated upon but are reflections of the differences in the probability densities as discussed in the preceding sections. However, it should be noted that the entire electron charge distribution for an electron contributes to $v_1(r)$ and $z_1(r)$ for each value of $r$, not just that part of the charge lying within the sphere of radius $r$ (see section 7.24). Thus, there is not necessarily a simple correlation of the
TABLE 30. Equivalent Nuclear Charge \(-z_{ls}\) or Screening Parameter for a Single Electron in the 1s Subshell of the Boron Atom (Unit Charge Equals \(-e\))

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TABLE 31. Equivalent Nuclear Charge-\(z_{2s}\), or Screening Parameter for a Single Electron in the 2s Subshell of the Boron Atom (Unit Charge Equals - e)

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TABLE 32. Equivalent Nuclear Charge $-\frac{e}{2p^3}$ or Screening Parameter for a Single Electron in the 2p Subshell of the Boron Atom
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FIGURE 10

EQUIVALENT NUCLEAR CHARGE, OR SCREENING PARAMETER, FOR A SINGLE ELECTRON IN THE 1S SUBSHELL OF THE BORON ATOM
Figure 11: Equivalent nuclear charge, or screening parameter, for a single electron in the 2s subshell of the boron atom.
FIGURE 12  EQUIVALENT NUCLEAR CHARGE, OR SCREENING PARAMETER, FOR A SINGLE ELECTRON IN THE 2P ORBITAL OF THE BORON ATOM.
differences in $z_1(r)$ with the differences in probability density for the three kinds of orbitals.

### 7.53 Total Effective Nuclear Charge

The total effective nuclear charge $Z_{at}$ as defined by Eq. (72) is the charge at the nucleus which would (in the absence of the electrons) produce the same value of the potential at $r$ as actually exists in the neutral atom. This is the potential which would act on an infinitesimal added test charge, and not the potential in which the individual electrons move. The latter potential is obtained in the Hartree approximation by subtracting from $Z_{at}$ the equivalent nuclear, $z_1(r)$, of the given electron as discussed in the preceding section. The values of $Z_{at}$ are given in Table 33 and plotted in Figure 13.

The Hartree-Fock values of $Z_{at}$ given for configuration $1s^22s^22p$ are for the unperturbed configuration, and those for the perturbing $1s^22p^3$ configuration represent a correction function to be added with appropriate weight to the former values to correct for configuration interaction. These two values of $Z_{at}$ correspond to $Z_1(r)$ and $Z_2(r)$ of Eqs. (113) and (114), respectively. The weighted average value of $Z_{at}$ as computed from Eq. (112), and the corresponding weighted total electron probability density, $W(r)$, as given by Eqs. (109-111), are given in Table 34. The value used for $a_{12}$ is that given in Eq. (107). The values of these functions given by Glembotskii, et al. are shown for comparison. The agreement is satisfactory and may be regarded as a verification of the reconstruction of their potentials by numerical integration of the probability densities in the present investigation.
TABLE 33. Total Effective Nuclear Charge, $Z_{at}$ for the Boron Atom

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FIGURE 13  TOTAL EFFECTIVE NUCLEAR CHARGE, $Z_{at}$, FOR THE BORON ATOM
TABLE 34. Total Probability Density and Effective Nuclear Charge of the Boron Atom in the Two-Configuration Approximation

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Chapter 8. Density Matrix Formulation of Hartree-Fock

Self-consistent Field Molecular Orbital Theory

8.1 Introduction

The secular equation for α-rhombohedral boron in the LCAO or tight-binding approximation has been formulated in Chapter 6 in terms of the standard integrals given in Eqs. (36a-d). These integrals are all of the form

\[ \langle \eta_i | H | \eta_j \rangle = \int \eta_i^* H \eta_j \, d\tau, \quad (136) \]

where \( \eta_i \) and \( \eta_j \) are selected from properly oriented atomic orbitals of type 2s, 2p\( \sigma \), 2p\( \pi \), or 2p\( \pi^* \) for the \( i \)th and \( j \)th atoms, and \( H \) is an effective one-electron Hamiltonian operator yet to be described (in Chapter 6 the integral in Eq. (136) was denoted by \( \langle \eta_i^* | H | \eta_j \rangle \) but hereafter the conventional practice of not indicating explicitly the complex conjugation of atomic orbitals or wave functions in the symbol for a matrix element or integral will be followed). The various approximations for the atomic orbitals of boron have been considered and critically compared in Chapter 7, and the conclusion reached that the Slater-type orbitals are reasonably good approximations to the more accurate Hartree-Fock (or Hartree) functions. The Slater-type orbitals described in Section 7.4 will be used for the numerical calculations of the present investigation because of the availability of complete tabulations of the required integrals.
It is clear that the analysis up to this point is somewhat formal because of the complete lack of specification of the form of the effective one-electron Hamiltonian, $H$. The development up to this point is equivalent to that of the naive or semi-empirical version of molecular orbital theory, or to the interpolation method of Slater and Koster (in fact a modified version of their formalism has been used in Chapter 6). As is well known, in semi-empirical molecular orbital theory the problem of finding an effective one-electron Hamiltonian and evaluating therefrom the integrals of Eq. (136) is avoided by simply treating these integrals (called Coulomb integrals for $i = j$ and resonance integrals for $i \neq j$) as adjustable parameters at the end of the calculation. Usually the resonance integrals are assumed to be proportional to the corresponding overlap integrals,

$$\langle \eta_i | H | \eta_j \rangle = k S_{i,j}^* (i \neq j), \quad (137)$$

$$S_{i,j} = \langle \eta_i \mid \eta_j \rangle = \int \eta_i^* \eta_j \, d\tau. \quad (138)$$

Since the integrals $S_{i,j}$ are readily evaluated the calculation of the resonance integrals is reduced to the determination of a single parameter $k$. This is, for example, the procedure used by Longuet-Higgins and Roberts in their molecular orbital theory of an isolated boron dodecahedron discussed in Section 2.2. This procedure is, of course, quite empirical and unsatisfactory from a fundamental viewpoint, hence the description of this approach as naive or semi-empirical.

In considering possible procedures for carrying out such calculations on a reasonably absolute basis, it should be noted that the Hartree and Hartree-Fock methods provide such a basis for the calculation of
atomic energy states and wave functions as discussed in Chapter 7. The Hartree-Fock method is the more accurate of the two because it makes use of a properly anti-symmetrized many-electron wave function, and further improvement in accuracy may be obtained by considering configurational interaction. Obviously there is no difficulty in principle in extending the Hartree or Hartree-Fock methods to molecules or even to crystals, but without additional approximations the calculations become enormously more difficult because of the loss of spherical symmetry. In order to make the calculation practicable it is virtually necessary to use atomic orbitals evaluated for a central field, e.g., Slater, Hartree, or Hartree-Fock atomic orbitals, and to regard these orbitals as fixed throughout the molecular orbital calculation. In the so-called LCAO methods the molecular orbitals are represented as linear combinations of the atomic orbitals. The problem is then reduced to the adjustment of the constant coefficients in the linear combinations defining the occupied molecular orbitals so as to minimize the ground-state energy in accordance with the variation theorem.

In the approximation analogous to that of Hartree for atoms (see Section 7.1) the complete wave function for the molecule is assumed to be a simple product of occupied molecular orbitals. If the existence of a formal but unspecified one-electron Hamiltonian $H$ is assumed, the minimization procedure then leads to the secular equation of naive molecular orbital theory involving integrals of the type in Eq. (136), with the difficulties discussed above. It is also possible to carry out the Hartree calculation using a product-type wave function and the true
many-electron Hamiltonian for the entire system. This Hamiltonian is
easily written down, and is the sum of (i) the kinetic energy operator
for each electron, (ii) the attractive Coulomb potential between each
electron and each nucleus, and (iii) the repulsive Coulomb potential
between each pair of electrons. This calculation yields a set of equa-
tions similar to Hartree's equation for an atom. It will be recalled
that in the latter case the effective potential in which a single elec-
tron is found to move is that of the atomic nucleus and the total mean
electron charge density, less the field produced by the charge of one
electron distributed over the atomic orbital occupied by the given
electron with a density proportional to the squared amplitude of that
orbital. This charge which is removed or subtracted in calculating the
potential for a given electron may be called the self-charge, and is the
Hartree approximation to the "Fermi hole" which represents the decreased
probability of other electrons occurring in the near vicinity of a given
electron.

The analogous procedure in the molecular case leads to an effec-
tive one-electron potential for an electron in a given molecular orbital
corresponding to the subtraction from the field of the nuclei and total
mean electron charge density the field produced by the charge of one
electron distributed over the given molecular orbital with a density
proportional to the squared amplitude of the latter. Because of the
extended form of most molecular orbitals the self-charge or Fermi hole
becomes diffuse or delocalized, rather than being localized as in the
atomic case. It is clear that in a large molecule the hole essentially
disappears, and that it vanishes completely in the case of an (infinite)
crystal in which the molecular orbital becomes a Bloch wave function extending over the entire crystal. In such cases the Hartree method becomes unrealistic because each electron moves effectively in the field of the nuclei and of the total electron charge. As a result, when the electron is near a given atom, the field is that of a neutral atom rather than a singly-charged ion as it should be. It is essentially for this reason that the unmodified Hartree method is not useful for molecules and crystals.

Slater\(^{54}\) has emphasized the fact that the difficulty associated with the delocalization of the Fermi hole in the Hartree method no longer exists in the application to an extended system of the Hartree-Fock method, in which the wave function is a properly anti-symmetrized product of occupied molecular orbitals. The exchange terms obtained correspond to the introduction of a Fermi hole which is largely localized in the vicinity of the given electron and moves about as it moves (this is important, as the electron still generally occupies a delocalized molecular orbital or Bloch wave function). The "shape" or distribution of the charge in the Fermi hole varies somewhat as the electron moves about and is also dependent on the molecular orbital occupied by the electron. Slater has proposed a simplified hole for electrons in crystals (especially metals) which is averaged over all occupied molecular orbitals but still depends on the mean charge density at the position of the electron. Slater's method yields differential equations for the wave functions (molecular orbitals or Bloch functions) occupied by the electrons. As they stand they are suitable for application to systems in which a method is available for evaluating the one-electron wave
functions by solution of the differential equations, without resort to their expansion in terms of a fixed set of basis functions such as is used in the LCAO approximation. However, Slater's results suggest that the extension of the Hartree-Fock method to molecules in the LCAO approximation, or to crystals in the analogous tight-binding approximation, should also remove the difficulty associated with the delocalization of the Fermi hole.

The successful adaptation of the self-consistent field Hartree-Fock method to molecular orbital theory in the LCAO approximation was accomplished by Roothaan in a paper which has now become a classic in its field (Roothaan's original paper considered only singlet or closed-shell systems but the method has been extended to open shells by Roothaan and Hazinaga). In Roothaan's method the differential equations of the general Hartree-Fock theory are replaced by a matrix eigenvalue equation, as would be expected for the LCAO approximation used. The roots of the associated secular equation represent the "energies" of the molecular orbitals (although as will be made clear later the total energy of the many-electron system is not simply the sum of these energy parameters for the occupied molecular orbitals). The eigenvector of the matrix equation associated with a given root has as its components the coefficients of the basis functions (atomic orbitals) in the corresponding molecular orbital. Roothaan's matrix is a representation of the Hartree-Fock operator and differs from the matrix representing the Hamiltonian in the naive theory in the fact that the matrix elements depend on the form of the occupied molecular orbitals, or the corresponding eigenvectors. The solution must satisfy a self-consistency condition
according to which the eigenvectors corresponding to the occupied orbitals yield the Hartree-Fock matrix of which they are eigenvectors.

A few years prior to Roothaan's development of the LCAO Hartree-Fock molecular orbital theory, Coulson and Longuet-Higgins had made a number of refinements in semi-empirical molecular orbital theory, especially for conjugated systems. In particular they had introduced the concept of atom charge density and bond order parameters represented by certain sums over binary products of the coefficients in the LCAO molecular orbitals (as well as certain derivatives of these quantities called mutual polarizabilities of two atoms or of a bond and atom). Lowdin subsequently formulated the Hartree-Fock expression for the energy of an ionic crystal in terms of equivalent charge and bond order parameters. However, Lowdin's formulation was for relatively simple crystals such as the alkali halides, for which the form of the Bloch functions is completely determined by the symmetry of the crystal, and he did not therefore need to use the Hartree-Fock operator in the LCAO approximation (see footnote 7a of Lowdin's first paper).

Shortly after the publication of Roothaan's paper in 1951 it was pointed out by Taylor that not only the expression for the total energy but also the elements of Roothaan's Hartree-Fock matrix operator could be concisely expressed in terms of Coulson and Longuet-Higgins' charge and bond order parameters. Moreover, Taylor pointed out the close relation of these parameters to the expression for the Dirac density matrix in the LCAO approximation, including the idempotent property of the density matrix, as indicated by the title of his note, "Density Matrix Formulation of LCAO Molecular Orbital Theory." Although
very brief, this communication contains all the essential equations of
the density matrix formulation for the closed-shell case. Subsequently,
and apparently independently, the density matrix formulation of Hartree-
Fock self-consistent field molecular orbital theory, including the LCAO
approximation, has been developed in great detail by Lowdin, McWeeny, and Chirgwin.

For the purposes of the present investigation the concise formulation of the final equations presented by Taylor is entirely sufficient,
and in fact more convenient than the more elaborate presentations by
later authors. The remainder of this chapter presents an expanded
version of the density matrix form of the theory as given by Taylor, including derivations and discussion omitted there, and is based on
unpublished notes of this author. In order to obtain greater generality
a discussion of the generalized density matrices introduced by Lowdin
are also included.

8.2 Atomic and Molecular Orbitals

In the present discussion based on the LCAO or tight-binding
approximation it is assumed that the molecular orbitals in a molecule,
or the occupied wave functions in a solid, may be approximated as linear
combinations of a selected set of atomic orbitals for the atoms in the
system. In the subsequent application of the method it will be desirable
to introduce indices indicating the atom on which an orbital is located
and also the particular orbital of that atom. However, in the present
section it will be sufficient to indicate the atomic orbitals by a
single index, as \( \chi_\alpha = \chi_\alpha (r) \), where \( \alpha = 1, 2, \ldots, \nu \). Of course
the total number of atomic orbitals, \( \nu \), may be extremely large in crystal, but this does not affect the formal development in this section. The molecular orbitals may then be represented as

\[
\phi_i(r) = \sum_{\alpha=1}^{\nu} c_{\alpha i} \chi_\alpha(r), \quad (i = 1, 2, \ldots, n),
\]

(139)

where the \( c_{\alpha i} \) are constant coefficients to be determined. Hereafter, to avoid constant repetition, the \( \phi_i \)'s will be referred to as molecular orbitals unless the case of crystal wave functions is being considered explicitly. The number of occupied molecular orbitals in the ground state of the system is denoted by \( n \). It is possible to form \( \nu \) linearly independent linear combinations of the \( \nu \) atomic orbitals, of the type indicated in Eq. (139). However, in a stable system only a certain fraction of these will be occupied in the ground state of the system. The occupied molecular orbitals will correspond to the \( n \) eigenvectors of the secular equation having the lowest energy. The remaining \( \nu - n \) eigenvectors are of some interest as approximations to excited molecular orbitals\(^6\) but do not enter into the formulation of the secular equation itself in Roothaan's LCAO self-consistent field method.

The condition imposed by orthogonality of the molecular orbitals, \( \phi_i \), will next be considered. This condition may be formulated as

\[
\int \phi_i^*(\vec{r}) \phi_j(\vec{r}) \, d\vec{r} = \delta_{ij},
\]

(140)

where \( \delta_{ij} \) is the Kronecker delta. Substitution of Eq. (139) in Eq. (140) yields

\[
\sum_{\alpha=1}^{\nu} c_{\alpha i}^* S_{\alpha \beta} c_{\beta j} = \delta_{ij}, \quad (i, j = 1, 2, \ldots, n),
\]

(141)
where \( S_{\alpha\beta} \) is the overlap integral for the \( \alpha \)th and \( \beta \)th atomic orbitals,

\[
S_{\alpha\beta} = \int \chi_\alpha^*(\vec{r}) \chi_\beta(\vec{r}) \, d\vec{r} \quad (142)
\]

The atomic orbitals are assumed to be normalized, so that \( S_{\alpha\alpha} = 1 \), but are not necessarily orthogonal to one another so that in general \( S_{\alpha\beta} \neq 0 \) (\( \alpha \neq \beta \)). The range of integration in Eq. (140) requires some discussion. The atomic orbitals, \( \chi_\alpha \), decrease sufficiently rapidly with \( |\vec{r}| \) so that the normalization integral of Eq. (142) (for the case \( \alpha = \beta \)) converges when extended to infinity, and it is understood that the atomic orbitals are normalized over the infinite range. It is clear from the form of the molecular orbitals of Eq. (139) that the same situation prevails for the molecular orbitals of a molecule containing a finite number of atoms. The normalization integral in Eq. (140) then also extends over the infinite range of \( \vec{r} \). However, the latter integrals would diverge for an infinite periodic crystal if treated in this way.

This difficulty may be overcome by assuming a cyclic lattice of the type introduced by Born and von Karman in connection with lattice vibrations. The range of integration of the integrals in Eq. (140) may then be restricted to a single "block" of this cyclic lattice, so that an unambiguous normalization of the molecular orbitals is obtained. Moreover, if this block is sufficiently large the range of integration in Eq. (142) may still be regarded as extending to infinity because of the rapid fall off of the atomic orbitals with increasing \( |\vec{r}| \).

The overlap matrix, \( (S) \), for the atomic orbitals is defined as the square Hermitian matrix having \( S_{\alpha\beta} \) as the element in its \( \alpha \)th row.
and \( \beta \) th column. If \( z_1, z_2, \ldots, z_\nu \) are \( \nu \) arbitrary complex numbers, not all of which vanish, then

\[
\int \left| \sum_{\alpha=1}^\nu z_\alpha \chi_\alpha (\mathbf{r}) \right|^2 d\mathbf{r} = \sum_{\alpha=1}^\nu S_{\alpha\beta} Z_\alpha^* Z_\beta = 0, \tag{143}
\]

since the \( \nu \) atomic orbitals are linearly independent and the relation

\[
\sum_{\alpha=1}^\nu z_\alpha \chi_\alpha (\mathbf{r}) = 0, \tag{144}
\]

cannot be satisfied for all \( \mathbf{r} \). It follows from Eq. (143) that \( (S) \) is positive-definite as well as Hermitian, so that all its roots are real and positive. This is of interest in connection with the diagonalization of \( (S) \) and the solution of the secular equation.

The molecular orbital \( \psi_i (\mathbf{r}) \) of Eq. (139) describes only the spatial coordinates \( \mathbf{r}_i = (x_i, y_i, z_i) \) of the \( i \) th electron. To obtain a complete description the molecular orbital must be multiplied by a spin orbital \( \sigma_i (s) \), where \( s \) is the spin coordinate of the \( i \) th electron, and \( \sigma_i (s) \) is an eigenfunction of the operator representing the \( z \)-component of the angular momentum of an electron. Only two such eigenfunctions, \( \sigma_+ (s) \) and \( \sigma_- (s) \) exist, corresponding to the eigenvalues 1/2 and -1/2, respectively, for the \( z \)-component of angular momentum (in units of \( h/2\pi \)). These two functions are necessarily orthogonal, and are assumed to be normalized, so that

\[
\int \sigma_+^* \sigma_+ d s = \int \sigma_-^* \sigma_- d s = 1, \tag{145}
\]
\[
\int \sigma_+^* \sigma_- d s = 0 \tag{146}
\]
The product $\phi^{(s^+)}_1 (\mathbf{r}_1^+) \sigma^+ (s_1)$ is referred to as a molecular spinorbital.

8.3 Hartree-Fock Wave Function for a Single Configuration of the Many-Electron System

The general wave function for an N-electron system will be represented by

$$\psi = \psi (\mathbf{r}_1, \ldots, \mathbf{r}_N; s_1, \ldots, s_N).$$

(147)

The antisymmetry principle for elementary physical particles requires that

$$P \psi = (-1)^P \psi,$$

(148)

where $P$ is an arbitrary permutation of the $N$ electrons and $p$ is the parity of $P$. In the Hartree approximation the wave function for the system is formed as a simple product of molecular spinorbitals, but such a function fails to satisfy the requirement of antisymmetry. A function satisfying Eq. (148) is provided by the antisymmetrized product

$$\Phi = (N!)^{-\frac{1}{2}} \sum_P (-1)^P \phi_1 (\mathbf{r}_1^+) \sigma_1 (s_1) \phi_2 (\mathbf{r}_2^+) \sigma_2 (s_2) \cdots$$

$$\phi_N (\mathbf{r}_N^+) \sigma_N (s_N),$$

(149)

where $P$ operates on the spatial and spin coordinates of the electrons and the sum extends over the $N!$ permutations of the symmetric group on $N$ objects. If the permutations of this group are represented by the set $\{P\}_N$, then $\{P'P\}_N$ with $P'$ an arbitrary member of the group represents simply an inconsequential reordering of the set $\{P\}$. Furthermore the parity of $P'P$ is $p' + p$. It follows that

$$P' \Phi = (-1)^{P'} \Phi,$$

(150)
as stated. In view of the definition of a determinant, \( \nu \) may also be written in the form due to Slater,

\[
\Phi = (\text{det})^{-\frac{1}{2}} \begin{vmatrix}
\phi_1(\vec{r}_1) \sigma_1^1(s_1) & \phi_2(\vec{r}_1) \sigma_2^1(s_1) & \cdots & \phi_N(\vec{r}_1) \sigma_N^1(s_1) \\
\phi_1(\vec{r}_2) \sigma_1^2(s_2) & \phi_2(\vec{r}_2) \sigma_2^2(s_2) & \cdots & \phi_N(\vec{r}_2) \sigma_N^2(s_2) \\
\phi_1(\vec{r}_N) \sigma_1^N(s_N) & \phi_2(\vec{r}_N) \sigma_2^N(s_N) & \cdots & \phi_N(\vec{r}_N) \sigma_N^N(s_N)
\end{vmatrix}
\]

(151)

from which it is clear that \( \Phi \) vanishes identically if any two of the molecular spinorbitals are identical. From this fact and Eqs. (140), (145) and (146) it follows that

\[
\int \cdots \int \Phi^* \Phi \ d\vec{r}_1 \ d s_1 \cdots d\vec{r}_n \ d s_n \\
= (\text{det})^{-1} \int \cdots \int \left\{ \sum_{\mathbf{P}, \mathbf{L}} (-1)^{\mathbf{P} \cdot \mathbf{L}} \ \phi^*_1 \sigma_1^1 \cdots \phi^*_N \sigma_N^1 \right\} \\
\left\{ \sum_{\mathbf{P}} (-1)^{\mathbf{P}} \ \phi_1 \sigma_1 \cdots \phi_N \sigma_N \right\} \ d\vec{r} \ d s \\
= (\text{det})^{-1} \int \cdots \int \left\{ \sum_{\mathbf{P}} \ |\phi_1 \sigma_1|^2 \cdots |\phi_N \sigma_N|^2 \right\} \ d\vec{r} \ d s \\
= 1,
\]

(152)

where \( d\vec{r} \ d s = d\vec{r}_1 \cdots d\vec{r}_N \ d s_1 \cdots d s_N \). Thus, \( \Phi \) of Eq. (149) or (151) is normalized.

A single antisymmetrized product of the form in Eq. (149) or (151), with a particular assignment of molecular spinorbitals to each electron, represents a single configuration of the system. In general the wave function for the entire system may be represented as a linear combination of antisymmetrized products for a finite (or infinite) number of configurations (corresponding to configuration interaction or
superposition). However, the present discussion is restricted for the most part to the case in which the ground state is represented by a single closed-shell configuration. In this case each of the molecular orbitals, \( \phi_1 \) in Eq. (149) or (151) occurs twice, once with the spin function \( \sigma_+ \) and once with \( \sigma_- \). Furthermore, the number of electrons is then twice the number of orbitals, or \( N = 2n \). Thus, the wave function of the system has the form

\[
\Psi = [(2n)!]^{-1/2} \sum \frac{(-1)^P}{P!} \phi_1 \sigma_+ \phi_1 \sigma_- \phi_2 \sigma_+ \phi_2 \sigma_- \cdots \phi_n \sigma_- \tag{153}
\]

8.4 Hamiltonian Operator and Energy for the Many-Electron System

In general the Hamiltonian operator for a system of many particles will be of the form

\[
H = H_0 + \sum_{i=1}^{N} H_i + \sum_{i=1}^{N} \sum_{j=1}^{i-1} H_{ij}, \tag{154}
\]

where \( H_0 \) is independent of the coordinates or momenta of the particles under consideration, \( H_i \) depends on the coordinates or momenta of the \( i \) th particle only, \( H_{ij} \) on the coordinates and momenta of the \( i \) th and \( j \) th particles, etc. A similar analysis may be made of other operators of physical interest, for example, those representing orbital angular momentum or spin. For systems of fundamental particles which interact through pair forces, there appears to be no need at present for considering terms such as \( H_{ijk} \) involving the coordinates or momenta of three or more particles. In the present application to many-electron systems such as molecules or crystals it is assumed that the separation of the motion of the atomic nuclei and the electrons has been effected by the
Born-Oppenheimer method. The equilibrium nuclear coordinates then enter the problem of electron motion simply as parameters which determine a constant term in the energy (or $H_0$), as well as determining the fixed part of the potential field in which the electrons move. Thus,

$$H_0 = \sum_{a,b} \frac{Z_a Z_b}{r_{ab}}, \quad (155)$$

where $Z_a$ and $Z_b$ are the atomic numbers of the $a$th and $b$th nuclei, and $r_{ab}$ the distance separating them.

The one-electron term, $H_1$, is the sum of operators representing the kinetic energy and the potential field arising from the nuclei,

$$H_1 = -(1/2) \nabla_i^2 + \sum_a \frac{Z_a}{r_{ai}}. \quad (156)$$

Here $\nabla_i^2$ is the Laplacian operator in the coordinates of the $i$th electron, $r_{ai}$ is the distance from the $a$th nucleus to the $i$th electron, and the sum extends over all nuclei. Finally, the Coulomb interaction of the $i$th and $j$th electrons is represented by the term

$$H_{ij} = \frac{1}{r_{ij}}. \quad (157)$$

where $r_{ij}$ is the distance between this pair of electrons. Equations (155) to (157) have been written in the form they take with atomic units, in which the mass and charge of the electron are unity, and the unit of distance is the Bohr radius, $a_0$, of the hydrogen atom. In addition, all spin-orbit or spin-spin terms in the Hamiltonian are ignored in the approximation considered here.
If the many-electron system is represented by the wave function \( \psi \) of Eq. (147), then according to a fundamental axiom of quantum mechanics its energy is given by

\[
E = \frac{\int \cdots \int \psi^* \mathcal{H} \psi \, d\mathbf{r} \, d\mathbf{s}}{\int \cdots \int \psi^* \psi \, d\mathbf{r} \, d\mathbf{s}}
\]  
(158)

The true or exact wave function for a stationary state is necessarily an eigenfunction of the (exact) Hamiltonian operator \( \mathcal{H} \), and \( E \) as calculated from Eq. (158) will then be the corresponding eigenvalue of \( \mathcal{H} \). On the other hand, if \( \psi \) is an approximate wave function which is not an eigenfunction of \( \mathcal{H} \), Eq. (158) still yields the mean value of the energy for this state. According to the variation theorem the best approximation of a given type to the ground-state energy and wave function is obtained by minimizing the energy \( E \) as calculated from Eq. (158). This is, in fact, the general procedure by which the Hartree-Fock differential equations of atomic or molecular orbital theory are derived. That is, \( \psi \) in Eq. (158) is approximated by a single determinantal wave function of the form given in Eq. (151), and the condition that \( E \) be a minimum, or \( \delta E = 0 \), then leads to simultaneous integro-differential equations determining the orbitals, \( \phi_1, \ldots, \phi_N \).

The Hartree-Fock equations were originally derived for the atomic case by Fock and Slater, and their application to the calculation of molecular orbitals has been discussed by Roothaan. The Hartree-Fock equations are formally identical for the atomic and molecular cases if the molecular orbitals are left in a general form, but the numerical integration of the equations is not practicable in the latter case.
because of the loss of spherical symmetry. Roothaan therefore specialized the equations to the form they take in the LCAO approximation in which the molecular orbitals are represented as linear combinations of a fixed set of atomic orbitals, as in Eq. (139). The general integro-differential Hartree-Fock equations then reduce to a matrix eigenvalue equation for the calculation of the expansion coefficients $c_{\alpha_1}$ of Eq. (139). However, instead of duplicating Roothaan's analysis based on the specialization of the Hartree-Fock equations to the LCAO approximation, the present discussion will be based on an equivalent procedure first proposed by Taylor\footnote{Taylor.} and studied in detail by McWeeny.\footnote{McWeeny.} In this procedure the expression for the energy is obtained in LCAO form prior to its minimization, thus leading directly to the matrix equations of Roothaan without the necessity for his rather cumbersome reduction of the Hartree-Fock equations. This procedure is also adapted to the density matrix approach which it is desired to emphasize.

It can be assumed without loss of generality that the wave function, $\psi$, in Eq. (158) is normalized,

$$ \int \cdots \int \psi^* \psi \, d \mathbf{r}_1 \cdots d \mathbf{r}_N \, d s_1 \cdots d s_N $$

as the equivalent condition will be imposed subsequently on the elements of the density matrix. Substitution of Eq. (154) for $\mathbf{H}$ into Eq. (158) and use of Eq. (159) now yields

$$ E = E_0 + E_1 + E_2, $$

where

$$ E_0 = \int \cdots \int \psi^* \mathbf{H}_0 \psi \, d \mathbf{r} \, d s = \mathbf{H}_0, $$

(161)
(since \( H_0 \) is independent of the electron coordinates and momenta) and

\[
E_1 = \sum_{i=1}^{N} \int \ldots \int \psi^* H_i \psi \, d\mathbf{r} \, d\mathbf{s}, \quad (162)
\]

\[
E_2 = \sum_{i=1}^{N} \sum_{j=1}^{i-1} \int \ldots \int \psi^* H_{ij} \psi \, d\mathbf{r} \, d\mathbf{s}. \quad (163)
\]

Because of the identity of the \( N \) electrons, the Hamiltonian of the system, \( H \) of Eq. (154), is invariant to an arbitrary permutation of the electron coordinates and momenta. Thus, \( H_i \) and \( H_{ij} \) are the same functions of the coordinates and momenta of the \( i \)th and \( j \)th electrons that \( H_1 \) and \( H_{12} \) are of those of electrons 1 and 2, respectively (this is of course also clear from Eqs. (156) and (157)). Therefore, if \( P \) is a general permutation of the symmetric group of order \( N! \) on the \( N \) electrons, \( E_1 \) and \( E_2 \) can be represented as

\[
E_1 = \frac{1}{(N-1)!} \sum_{P} \int \ldots \int \psi^* (P H_1) \psi \, d\mathbf{r} \, d\mathbf{s}
\]

\[
= \frac{1}{(N-1)!} \sum_{P} \int \ldots \int (P^{-1} \psi)^* H_1 (P^{-1} \psi) \, d\mathbf{r} \, d\mathbf{s}
\]

\[
= N \int \ldots \int \psi^* H_1 \psi \, d\mathbf{r} \, d\mathbf{s}, \quad (164)
\]

\[
E_2 = \frac{1}{21 (N-2)!} \sum_{P} \int \ldots \int \psi^* (P H_{12}) \psi \, d\mathbf{r} \, d\mathbf{s}
\]

\[
= \frac{1}{21 (N-2)!} \sum_{P} \int \ldots \int (P^{-1} \psi)^* H_{12} (P^{-1} \psi) \, d\mathbf{r} \, d\mathbf{s}
\]

\[
= \binom{N}{2} \int \ldots \int \psi^* H_{12} \psi \, d\mathbf{r} \, d\mathbf{s}, \quad (165)
\]

in view of Eq. (148).
8.5 Density Matrix Formulation of Molecular Orbital Theory

8.51 General Formulation of Density Matrices

Equations (164) and (165), or the analogous equations for the mean values of other one- and two-electron operators, suggest the utility of introducing quantum-mechanical density matrices. Such matrices were first introduced by Fock\textsuperscript{42} and Dirac\textsuperscript{75} for wave functions of the Hartree-Fock type of Eq. (151). The original discussions of these authors provided the basis for the first density matrix formulation of LCAO molecular orbital theory by Taylor,\textsuperscript{71} and is sufficient for the present investigation. However, Lowdin\textsuperscript{72} has subsequently given a generalized discussion of density matrices, particularly with regard to the matrices of higher order, which provides greater insight into their significance and properties. We will therefore follow Lowdin in defining the generalized density matrices of successive orders.

\[ \rho_2 (\vec{r}_1, s_1, \vec{r}_2, s_2; \vec{r}_1', s_1', \vec{r}_2', s_2') = \binom{N}{2} \int \cdots \int \psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; s_1, s_2, \cdots, s_N) \times \psi^*(\vec{r}_1', \vec{r}_2', \cdots, \vec{r}_N; s_1', s_2', \cdots, s_N) (d \vec{r}_1) (d s_1) (d \vec{r}_2) (d s_2), \]  

(166)

\[ \rho_m (\vec{r}_1, s_1, \cdots, \vec{r}_m, s_m; \vec{r}_1', s_1', \cdots, \vec{r}_m', s_m') = \binom{N}{m} \int \cdots \int \psi(\vec{r}_1, \cdots, \vec{r}_m, \vec{r}_{m+1}, \cdots, \vec{r}_N; s_1, \cdots, s_m) \]  

(167)
where \( (d r)^I_{1...m} = d r_{m+1} \ldots d r_N \) and \( (d s)^I_{1...m} = d s_{m+1} \ldots d s_N \),

and

\[
\begin{align*}
\rho_N(r_1 s_1, \ldots, r_N s_N; r'_1 s'_1, \ldots, r'_N s'_N) & = \psi(r'_1, \ldots, r'_N; s_1, \ldots, s_N) \psi^*(r_1, \ldots, r_N; s'_1, \ldots, s'_N).
\end{align*}
\]

(169)

The first-order density matrix, \( \rho_1 \), was denoted by \( \rho \) by Fock and Dirac, and as \( \gamma \) by Lowdin; the latter designates \( \rho_m \) as \( \gamma^m \) for \( m \geq 2 \). The following obvious recursion relation exists between each pair of density matrices of successive orders.

\[
\begin{align*}
\rho_{m-1}(r_1 s_1, \ldots, r_{m-1} s_{m-1}; r'_1 s'_1, \ldots, r'_{m-1} s'_{m-1}) &= \left( \frac{m}{N-m+1} \right) \int \rho_m(r_1 s_1, \ldots, r_{m-1} s_{m-1}; r_m s_m; r'_1 s'_1, \ldots, r'_{m-1} s'_{m-1}, r_m s_m) \, d r_m d s_m.
\end{align*}
\]

(170)

The density matrices are Hermitian,

\[
\begin{align*}
\rho_m(r_1 s_1, \ldots, r_m s_m; r'_1 s'_1, \ldots, r'_m s'_m) = \rho_m^*(r'_1 s'_1, \ldots, r'_m s'_m; r_1 s_1, \ldots, r_m s_m).
\end{align*}
\]

(171)

They are also antisymmetric in each set of indices separately. That is \( \rho_m \) is changed in sign by an interchange of any two of the space-spin coordinate pairs \( r_1 s_1, \ldots, r_m s_m \), and similarly for \( r'_1 s'_1, \ldots, r'_m s'_m \). These results follow directly from Eqs. (148) and (168).
The diagonal elements of the density matrix may be denoted by the condensed notation

$$\rho_m (\vec{r}_1 s_1, \ldots, \vec{r}_m s_m) = \rho_m (\vec{r}_1 s_1, \ldots, \vec{r}_m s_m; \vec{r}_1 s_1, \ldots, \vec{r}_m s_m).$$  

(172)

They are simply related to the distribution functions for the coordinates and spins of m-electron sets. Thus, from the fundamental hypothesis of Born regarding the interpretation of the Schrodinger wave function,

$$\rho_N (\vec{r}_1 s_1, \ldots, \vec{r}_N s_N) d \vec{r}_1 d s_1 \ldots d \vec{r}_N d s_N$$

$$= |\psi(\vec{r}_1, \ldots, \vec{r}_N; s_1, \ldots, s_N)|^2 d \vec{r}_1 d s_1 \ldots d \vec{r}_N d s_N (173)$$

is the probability that electrons 1 to N have simultaneously values for their coordinates in \(d \vec{r}_1, \ldots, d \vec{r}_N\) and spins in \(d s_1, \ldots, d s_N\), respectively. It follows immediately that

$$\rho_m (\vec{r}_1 s_1, \ldots, \vec{r}_m s_m) d \vec{r}_1 \ldots d \vec{r}_m d s_1 \ldots d s_m$$

$$= \binom{N}{m} d \vec{r}_1 \ldots d \vec{r}_m d s_1 \ldots d s_m \int \cdots \int |\psi|^2 (d \vec{r})_1 \ldots m$$

$$\left(d s\right)_1 \ldots m (174)$$

is the number of ways of selecting sets of m electrons multiplied by the probability that the electrons in any one of these sets will, when ordered from 1 to m, have simultaneously values for their coordinates in \(d \vec{r}_1, \ldots, d \vec{r}_m\) and spins in \(d s_1, \ldots, d s_m\), respectively, without regard to the values of the coordinates and spins for the remaining \(N-m\) electrons. We now define the m-electron distribution function (which was not introduced by Lowdin, but is the form given by Corson\footnote{\textsuperscript{77}} as follows

$$P_m (\vec{r}_1 s_1, \ldots, \vec{r}_m s_m) = m! \rho_m (\vec{r}_1 s_1, \ldots, \vec{r}_m s_m).$$  

(175)
Then

$$P_m (\mathbf{r}_1 s_1, \ldots, \mathbf{r}_m s_m) \ d \mathbf{r}_1 \ldots d \mathbf{r}_m d s_1 \ldots d s_m \quad (176)$$

is the probability that \( m \) electrons will have simultaneously the indicated values of coordinates and spins, without regard to the identity or ordering of these \( m \) electrons, or the values of the coordinates or spins for the remaining electrons. It is clear from Eqs. (148), (174), and (175) that \( \rho_m \) and \( P_m \) are invariant to an arbitrary permutation of the coordinates of electrons 1 to \( m \).

Aside from \( \rho_N = |\psi|^2 \), the density matrices \( \rho_1 \) and \( \rho_2 \) are of greatest importance.

$$\rho_1 (\mathbf{r}_1 s_1) \ d \mathbf{r}_1 d s_1 = N d \mathbf{r}_1 d s_1 \int \ldots \int |\psi|^2 (d \mathbf{r})^I_1 (d s)_1 \quad (177)$$

is the probability that one electron will occupy \( d \mathbf{r}_1 d s_1 \), without regard to the identity of this electron or the positions and spins of the remaining electrons. Clearly \( P_1 (\mathbf{r}_1 s_1) = \rho_1 (\mathbf{r}_1 s_1) \). The electron density in coordinate-spin space, or mean number of electrons per unit volume at \( \mathbf{r}_1 \) having spin in \( d s_1 \), is a physically important quantity. It will be denoted by \( \rho (\mathbf{r}_1 s_1) \), and is defined by the condition that

$$\rho (\mathbf{r}_1 s_1) \ d \mathbf{r}_1 d s_1 \quad (178)$$

be the mean number of electrons in \( d \mathbf{r}_1 d s_1 \). For vanishingly small \( d \mathbf{r}_1 \) the only possibilities which need to be considered are the occurrence of no electron or one electron in \( d \mathbf{r}_1 \), since the probability of occurrence of two electrons is of order \( (d \mathbf{r}_1)^2 \). It follows that the
expression (178) is also the probability of occurrence of one electron in \(d \mathbf{r}_1 \, d s_1\), so that
\[
\rho(\mathbf{r}_1 \, s_1) = \rho_{11}(\mathbf{r}_1 \, s_1) = P_1(\mathbf{r}_1 \, s_1)
\] (179)
and these three quantities are interchangeable.

From Eqs. (174) and (175),
\[
P_2(\mathbf{r}_1 \, s_1; \mathbf{r}_2 \, s_2) \, d \mathbf{r}_1 \, d \mathbf{r}_2 \, d s_1 \, d s_2
\]
\[
= 2 \rho_2(\mathbf{r}_1 \, s_1; \mathbf{r}_2 \, s_2) \, d \mathbf{r}_1 \, d \mathbf{r}_2 \, d s_1 \, d s_2
\]
\[
= N (N - 1) \, d \mathbf{r}_1 \, d \mathbf{r}_2 \, d s_1 \, d s_2 \int \ldots \int |\psi|^2 \, (d \mathbf{r})_{12} \, (d s)_{12}
\] (180)
is the probability that a pair of electrons will simultaneously occupy \(d \mathbf{r}_1 \, d s_1\) and \(d \mathbf{r}_2 \, d s_2\), without regard to the identity or ordering of these two electrons, or the positions or spins of the remaining electrons. As already indicated for the general case, \(P_2\) is symmetric to electron interchange.

There is also some interest attached to the conditional pair-distribution function, \(P_{12}\) such that \(P_{12} \, d \mathbf{r}_2 \, d s_2\) is the probability that an electron will occupy \(d \mathbf{r}_2 \, d s_2\) if another electron having spin in \(d s_1\) is known to be in \(d \mathbf{r}_1\). It is obvious that
\[
\rho(\mathbf{r}_1 \, s_1) \, d \mathbf{r}_1 \, d s_1 \, P_{12}(\mathbf{r}_1 \, s_1; \mathbf{r}_2 \, s_2) \, d \mathbf{r}_2 \, d s_2
\]
\[
= P_2(\mathbf{r}_1 \, s_1; \mathbf{r}_2 \, s_2) \, d \mathbf{r}_1 \, d \mathbf{r}_2 \, d s_1 \, d s_2,
\] (181)
since the left- and right-hand sides of this equation represent different ways of expressing the same probability. Therefore,
or, in view of Eqs. (172) and (175),

\[ P_{12} \left( \vec{r}_1 s_1; \vec{r}_2 s_2 \right) = (N - 1) \int \cdots \int \left| \psi \right|^2 \left( d \vec{r}_{12} \right) \left( d s \right)_{12} \]  

(183)

In general \( P_{12} \) is not symmetric,

\[ P_{12} \left( \vec{r}_1 s_1; \vec{r}_2 s_2 \right) \neq P_{12} \left( \vec{r}_2 s_2; \vec{r}_1 s_1 \right). \]  

(184)

Equations (182) and (183) have an important connection with the so-called Fermi hole. As has been stated previously, the density matrices of any order are antisymmetric in the primed and unprimed coordinates separately. In particular, for non-diagonal elements of \( \rho_2 \),

\[ \rho_2 \left( \vec{r}_2 s_2, \vec{r}_1 s_1; \vec{r}_1^i s_1^i, \vec{r}_2^i s_2^i \right) = - \rho_2 \left( \vec{r}_1 s_1, \vec{r}_2 s_2; \vec{r}_1^i s_1^i, \vec{r}_2^i s_2^i \right) \]  

(185)

and therefore the diagonal elements of \( \rho_2 \) vanish,

\[ \rho_2 \left( \vec{r}_1 s_1, \vec{r}_1 s_1 \right) = \rho_2 \left( \vec{r}_1 s_1, \vec{r}_1 s_1; \vec{r}_1 s_1, \vec{r}_1 s_1 \right) = 0. \]  

(186)

From Eqs. (182) and (186),

\[ P_{12} \left( \vec{r}_1 s_1, \vec{r}_1 s_1 \right) = 0 \]  

(187)

so that if an electron with spin in \( d s_1 \) is at \( \vec{r}_1 \) there is zero probability that another electron with the same spin will simultaneously occupy this position in space. This restriction due to antisymmetry does not, of course, apply to electrons of differing (opposite) spin. However, it may be assumed that the probability of the latter occurrence will be relatively small as a result of the Coulomb repulsion between two
electrons and the requirement (based on the variation theorem) that the sum of the potential and kinetic energies of the system be minimized.

If the exact wave function, $\psi$, of the system were known and inserted in Eq. (183) the resulting distribution function for electron pairs, $P_{12}$, would represent correctly not only the antisymmetry effect but also the so-called electron correlation due to the Coulomb forces. An exact expression for the mean potential of an electron of spin $s_1$ at $\vec{r}_1$ due to the other $N-1$ electrons may be obtained from Eq. (183), and is (in atomic units)

$$ V(\vec{r}_1 s_1) = - \sum_{2} P_2(\vec{r}_1 s_1; \vec{r}_2 s_2) \left( \frac{1}{r_{12}} \right) d_{s_2} \left( d_{s_1} \right) $$

Further analysis is not profitable unless the nature of the wave function is specified in more detail, particularly with regard to the electron spins (see, for example, Slater).

This section will be concluded by giving the expressions for the energy in terms of density matrices. The energy, $E$, has previously been separated into a part $E_0$ independent of the electron coordinates, a part $E_1$ which is a sum of one-electron terms, and a part $E_2$ which is a sum of two-electron terms (of Eqs. (160-165)). The density matrices are defined by Eqs. (166-169). We now introduce the convention of Lowdin that an operator such as $H$ operating on a density matrix of any given order operates only on the unprimed coordinates. It then follows, from Eqs. (164) and (166) that
\[
\begin{align*}
E_1 &= \int \left[ H_1 \rho \left( \mathbf{r}_1, s_1; \mathbf{r}_1', s_1' \right) \right] \mathbf{r}_1' = \mathbf{r}_1, s_1' = s_1 \ d \mathbf{r}_1 \ d s_1 \\
&= \text{Trace} \left( H_1 \rho \right) \\
\end{align*}
\]  
(189)

Similarly, from Eqs. (165) and (167),
\[
\begin{align*}
E_2 &= \int \int \left[ H_{12} \rho_2 \left( \mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \mathbf{r}_1', s_1'; \mathbf{r}_2', s_2' \right) \right] \mathbf{r}_1' = \mathbf{r}_1, s_1' = s_1 \\
&\quad \mathbf{r}_2' = \mathbf{r}_2, s_2' = s_2 \\
x d \mathbf{r}_1 \ d \mathbf{r}_2 \ d s_1 \ d s_2 = \text{Tr} \left( H_{12} \rho_2 \right) \\
\end{align*}
\]  
(190)

8.52 Formulation of Density Matrices for a Single Configuration in Terms of Molecular Orbitals

If the wave function \( \psi \) of the system is approximated by a single antisymmetrized product, \( \psi \), of molecular orbitals of the form given by Eq. (149), or the equivalent Slater determinant of Eq. (151), the density matrices defined by Eqs. (166-169) assume special forms of considerable interest and utility. On using Eqs. (149) and (166), and the orthonormality of the molecular spin orbitals, the first-order density matrix becomes
\[
\rho_1 \left( \mathbf{r}_1, s_1; \mathbf{r}_1', s_1' \right) \\
= \frac{1}{(N-1)!} \int \ldots \int \left\{ \sum_{P} \left( -1 \right)^{P} P \ \phi_1 \left( \mathbf{r}_1 \right) \sigma_1^{-} \left( s_1 \right) \phi_2 \left( \mathbf{r}_2 \right) \sigma_2^{-} \left( s_2 \right) \ldots \right\} \\
\phi_N \left( \mathbf{r}_N \right) \sigma_N^{-} \left( s_N \right) \ x \left\{ \sum_{P'} \left( -1 \right)^{P'} P' \ \phi_1^{*} \left( \mathbf{r}_1^{*} \right) \sigma_1^{-*} \left( s_1^{*} \right) \phi_2^{*} \left( \mathbf{r}_2^{*} \right) \ldots \right\} \\
\sigma_2^{-*} \left( s_2^{*} \right) \ldots \phi_N^{*} \left( \mathbf{r}_N^{*} \right) \sigma_N^{-*} \left( s_N^{*} \right) \right\} \ (d \mathbf{r}_1) \ (d s_1)
In this form the first-order density matrix possesses an important idempotent property not possessed by the generalized density matrix of Eq. (166). That is,

\[
\int \rho_1 (\vec{r}^1 s^1; \vec{r} s) \rho_1 (\vec{r} s; \vec{r}'' s'') \, d \vec{r} \, d s \\
= \int \sum_{i=1}^{N} \varphi_i (\vec{r}^1) \sigma_i^- (s^1) \varphi_i^* (\vec{r}) \sigma_i^+ (s) \, d \vec{r} \, d s \\
= \sum_{j=1}^{N} \varphi_j (\vec{r}) \sigma_j^- (s) \varphi_j^* (\vec{r}'') \sigma_j^+ (s'') \, d \vec{r} \, d s \\
= \sum_{i=1}^{N} \varphi_i (\vec{r}^1) \sigma_i^- (s^1) \varphi_i^* (\vec{r}'') \sigma_i^+ (s'') \\
= \rho_1 (\vec{r}^1 s^1; \vec{r}'' s''),
\]

in view of the orthonormality of the molecular spinorbitals.

The diagonal elements of the first-order density matrix, Eq. (191), are

\[
\rho_1 (\vec{r}^1 s_1) = \sum_{i=1}^{N} \left| \varphi_i (\vec{r}^1) \right|^2 \left| \sigma_i^- (s_1) \right|^2,
\]

and have the interpretation discussed following Eq. (177). Integration over the spin coordinate, \(s_1\), yields the total electron density as a function of the spatial coordinates alone,

\[
\rho_1 (\vec{r}) = \sum_{i=1}^{N} \left| \varphi_i (\vec{r}_1) \right|^2.
\]
For a single closed-shell configuration each molecular orbital occurs
twice in the summation, and

$$\rho_1 (r) = 2 \sum_{i=1}^{n} \varphi_1 (r^i_1)^2.$$  \hspace{1cm} (195)

In Eq. (195) sum is over the n distinct molecular orbitals occupied by

$$N = 2n$$
electrons.

It will now be shown that the density matrix of order n \((m = 1, 2, ..., N)\) has the form

$$\rho_m (r_1 s_1; r_2 s_2; ..., r_m s_m; r'_1 s'_1, r'_2 s'_2, ..., r'_m s'_m)$$

$$= \frac{1}{m!} \begin{vmatrix} \rho_1 (r_1 s_1; r'_1 s'_1) \rho_1 (r_1 s_1; r'_2 s'_2) \ldots \rho_1 (r_1 s_1; r'_m s'_m) \\ \rho_1 (r_2 s_2; r'_1 s'_1) \rho_1 (r_2 s_2; r'_2 s'_2) \ldots \rho_1 (r_2 s_2; r'_m s'_m) \\ \rho_1 (r_m s_m; r'_1 s'_1) \rho_1 (r_m s_m; r'_2 s'_2) \ldots \rho_1 (r_m s_m; r'_m s'_m) \end{vmatrix} $$  \hspace{1cm} (196)

Equation (196) is, of course, an identity for \(m = 1\). Its validity
for \(m = N\) is established by substitution of Eq. (151) for \(\psi\), and its
Hermitian conjugate for \(\psi^*\), in Eq. (169) and multiplying together the
two determinants according to the usual rule for matrix multiplication.

In order to establish the validity of Eq. (196) for all values of \(m\) it
is therefore sufficient to show that if Eq. (196) holds for an arbitrary
value \(m\) it holds also for \(m - 1\). The following proof is a somewhat more
The determinant in Eq. (196) may be expanded according to cofactors of its last column, yielding

\[
\rho_m (\vec{r}_1 s_1, \vec{r}_2 s_2, \ldots, \vec{r}_m s_m ; \vec{r}_1^f s_1^f, \vec{r}_2^f s_2^f, \ldots, \vec{r}_m^f s_m^f) = (1/m!) \sum_{k=1}^{m-1} \sum_{k'=1}^{m-1} (-1)^{m-k-k'} \rho_1 (\vec{r}_k s_k; \vec{r}_k^f s_m^f) \rho_1 (\vec{r}_k^f s_k^f; \vec{r}_k^f s_k^f) \rho_1 (\vec{r}_k^f s_k^f; \vec{r}_k^f s_k^f) \rho_1 (\vec{r}_m s_m; \vec{r}_m^f s_m^f) \rho_1 (\vec{r}_m^f s_m^f; \vec{r}_m^f s_m^f) \rho_1 (\vec{r}_m^f s_m^f; \vec{r}_m^f s_m^f)
\]

where \( D_{k k'}^{(m)} \) is the minor of the element \( \rho_1 (\vec{r}_k s_k; \vec{r}_k^f s_m^f) \) in \( k \) th row, \( k' \) column of the determinant. Next, set \( \vec{r}_m = \vec{r}_m^f \) and \( s_m = s_m^f \) in Eq. (198), and integrate over \( \vec{r}_m \) and \( s_m \) to obtain
Here use has been made of the idempotent property of the first-order density matrix, Eq. (194), and the fact that the integral of the diagonal elements (or trace) of the first-order density matrix is N, as is clear from Eq. (177) or (193). Equation (199) may be rearranged to the form

\[
\left[ \frac{1}{(m-1)!} \right] D \left\{ \rho_{1} (\vec{r}_{1} s_{1}; \vec{r}_{1} s_{1}^{f}) \rho_{1} (\vec{r}_{2} s_{2}; \vec{r}_{2} s_{2}^{f}) \cdots \rho_{1} (\vec{r}_{m-1} s_{m-1}; \vec{r}_{m-1} s_{m-1}^{f}) \right\} = (\frac{N-m+1}{m!}) \int \rho_{m} (\vec{r}_{1} s_{1}, \cdots, \vec{r}_{m-1} s_{m-1}; \vec{r}_{m} s_{m}, \vec{r}_{m} s_{m}^{f}) \cdots (m-1) \\
\int \rho_{m} (\vec{r}_{1} s_{1}, \cdots, \vec{r}_{m-1} s_{m-1}; \vec{r}_{m} s_{m}, \vec{r}_{m} s_{m}^{f}) d\vec{r}_{m} d s_{m} \tag{200}
\]

Comparison with the general recursion relating \( \rho_{m-1} \) and \( \rho_{m} \), as given in Eq. (170), establishes the validity of Eq. (196) for all values of m from 1 to N, since it is known to hold for m = N. It has thus been established that the density matrices of all orders may be expressed in terms of the first-order density matrices for the special case in which the wave function of the N-electron system is represented by a single
determinant of the form given in Eq. (151), corresponding to a single configuration. It is important to notice, however, that the diagonal elements of the density matrices of order higher than the first are not expressible simply in terms of the diagonal elements of the first-order matrix, but depend also on the off-diagonal elements of the latter. Of particular interest in connection with the evaluation of the electron-pair repulsion energy, $E_2$, is the second-order density matrix, which is given by

$$\rho_2(\vec{r}_1 s_1, \vec{r}_2 s_2; \vec{r}'_1 s'_1, \vec{r}'_2 s'_2)$$

According to Eq. (175) the probability distribution function $P_2(\vec{r}_1 s_1, \vec{r}_2 s_2)$, for electron pairs is obtained by setting the primed and unprimed coordinates equal in Eq. (201), and multiplying by 2! The function $P_2$ has been applied to the study of the spatial correlation of electron pairs in molecules by Lennard-Jones.

8.53 Resolution According to Spin of Density Matrices for a Single Configuration

The first-order density matrix is defined by Eq. (166). For the case in which the wave function, $\psi$, of the system is given by a single antisymmetrized product, $\phi$, of molecular orbitals, as in Eq. (149) or (151), the first-order density matrix reduces to the simple form given in Eq. (191). In this equation the sum is over the molecular spinorbitals occupied by the $N$ electrons. Now let $N_+$ and $N_-$ be the
number of electrons, for given $\phi$, having spin projections of $+1/2$ and $-1/2$ (in units of $h/2\pi$), respectively; of course $N_+ + N_- = N$. Then Eq. (191) can be rewritten as

$$\rho_1 (\vec{r}_1, \vec{r}_1'; s_1; s_1') = \rho_+ (\vec{r}_1, \vec{r}_1') \sigma_+ (s_1) \sigma_+^* (s_1') + \rho_- (\vec{r}_1, \vec{r}_1') \sigma_- (s_1) \sigma_-^* (s_1'),$$

(202)

where

$$\rho_+ (\vec{r}_1, \vec{r}_1') = \sum_{i=1}^{N_+} \phi_i (\vec{r}_1) \phi_i^* (\vec{r}_1'),$$

(203a)

$$\rho_- (\vec{r}_1, \vec{r}_1') = \sum_{j=1}^{N_-} \phi_j (\vec{r}_1) \phi_j^* (\vec{r}_1').$$

(203b)

In Eq. (203a) the summation extends over the $N_+$ molecular orbitals occupied by electrons with positive spin, and in Eq. (203b) over the $N_-$ orbitals occupied by electrons with negative spin. It follows from the exclusion principle that $\rho_+$ represents a sum over distinct, and therefore orthogonal, molecular orbitals and similarly for $\rho_-$ (however, the same molecular orbital may occur once in $\rho_+$ and once in $\rho_-$. Consequently, both $\rho_+$ and $\rho_-$ have the idempotent property,

$$\int \rho_+ (\vec{r}_1, \vec{r}_1') \rho_+ (\vec{r}_1, \vec{r}_1'') d\vec{r}_1 = \rho_+ (\vec{r}_1, \vec{r}_1'')$$

(204)

(compare the derivation of Eq. (192)). $\rho_+$ and $\rho_-$ are the space parts of the first-order density matrix for electrons of positive and negative spin respectively.

It has been shown in Section 8.52 that in the single-configurational case under consideration, all higher order density matrices can be expressed in terms of the first-order matrix through Eq. (196); it
follows from Eq. (202) that they can also be expressed in terms of $\rho_+^1$ and $\rho_-^1$ and the spin functions. The electron density in coordinate-spin space is given by the diagonal elements of the first-order density matrix, or Eq. (193), which may now be rewritten as

$$\rho_1^1(\vec{r}_1, s_1) = \rho_+^1(\vec{r}_1) |\sigma_+^1(s_1)|^2 + \rho_-^1(\vec{r}_1) |\sigma_-^1(s_1)|^2,$$

(205)

with

$$\rho_+^1(\vec{r}_1) = \rho_+^1(\vec{r}_1, \vec{r}_1) = \sum_{i=1}^{N_+} |\phi_i^1(\vec{r}_1)|^2,$$

(206a)

$$\rho_-^1(\vec{r}_1) = \rho_-^1(\vec{r}_1, \vec{r}_1) = \sum_{j=1}^{N_-} |\phi_j^1(\vec{r}_1)|^2.$$

(206b)

It follows from the properties of $\sigma_+^1$ and $\sigma_-^1$ that $\rho_+^1(\vec{r}_1)$ and $\rho_-^1(\vec{r}_1)$ are the densities in ordinary space of electrons of positive and negative spin, respectively. The total electron density in ordinary space is

$$\rho_1^1(\vec{r}_1) = \rho_+^1(\vec{r}_1) + \rho_-^1(\vec{r}_1).$$

(207)

It is also clear from the normalization of the molecular orbitals that

$$\rho_+^1(\vec{r}_1) d\vec{r}_1 = \int \rho_+^1(\vec{r}_1, \vec{r}_1) d\vec{r}_1 = \text{Tr} \rho_+^1(\vec{r}_1, \vec{r}_1') = N_+$$

(208)

It is of interest also to introduce the product of the density matrices $\rho_+$ and $\rho_-^{79}$

$$\omega(\vec{r}_1', \vec{r}_2') = \int \rho_+^1(\vec{r}_1', \vec{r}_1) \rho_-^1(\vec{r}_1, \vec{r}_2') d\vec{r}_1 = \int \rho_-^1(\vec{r}_1', \vec{r}_1') d\vec{r}_1.$$

$$\rho_+^1(\vec{r}_1, \vec{r}_1') d\vec{r}_1$$
\[
\begin{align*}
&= \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} \phi_i (r_1^i) \phi_j^* (r_1^j) \int \phi_i^* (r_1) \phi_j^* (r_1) \, d r_1 \\
&= \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} \delta_{ij} \phi_i (r_1^i) \phi_i^* (r_1^i),
\end{align*}
\]

in view of Eq. (140). Thus,

\[
\text{Tr} \omega = \int \omega (\hat{r}_1, \hat{r}_1) \, d \hat{r}_1 = \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} \delta_{ij} = N(\pm),
\]

where \(N(\pm)\) is the number of molecular orbitals occupied by electrons of both positive and negative spin, that is, the number of doubly-occupied molecular orbitals.

For a closed-shell configuration, each of \(n\) molecular orbitals is occupied by two electrons with opposed spins, \(N_+ = N_- = N/2 = n\), and the two sets of molecular orbitals indicated by subscripts \(i\) and \(j\) in the preceding equations are identical. In this case, therefore, \(\rho_+\) and \(\rho_-\) become identical, and the first-order density matrix reduces to

\[
\rho_1 (r_1^s_1; r_1^s_1') = \rho(r_1^s_1, r_1^s_1') \left\{ \sigma_+ (s_1) \sigma_-^*(s_1') + \sigma_- (s_1) \sigma_+^*(s_1') \right\},
\]

(211)

with

\[
\rho(r_1^s_1, r_1^s_1') = \sum_{i=1}^{n} \phi_i (r_1^s_1) \phi_i^* (r_1^s_1').
\]

(212)

The densities of electrons with positive and negative spins become equal,

\[
\rho_\pm (r_1^s_1) = \rho(r_1^s_1, r_1^s_1) = \sum_{i=1}^{n} \left| \phi_i (r_1^s_1) \right|^2,
\]

(213)
and the total electron density in ordinary space is

\[ \rho(\mathbf{r}_1) = \rho^+ (\mathbf{r}_1) + \rho^- (\mathbf{r}_1) = 2 \sum_{i=1}^{n} \left| \phi_i (\mathbf{r}_1) \right|^2. \]  

(214)

Since by the exclusion principle the \( n \) doubly-occupied orbitals are distinct, and therefore orthogonal, it is clear that \( \rho(\mathbf{r}_1, \mathbf{r}_1') \) also possesses the idempotent property analogous to Eq. (204). Furthermore, all higher-order density matrices can be expressed in terms of \( \rho(\mathbf{r}_1, \mathbf{r}_1') \) and the spin functions through Eqs. (196) and (211). It is therefore appropriate to refer to \( \rho(\mathbf{r}_1, \mathbf{r}_1') \) as the space part of the first-order density matrix, although in general the spin factor in Eq. (211) must be included in the complete density matrix in computing mean values. The analog of Eq. (208) is

\[ \int \rho^+ (\mathbf{r}_1) \, d\mathbf{r}_1 = \int \rho(\mathbf{r}_1, \mathbf{r}_1) \, d\mathbf{r}_1 = \text{Tr} \rho(\mathbf{r}_1, \mathbf{r}_1) = n = 1/2 \, N \]  

(215)

From the idempotent property it follows that for the closed-shell case

\[ \omega(\mathbf{r}_1', \mathbf{r}_1'') = \int \rho(\mathbf{r}_1, \mathbf{r}_1) \rho(\mathbf{r}_1, \mathbf{r}_1) \, d\mathbf{r} = \rho(\mathbf{r}_1, \mathbf{r}_1), \]  

(216)

so that from Eqs. (210), (215) and (216)

\[ \text{Tr} \omega = N(\pm) = n, \]  

(217)

corresponding to the double-occupancy of all the molecular orbitals.

8.54 Energy for a Single Configuration in Terms of Molecular Orbitals

The general expression for the one-electron part of the energy, \( E_1 \), in terms of the first-order density matrix is given in Eq. (189). An expression for \( E_1 \) in terms of integrals over molecular orbitals for
the ease of a single configuration may now be obtained by substitution in
Eq. (189) of the resolved form of the first-order density matrix given by
Eqs. (202) and (203a,b). On recalling that $H_1$ in Eq. (189) operates
only on the unprimed coordinates this yields

$$E_1 = \sum_{i=1}^{N_+} \int \int \phi_i^* \left( \vec{r}_1 \right) \sigma_+ \left( s_1 \right) H_1 \phi_i \left( \vec{r}_1 \right) \sigma_+ \left( s_1 \right) d \vec{r}_1 d s_1$$

$$+ \sum_{j=1}^{N_-} \int \int \phi_j^* \left( \vec{r}_1 \right) \sigma_- \left( s_1 \right) H_1 \phi_j \left( \vec{r}_1 \right) \sigma_- \left( s_1 \right) d \vec{r}_1 d s_1. \quad (218)$$

(In Sections 8.51 and 8.52 a single integral sign was used for simplicity
to indicate integration over both the space and spin variables, $\vec{r}$ and $s$,
for each electron; in Eq. (218) and hereafter separate integral signs
will be used as it is desired to carry out explicitly the integrations
over the spin variables.)

If $H_1$ does not depend upon the spin variable $s_1$, which will be
the case for the Hamiltonian of atomic and molecular systems if spin-
orbit coupling is neglected, the integration over the spin variables in
Eq. (218) yields, in view of Eq. (145),

$$E_1 = \sum_{i=1}^{N^+} H_1 + \sum_{i=1}^{N^-} H_i. \quad (219)$$

where $H_1$ is the one-electron integral

$$H_1 = \int \phi_i^* \left( \vec{r}_1 \right) H_1 \phi_i \left( \vec{r}_1 \right) d \vec{r}_1, \quad (220)$$

and similarly for $H_i$. (In Section 8.3 $H_1$ was used to denote the operator
$H_1$ for the $i$ th electron but there is no longer a need for this notation
in view of the expression of $E_1$ in terms of a typical one of these
operators $H_i$ in Eqs. (164) and (189), and hereafter $H_i$ will signify the diagonal matrix element of $H_i$ with respect to the $i$th molecular orbital, as in Eq. (220). The operator $H_i$ is obtained by setting the index $i$ equal to 1 in Eq. (157). Substitution in Eq. (220) then yields

$$H_i = T_i + \sum_a Z_a J_{ai} \quad (221)$$

where

$$T_i = -(1/2) \int \phi_i^* (\mathbf{r}_1) \nabla_1^2 \phi_i (\mathbf{r}_1) d \mathbf{r}_1 \quad (222)$$

is the kinetic energy integral for the $i$th molecular orbital, and

$$J_{ai} = \int \phi_i^* (\mathbf{r}_1) (1/r_{al}) \phi_i (\mathbf{r}_1) d \mathbf{r}_1 \quad (223)$$

is the nuclear attraction integral for the $a$th nucleus and $i$th molecular orbital. $Z_a$ is the atomic number for the $a$th nucleus, and $r_{al}$ the distance of electron 1 from the $a$th nucleus.

The reduction of the two-electron part of the energy, $E_2$, is similar but somewhat more involved. The general expression for $E_2$ has been reduced in Eq. (190) to a form depending on the second-order density matrix, $\rho_2$, and the electron-pair interaction operator, $H_{12}$. For the case of a single configuration $\rho_2$ is expressed in terms of the first-order density matrix $\rho_1$ by Eq. (201). On substituting Eqs. (202) and (203 a,b) for $\rho_1$ in Eq. (201), expanding the determinant and inserting the resulting expression for $\rho_2$ in Eq. (190), and noting that $H_{12}$ acts only on the unprimed variables in the latter equation, there is obtained,

$$E_2 = (1/2) \left\{ \sum_{i=1}^{N_+} \sum_{i'=-1}^{N_+} (J_{i^+, 1^+:} - K_{i^+, 1^+:}) + \sum_{j=1}^{N_-} \sum_{j'=-1}^{N_-} (J_{j^-, 1^+:} - K_{j^-, 1^+:}) \right\} + 2 \sum_{i=1}^{N_+} \sum_{j=-1}^{N_-} (J_{1^+, j^+:} - K_{1^+, j^+:}) \quad (224)$$
where

\[ J_{k \pm, k' \pm} = \int \int \int \int \phi_k^* (r_1) \sigma_\pm (s_1) \phi_{k'}^* (r_2) \sigma_\pm (s_2) \times H_{12} \phi_k (r_1) \sigma_\pm (s_1) \phi_{k'} (r_2) \sigma_\pm (s_2) \, dr_1 \, ds_1 \, dr_2 \, ds_2 \]  

(225a)

is a generalized Coulomb integral with spin included, and

\[ K_{k \pm, k' \pm} = \int \int \int \int \phi_k^* (r_2) \sigma_\pm (s_2) \phi_{k'}^* (r_1) \sigma_\pm (s_1) \times H_{12} \phi_k (r_1) \sigma_\pm (s_1) \phi_{k'} (r_2) \sigma_\pm (s_2) \, dr_1 \, ds_1 \, dr_2 \, ds_2 \]  

(225b)

is a generalized exchange integral (it should be noted that there are only 4 possibilities for the signs of the spin functions in the integrals on the right-hand side of Eqs. (225 a, b), because the spin functions associated with the \( \phi_k \) and \( \phi_k^* \) must be either \( \sigma_+ \) and \( \sigma_+^* \) or \( \sigma_- \) and \( \sigma_-^* \) respectively, and similarly for \( \phi_{k'} \) and \( \phi_{k'}^* \)).

If \( H_{12} \) does not depend upon the spin variables, which will be the case for the Hamiltonian operator if spin-spin coupling is ignored (it may be noted in passing that other two-electron operators involving spin are also of interest, for example, the operator for the square of the total electron spin, which Dirac has represented as a permutation operator on pairs of spin coordinates), then the integrations over the spin variables in Eqs. (225 a, b) may be carried out explicitly and yields, in view of Eqs. (145) and (146),

\[ J_{k \pm, k' \pm} = J_{k k'} \]  

(226a)

\[ K_{k \pm, k' \pm} = K_{k - k'} = K_{k' k} \]  

(226b)
where

\[ K_{k^+}^{+}, k^+_{-} = K_{k^-}^{+}, k^+_{+} = 0, \] (226c)

\[ J_{kk} = \int \int \hat{\varphi}_k^*(\vec{r}_1) \hat{\varphi}_k^*(\vec{r}_2) H_{12} \hat{\varphi}_k(\vec{r}_1) \hat{\varphi}_k^*(\vec{r}_2) \, d \vec{r}_1 \, d \vec{r}_2, \] (227a)

\[ K_{kk} = \int \int \hat{\varphi}_k^*(\vec{r}_2) \hat{\varphi}_k^*(\vec{r}_1) H_{12} \hat{\varphi}_k(\vec{r}_1) \hat{\varphi}_k^*(\vec{r}_2) \, d \vec{r}_1 \, d \vec{r}_2, \] (227b)

It should be noted that these integrals are real for Hermitian operators, \( H_{12} \), and that \( J_{kk} = J_{k^+k^+}^{+}, K_{kk} = K_{k^+k^+}^{+} \), and

\[ J_{kk} = K_{kk} \] (228)

(similar relations hold for the general integrals in Eqs. (225 a, b)).

For the case in which \( H_{12} \) does not depend upon spin variables it follows from Eqs. (224) and (226 a, b, d) that the two-electron energy for a single configuration assumes the form

\[
E_2 = (1/2) \left[ \sum_{i=1}^{N_+} \sum_{i'=1}^{N_+} (J_{ii'} - K_{ii'}) + \sum_{j=1}^{N_-} \sum_{j'=1}^{N_-} (J_{jj'} - K_{jj'}) + 2 \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} J_{ij} \right]
\] (229)

For the case of interest here \( H_{12} \) is simply the Coulomb interaction operator for the pair of electrons, \( H_{12} = 1/r_{12} \) (see Eq. (157)), and the integrals \( J_{kk} \) and \( K_{kk} \) of Eqs. (227 a, b) are then simply the ordinary Coulomb and exchange integrals, respectively. For a closed-shell configuration, for which the set of \( N_+ \) orbitals \( \varphi_i \) and the set of \( N_- \) orbitals \( \varphi_j \) are identical, corresponding to double occupancy of a single set of \( n \) molecular orbitals \( n = N_+ = N_- = N/2 \), the sums over \( i \) (or \( i' \)) and \( j \) (or \( j' \)) in Eqs. (219) and (229) become identical. The one-electron energy then reduces to
\[ E_1 = 2 \sum_{i=1}^{n} H_i, \quad (230) \]

and the two-electron energy to

\[ E_2 = \sum_{i,j=1}^{n} (2 J_{ij} - K_{ij}). \quad (231) \]

Although Eq. (231) is the usual representation of \( E_2 \) in this case, it should be noted that it contains terms which cancel identically, in view of Eq. (228).

8.6 Density Matrix Formulation of Self-Consistent Field Molecular Orbital Theory in the LCAO Approximation for a Single Configuration

8.61 Density Matrices in the LCAO Approximation

We now return to the LCAO approximation discussed in Section 8.2 in which each molecular orbital, \( \psi_i \), is approximated as a linear combination of atomic orbitals, \( \chi_\alpha \), as in Eq. (139). Substitution of this equation in Eqs. (203 a,b) yields, after rearrangement,

\[ \rho_{\pm}(\mathbf{r}_1', \mathbf{r}_1) = \sum_{\alpha, \beta = 1}^{N} \rho_{\alpha \beta}^{\pm} \chi_\alpha(\mathbf{r}_1') \chi_\beta^*(\mathbf{r}_1), \quad (232) \]

where

\[ \rho_{\alpha \beta}^{+} = \sum_{i=1}^{N_+} c_{\alpha i} c_{\beta i}^*, \quad (233a) \]

\[ \rho_{\alpha \beta}^{-} = \sum_{i=1}^{N_-} c_{\alpha j} c_{\beta j}^*. \quad (233b) \]
It is logical to refer to the $v \times v'$ matrices having as their elements $\rho^+_{\alpha\beta}$ and $\rho^-_{\alpha\beta}$ as the representatives relative to the basis functions, $\chi_{\alpha}(\vec{r}_1)$, of the parts of the first-order density matrix associated with positive and negative spin, respectively. These two matrices may conveniently be denoted by $(\rho^+)$ and $(\rho^-)$, respectively, or by $(\rho^\pm)$ when referred to in common. Substitution of Eq. (232) in the idempotent condition for the continuous density matrix $\rho^\pm(\vec{r}_1, \vec{r}_1')$, or Eq. (204), yields

$$\int \rho^\pm(\vec{r}_1, \vec{r}_1') \rho^\pm(\vec{r}_1', \vec{r}_1'') d\vec{r}_1$$

$$= \sum_{\alpha, \beta = 1}^{v'} \sum_{\gamma, \delta = 1}^{v'} \rho^\pm_{\alpha\beta} \rho^\pm_{\gamma\delta} \chi_{\alpha}(\vec{r}_1') \chi^*_{\gamma}(\vec{r}_1') \int \chi^*_{\beta}(\vec{r}_1) \chi_{\delta}(\vec{r}_1) d\vec{r}_1$$

$$= \sum_{\alpha, \beta = 1}^{v'} \chi_{\alpha}(\vec{r}_1') \chi^*_{\beta}(\vec{r}_1') \sum_{\gamma, \delta = 1}^{v'} \rho^\pm_{\alpha\beta} s_{\beta\gamma} \rho^\pm_{\gamma\delta}$$

$$= \rho^\pm(\vec{r}_1, \vec{r}_1'') = \sum_{\alpha, \beta = 1}^{v'} \rho^\pm_{\alpha\beta} \chi_{\alpha}(\vec{r}_1') \chi^*_{\beta}(\vec{r}_1'). \tag{234}$$

Thus,

$$\sum_{\alpha, \beta = 1}^{v'} \rho^\pm_{\alpha\beta} s_{\beta\gamma} \rho^\pm_{\gamma\delta} = \rho^\pm_{\alpha\delta}, \tag{235}$$

or more compactly,

$$(\rho^\pm S)(\rho^\pm) = (\rho^\pm). \tag{236}$$

Here $(S)$ is the overlap matrix with elements $s_{\alpha\beta}$ defined by Eq. (142).

This is the analog for the discrete matrices $(\rho^\pm)$ of the idempotent
condition. It will be noted that if the atomic orbitals are orthonormal, 
$(S) = (I)$, where $(I)$ is the $\nu \times \nu$ unit matrix, and Eq. (236) reduces to a true idempotency condition,

$$(\rho^{\pm})^2 = (\rho^{\pm})_.$$

(237)

To avoid duplication, discussion of the use of orthogonalized atomic orbitals will be deferred until after the closed-shell case has been considered.

As discussed in Section 8.53, the charge densities of electrons of positive or negative spin (measured in atomic units, or electrons per unit volume) are given by the diagonal elements of $\rho_\pm (\vec{r}_1, \vec{r}_1)$, or

$$\rho_\pm (\vec{r}_1) = \rho_\pm (\vec{r}_1, \vec{r}_1) = \sum_{\alpha, \beta} \rho_{\alpha, \beta} \chi_\alpha (\vec{r}_1) \chi^*_\beta (\vec{r}_1).$$

(238)

Substitution of Eq. (238) in Eq. (208) yields

$$\text{Tr} (\rho^{\pm}) (S) = \sum_{\alpha, \beta} \rho_{\alpha, \beta} S_{\beta \alpha} = N^{\pm}$$

(239)

which is the LCAO form of the normalization conditions for total positive and negative charge. In view of Eq. (239) and the relation $S_{\alpha \alpha} = 1$,

$$Q^{\pm}_d = \rho_{\alpha, \alpha}$$

(240)

represents the mean charge or number of electrons of positive or negative spin occupying the $\alpha$th atomic orbital, while for $\alpha \neq \beta$ ,

$$p^{\pm}_{\alpha, \beta} = p^{\pm}_{\beta, \alpha} = \rho^{\pm}_{\alpha, \beta} S_{\alpha \beta} + \rho^{\pm}_{\beta, \alpha} S_{\beta \alpha} = \rho^{\pm}_{\alpha, \beta} S_{\alpha \beta} + (\rho^{\pm}_{\alpha, \beta})^* S_{\beta \alpha}$$

(241)

represents the mean excess or deficiency of charge or number of electrons
of positive or negative spin in the region of overlap of the $\alpha^{th}$ and $\beta^{th}$ atomic orbitals. The totals of the corresponding quantities without regard to spin are

$$Q_\alpha = Q_\alpha^+ + Q_\alpha^- = \rho_\alpha^+ + \rho_\alpha^-,$$

and

$$P^\alpha_\beta + P_\alpha^+ + P^- = (\rho_\alpha^+ + \rho_-) S^* + (\rho_\alpha^+ + \rho_-)^* S_\alpha^\beta$$

(243)

For a closed-shell configuration, similarly, the space part of the density matrix given by Eq. (212) reduces in the LCAO approximation to

$$\rho(r_1, r'_1) = \sum_{\alpha, \beta = 1}^{\nu} \rho_{\alpha\beta} \chi_\alpha(r_1) \chi_\beta^*(r'_1)$$

(244)

where

$$\rho_{\alpha\beta} = \sum_{i=1}^{n} c_{\alpha i} c_{\beta i}^*$$

(245)

($n = N_+ = N_-)$. That is, $\rho_+ (r_1, r'_1)$ and $\rho_- (r_1, r'_1)$ reduce to the common form $\rho(r_1, r'_1)$, and $\rho_\alpha^+$ and $\rho_\alpha^-$ to $\rho_\alpha^\beta$. The $\nu \times \nu$ matrix with elements $\rho_{\alpha\beta}$ to which $(\rho_+)$ and $(\rho_-)$ both reduce in the closed-shell case will be denoted by $\rho)$, and is the representative relative to the basis functions $\chi_\alpha(r_1)$ of the space part of the first-order density matrix. The idempotent condition becomes

$$\sum_{\beta, \gamma = 1}^{\nu} \rho_{\alpha\beta} S_{\beta\gamma} \rho_{\gamma\delta} = \rho_{\alpha\delta}$$

(246)

or
a result first given by Taylor.\textsuperscript{\text{71}}

For the closed-shell case the charge densities of electrons of positive and negative spin become equal, and it is convenient to deal with the total charge density or number of electrons of both spins per unit volume,

\[
\rho(r_1) = \rho_+ (r_1) + \rho_- (r_1) = 2 \sum_{\alpha, \beta = 1}^{\nu} \rho_{\alpha \beta} \chi^*_\alpha (r_1) \chi^*_\beta (r_1). \tag{248}
\]

The normalization condition for total charge becomes

\[
2 \text{Tr} (\rho)(S) = 2 \sum_{\alpha, \beta = 1}^{\nu} \rho_{\alpha \beta} S_{\beta \alpha} = N_+ + N_- = N \tag{249}
\]

where \(N\) is the total number of electrons, or\textsuperscript{71}

\[
\text{Tr} (\rho) (S) = \sum_{\alpha, \beta = 1}^{\nu} \rho_{\alpha \beta} S_{\beta \alpha} = n, \tag{250}
\]

where \(n = N/2\) is the number of occupied molecular orbitals.

The total mean charge or number of electrons of both positive and negative spins in the \(\alpha\) th atomic orbital is

\[
Q_\alpha = Q_\alpha^+ + Q_\alpha^- = \rho^+ + \rho^- = 2\rho_{\alpha \alpha}, \tag{251}
\]

and the total excess or deficiency of charge or number of electrons of both positive and negative spins in the region of overlap of the \(\alpha\) th and \(\beta\) th atomic orbitals is, for \(\alpha \neq \beta\),

\[
P^+_{\alpha \beta} = P^+_{\alpha \beta} + P^-_{\alpha \beta} = 2 (\rho_{\alpha \beta} S_{\alpha \beta} - \rho_{\alpha \beta} S_{\beta \alpha}) = 2 (\rho_{\alpha \beta} S_{\alpha \beta} + \rho_{\alpha \beta} S_{\alpha \beta}) \tag{252}
\]
Equations (251) and (252) are identical with those given by Taylor,\textsuperscript{71} except that the electronic charge was there indicated explicitly by $e$. It is evident that $Q_\alpha$ (or $Q_\alpha^\pm$) is real and positive, while $P_{\alpha\beta}$ (or $P_{\alpha\beta}^\pm$), $\alpha \neq \beta$, is real but may be positive, negative, or zero. If the $\alpha$\textsuperscript{th} and $\beta$\textsuperscript{th} atomic orbitals are centered on different atoms, and $P_{\alpha\beta}$ is positive and relatively large (which requires that the two atoms be relatively near one another as the overlap integral, $S_{\alpha\beta}$, decreases exponentially with interatomic distance) then it is reasonable to regard the $\alpha$\textsuperscript{th} and $\beta$\textsuperscript{th} orbitals as forming a "bond" between the pair of atoms in question. If $P_{\alpha\beta}$, $\alpha \neq \beta$ is negative and relatively large the $\alpha$\textsuperscript{th} and $\beta$\textsuperscript{th} atomic orbitals may be regarded as "anti-bonding," and if the magnitude of $P_{\alpha\beta}$ is very small or zero, as "non-bonding." It should be noted that although $P_{\alpha\beta}$ may be negative, this quantity represents only the excess or deficiency of electrons in the region of overlap of the $\alpha$\textsuperscript{th} and $\beta$\textsuperscript{th} atomic orbitals. The total number of electrons assignable to a bond involving the $\alpha$\textsuperscript{th} and $\beta$\textsuperscript{th} orbitals, for the case in which these two orbitals do not participate significantly in the formation of any other bonds, is

$$Q_{\alpha\beta} = Q_\alpha + P_{\alpha\beta} + Q_\beta^* \quad (253)$$

The quantity $Q_{\alpha\beta}$ is necessarily positive, since from Eqs. (142), (245), and (251-253),

$$Q_{\alpha\beta} = 2 \left\{ \rho_\alpha + (\rho_{\alpha\beta} S_{\alpha\beta}^* + \rho_{\alpha\beta}^* S_{\alpha\beta} + \rho_{\beta\beta}) \right\} \quad (251)$$

$$= 2 \sum_{i=1}^{n} \left\{ c_{\alpha i} c_{\alpha i}^* + c_{\alpha i} c_{\beta i}^* \int \chi_\alpha(\vec{r}_1) \chi_\beta^* (\vec{r}_1) d \vec{r}_1 + c_{\alpha i} c_{\beta i} \int \chi_\beta(\vec{r}_1) \chi_\alpha^* (\vec{r}_1) d \vec{r}_1 \right\} \quad (252)$$
In obtaining the third equality in Eq. (25*0 use is made of the normalization of the atomic orbitals, \( S_{\alpha\alpha} = 1 \). The inequality in the last line follows from the linear independence of the atomic orbitals, as a result of which the squared modulus in the integrand on the third line of Eq. (254) cannot vanish everywhere. If the \( \alpha \) th and \( \beta \) th participate to a significant degree in other bonds, Eq. (253) must be modified to the form

\[
Q_{\alpha\beta} = Q_{\alpha} \left( f_{\alpha\beta} + P_{\alpha\beta} \right) + Q_{\beta} f_{\beta\alpha} \quad (255)
\]

where \( f_{\alpha\beta} \) is the fraction of the number of electrons in the \( \alpha \) th atomic orbital that is to be assigned to the \( \alpha\beta \) th bond, and similarly for \( f_{\beta\alpha} \). Equation (253) is thus simply an idealized limiting form of Eq. (255) for the case \( f_{\alpha\beta} = f_{\beta\alpha} = 1 \). Probably the simplest and most important application of Eq. (255) is to the mobile or \( \pi \) electrons in conjugated hydrocarbon systems. If only the \( \pi \) electrons are included in the molecular orbital calculation, each atomic orbital, \( \chi_{\alpha} \), is a \( p \pi \) orbital. Each such orbital within a conjugated ring participates in two \( \pi \) -bonds, one with the adjacent \( p \pi \) orbital on either side, except for \( p \pi \) orbitals at the junction of two (or three) rings, which participate in three such \( \pi \) -bonds (in this approximation \( \pi \) -bonds formed "across the ring" are neglected). It is evident from the equivalence of the six \( p \pi \) atomic orbitals in benzene that \( f_{\alpha\alpha} + 1 = 1/2 \) (all \( \alpha \)). However, no clear criterion exists for the determination of \( f_{\alpha\beta} \) in the general case, and in fact these quantities may be fixed somewhat
arbitrarily provided only that $Q_{\alpha\beta}$ as defined by Eq. (255) remain positive for all $\alpha$ and $\beta$.

The preceding analysis of bond charges is based on Eqs. (251) and (252) of Taylor.\textsuperscript{71} Coulson and Longuet-Higgins\textsuperscript{69} had given earlier a somewhat similar analysis of (mobile) atomic charges and "mobile bond order" (a term introduced by them) in conjugated systems. Their "atomic charge, $q_\alpha$, refers only to electrons in the $p\pi$ orbital on the $\alpha$ th atom, and is thus entirely equivalent to $Q_\alpha$ of Eq. (242) or (251). Their mobile bond order, $p_{\alpha\beta}$, between the $p\pi$ orbitals on adjacent carbon atoms (the bond order is defined to be zero for non-adjacent atoms) is equivalent to $\rho_{\alpha\beta}^+ + \rho_{\alpha\beta}^-$ in general, or to $2\rho_{\alpha\beta}$ for the case of a closed shell. Thus $P_{\alpha\beta}$ as defined by Eq. (243) is equivalent to $p_{\alpha\beta}^* S_{\alpha\beta}^* + p_{\alpha\beta}^* S_{\alpha\beta}^*$ or to $2p_{\alpha\beta} S_{\alpha\beta}$ for the usual case in which the atomic and molecular orbitals are real. It is found in general that $p_{\alpha\beta} > 0$ for adjacent $p\pi$ orbitals in conjugated systems, and since $S_{\alpha\beta} > 0$ for similarly directed $p\pi$ orbitals, it follows that $P_{\alpha\beta} > 0$. Although the mobile bond order has proved useful in the theoretical treatment of atom (or orbital) and bond polarizabilities,\textsuperscript{69} the quantity $P_{\alpha\beta}$ has the advantage that it indicates the actual excess or deficiency of electrons in the overlap region (while $Q_{\alpha\beta}$ indicates the total number of electrons associated with the bond).

If the atomic orbitals are orthogonalized to one another, for example by the procedure of Lowdin,\textsuperscript{31} then $S_{\alpha\beta} = 0$ for $\alpha \neq \beta$, and $P_{\alpha\beta} = 0$ even for the case $p_{\alpha\beta} \neq 0$. That is, even though the mobile bond order of Coulson and Longuet-Higgins might be non-vanishing and
positive in this case, there would exist no excess concentration of electron charge in the region between the atoms over and above that in the two orthogonalized atomic orbitals. As it is well established that chemical bonding is correlated with the existence of an increased charge density in the region between the two atoms, it seems sensible to use a formalism such as that developed here in which the excess charge is directly revealed, rather than concealed by the introduction of artificially orthogonalized "atomic" orbitals (similar remarks apply to the anti-bonding case in which the present formulation reveals directly the deficiency in charge between the atoms). Slater has given a detailed discussion which shows that Lowdin's orthogonalized atomic orbitals do not form an effective bonding molecular orbital in the case of the $H_2$ molecule, which supports the preceding viewpoint.

The present discussion is based on the earliest formulation of self-consistent field LCAO molecular orbital theory in density matrix form by Taylor, who based his treatment on the use of ordinary non-orthogonalized atomic orbitals. The overlap matrix, $(S)$, or overlap integrals, $S_{\alpha\beta}$, thus appear explicitly in the equations, such as the idempotency condition, Eqs. (235-6) or (246-7), the normalization of charge condition, Eqs. (239) or (250), and also the secular equation to be obtained subsequently, Eqs. (310) or (337). In the subsequent discussions of Lowdin and others the tendency has been to emphasize the formulation in terms of orthogonalized atomic orbitals (although Lowdin gives the other version also). The use of orthogonalized atomic orbitals gives the equations a greater formal simplicity, but it is not
clear that this compensates for its disadvantages which are considerable. Aside from providing less insight into the charge distribution, as discussed above, the orthogonalized atomic orbitals are partially delocalized linear combinations of several adjacent atomic orbitals. This adds enormously to the labor involved in the evaluation of the one- and two-electron quantum integrals, especially when these involve (orthogonal) atomic orbitals on two, three, or four atoms.

In view of these practical disadvantages of orthogonalized atomic orbitals, and the fact that the formulation of the density matrix theory in terms of ordinary localized and non-orthogonal atomic orbitals is equally correct and rigorous (and in fact mathematically equivalent), no apology need be made for the use of non-orthogonal atomic orbitals with the explicit inclusion of overlap effects. It may also be noted that Roothaan based his original LCAO form of self-consistent field molecular orbital theory (prior to the density matrix formulations of Taylor and others) on non-orthogonal atomic orbitals.

### 8.62 Energy for a Single Configuration in the LCAO Approximation

The energy for the case of a single configuration has been expressed in terms of integrals over molecular orbitals in Section 8.54. Only the cases in which the one- and two-electron operators, $H_1$ and $H_{12}$, do not depend upon the spin coordinates will be considered hereafter. Substitution of the LCAO approximation, Eq. (139), for the molecular orbitals in Eq. (220), insertion of the resulting expressions for $H_1$ and
H_j in Eq. (219), and inversion of the order of summation, yields for the one-electron part of the energy

\[ E_1 = \sum_{\alpha, \beta = 1}^{\nu} (\rho_{\alpha\beta}^+ + \rho_{\alpha\beta}^-) H_{\beta\alpha} \]  

(256)

Here \( \rho_{\alpha\beta}^\pm \) is defined by Eqs. (233 a,b), and \( H_{\alpha\beta} \) is the matrix element of the one-electron operator \( H_1 \) with respect to the indicated atomic orbitals,

\[ H_{\alpha\beta} = \int \chi_\alpha^* (\vec{r}_1) H_1 \chi_\beta (\vec{r}_1) d\vec{r}_1. \]  

(257)

Designating by \( (H_1) \) the \( \nu \times \nu \) matrix with elements \( H_{\alpha\beta} \), Eq. (256) may be written

\[ E_1 = \text{Tr} \left[ (\rho^+) + (\rho^-) \right] (H_1). \]  

(258)

Substitution of Eq. (156) (with \( i = 1 \)) for \( H_1 \) in Eq. (257) yields

\[ H_{\alpha\beta} = T_{\alpha\beta} + \sum_a Z_a J_{a,\alpha\beta} \]  

(259)

where

\[ T = - (1/2) \int \chi_\alpha^* (\vec{r}_1) \nabla_1^2 \chi_\beta (\vec{r}_1) d\vec{r}_1 \]  

(260)

is the kinetic energy integral, and

\[ J_{a,\alpha\beta} = \int \chi_\alpha^* (\vec{r}_1) (1/r_{al}) \chi_\beta (\vec{r}_1) d\vec{r}_1 \]  

(261)

is the nuclear attraction integral for the \( a \)th nucleus, and for the indicated pair of atomic orbitals. For a closed-shell configuration Eqs. (256) and (258) reduce to

\[ E_1 = 2 \sum_{\alpha, \beta = 1}^{\nu} \rho_{\alpha\beta} H_{\beta\alpha} \]  

(262)
and

$$E_1 = 2 \mathcal{T} r (\rho) (H_1), \quad (263)$$

respectively.

The reduction of the two-electron part of the energy, $E_2$, for the LCAO case is similar but more tedious. Substitution of Eq. (139) for the molecular orbitals into Eqs. (227 a,b) yields

$$J_{kk'} = \sum_{\alpha', \beta', \gamma', \delta} c_{\alpha k} c_{\beta k} c_{\gamma k'} c_{\delta k'} J_{\beta \delta, \alpha \gamma} \quad (264a)$$

$$K_{kk'} = \sum_{\alpha', \beta', \gamma', \delta} c_{\alpha k} c_{\beta k} c_{\gamma k'} c_{\delta k'} J_{\beta \delta, \gamma \alpha} \quad (264b)$$

where, for the case $H_{12} = r_{12}^{-1}$,

$$J_{\alpha \beta, \gamma \delta} = \int \int \chi_\alpha^* (\vec{r}_1) \chi_\beta^* (\vec{r}_2) r_{12}^{-1} \chi_\gamma (\vec{r}_1) \chi_\delta (\vec{r}_2) d \vec{r}_1 d \vec{r}_2. \quad (265)$$

That is, $J_{\alpha \beta, \gamma \delta}$ is a two-electron integral having in its integrand as many as four distinct atomic orbitals, although in special cases two or more of these atomic orbitals may be identical. The integral is referred to as an $n$-center integral, where $n$ is the number of distinct atoms on which the atomic orbitals in the integrand are centered, and may assume the values 1, 2, 3, or 4. Both the Coulomb integrals, $J_{kk'}$, and the exchange integrals, $K_{kk'}$, defined with respect to the molecular orbitals as in Eqs. (227a,b), are expressible in terms of the two-electron atomic orbital integrals $J_{\alpha \beta, \gamma \delta}$ by appropriate permutation of indices, as shown by Eqs. (264a,b). Thus, it is unnecessary to
maintain a distinction between Coulomb and exchange integrals in defining the general two-electron integral over atomic orbitals in the LCAO approximation. Nevertheless, as will be seen subsequently, for the two-center case in which also only two of the four atomic orbitals are distinct, \( J_{\alpha\beta,\gamma\delta} \) may assume the form of a Coulomb or exchange integral defined with respect to a pair of atomic orbitals.

Substitution of Eqs. (264 a,b) into Eq. (229), inversion of the order of summation over molecular and atomic orbitals in the several terms on the right-hand side of the latter equation, and use of Eqs. (233 a,b) yields the following compact expression for the two-electron energy in terms of the elements of the density matrices \((\rho^+)\) and \((\rho^-)\),

\[
E_2 = \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta} \left( \rho^+_{\alpha\beta} \rho^+_{\gamma\delta} + \rho^-_{\alpha\beta} \rho^-_{\gamma\delta} \right) 
\]

\[
\times \left( J_{\beta\delta,\alpha\gamma} - J_{\beta\delta,\gamma\alpha} \right) + 2 \rho^+_{\alpha\beta} \rho^-_{\gamma\delta} J_{\beta\delta,\alpha\gamma} \tag{266}
\]

For a closed-shell configuration, for which \(\rho^+_{\alpha\beta} = \rho^-_{\alpha\beta} = \rho_{\alpha\beta} \), with \(\rho_{\alpha\beta}\) defined by Eq. (245), the two-electron energy reduces further to

\[
E_2 = \sum_{\alpha, \beta, \gamma, \delta} \rho_{\alpha\beta} \rho_{\gamma\delta} \left( 2J_{\beta\delta,\alpha\gamma} - J_{\beta\delta,\gamma\alpha} \right) \tag{267}
\]

As will be shown shortly in more detail the two-electron energy, \(E_2\), has a close relation to the mean electron charge distribution.

Equation (238) or (248) shows that the charge density function is a sum of binary products of atomic orbital functions with coefficients which are elements of the discrete first-order density matrix, the typical
term being of the form \( \rho_{\alpha\beta} \chi_\alpha (\mathbf{r}_1) \chi_\beta^* (\mathbf{r}_1) \). Thus, \( \chi_\alpha (\mathbf{r}_1) \times \chi_\beta^* (\mathbf{r}_1) \) may be regarded as an elementary charge distribution function, associated with the \( \alpha \beta \) th "bond" if \( \alpha \neq \beta \), or with the \( \alpha \) th atomic orbital if \( \alpha = \beta \). The two-electron integral \( J_{\alpha\beta,\gamma\delta} \) of Eq. (265) has been written in the conventional way, with the arrangement of the four atomic orbitals in the integrand (which may or may not be all distinct) patterned after that of the Coulomb and exchange integrals defined in terms of molecular orbitals in Eqs. (227 a,b). That is, the functions with arguments \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) are written following, and the complex-conjugated functions preceding, the operator \( H_{12} \). However, since the operator \( H_{12} \) in the cases under discussion is simply the multiplicative factor \( r_{12}^{-1} \), the factors in the integrand may be rearranged at will.

Following Taylor\(^ {71} \) the two-electron integral may therefore also be written in the form

\[
I_{\alpha\beta,\gamma\delta} = \int \chi_\alpha^* (\mathbf{r}_1) \chi_\beta (\mathbf{r}_1) r_{12}^{-1} \chi_\gamma^* (\mathbf{r}_2) \chi_\delta (\mathbf{r}_2) \ d\mathbf{r}_1 \ d\mathbf{r}_2
\]

(268)

in which the two atomic orbital functions with \( \mathbf{r}_1 \) as their argument are grouped together, and similarly for \( \mathbf{r}_2 \). This emphasizes the elementary charge distribution functions, and is particularly appropriate since \( I_{\alpha\beta,\gamma\delta} \) clearly represents the classical Coulomb energy of interaction (in atomic units) of the charge distributions \( \chi_\alpha^* (\mathbf{r}_1) \chi_\beta (\mathbf{r}_1) \) and \( \chi_\gamma^* (\mathbf{r}_2) \chi_\delta (\mathbf{r}_2) \). Roothaan,\(^ {83} \) in an extensive theoretical analysis of two-center quantum integrals, has recognized the advantage of writing the two-electron integrals in the manner of Eq. (268) in order to emphasize
the concept of charge distribution (see Eqs. (26) and (30) of Roothaan's paper). Although Lowdin has generally followed convention in writing these integrals, he has also pointed out (reference 84, pages 110-111) the advantages, both mnemonic and from the viewpoint of physical insight, in writing these integrals so as to emphasize the charge densities. It is true that the numerical tabulations of these integrals follow the conventional notation and arrangement of factors in the integrand. However, the connection with the conventional form is readily made through the relation (see Eqs. (265) and (268)).

\[ I_{\alpha\beta,\gamma\delta} = J_{\alpha\delta,\beta\gamma} \]  

that is, to go from either form to the other simply interchange the two interior indices. Each form of integral is clearly invariant to interchange of \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \), so that

\[ J_{\alpha\beta,\gamma\delta} = J_{\beta\delta,\alpha\gamma} = J_{\gamma\delta,\alpha\beta} = J_{\delta\gamma,\beta\alpha} \]  

and

\[ I_{\alpha\beta,\gamma\delta} = I_{\gamma\delta,\alpha\beta} = I_{\beta\delta,\gamma\alpha} = I_{\delta\gamma,\beta\alpha} \]  

Additional symmetry relations exist if the atomic orbitals are real, as is ordinarily the case, or if two or more of the atomic orbitals in the integrand are identical.

Use of Eqs. (266), (267), and (269) now yields for the two-electron energy in the general case,
or for the closed-shell case,

\[
E_2 = \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta = 1}^{2^j} \left\{ \left( \rho_+^{\alpha \beta} + \rho_-^{\alpha \beta} + \rho_+^{\beta \alpha} + \rho_-^{\beta \alpha} \right) \left( I_{\beta \alpha, \delta \gamma} - I_{\beta \gamma, \delta \alpha} \right) + 2 \rho_+^{\alpha \beta} \rho_-^{\beta \alpha} I_{\beta \alpha, \delta \gamma} \right\}.
\]  

(271)

Comparison with Eqs. (256), (262), (266), and (267) shows the advantage, simply from a mnemonic viewpoint, of the modified notation for the integrals given in Eq. (268). This is made still clearer by the discussion of the Coulomb part of the energy which follows.

The two-electron energy is often called the interelectronic repulsion energy, since in view of Eq. (163) it represents the mean value of the Coulomb repulsion terms, \( H_{ij} = 1/|r_{ij}| \), in the Hamiltonian operator for the system. In order to make clearer the significance of Eqs. (271-2) for \( E_2 \) in the LCAO case it is useful to give the following analysis. The total mean electron charge density, including electrons of both positive and negative spin, is

\[
p(\mathbf{r}) = \rho_+^{\alpha \beta}(\mathbf{r}) + \rho_-^{\alpha \beta}(\mathbf{r}) = \sum_{\alpha, \beta = 1}^{2^j} \left( \rho_+^{\alpha \beta} + \rho_-^{\alpha \beta} \right) \chi_\alpha(\mathbf{r}) \chi^*_\beta(\mathbf{r}).
\]

(273)

from Eq. (238). If this mean charge density is regarded as a static continuous charge distribution, the classical coulombic interaction
(repulsion) energy of this charge distribution with itself may be computed. Letting $r_{12} = |\vec{r}_1 - \vec{r}_2|$, this yields (in atomic units)

$$E_2^c = (1/2) \int \int \rho(\vec{r}_1) r_{12}^{-1} \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

$$= (1/2) \int \int \left\{ \sum_{\alpha, \beta = 1}^{\nu} \left( \rho_{\alpha \beta}^+ \rho_{\alpha \beta}^- \right) \chi_{\alpha}(\vec{r}_1) \chi_{\beta}^*(\vec{r}_1) \right\} r_{12}^{-1}$$

$$\left\{ \sum_{\gamma, \delta = 1}^{\nu} \left( \rho_{\gamma \delta}^+ \rho_{\gamma \delta}^- \right) \chi_{\gamma}(\vec{r}_2) \chi_{\delta}^*(\vec{r}_2) \right\} d\vec{r}_1 d\vec{r}_2$$

$$= (1/2) \sum_{\alpha, \beta, \gamma, \delta = 1}^{\nu} \left( \rho_{\alpha \beta}^+ \rho_{\gamma \delta}^+ + \rho_{\alpha \beta}^- \rho_{\gamma \delta}^- + \rho_{\alpha \beta}^+ \rho_{\gamma \delta}^- + \rho_{\alpha \beta}^- \rho_{\gamma \delta}^+ \right)$$

$$\int \chi_\beta^*(\vec{r}_1) \chi_\alpha(\vec{r}_1) r_{12}^{-1} \chi_\delta^*(\vec{r}_2) \chi_\gamma(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

$$= (1/2) \sum_{\alpha, \beta, \gamma, \delta = 1}^{\nu} \left[ \left( \rho_{\alpha \beta}^+ \rho_{\gamma \delta}^+ + \rho_{\alpha \beta}^- \rho_{\gamma \delta}^- \right) + 2 \rho_{\alpha \beta}^+ \rho_{\gamma \delta}^- \right]$$

$$\times I_{\beta \gamma \delta \alpha}$$  \hspace{1cm} (274)

where Eqs. (268), (270b), and (273) have been used. The factor 1/2 enters because the integration over all values of $\vec{r}_1$ and $\vec{r}_2$ counts the interaction of the charge in each pair of volume elements twice.

Comparison of Eqs. (271) and (274) shows that two-electron energy, $E_2$, is the sum of the Coulomb energy and an exchange energy,

$$E_2^e = - (1/2) \sum_{\alpha, \beta, \gamma, \delta = 1}^{\nu} \left( \rho_{\alpha \beta}^+ \rho_{\gamma \delta}^+ + \rho_{\alpha \beta}^- \rho_{\gamma \delta}^- \right) I_{\beta \gamma \delta \alpha}$$  \hspace{1cm} (275)
That is

\[ E_2 = E_2^c + E_2^e. \]  
(276)

For the closed-shell case \( E_2 \) is given by Eq. (272), and the Coulomb and exchange energies by

\[ E_2^c = 2 \sum_{\alpha \beta \gamma \delta = 1}^{z'} \rho_{\alpha \beta} \rho_{\gamma \delta} I_{\alpha \beta, \gamma \delta}. \]  
(277)

\[ E_2^e = - \sum_{\alpha \beta \gamma \delta = 1}^{z'} \rho_{\alpha \beta} \rho_{\gamma \delta} I_{\beta \gamma, \delta \alpha}. \]  
(278)

A similar division of the energy \( E_2 \) into a Coulomb and exchange part was found in Eqs. (229) and (231), which express \( E_2 \) in terms of Coulomb integrals, \( J_{kk} \), and exchange integrals, \( K_{kk} \), defined in terms of molecular orbitals by Eqs. (227 a,b). It is readily seen that \( E_2^c \) and \( E_2^e \) as defined here represent in the LCAO case the sum of the Coulomb and exchange terms, respectively, as given in Eqs. (229) or (231).

It is clear from their definitions in terms of molecular orbitals in Eqs. (206 a,b) that \( \rho^+ (\mathbf{r}_1) \) and \( \rho^- (\mathbf{r}_1) \), and therefore also their sum, \( \rho (\mathbf{r}_1) \), are non-negative functions for all values of \( \mathbf{r}_1 \). As a result the Coulomb energy, \( E_2^c \), as defined by Eq. (274) is necessarily positive. This is also clear from Eqs. (227a), (229), and (231), since the Coulomb integrals \( J_{kk} \) are non-negative. It is less obvious that the exchange integrals, \( K_{kk} \), of Eq. (227b) are non-negative, but this has been proved by Roothaan. It follows, because of the negative coefficients with which the exchange integrals enter into Eqs. (229) and (231), that the total exchange energy is negative. The exchange
energy, $E_e^e$, as expressed by Eq. (275) or (278) for the LCAO case, must therefore also be negative.

The exchange energy therefore represents a decrease in the inter-electron repulsion energy as computed on the assumption of a static continuous charge distribution. This decrease is a result of the exclusion principle, or the use of the anti-symmetrized wave function of Eq. (153) for the closed-shell case, which evidently tends on the average to keep the electrons further apart than would be the case for a wave function constructed from the same molecular orbitals but not anti-symmetrized. This phenomenon was investigated in detail by Wigner and Seitz, and leads to the concept of the Fermi hole, which has been discussed from the viewpoint of the second-order density matrix in Section 8.51. Although the exchange energy is a negative quantity, it is clear that the total two-electron energy, $E_e$, is a positive quantity (whether computed from the approximate single-configuration wave function considered here or the exact wave function for the system) because in view of Eqs. (157) and (163) it represents the mean value of a quantity which is non-negative (and which vanishes only in the limit in which the distance between every pair of electrons in the system approaches infinity).

8.63 Secular Equation for a Single Configuration in the Self-consistent Field LCAO Approximation

a. Reduction of the first differential of the energy.---In the present section the secular equation for self-consistent field molecular orbital theory in the LCAO approximation will be obtained by minimization of the energy of the system. This will be accomplished in part using the compact expressions for the energy in terms of elements of the LCAO
density matrix as obtained in the preceding section. This method is considerably simpler and easier to follow than Roothaan's original method for the derivation of the secular equation based on the use of Coulomb- and exchange-type integral operators.

The total energy, $E$, of the system is the sum of $E_0$, $E_1$, and $E_2$, as indicated by Eq. (160). The internuclear repulsive energy (or in some approximations the "core" and "core-repulsion" energies) is a function of the nuclear parameters through Eq. (155), and is constant if these remain fixed. In the present section only variations of the form of the electronic wave functions or molecular orbitals (or of the corresponding density matrices) are considered, the nuclear parameters (charges and coordinates) being assumed fixed. Thus, the variation of $E_0$ vanishes, and does not have to be considered further. However, if after determining the best molecular orbitals and total wave function for given nuclear parameters it is desired to investigate the variation of the total energy $E$ with variation of the latter (in order, for example, to minimize $E$ also with respect to the nuclear parameters), it then becomes necessary to include the variation of $E_0$ in computing the variation of $E$.

For the case of fixed nuclear parameters, as just discussed, the variation of $E$ is given by

$$\delta E = \delta E_1 + \delta E_2.$$  

(279)

Here $E_1$ is the one-electron part of the energy representing the mean energy of the electrons in the fields of the nuclei, and $E_2$ is the two-electron part of the energy or the electron-pair repulsion energy. For the open-shell case, $E_1$ and $E_2$ are given in terms of the elements $\rho^{\pm}_{\alpha\beta}$ of the LCAO density matrices, ($\rho^+$) and ($\rho^-$), by Eqs. (256) and (271).
On taking the variation of these expressions and substituting in Eq. (279), there is obtained after rearrangement,

$$\delta E = \sum_{\alpha \beta} (F^+_{\alpha \beta} \delta \rho^+_{\alpha \beta} + F^-_{\alpha \beta} \delta \rho^-_{\alpha \beta}),$$

where

$$F^\pm_{\alpha \beta} = H_{\alpha \beta} + \sum_{\gamma \delta} \left[ \rho^\pm_{\alpha \beta} (I_{\alpha \gamma, \delta \gamma} - I_{\alpha \gamma, \delta \beta}) + \rho^\pm_{\gamma \delta} I_{\alpha \gamma, \delta \gamma} \right].$$

The Hartree-Fock operators for electrons of positive and negative spin are represented in the LCAO approximation by the Hermitian matrices \((F^+)\) and \((F^-)\), with elements \(F^+_{\alpha \beta}\) and \(F^-_{\alpha \beta}\), respectively. In terms of these matrices, Eq. (280) may be written

$$\delta E = \text{Tr} \left[ (F^+)(\delta \rho^+) + (F^-)(\delta \rho^-) \right],$$

where \((\delta \rho^\pm)\) is a matrix having as its \(\alpha \beta\) th element \(\delta \rho^\pm_{\alpha \beta}\). For the closed-shell case, \(\rho_{\alpha \beta} = \rho^\pm_{\alpha \beta}\), and the preceding relations reduce to

$$\delta E = 2 \sum_{\alpha \beta} F_{\alpha \beta} \delta \rho_{\alpha \beta} = 2 \text{Tr} \left[ (F)(\delta \rho) \right],$$

where \((F)\) is the Hermitian matrix with elements

$$F_{\alpha \beta} = H_{\alpha \beta} + \sum_{\gamma \delta} \rho_{\gamma \delta} (2 I_{\alpha \gamma, \delta \gamma} - I_{\alpha \gamma, \delta \beta}),$$

and \((\delta \rho)\) is the matrix having \(\delta \rho_{\alpha \beta}\) as its \(\alpha \beta\) th element. This representation of the matrix \((F)\) of the self-consistent field LCAO molecular orbital theory of Roothaan in terms of the elements of the LCAO density matrix, \((\rho)\), was first given by Taylor.

In order to proceed further with the minimization of the energy and the formulation of the secular equation it is convenient to introduce at this point a representation of the LCAO density matrices, \((\rho^\pm)\) or
(ρ), as products of matrices having as their elements the coefficients $c_{α_1}$ which determine the form of the molecular orbitals through Eq. (139). In order to treat correctly the open-shell case it now becomes necessary to divide the occupied molecular orbitals into three sets as follows:

1. the set of $N(±)$ molecular orbitals occupied by a pair of electrons with opposed spins which constitutes the "closed-shell" part of the configuration (in this connection see Eq. (210));
2. the $n_+$ molecular orbitals occupied by a single electron with positive spin;
3. the $n_-$ molecular orbitals occupied by a single electron with negative spin.

These three sets of molecular orbitals may be regarded as forming the elements of row matrices which will be denoted by $(φ(±), φ_+, φ_-)$, respectively. The complete set of $N_+ = N(±) + n_+$ molecular orbitals occupied by an electron with positive spin may be represented by the partitioned row matrix $(φ(±), φ_+)$, the complete set of $N_- = N(±) + n_-$ molecular orbitals occupied by an electron with negative spin by $(φ(±), φ_-)$, and the set of all $n$ distinct molecular orbitals, whether doubly or singly occupied, by

$$(φ) = (φ(±), φ_+, φ_-).$$  \hspace{1cm} (285)$$

It is clear that

$$n = N(±) + n_+ + n_-.$$  \hspace{1cm} (286)$$

and that the total number of electrons is

$$N = 2 N(±) + n_+ + n_- = n + N(±) = N_+ + N_- - N(±).$$  \hspace{1cm} (287)$$

For a closed-shell configuration, with all $n$ occupied molecular orbitals doubly occupied, $n_+ = n_− = 0$, $N_+ = N_- = N(±) = n$, $N = 2n$, and
\( \phi = (\phi_{\pm}) \). The \( \nu \) atomic orbitals, \( \chi_{\alpha} (\alpha = 1, \ldots, \nu) \) from which the molecular orbitals are formed according to Eq. (139) will be represented as the row matrix \( (\chi) \). In view of the latter equation the linear transformations from atomic orbitals to the three sets of molecular orbitals defined above may be represented in matrix form as

\[
(\phi_{\pm}) = (\chi)(C_{\pm}), \hspace{1cm} (288a)
\]

\[
(\phi_+) = (\chi)(C_+), \hspace{1cm} (288b)
\]

\[
(\phi_-) = (\chi)(C_-). \hspace{1cm} (288c)
\]

Here \( (C_{\pm}), (C_+), \) and \( (C_-) \) are matrices having \( \nu \) rows each but \( N_{\pm}, n_+, \) and \( n_- \) columns, respectively, and having as the element in their 1\( \text{st} \) column and \( \alpha \text{th} \) row the coefficient \( c_{\alpha i} \) of \( \chi_{\alpha} \) in the molecular orbital in the \( i \text{th} \) position (column) of \( (\phi_{\pm}), (\phi_+), \) or \( (\phi_-), \) respectively.

Thus, the columns of \( (C_{\pm}), (C_+), \) and \( (C_-) \) are in one-to-one correspondence with the \( n \) distinct occupied molecular orbitals, and will be found to constitute the eigenvectors of the LCAO secular equation. The complete sets of \( N_+ \) or \( N_- \) molecular orbitals occupied by electrons of positive or negative spin may be represented as

\[
(\phi_{\pm}, \phi_+) = (\chi)(C_{\pm}, C_+), \hspace{1cm} (289a)
\]

or

\[
(\phi_{\pm}, \phi_-) = (\chi)(C_{\pm}, C_-), \hspace{1cm} (289b)
\]

respectively, and the set of all \( n \) occupied molecular orbitals as

\[
(\phi) = (\phi_{\pm}, \phi_+, \phi_-) = (\chi)(C_{\pm}, C_+, C_-), \hspace{1cm} (290)
\]

in terms of matrices partitioned as indicated. For a closed-shell configuration, the matrices \( (C_+) \) and \( (C_-) \) do not exist, and \( (C_{\pm}) \) will
be denoted by \((\psi)\), so that
\[
(\psi) = (\phi_{(\pm)}) = (\lambda)(C_{(\pm)}) = (\lambda)(C).
\] (291)

In this case \((\phi)\) is a row matrix having the \(n\) molecular orbitals as its elements, and \((C)\) is a \(\nu \times n\) matrix.

The elements \(\rho_{\alpha\beta}^{\pm}\) of the \(\nu \times \nu\) LCAO density matrices \((\rho^+\) and \((\rho^-)\) are defined by Eqs. (233 a,b). It is readily seen that these matrices may be represented as products of the eigenvector or \(C_\pm\) matrices in the form,
\[
(\rho^+) = (C_{(\pm)})(C_{(\pm)})^\dagger + (C_+)(C_+)^\dagger, \quad (292a)
\]
\[
(\rho^-) = (C_{(\pm)})(C_{(\pm)})^\dagger + (C_-)(C_-)^\dagger. \quad (292b)
\]

Here the dagger indicates the Hermitian conjugate of a matrix, or the complex conjugate of the transposed matrix. For the closed-shell case,
\[
(\rho) = (\rho^+) = (\rho^-) = (C_{(\pm)})(C_{(\pm)})^\dagger = (C)(C)^\dagger. \quad (293)
\]

From Eqs. (292 a,b) the variation of \((\rho^{\pm})\) is represented to terms of first degree in the variations \(\delta c_{a1}\) of the coefficients defining the molecular orbitals by
\[
(\delta \rho^+) = (\delta C_{(\pm)})(C_{(\pm)})^\dagger + (C_{(\pm)})(\delta C_{(\pm)})^\dagger + (\delta C_+)(C_+)^\dagger + (C_-)(\delta C_-)^\dagger. \quad (294)
\]

This and subsequent equations in which both \((\pm)\) and \(+\) signs occur represent in actuality a pair of equations, in one of which the signs are to be taken as \((\pm)\) and \(+\), and in the other as \((\pm)\) and \(-\). The matrices \((\delta C_{(\pm)}), (\delta C_+), \) and \((\delta C_-)\) have as their elements the variations \(\delta c_{a1}\) of the elements \(c_{a1}\) in the corresponding positions of the matrices \((C_{(\pm)}), (C_+), \) and \((C_-)\), respectively. Substitution of \((\delta \rho^{\pm})\) from Eq. (294) into Eq. (282) yields for the variation of the energy
We now use the fact that the trace of a sum of matrices is the sum of the traces of the corresponding matrices, and the invariance of the trace of a product of matrices to a cyclic permutation of the factors (note that if the matrices are conformable for multiplication with the original order of factors and the product is a square matrix as it must be if the trace is defined then the matrices remain conformable and the product square following a cyclic permutation of the factors) to put Eq. (295) in a form in which the matrices of the variations occur as postmultipliers in each product. When this result is again written as the trace of a single matrix for compactness there is obtained

\[
\delta E = \text{Tr} \left\{ (C^\pm)^\dagger \left[ (F^+ + F^-) (C^\pm)^\dagger + (C^\pm) (\delta C^\pm)^\dagger \right] + \left( (\delta C^+)^\dagger + (C^+)(\delta C^+)^\dagger \right) \right\}. \tag{295}
\]

For the closed-shell case, from Eq. (293),

\[
(\delta p) = (\delta C)(C)^\dagger + (C)(\delta C)^\dagger. \tag{297}
\]

and substitution in Eq. (293) followed by a rearrangement similar to that used in obtaining Eq. (296) yields

\[
E = 2 \text{Tr} \left\{ (C)^\dagger (F)(\delta C) + (F)(C)(\delta C)^\dagger \right\}. \tag{298}
\]

b. **Orthonormality conditions.**—The minimization of the energy must be carried out subject to the conditions of orthonormality imposed on the molecular orbitals in the preceding theoretical analysis. These conditions are that the set of N distinct molecular spinorbitals,
\( \phi_i \sigma^-_i \) \((i = 1, \ldots, N; \sigma^- = \sigma^+ \text{ or } \sigma^-)\) which are used in the construction of the antisymmetrized wave function \( \Phi \) of the \( N \) electron system for the given configuration (see Eqs. (149) or (151)) must be normalized and mutually orthogonal. This requirement enters the theoretical treatment in connection with the normalization of \( \Phi \) as in Eq. (152), and the reduction of the first-order density matrix of the system as given in Eq. (191). For the single configuration case the second-order density matrix is determined by the first-order matrix through Eq. (196).

Furthermore, the general density matrix formulation of the one- and two-electron parts of the energy as in Eqs. (189) and (190), shows that these are completely determined by the first- and second-order density matrices. It follows that the normalization and mutual orthogonality of the set of \( N \) distinct molecular spinorbitals are the only auxiliary conditions required to be placed upon these orbitals in connection with the minimization of the energy of the system. The \( N \) molecular spinorbitals are necessarily distinct, as otherwise the wave function \( \Phi \) of the system would vanish identically in accordance with the Pauli exclusion principle. However the molecular orbitals, \( \phi_i \), or space parts of the spinorbitals are not in general distinct.

As discussed above the \( n \) occupied molecular orbitals may be divided into three sets, \((\phi_\pm)\), \((\phi_+)\), and \((\phi_-)\), containing \( n_\pm \), \( n_+ \), and \( n_- \) distinct molecular orbitals, respectively (see Eqs. (285) and (286)). Each of the molecular orbitals in the set \( \phi_\pm \) occurs as a factor in two molecular spinorbitals, once with the spin function \( \sigma^- \) and once with \( \sigma^+ \). Each of the molecular orbitals in the sets \((\phi_+)\) and \((\phi_-)\)
occurs in only a single spinorbital, with spin functions $\sigma_+^+$ and $\sigma_-^-$ for orbitals in the two sets, respectively. Thus the total sets of molecular orbitals occurring with spin factors $\sigma_+^+$ and $\sigma_-^-$ are $(\phi_{(\pm)}^+, \phi_{(\pm)}^-)$ and $(\phi_{(\pm)}^+, \phi_{(\pm)}^-)$, respectively. It is clear from the orthonormality of the spin factors, Eqs. (145) and (146), combined with the required ortho-normality of the molecular spinorbitals, that: 1) each of the $n$ molecular orbitals must be normalized in accordance with Eq. (140); 2) the molecular orbitals within each of the sets $(\phi_{(\pm)}^+), (\phi_{(\pm)}^-)$, and $(\phi_{(\pm)}^-, \phi_{(\pm)}^-)$ must be mutually orthogonal in accordance with Eq. (140); 3) each of the molecular orbitals in the sets $(\phi_{(\pm)}^+)$ and $(\phi_{(\pm)}^-)$ must be orthogonal to each in the set $(\phi_{(\pm)}^+); 4)$ the molecular orbitals in the set $(\phi_{(\pm)}^+)$ are not required to be orthogonal to those in the set $(\phi_{(\pm)}^-)$ as orthogonality of the corresponding spinorbitals is assured by the spin factors; and 5) no molecular orbital in $(\phi_{(\pm)}^+)$ may be identical with an orbital in $(\phi_{(\pm)}^-)$ as otherwise this orbital would be assigned to $(\phi_{(\pm)}^+)$, and the three sets are mutually exclusive by definition.

The required orthonormality conditions as stated in items (1-3) above impose conditions of the type given in Eq. (141) on the coefficients $c_{\alpha \beta}$ determining the form of the molecular orbitals in the LCAO approximation. These conditions may be conveniently represented in matrix form as

$$
(C_{(\pm)}^+)^T (S)(C_{(\pm)}) = (I_{(\pm)}),
$$

(299a)

$$
(C_{(\pm)}^-)^T (S)(C_{(\pm)}) = (I_{(\pm)}),
$$

(299b)

$$
(C_{(\pm)}^+)^T (S)(C_{(\pm)}^-) = (0)
$$

(299c)

Here $(S)$ is the $\nu \times \nu$ Hermitian or self-conjugate overlap matrix with elements $S_{\alpha \beta}$ defined by Eq. (142). Equations (299b) and (299c) each
represent a pair of equations in which the $\pm$ signs (but not the $(\pm)$ sign) are all taken as + or all as - signs, respectively. $(I_{(\pm)})$ and $(I_{\pm})$ are (square) unit matrices of dimension $N_{(\pm)}$ and $n_{\pm}$, respectively, and $(0)$ in Eq. (296c) represents the $N_{(\pm)} \times n_{\pm}$ null matrix. If in addition to the preceding orthonormality conditions required by the assumptions made in the theoretical analysis it were desired to impose also the condition that molecular orbitals in the set $(\phi_+)$ be orthogonal to those in the set $(\phi_-)$, then there would be the added condition

$$(c_+)^\dagger (s)(c_-) = (0), \quad (299d)$$

where $(0)$ represents the $n_+ \times n_-\text{null matrix (note that the Hermitian conjugates of Eqs. (296c) and 299d do not yield independent conditions).}$

However, in view of item (4) above the last condition is optional and not required. For a closed-shell configuration the single required auxiliary condition is Eq. (299a) which reduces to

$$(c)^\dagger (s)(c) = (I), \quad (300)$$

where $(I)$ is the $n$-dimensional unit matrix.

From Eqs. (299a,b) and (299a,b,c) there is obtained

$$
(r_{\pm}^\dagger)(s)(r_{\pm}) = (c_{(\pm)}(I_{(\pm)})(c_{(\pm)})^\dagger + (c_{(\pm)}(0)(c_{(\pm)})^\dagger
+ (c_{\pm})(0)(c_{\pm})^\dagger + (c_{\pm})(I_{\pm})(c_{\pm})^\dagger
= (c_{(\pm)}(c_{(\pm)})^\dagger + (c_{\pm})(I_{\pm})(c_{\pm})^\dagger
= (r_{\pm})
\quad (301)$$

Similarly for the closed-shell case Eqs. (293) and (300) yield

$$(r)(s)(r) = (c)(I)(c)^\dagger = (c)(c)^\dagger = (r). \quad (302)$$

These represent matrix derivations of the idempotency conditions, Eqs. (235) or (236), and Eqs. (246) or (247), for the LCAO density matrices for the general case of non-orthogonalized atomic orbitals. Thus the
idempotency of the density matrices is equivalent to the orthonormality conditions on the molecular orbitals (the optional nature of the orthogonality conditions represented by Eq. (299d) is confirmed by the fact that this relation is not required for the derivation of Eq. (301)). It is possible to devise procedures for the direct minimization of the energy as expressed in terms of elements of the LCAO density matrices, using Eq. (282) or (283) for $\delta E$ and applying the idempotency conditions on the variations ($\delta \rho^\dagger$) or ($\delta \rho$) of the density matrices as required by Eqs. (301) or (302), respectively. Such a procedure was first suggested by Taylor, and an ingenious method of steepest descents for accomplishing this has been developed by McWeeny. However, this procedure is not as well tested and is probably more difficult than the solution of the LCAO self-consistent secular equation for the molecular orbitals. Although all observable properties of a given state are determined the density matrices for that state, the knowledge of the form and "energy" of the individual molecular orbitals obtained by solution of the secular equation makes possible the semi-quantitative consideration of phenomena involving excitation of electrons to higher states without the necessity of elaborate additional calculations to obtain the energies of the excited states.

c. Minimization of energy for open-shell configurations by Lagrange's method. The normalization and orthogonality conditions in the form required for the derivation of the secular equation for the single-configuration open-shell case are obtained by taking the variation of Eqs. (299 a-d), with the retention of only terms of first degree in the variations of the $c_{\omega i}$'s or the C-matrices, to yield
In accordance with the method of Lagrange these auxiliary conditions are now premultiplied by matrices having as their elements the Lagrangian multipliers. On taking the traces of each side of the resulting matrix equations and carrying out a cyclic rearrangement of the factors similar to that made in obtaining Eq. (296) there is obtained

\[
\begin{align*}
\text{Tr} \left\{ (S)(C_+)^+ (L_+)(C_+)^+ (S)(\delta C_+)^+ \right\} & = 0 \quad (304a) \\
\text{Tr} \left\{ (S)(C_+)^+ (L_+)(C_+)^+ (S)(\delta C_+)^+ \right\} & = 0 \quad (304b) \\
\text{Tr} \left\{ (S)(C_+)^+ (L_+)(C_+)^+ (S)(\delta C_+)^+ \right\} & = 0 \quad (304c) \\
\text{Tr} \left\{ (S)(C_+)^+ (L_+)(C_+)^+ (S)(\delta C_+)^+ \right\} & = 0 \quad (304d)
\end{align*}
\]

Here \((L_+)(C_+)^+\) and \((L_+)(C_+)^+\) are square matrices of Lagrangian multipliers of dimension \(N_+(C_+)\) and \(n_+\), respectively; \((L_+)(C_+)^+)\) and \((L_+)(C_+)^+)\) are \(n_+ x N_+(C_+)\) and \(n_+ x n_+\) matrices. In addition the equations obtained by setting equal to zero the traces of the Hermitian conjugates of the expressions within the braces in Eqs. (304c) and (304d) yield independent conditions, because \((\delta C_+)^+, (\delta C_+)^+\) and \((\delta C_+)^+, (\delta C_+)^+\) are all regarded as independently variable following the introduction of the Lagrangian multipliers. This yields after cyclic rearrangement the equations

\[
\begin{align*}
\text{Tr} \left\{ (S)(C_+)^+ (L_+)(C_+)^+ (S)(\delta C_+)^+ \right\} & = 0 \quad (304e)
\end{align*}
\]
Furtherm ore each of Eqs. (304 b, c, e) represent a pair of independent equations, as explained following Eq. (294)

On adding each of the independent condition equations represented by Eqs. (304 a-f) to Eq. (296), and noting that $E$ must vanish for the conditional minimum of the energy, there is obtained a single matrix equation homogeneous and linear in the variations $(\delta C_+)$, $(\delta C_-)$, $(\delta C_+)^\dagger$, $(\delta C_-)^\dagger$, and $(\delta C_+)^\dagger$. As the elements of each of the latter six matrices are now arbitrarily variable the matrix coefficient of each in this equation must be a null matrix. On setting equal to zero the coefficients of $(\delta C_+)^\dagger$, $(\delta C_-)^\dagger$, and $(\delta C_-)^\dagger$, the following three equations are obtained,

\[
\begin{align*}
\left[F^+(C_+) + (F^-(C_-))\right] &= (S) \left[[C_+](L_+)(\pm) + (C_+)(L_+\pm) + (C_-)(L_-\pm)\right], \\
(F^+(C_+) &= (S) \left[[C_-](L_-)(\pm) + (C_+)(L_+\pm) + (C_-)(L_-\pm)\right], \\
(F^-(C_-) &= (S) \left[[C_+](L_+)(\pm) + (C_-)(L_-\pm)\right].
\end{align*}
\]

Setting equal to zero the coefficients of $(\delta C_+)$, $(\delta C_-)$, and $(\delta C_-)$, and then taking the Hermitian conjugates of the resulting equations, yields three equations identical with Eqs. (305 a, b, c) except for the replacement of the matrices $(L_+(\pm), (L_+\pm)$ and $(L_-\pm)$ by their Hermitian conjugate matrices. If these two sets of equations are to be consistent it is therefore necessary that these three matrices be Hermitian, or that

\[
\begin{align*}
(L_+(\pm), (L_+\pm) &= (L_+(\pm), (L_+\pm)), \\
(L_-\pm) &= (L_-\pm).
\end{align*}
\]
Equations (305 a,b,c), together with the restrictions of Eqs. (306 a,b), constitute a set of simultaneous linear matrix equations for the determination of the matrices \((C_{(+)}), (C_{+}), \text{ and } (C_{-})\), or the molecular orbitals, which minimize (or more generally make stationary) the total electronic energy of the system. Unfortunately the solution of these equations is greatly complicated by the occurrence of the Lagrangian multipliers connecting pairs of the matrices \((C_{(+)}), (C_{+}), \text{ and } (C_{-})\), or different columns of the same matrix. The extent to which such Lagrangian multipliers can be removed will now be considered.

Let arbitrary unitary transformations of the molecular orbitals within each of the sets \((\phi_{(+)}), (\phi_{+}), \text{ and } (\phi_{-})\) be represented by

\[
(\phi^{'}_{(+)} = (\phi_{(+)}) (U_{(+)})^*, \tag{307a}
\]

\[
(\phi^{'}_{+}) = (\phi_{+}) (U_{+}). \tag{307b}
\]

Here \((U_{(+)}) \text{ and } (U_{+})\) are (square) unitary matrices of dimension \(N_{(+)}\) and \(n_{+}\), respectively, and \((\phi^{'}_{(+)}\) and \((\phi^{'}_{+})\) are row matrices having as their elements the transformed molecular orbitals. On substituting into Eqs. (307 a,b) the Eqs. (288 a,b,c) for the original molecular orbitals, the transformed molecular orbitals are found to be related to the atomic orbitals by the linear transformations,

\[
(\phi^{'}_{(+)} = (\chi)(C^{'}_{(+)}), \tag{308a}
\]

\[
(\phi^{'}_{+}) = (\chi)(C^{'}_{+}). \tag{308b}
\]

with

\[
(C^{'}_{(+)} = (C_{(+)}) (U_{(+)}, \tag{309a}
\]

\[
(C^{'}_{+}) = (C_{+}) (U_{+}). \tag{309b}
\]
Solution of Eqs. (309 a, b) for \((C_{\pm})\) and \((C^\dagger_{\pm})\), and substitution for the latter matrices in Eqs. (305 a, b, c) yields
\[
\begin{align*}
[f^+ + (F^-)](C_{\pm}) &= (S) \left[ (C_{\pm}^\dagger)(\epsilon_{\pm},(\pm)) + (C^\dagger_{\pm})(\epsilon_{\pm},(\pm)) + (C^\dagger_{\pm})(\epsilon_{\pm},(\pm)) \right], \\
(F^+)(C^\dagger_{\pm}) &= (S) \left[ (C_{\pm}^\dagger)(\epsilon_{\pm},(\pm)) + (C^\dagger_{\pm})(\epsilon_{\pm},(\pm)) + (C^\dagger_{\pm})(\epsilon_{\pm},(\pm)) \right], \\
(F^-)(C^\dagger_{\pm}) &= (S) \left[ (C_{\pm}^\dagger)(\epsilon_{\pm},(\pm)) + (C^\dagger_{\pm})(\epsilon_{\pm},(\pm)) + (C^\dagger_{\pm})(\epsilon_{\pm},(\pm)) \right],
\end{align*}
\]
where
\[
\begin{align*}
(\epsilon_{\pm},(\pm)) &= (U_{\pm})^\dagger (L_{\pm},(\pm)) (U_{\pm}), \\
(\epsilon_{\pm},(\pm)) &= (U_{\pm})^\dagger (L_{\pm},(\pm)) (U_{\pm}), \\
(\epsilon_{\pm},(\pm)) &= (U_{\pm})^\dagger (L_{\pm},(\pm)) (U_{\pm}), \\
(\epsilon_{\pm},(\pm)) &= (U_{\pm})^\dagger (L_{\pm},(\pm)) (U_{\pm}).
\end{align*}
\]

Since every Hermitian matrix can be diagonalized by a unitary transformation, the unitary matrices \((U_{\pm})\) and \((U^\dagger_{\pm})\) can be chosen to diagonalize \((L_{\pm},(\pm))\) and \((L_{\pm},(\pm))\). The matrices \((\epsilon_{\pm},(\pm))\) and \((\epsilon_{\pm},(\pm))\) will then be diagonal matrices having real elements on their diagonals (since the roots of Hermitian matrices are real). The matrices \((\epsilon_{\pm},(\pm))\) and \((\epsilon_{\pm},(\pm))\), which are rectangular in general, will still have non-vanishing elements or Lagrangian multipliers at each position. However, as previously pointed out the imposition of the orthogonality condition (299d) is optional for the single-configuration case. Omission of this condition relaxes the restrictions on the singly occupied molecular orbitals and by the variation theorem of quantum mechanics must lower (or leave stationary) the energy and improve (or leave unchanged) the wave function of the system. Omission of the conditions of Eq. (299d), or the equivalent Eq. (303d), is equivalent to setting \((L_{\pm},(\pm))\) equal to...
the $n_+ \times n_+$ null matrix in the subsequent equations. It follows from Eq. (31ld) that $(\epsilon_{+,0})$ reduces to the same null matrix in this case.

The only non-vanishing non-diagonal Lagrangian multipliers connecting different columns of the matrices $(C^+_1)$, $(C^+_2)$, and $(C^-)$ in Eqs. (310 a,b,c) will then be the elements of the matrices $(\epsilon(\pm),+)$, $(\epsilon(\pm),-)$, and their Hermitian conjugates. These matrices have the effect of coupling the doubly-occupied molecular orbitals with those which are singly-occupied, whether by electrons of positive or negative spin. In general it is not possible to remove this coupling by a further unitary transformation which mixes molecular orbitals in two or more of the sets $(\phi(\pm))$, $(\phi_+)$, and $(\phi_-)$, without at the same time introducing equivalent coupling terms into the left-hand sides of these equations.

It should be noted, however, that Eqs. (310 a,b,c) would still represent a set of coupled equations for the coefficients determining the form of the molecular orbitals even if it were possible to remove all non-diagonal Lagrangian multipliers on the right-hand sides of these equations. This is a result of the fact that the elements of the matrices $(F^\pm)$ on the left-hand sides of these equations, which are given by Eqs. (281), depend on the elements $\rho_{\alpha\beta}^\pm$ of the first-order density matrices $(\rho^\pm)$ (note that $(F^+)$ and $(F^-)$ each depend on both $(\rho^+)$ and $(\rho^-)$). But the density matrices depend, through Eqs. (233 a,b) or the equivalent Eqs. (292 a,b), on the form of all the occupied molecular orbitals. This coupling of the molecular orbitals through the form of the matrices $(F^\pm)$, which are the representations for the LCAO case of the Hartree-Fock operators, is a reflection of the fact that the electrons are required to move in a self-consistent field. It is of some
importance to show that the matrices \( \rho^\pm \) are invariant to the unitary transformations of the molecular orbitals represented by Eqs. (307 a,b).

Thus, from Eqs. (292 a,b) and (309 a,b),

\[
\rho^\pm = (C^\pm_+)(U^\pm_+)^\dagger (U^\pm_+)(C^\pm_+)^\dagger + (C^\pm_\pm)(U^\pm_\pm)^\dagger (U^\pm_\pm)(C^\pm_\pm)^\dagger
\]

\[
= (C^\pm_+)(C^\pm_+)^\dagger + (C^\pm_\pm)(C^\pm_\pm)^\dagger.
\]

(312)

which is the same result obtained by direct substitution of \( (C^\pm_+) \) and \( (C^\pm_\pm) \) for \( (C_+) \) and \( (C_\pm) \), respectively, in Eqs. (292 a,b). It follows that the matrices \( \rho^\pm \) are also invariant to such unitary transformations. However, these matrices are not invariant in general to transformations which mix molecular orbitals from two or more of the sets \( (\phi^\pm_+) \), \( (\phi^\pm_-) \), and \( (\phi^\pm) \). This represents a further obstacle to removing the non-diagonal Lagrangian multipliers represented by the elements of the matrices \( (\epsilon^\pm_+) \) (and \( (\epsilon^\pm_-) \) if orthogonality of the sets \( (\phi^\pm_+) \) and \( (\phi^\pm_-) \) is required). For further discussion of the open-shell case reference should be made to Lefebvre, Roothaan, and Huzinaga.

\[\text{d. Minimization of energy and secular equation for closed-shell configurations.} \]

The minimization of the energy in the closed-shell case is not only simpler but can be carried to a more satisfactory conclusion. The orthonormality conditions in this case are represented by the single matrix relation, Eq. (300). The auxiliary condition for the minimization obtained by taking the variation of Eq. (300) is

\[
(\delta C)^\dagger (S)(C) + (C)^\dagger (S)(\delta C) = (0),
\]

(313)

where the overlap matrix \( (S) \) is Hermitian and of dimension \( \nu \times \nu \), \( (C) \) and \( (\delta C) \) are \( \nu \times n \) matrices, and \( (0) \) is the \( n \times n \) null matrix. On premultiplying both sides of Eq. (313) by the \( n \times n \) matrix of Lagrangian
multipliers, \( L \), taking the trace, and rearranging cyclically as in the
derivation of Eq. (296), there is obtained

\[
\text{Tr} \left\{ (S)(C)(L)(\delta C)^\dagger + (L)(C)^\dagger (S)(\delta C) \right\} = (0).
\]  

(314)

On dividing Eq. (298) by a factor of two, setting \( \delta E = 0 \), and subtracting
the resulting equation from Eq. (314), the following matrix equation
homogeneous and linear in \((\delta C)\) and \((\delta C)^\dagger\) is obtained,

\[
\text{Tr} \left\{ \left[ (F)(C) - (S)(C)(L) \right] (\delta C)^\dagger + \left[ (C)^\dagger (F) - (L)(C)^\dagger (S) \right] (\delta C) \right\} = (0).
\]  

(315)

Since \((\delta C)\) and \((\delta C)^\dagger\) are now independently variable their coefficients
must vanish, which requires that

\[
(C)^\dagger (F) = (L)(C)^\dagger (S),
\]  

(316a)

and

\[
(F)(C) = (S)(C)(L).
\]  

(316b)

Taking the Hermitian conjugate of Eq. (316a) yields (since \((F)\) and \((S)\)
are Hermitian)

\[
(F)(C) = (S)(C)(L)^\dagger,
\]  

(316c)

and comparison of this result with Eq. (316b) shows that \((L)\) must be
Hermitian, or

\[
(L)^\dagger = (L).
\]  

(317)

We next introduce a unitary transformation of the molecular
orbitals,

\[
(\phi') = (\phi)(U),
\]  

(318)

where \((U)\) is an \( n \times n \) unitary matrix and \((\phi')\) as a row matrix having the
\( n \) transformed molecular orbitals as its elements. On substituting
Eq. (291) for the original molecular orbitals, \((\phi)\), into Eq. (318) the
transformed molecular orbitals are found to be related to the atomic orbitals by the linear transformation

\[(\phi') = (\lambda)(C'), \quad (319)\]

with

\[(C') = (C)(U), \quad (320a)\]
\[(C) = (C')(U)^+. \quad (320b)\]

From Eqs. (293) and (320b),

\[(\rho) = (C')(U)^+ (U)(C')(U)^+ = (C')(C')(U)^+ = (\rho'), \quad (321)\]

so that the LCAO first-order density matrix (\(\rho\)), and all its elements \(\rho_{\alpha\beta}\), are invariant to the transformation. Therefore, in view of Eq. (284), the matrix (\(F\)) is also invariant to the transformation. Substitution of Eq. (320b) for (\(C\)) in Eq. (316b), and postmultiplication of both sides of the resulting equation by (\(U\)) yields

\[(F)(C') = (S)(C')(\epsilon), \quad (322)\]

with

\[(\epsilon) = (U)^+ (L)(U). \quad (323)\]

The unitary transformation matrix (\(U\)), arbitrary to this point, is now chosen to diagonalize the Hermitian matrix (\(L\)). Then (\(\epsilon\)) is a diagonal matrix having as its diagonal elements the roots (which are necessarily real) of (\(L\)). Since the original molecular orbitals, (\(\phi\)), and matrix, (\(C\)), are no longer of interest, the primes will be dropped hereafter from (\(\phi'\)) and (\(C'\)). Alternatively, the original (\(\phi\)) and (\(C\)) may be regarded as having been chosen so that (\(L\)) reduced to the diagonal matrix (\(\epsilon\)). The equation for the determination of (\(C\)), Eq. (322), is therefore rewritten as

\[(F)(C) = (S)(C)(\epsilon). \quad (324)\]
In order to proceed further it is necessary to indicate more explicitly the structure of the matrices \((\phi), (\chi), (C), \text{ and } (\xi)\). Thus,

\[
(\phi) = (\phi_1, \ldots, \phi_n),
\]

\[
(\chi) = (\chi_1, \ldots, \chi_n),
\]

where \(\phi_i (i = 1, \ldots, n)\) represents a typical one of the \(n\) molecular orbitals, and \(\chi_\alpha (\alpha = 1, \ldots, \nu)\) a typical one of the \(\nu\) atomic orbitals. In the closed-shell case under consideration each of the \(n\) molecular orbitals, \(\phi_i\), is occupied by a pair of electrons with opposed spins, leading to \(N = 2n\) orthonormal molecular spinorbitals, \(\phi_i \sigma^+\) and \(\phi_i \sigma^- (i = 1, \ldots, n)\), and the antisymmetrized wave function for the system of \(N\) electrons given by \(\bar{\Phi}\) of Eq. (153). From Eq. (139),

\[
\phi_i = (\chi)(c_i), \quad (i = 1, \ldots, n),
\]

where

\[
(c_i) = \begin{bmatrix}
  c_{i1} \\
  \vdots \\
  c_{i\nu}
\end{bmatrix}
\]

is a column matrix or vector having as its elements the coefficients of the atomic orbitals in the linear combination of these orbitals represented by \(\phi_i\). Comparison of Eq. (291), which defines \((C)\), with Eqs. (327) and (328) shows that \((c_i)\) is the \(i\)th of the \(\nu \times n\) matrix \((C)\), so that the latter may be represented in partitioned form as

\[
(C) = (c_1, \ldots, c_i, \ldots, c_n).
\]
The diagonal $n \times n$ matrix $(\epsilon)$ in Eqs. (323) and (324) may be represented as

$$(\epsilon) = (\epsilon_1, \ldots, \epsilon_1, \ldots, \epsilon_n)_{\text{diag.}}$$

(330)

where the $\epsilon_i$ ($i = 1, \ldots, n$) are real constants. It then follows readily from the rules of matrix multiplication that

$$(C)(\epsilon) = (\epsilon_1 c_1, \ldots, \epsilon_1 c_1, \ldots, \epsilon_n c_n),$$

(331)

where $\epsilon_i c_1$ is the column matrix

$$\begin{bmatrix}
\epsilon_1 c_{11} \\
\vdots \\
\epsilon_n c_{n1}
\end{bmatrix}$$

Substitution of Eqs. (329) and (331) into Eq. (324) now setting equal corresponding columns of the matrix products on either side of the latter equations now yields

$$(F)(c_i) = (S)(c_i), \ (i = 1, \ldots, n),$$

(333)

or

$$[(F) - \epsilon_i (S)] (c_i) = (0), \ (i = 1, \ldots, n),$$

(334)

where $(0)$ is the $\nu \times 1$ null matrix. The elements of the $\nu \times \nu$ Hermitian matrices $(S)$ and $(F)$ are given by Eqs. (142) and (284), so that Eqs. (334) are equivalent to $n$ sets of simultaneous linear homogeneous equations for the determination of the $c_{\alpha i}$'s, the $i$ th such set being

$$\sum_{\beta=1}^{\nu} (F_{\alpha \beta} - \epsilon_i S_{\alpha \beta}) c_{\beta i} = 0, \ (\alpha = 1, \ldots, \nu).$$

(335)
As is well known the condition that these \( \nu \) equations have a solution (other than the trivial solution \( c_{\beta 1} = 0, \beta = 1, \ldots, \nu \), or \( (c_1) = (0) \), which is of no interest) is the vanishing of the determinant of the coefficients. Thus,

\[
\begin{vmatrix} F_i - \xi_i (S) \end{vmatrix} = \begin{vmatrix} F_{\alpha \beta} - \xi_i S_{\alpha \beta} \end{vmatrix} = 0, \quad (i = 1, \ldots, n). \tag{336}
\]

Expansion of the determinant on the left-hand side of the equation

\[
\begin{vmatrix} (F) - \xi (S) \end{vmatrix} = \begin{vmatrix} F_{\alpha \beta} - \xi S_{\alpha \beta} \end{vmatrix} = 0 \tag{337}
\]

leads to an algebraic equation of degree \( \nu \) in the parameter \( \xi \). By the fundamental theorem of algebra this equation has \( \nu \) roots, \( \xi^{(j)} (j = 1, \ldots, \nu) \), which are not necessarily distinct (that is, multiple roots may occur). In view of Eqs. (336) the \( n \) parameters \( \xi_i \) must be selected from the set of \( \nu \) roots \( \xi^{(j)} \) of Eq. (337). In order to minimize the total energy, \( E \), of the system the \( n \) algebraically smallest of the \( \nu \) roots \( \xi^{(j)} \) (as previously shown the roots are real) must be selected to form the set of parameters \( \xi_i \), multiple roots being repeated a number of times equal to their multiplicity before proceeding to the next highest root. Substitution of each such root \( \xi_i \) into Eqs. (334) leads to a solvable set of \( \nu \) simultaneous homogeneous linear equations for the relative values of the coefficients \( c_{\beta 1} (\beta = 1, \ldots, \nu) \), or the unnormalized vector \((c_1)\). The normalization of the vectors \((c_1)\) is to be carried out in conformity with Eqs. (141) or (300), which are equivalent to

\[
(c_1)^\dagger (S) (c_1) = 1, \quad (i = 1, \ldots, n). \tag{338}
\]

It will be assumed that each of the \( n \) vectors has been multiplied by an appropriate constant factor such that they are normalized with
respect to the matrix \( (S) \) as in Eqs. (338). It should be noted that the expression on the left-hand side of Eq. (338) is necessarily real and positive because \( (S) \) is Hermitian and the matrix of a positive-definite quadratic form (see Eq. (143)). Thus the normalization factor will be real. The normalized vectors will of course still satisfy Eqs. (333) to (335) with the same values of the \( \epsilon_i \)'s because of the linear nature of these equations. The normalized vector \( (c_i) \) and the corresponding value of \( \epsilon_i \) will be referred to hereafter as the \( i \) th eigenvector and eigenvalue, respectively.

However, it should be noted that these equations are not eigenvalue equations of the most familiar type, because of the occurrence of the matrix \( (S) \) and the fact that matrix elements of \( (F) \) are dependent on the form of the eigenvectors. Now replace the index \( i \) by \( j \) and take the Hermitian conjugate of Eq. (333) to obtain

\[
(c_j)^\dagger (F) = \epsilon_j^* (c_j)^\dagger (S).
\]

Premultiplication of Eq. (333) by \( (c_j)^\dagger \), postmultiplication of Eq. (339) by \( (c_i) \), and subtraction of the latter result from the former then yields

\[
(\epsilon_i - \epsilon_j^*)(c_j)^\dagger (S)(c_i) = 0
\]

If \( i = j \), the quadratic form in Eq. (340) cannot vanish because of the positive-definiteness of \( (S) \) and \( \epsilon_i = \epsilon_i^* \), confirming the reality of the eigenvalues associated with the Hermitian matrices \( (F) \) and \( (S) \). If \( i \neq j \) and also \( \epsilon_i \neq \epsilon_j \), then

\[
(c_j)^\dagger (S)(c_i) = 0, \quad (\epsilon_i \neq \epsilon_j),
\]

so that eigenvectors associated with different eigenvalues are necessarily "orthogonal with respect to \( (S) \)" (this terminology will be used
if two vectors satisfy a relation similar to Eq. (341) for a given matrix \((S)\)). Eigenvectors for which the associated eigenvalues have the same numerical value are not necessarily orthogonal with respect to \((S)\) as in Eq. (341). However in this case mutually orthogonal and normalized combinations of a linearly independent set of such eigenvectors can always be formed by an adaptation of Schmidt's procedure (an arbitrary linear combination is clearly an eigenvector having the same eigenvalue). The number of linearly independent eigenvectors having the same eigenvalue is referred to as the degeneracy of the latter. Thus, in all cases, a set of \(n\) orthonormal eigenvectors can be found satisfying the conditions
\[
(c_j)^\dagger (S)(c_j) = \delta_{ij},
\]
which are the vector equivalent of Eqs. (141). Premultiplication of Eq. (333) by \((c_j)^\dagger\) and use of Eq. (342) now yields
\[
(c_j)^\dagger (F)(c_j) = \epsilon_i \delta_{ij}.
\]
Thus after orthogonalization with respect to \((S)\) the eigenvalues are also mutually orthogonal with respect to \((F)\). However, if normalized to unity with respect to \((S)\), as in Eq. (338), they are "normalized" to the corresponding eigenvalues with respect to \((F)\).

Now form the \(\nu \times n\) matrix \((C)\) having as its columns the \(n\) orthonormal eigenvectors \((c_i)\), arranged for convenience so that the corresponding eigenvalues form a monotonic sequence, as in Eq. (329). Then \((C)\) satisfies the matrix forms of the orthonormality condition, Eq. (300), and eigenvalue equation, Eq. (324). Premultiplication of Eq. (324) by \((C)^\dagger\) and use of Eq. (300) yields
\[
(C)^\dagger (F)(C) = (\epsilon_i).
\]
which is the matrix equivalent of Eq. (343) for the eigenvectors since \((\mathcal{E})\) is the diagonal matrix of the eigenvalues. On taking the trace of both sides of Eq. (344) and making a cyclic rearrangement there is obtained

\[
\text{Tr}\left[[F][F]^\dagger\right] = \text{Tr}\left[\mathcal{E}\right].
\]  

(345)

Furthermore,

\[
\text{Tr}\left[\mathcal{E}\right] = \sum_{i=1}^{n} \mathcal{E}_i,
\]

(346)

where for the closed-shell case under consideration the sum extends only over the eigenvalues associated with the \(n\) distinct eigenvectors, although the corresponding molecular orbitals are each occupied by a pair of electrons (thus the sum in Eq. (346) contains \(n\), not \(N = 2n\), terms; however each degenerate eigenvalue is summed a number of times equal to the number of the associated distinct degenerate and occupied eigenvectors).

Substitution of Eqs. (293) and (346) in Eq. (345) yields

\[
\sum_{i=1}^{n} \mathcal{E}_i = \text{Tr}\left[[F][F]^\dagger\right] = \sum_{\alpha,\beta=1}^{\nu} \rho_{\alpha\beta} F_{\beta\alpha}'.
\]

(347)

or from Eq. (284),

\[
\sum_{i=1}^{n} \mathcal{E}_i = \sum_{\alpha,\beta=1}^{\nu} \rho_{\alpha\beta} H_{\beta\alpha} + \sum_{\alpha,\beta,\gamma,\delta=1}^{\nu} \rho_{\alpha\beta} \rho_{\gamma\delta} (2 I_{\beta\alpha',\delta\gamma} - I_{\beta\gamma,\delta\alpha}).
\]

(348)

Comparison of this result with Eq. (262) for the one-electron energy, \(E_1\), and Eq. (272) for the two-electron energy, \(E_2\), shows that
From Eqs. (160), (272), and (349) the total electronic energy (exclusive of the internuclear repulsive energy $E_o$ of Eq. (155)) can be put in the form

$$E = E_1 + E_2$$

$$= 2 \sum_{i=1}^{n} \epsilon_i - E_2$$

$$= 2 \sum_{i=1}^{n} \epsilon_i - \sum_{\alpha', \beta', \gamma', \delta' = 1} (2 I_{\beta', \delta'} - I_{\gamma', \delta'}) \rho_{\alpha \beta} \rho_{\gamma \delta} (2 I_{\alpha', \delta'} - I_{\beta', \delta'}).$$

The factor two multiplying the sum over the eigenvalues in Eqs. (349) and (350) may be regarded as converting this to a sum over the molecular orbital "energies" or eigenvalues for each of the $N = 2n$ electrons.

However, Eq. (349) shows that in this sum the electron-pair repulsion energy, $E_2$, is counted twice, and must be subtracted from the sum as in Eq. (350) to obtain the correct total electron energy. This is a result of the fact that the negative of the eigenvalue, $-\epsilon_i$, is to the present degree of approximation the ionization energy of an electron in the $i$th molecular orbital, or the energy required to remove it to infinity (for stable molecules the eigenvalues are negative and the ionization energies positive). Equations (349) and (350) are equivalent for the LCAO molecular orbital theory to Eqs. (93) and (94), respectively, of the Hartree-Fock self-consistent field theory for atoms (except that there the $\epsilon$'s represent the positive ionization energies).

From its origin it is clear that the electron-pair repulsion energy, $E_2$,
is positive (see Eqs. (157) and (163)). It follows that the subtraction of $E_2$ from the sum of the eigenvalues as in Eq. (350) has the effect of making the molecule more stable than would be the case if the energy were taken as simply the sum of the molecular orbital energies for all electrons. It will be recalled that the latter procedure is used in naive or semi-empirical molecular orbital theory, as well as in the analogous one-electron band theory of crystals, although the error is assumed to be partially compensated there by the choice of an effective one-electron potential.

(e) Solution of the secular equation for the closed-shell case.

Procedures for the practical solution of the eigenvector-eigenvalue equation, Eq. (333), or corresponding secular equation, Eq. (337), for the closed-shell case will now be discussed. The major difficulty in the solution of these equations is connected with the "self-consistent field" aspect of the calculation. In the ordinary Hartree-Fock theory for atoms this is reflected in the fact that each one-electron atomic wave function or atomic orbital is an eigenfunction of a Hamiltonian operator containing an effective potential which itself depends on the form of all the occupied atomic orbitals. In the present application to molecular orbital theory in the LCAO approximation ($\Phi$) is the matrix representation of the Hartree-Fock Hamiltonian operator. As shown by Eq. (284) each of its elements, $F_{\alpha\beta}$, depends in general on all the elements, $\rho_{\gamma\delta}$, of the LCAO representation, ($\rho$), of the first-order density matrix (although in practice the dependence of $F_{\alpha\beta}$ on many of the elements $\rho_{\gamma\delta}$ may be unimportant as a result of the negligible value
of the two-electron integrals multiplying $\rho_{r\delta}$ in Eq. (284). Furthermore each element, $\rho_{r\delta}$, of the density matrix depends through Eq. (245) on the coefficients, $c_{\beta_1}$, which constitute the elements of the eigenvectors in Eq. (333) and which determine the molecular orbitals through Eq. (139).

It is therefore necessary to solve Eq. (333) by a procedure of successive approximations in which: (1) initial estimates of the elements $\rho_{r\delta}$ are inserted into Eq. (284) and the elements $F_{d\beta}$ calculated in zeroth approximation; (2) the zeroth approximation to $(F)$ is inserted in Eqs. (333) and (337) and these equations solved for the eigenvectors and eigenvalues in first approximation; (3) the elements of $\rho_{r\delta}$ are recalculated in first approximation from Eq. (245) choosing as the $n$ occupied eigenvectors those having the algebraically lowest eigenvalues; and (4) the matrix $(F)$ is recalculated from these improved values of the elements $\rho_{r\delta}$ and the process repeated until it is judged that convergence is sufficient according to some appropriate criterion. The latter might be based on the occurrence of sufficiently small changes in the total energy, $E$, the elements of the density matrix, $\rho_{r\delta}$, the eigenvalues, $\epsilon_1$, or the eigenvectors, $(c_1)$, in two successive steps of the calculation. The energy may be calculated at each step as the sum, $E = E_1 + E_2$, where $E_1$ is given by Eq. (262) and $E_2$ by Eq. (272), or alternatively in terms of the eigenvalues from Eq. (350). It may be anticipated from known general characteristics of the variation method that the convergence of the total energy will be more rapid than that of the eigenvectors (or molecular orbitals).
In each cycle of the preceding scheme of successive approximations it is necessary in step (2) to evaluate the eigenvalues, $\xi_i$, and eigenvectors, $(c_i)$, of Eq. (333). The matrix $F$ is treated as a constant matrix in this calculation, although it assumes a different form in successive cycles. On the other hand the overlap matrix $S$ is constant throughout successive cycles also. As previously remarked Eq. (333) is the characteristic equation of two matrices simultaneously and its solution is less simple than that of a single matrix. A similar characteristic equation occurs in the theory of harmonic vibrations of a mechanical system. In that case $S$ is replaced by the matrix of the positive-definite form representing the kinetic energy of the system, having effective masses as its elements. The matrix of the quadratic form for the potential energy, having "Hooke's law" force constants as elements, replaces $F$. The eigenvectors, $(c_i)$, represent the normal coordinates and the eigenvalues are $\xi_i = 4\pi^2 v_i^2$ where $v_i$ is the frequency of the $i$th normal mode (the similarity of the two problems is thus somewhat superficial as $\xi_i$ represents an orbital energy in the electronic problem while the vibrational energy quantum for the $i$th normal mode is $h v_i = \left(\hbar/2\pi\right)\xi_i^{1/2}$ with $\hbar$ Planck's constant). In both cases the matrices $(F)$ and $(S)$ are Hermitian (symmetric if real) and $(S)$ is in addition the matrix of a positive-definite form, features which greatly simplify the solution of Eq. (333).

Although a number of methods differing in detail exist for the solution of this equation or the secular equation, Eq. (337), all those in which the eigenvectors (as well as the eigenvalues) are found are equivalent to finding a linear transformation of the basis which
simultaneously diagonalizes the matrices (F) and (S), and further reduces the latter to the unit matrix. The eigenvalues then appear on the diagonal of (F), while the transformation matrix yields the molecular orbitals in the electronic problem and the normal coordinates in the vibrational problem. In practice the matrices (S) and (F) are diagonalized by successive transformations, so that the problem is in effect reduced to the simpler one of diagonalization of a single matrix, twice repeated. Programs for the diagonalization of large symmetric matrices on electronic digital computers now exist, so that the problem is adapted to machine calculation (at least for the case of real symmetric matrices). The classical method of Jacobi has, for example, been adapted for computers. The procedure for the successive diagonalization of (S) and (F) to be described here is the precise analog of that proposed by Taylor for the solution of the corresponding vibration problem. It has since been applied successfully by several investigators using electronic computers. The relation of the method to Lowdin's method of orthogonalized atomic orbitals will be developed in the discussion, and it will be shown that Lowdin's method always requires a greater number of mathematical operations.

In the following discussion the general case of Hermitian matrices (S) and (F) is considered, and the matrices of the transformations are then unitary (in part). In most applications (S) and (F) are real and Hermitian, therefore symmetric, and the transformation matrices real and unitary, therefore orthogonal. The conjunctive and collineatory transformations of the general case become congruent and collineatory for real
transformation matrices. However, even in the general case the eigenvalues are necessarily real.

In order to diagonalize \((S)\), consider the eigenvalue equation

\[
(S)(u_i) = s_i (u_i),
\]

which in itself has no direct physical significance (other than a relation to orthogonalized atomic orbitals). Here \((u_i)\) is a \(\nu \times 1\) column matrix and an eigenvector of \((S)\), with \(s_i\) the corresponding eigenvalue. For the non-null (non-trivial) eigenvectors to exist the eigenvalues must be roots of the characteristic equation of \((S)\),

\[
| (S) - s (I) | = 0,
\]

or

\[
| S_{\alpha\beta} - s \delta_{\alpha\beta} | = 0.
\]

Since the matrix \((S)\) is of dimension the expansion of the characteristic equation leads to an algebraic equation in \(s\) having roots, \(s_i \ (i = 1, \ldots, \nu)\). Substitution of each in turn into the simultaneous homogeneous linear equations

\[
[(S) - s_i (I)] (u_i) = 0, \ (i = 1, \ldots, \nu),
\]

and solution of the latter yields the elements of the eigenvectors \((u_i)\).

Let \((u_i)\) and \((u_j)\) be two such eigenvectors. Then from Eq. (351), using the Hermitian property of \((S)\),

\[
(u_j)^\dagger (S)(u_i) = s_i (u_j)^\dagger (u_i)
\]

and

\[
(u_j)^\dagger (S)(u_i) = s_j^* (u_j)^\dagger (u_i);
\]

subtraction of the second of these equations from the first then yields (compare the derivation of Eq. (340))

\[
(s_i - s_j^*)(u_j)^\dagger (u_i) = 0.
\]
If \( i = j \), \((u_i)^\dagger (u_i) > 0\), and \( s_i = s_i^* \), so that the roots \( s_i \) are real. That they are also positive, \( s_i > 0 \) (\( i = 1, \ldots, \nu \)), follows from the positive-definiteness of \((S)\) (see Eq. (143)) which requires that
\[
|S| = \prod_{i=1}^{\nu} s_i > 0. \tag{356}
\]
If \( i \neq j \) and \( s_i \neq s_j \) in Eq. (355), then \((u_j)^\dagger (u_i) = 0\); therefore two eigenvectors corresponding to different eigenvalues are orthogonal.

Furthermore by taking appropriate linear combinations of linearly independent eigenvectors corresponding to a degenerate eigenvalue an equal number of mutually orthogonal eigenvectors may be formed (these eigenvectors are indeterminate to the extent of a unitary transformation but this is of no consequence for the calculation). If, in addition, the eigenvectors are normalized to unity the complete set of eigenvectors will form an orthonormal set,
\[
(u_j)^\dagger (u_i) = \delta_{ij}, \quad (i, j = 1, \ldots, \nu). \tag{357}
\]
From Eqs. (351) and (357),
\[
(u_j)^\dagger (S)(u_i) = s_i \delta_{ij}, \quad (i, j = 1, \ldots, \nu) \tag{358}
\]
Now form a \( \nu \times \nu \) matrix \((U)\) having the eigenvectors \((u_i)\) as its columns (the order is immaterial). In view of Eqs. (357) and (358) \((U)\) is unitary,
\[
(U)^\dagger (U) = I, \tag{359a}
\]
or
\[
(U)^{-1} = (U)^\dagger, \tag{359b}
\]
and \((S)\) is diagonalized by the unitary (conjunctive and collineatory) transformation,
\[
(U)^\dagger (S)(U) = (s_i \delta_{ij}) \tag{360}
\]
Here \((s_1 \delta_{ij})\) is a diagonal matrix having the \(\nu\) eigenvalues, \(s_1\), as its diagonal elements (in the same order as that of the eigenvectors in \((U)\)).

It will be useful to introduce the positive Hermitian square root, \((s)^{\frac{1}{2}}\) of \((s)\). Let \((s_1^{\frac{1}{2}} \delta_{ij})\) be the diagonal matrix having the real positive square roots of the eigenvalues \(s_1\) on its diagonal. Then

\[
(s)^{\frac{1}{2}} = (U)(s_1^{\frac{1}{2}} \delta_{ij})(U)^\dagger
\]

is Hermitian, and from Eqs. (359) and (360),

\[
(s)^{\frac{1}{2}} (s)^{\frac{1}{2}} = (U)(s_1^{\frac{1}{2}} \delta_{ij})(U)^\dagger = (s).
\]

It is clear from Eq. (356) that both \((s)\) and \((s)^{\frac{1}{2}}\) are non-singular; the positive Hermitian reciprocal square root of \((s)\) may therefore be defined as

\[
(s)^{-\frac{1}{2}} = (s)^{\frac{1}{2}} = (U)(s_1^{-\frac{1}{2}} \delta_{ij})(U)^\dagger,
\]

where \(s_1^{-\frac{1}{2}}\) is the positive square root of \(s_1^{-1}\).

The preceding diagonalization of \((s)\) will now be related to two transformations to orthonormal basis orbitals. The original atomic orbitals, \(\chi_\alpha (\alpha = 1, \ldots, \nu)\), are represented by the row matrix \((\chi)\) (see Eq. (326)). The first set of orthonormal basis orbitals, \(\chi'_\alpha (\alpha = 1, \ldots, \nu)\), will be represented similarly by the row matrix \((\chi')\), and defined by the transformation

\[
(\chi') = (\chi)(U)(s_1^{-\frac{1}{2}} \delta_{ij}).
\]

In view of Eq. (142) the matrix \((s)\) may be represented as

\[
(s) = \int (\chi')\dagger(\chi) d\tau,
\]

with the understanding that the integral of a matrix is the matrix having as its elements the corresponding integrals of the elements of the matrix.
in the integrand. The overlap matrix \((S')\) for the orbitals \((\chi')\) is defined similarly, and on using Eqs. (364), (365), and (360) in that order, there is obtained

\[
(S') = \int (\chi')(\chi')^* \, d\mathbf{r}
\]

\[
= (s_{1j}^{-\frac{1}{2}} \delta_{1j}) (U)^\dagger (s)(U) (s_{1j}^{-\frac{1}{2}} \delta_{1j})
\]

\[
= (I).
\]  \hspace{1cm} \text{(366)}

Thus the basis orbitals \((\chi')\) are orthonormal as stated.

Semi-localized orthonormal basis orbitals, \(\chi''(\alpha = 1, \ldots, n')\), represented by the row matrix \((\chi'')\), may be obtained by carrying out a further unitary transformation of the form

\[
(\chi'') = (U)\gamma (\chi')(U)^\dagger.
\]  \hspace{1cm} \text{(367)}

From Eqs. (363) and (364),

\[
(\chi'') = (\chi)(s)^{-\frac{1}{2}}.
\]  \hspace{1cm} \text{(368)}

The overlap matrix for the orbitals \((\chi'')\) is found to be

\[
(S'') = \int (\chi'')(\chi'')^* \, d\mathbf{r}
\]

\[
= (U)^\dagger (S')(U)
\]

\[
= (I),
\]  \hspace{1cm} \text{(369)}

on using Eqs. (367), (366), and (359) in that order. The orthonormality of the orbitals \((\chi'')\) is of course a consequence of the fact that they are related by a unitary transformation to the orbitals \((\chi')\). The particular unitary transformation indicated in Eq. (367) is significant, however, because it leads to Eq. (368) and is connected with the semi-localized nature of the orbitals \((\chi'')\).

In order to establish this it will now be shown that under certain conditions a convergent series expansion may be obtained for the
matrix \((S)^{-\frac{1}{2}}\) defined by Eq. (363). Provided that all the eigenvalues of 
\((S)\) satisfy the inequality 
\[
|s_i - 1| < 1, \ (i = 1, \ldots, \nu), \tag{370}
\]
Eq. (363) may be represented as
\[
(S)^{-\frac{1}{2}} = (U)(\hat{1} + (s_i - 1)^{-\frac{1}{2}} \delta_{ij})(U)^+ = (U)(\hat{1} - (1/2)(s_i - 1) + (3/8)(s_i - 1)^2 - \ldots J \delta_{ij})(U)^+. \tag{371}
\]
From Eqs. (359) and (360),
\[
(S - I) = (S) - (I) = (U)(\hat{1} - J \delta_{ij})(U)^+ \tag{372}
\]
so that for all integral \(n\),
\[
(S - I)^n = (U)(\hat{1} - J \delta_{ij} J^n)(U)^+. \tag{373}
\]
The right-hand side of Eq. (371) may be reduced by means of Eqs. (359) and (373) to obtain the required series expansion,
\[
(S)^{-\frac{1}{2}} = (I) - (1/2)(S - I) + (3/8)(S - I)^2 - \ldots. \tag{374}
\]
Here \((S - I)\) is the matrix obtained by deleting the diagonal elements of 
\((S)\) (which are all unity) and retaining only the off-diagonal elements. 
\[
S_{\alpha\beta}(\alpha \neq \beta). \tag{374}
\]

In the limit of vanishingly small overlap between the atomic orbitals \((\chi)\), \(S_{\alpha\beta} \to 0\), \((\alpha \neq \beta)\), and \((S - I) \to (0)\) (the null matrix). Under the same conditions \(s_i \to 1\), \((i = 1, \ldots, \nu)\), so that the inequalities (370) will certainly be satisfied for sufficiently small overlap and Eq. (374) will become valid. Thus \((S)^{-\frac{1}{2}} \to (I)\), and from Eq. (368), \((\chi''') \to (\chi)\). Furthermore, when the degree of overlap is not so large that the inequalities (370) are violated, substitution of 
Eq. (374) in (368) yields
\[
(\chi''') = (\chi) - (1/2)(\chi)(S - I) + (3/8)(\chi)(S - I)^2 - \ldots. \tag{375}
\]
so that the atomic orbitals \((\chi)\) represent the leading terms in the expansion of the orbitals \((\chi''')\). However, the presence of the higher
order terms on the right-hand side of Eq. (375) shows that the orbitals \( \chi'' \) are only approximately localized. The effect of the first-order correction term in Eq. (375) is to add to each \( \chi''_{\alpha} \) terms linear in the atomic orbitals \( \chi_{\beta} \) with which \( \chi_{\alpha} \) overlaps, thus primarily orbitals adjacent to \( \chi_{\alpha} \). The second-order correction term adds terms linear in atomic orbitals \( \chi_{\gamma} \) which overlap the orbitals \( \chi_{\delta} \), etc. Thus the form of the orbitals \( \chi'' \) is relatively complex in spite of their orthogonality and semi-localized character.

These orbitals were first used by Löwdin, and are usually referred to as orthogonalized atomic orbitals. From Eq. (367),

\[
(\chi') = (\chi'')(u),
\]

so that the orthonormal basis orbitals \( \chi' \) defined by Eq. (364) are not in general localized even for the case of small overlap between the original atomic orbitals \( \chi \) (as \( (S) \rightarrow (I) \) the matrix \( (U) \) defined by Eq. (360) does not necessarily approach the unit matrix). In spite of this it will be shown that the orbitals \( \chi' \) are just as satisfactory for the solution of the secular equation as Löwdin's orbitals \( \chi'' \).

The first step in the solution of the secular equation, Eq. (324) or (337), corresponding to the diagonalization of the overlap matrix \( (S) \) and the introduction of orthonormal basis orbitals, \( \chi' \) or \( \chi'' \), has now been accomplished. The further detailed discussion will be restricted to the use of the basis orbitals \( \chi' \) of Eq. (364), which will be represented for convenience as

\[
(\chi') = (\chi)(v),
\]

with

\[
(v) = (u)(s_{ij}^{\frac{1}{2}} \delta_{ij}).
\]
In view of Eq. (368) the further treatment using Löwdin's orbitals is obtained by simply replacing \((\chi')\) by \((\chi'')\) and \((V)\) by \((S)^{-\frac{1}{2}}\) everywhere in the remaining equations of this section. Equations (363) and (378) show that the calculation of \((S)^{-\frac{1}{2}}\) involves one more matrix multiplication than that of \((V)\) (the discrepancy is even greater if \((S)^{-\frac{1}{2}}\) is calculated from the series expansion in Eq. (374) as originally proposed by Löwdin), so that the use of Löwdin's orbitals clearly increases the labor of the computation while providing no compensating advantage.

The eigenvector matrix \((C)\) of Eq. (324) determines the form of the molecular orbitals \((\phi)\) through Eq. (319) which may be rewritten as

\[
(\phi) = (\chi')(C) \tag{379}
\]

(it will be recalled that the primes were subsequently dropped from \((\phi')\) and \((C')\)). From Eqs. (377) and (378),

\[
(\chi) = (\chi')(V)^{-1} \tag{380}
\]

(Note that the matrix \((V)\) of Eq. (378) is not unitary), and substitution in Eq. (379) yields

\[
(\phi) = (\chi')(V)^{-1}(C) = (\chi')(C') \tag{381}
\]

with

\[
(C') = (V)^{-1}(C). \tag{382}
\]

Here we have introduced the matrix \((C')\) giving directly the transformation from the orthonormal basis orbitals \((\chi')\) to the molecular orbitals \((\phi)\) (the new matrix \((C')\) should not be confused with the matrix \((C')\) of Eqs. (319) to (322) which is represented as \((C)\) in all subsequent equations and is in fact the matrix \((C)\) of the present discussion).
Solution of Eq. (382) for (C) yields
\[ (C) = (V)(C'), \]  
(383)
and on substitution for (C) in Eq. (324) there is obtained
\[ (F)(V)(C') = (S)(V)(C')(\epsilon_i \delta_{ij}) \]  
(384)
where \((\epsilon_i \delta_{ij})\) is the diagonal matrix of eigenvalues of Eq. (330).

Premultiplication of both sides of Eq. (384) by the matrix
\[ (V)^\dagger = (s_i^{\frac{1}{2}} \delta_{ij})(V)^\dagger \]  
(385)
yields
\[ (V)^\dagger(F)(V)(C') = (V)^\dagger(S)(V)(C')(\epsilon_i \delta_{ij}). \]  
(386)
From Eqs. (360), (378), and (385),
\[ (V)^\dagger(S)(V) = (I). \]  
(387)
It is also convenient to introduce the transformed Hartree-Fock matrix,
\[ (F') = (V)^\dagger(F)(V). \]  
(388)
It should be noted that the transformations represented in Eqs. (387) and (388) are conjunctive (or congruent if \((V)\) is real) but are not collineatory and are consequently not unitary (or orthogonal if \((V)\) is real), since \((V)^\dagger \neq (V)^{-1}\). Substitution of Eqs. (387) and (388) in Eq. (386) yields
\[ (F')(C') = (C')(\epsilon_i \delta_{ij}), \]  
(389a)
or
\[ (F')(c'_i) = \epsilon_i(c'_i), (i = 1, \ldots, n), \]  
(389b)
where \((c'_i)\) is the \textit{i}th column of \((C')\). Equation (390) shows that \((c'_i)\) is an eigenvector of \((F')\) and \(\epsilon_i\) is the corresponding eigenvalue. The
eigenvalues \( \epsilon \) are therefore to be selected from the roots \( \epsilon \) of the characteristic equation of \((F^t)\),

\[
\left| (F^t) - \epsilon (I) \right| = 0, \quad (390a)
\]

or

\[
\left| (F^t) - \epsilon \delta_{\alpha \beta} \right| = 0. \quad (390b)
\]

The explicit expression for the elements of the matrix \((F^t)\) obtained from Eq. (388) is

\[
F_{\alpha \beta}^t = \sum_{k \lambda} (V)_k^\dagger (F)_{k \lambda} (V)_{\lambda \beta} \\
= \sum_{k \lambda} V_k^* \chi_{\lambda \beta} F_{k \lambda} \chi, \quad (391)
\]

where \( F_{k \lambda} \) is to be computed from Eq. (284) with \( \alpha \) replaced by \( k \) and \( \beta \) by \( \lambda \). The latter calculation requires the values of \( \rho_{\alpha \beta} \), the elements of the first-order density matrix \((\rho)\), which may be obtained by substitution of \((C)\) as computed from Eq. (383) into Eq. (293). An alternative procedure is to calculate the representative of the first-order density matrix for the orthonormal basis orbitals \((\chi')\), or

\[
(\rho') = (C')(C')^\dagger, \quad (392)
\]

and then \((\rho)\) from the transformation

\[
(\rho) = (V)(\rho')(V)^\dagger. \quad (393)
\]

Of course, as discussed in the first paragraph of part (e) of the present section it is necessary to have an initial estimate of \((\rho)\) (or possibly simply to set \( \rho_{\alpha \beta} = 0 \) for all \( \alpha \) and \( \beta \)) in order to calculate a zeroth approximation to \((F)\) and thus begin the solution of the secular equation. The immediately preceding relations for the calculation of \((\rho)\) from \((C')\) are applicable to the subsequent iterative steps of the solution which will presumably yield a self-consistent solution if repeated a sufficient
number of times. In this calculation \((C')\) is a rectangular \(\nu' \times n\) matrix now to be discussed, and \((\rho')\) and \((\rho)\) are \(\nu' \times \nu'\) Hermitian matrices.

It is clear from Eq. (388) and the Hermitian property of \((F)\) that \((F')\) is also Hermitian. Thus Eqs. (389) and (390) represent the characteristic equation of a Hermitian matrix and much of the preceding discussion of the characteristic equation and eigenvectors of the Hermitian matrix \((S)\) is applicable to the diagonalization of \((F')\). The only difference is that \((F')\) is not in general positive-definite, so that the eigenvalues \(\epsilon_i\) may be positive, negative, or zero (unlike the eigenvalues \(s_i\) of \((S)\) which are positive). A derivation analogous to that of Eq. (355) with \((S)\) replaced by \((F')\), \((u_1)\) by \((c_1')\), and \((s_i)\) by \((\epsilon_i)\), yields

\[
(\epsilon_i - \epsilon_j^*)(c_j')(c_i) = 0. \tag{394}
\]

It follows that the eigenvalues \(\epsilon_i\) are real (this has already been proved in another manner in connection with Eq. (340)), and that eigenvectors \((c_i')\) and \((c_j')\) of \((F')\) corresponding to different eigenvalues are orthogonal,

\[
(c_j')(c_i') = 0, \quad (\epsilon_i \neq \epsilon_j). \tag{395}
\]

If the eigenvectors are normalized to unity and those corresponding to degenerate eigenvalues are orthogonalized as discussed following Eq. (341), the eigenvectors of \((F')\) will then form an orthonormal set,

\[
(c_j')(c_i') = \delta_{ij}. \tag{396}
\]

Premultiplication of Eq. (389b) by \((c_j')\) and use of Eq. (396) yields

\[
(c_j')(F')(c_i') = \epsilon_i \delta_{ij}. \tag{397}
\]
Equations (396) and (397) should be compared with the corresponding Eqs. (342) and (343) for the eigenvectors \((c_i)\) of Eq. (333). In view of Eq. (396) the \(\nu\) linearly independent eigenvectors of \((F')\) may be taken to form the columns of a \(\nu \times \nu\) unitary matrix \((C'_0)\), such that
\[
(C'_0)^\dagger(C'_0) = (I),
\] (398)
with \((I)\) \(\nu \times \nu\) unit matrix. From Eq. (397),
\[
(C'_0)^\dagger(F')(C'_0) = (\varepsilon(j)\delta_{ij}),
\] (399)
where \((\varepsilon(j)\delta_{ij})\) is the \(\nu \times \nu\) diagonal having as diagonal elements all of the \(\nu\) eigenvalues \(\varepsilon(j)\) of \((F')\) (each repeated a number of times equal to its degeneracy). The matrix \((C'_0)\) which diagonalizes \((F')\), and the eigenvalues \(\varepsilon(j)\), may be calculated by standard methods.

As discussed following Eq. (337) the ground state energy is obtained by selecting the \(n\) algebraically lowest (most negative or least positive) eigenvalues \(\varepsilon_i\), \((i = 1, \ldots, n)\), and their \(n\) associated eigenvectors \((c_i)\), \((i = 1, \ldots, n)\), or the \(n\) corresponding columns of the unitary matrix \((C'_0)\). The rectangular \(\nu \times n\) matrix \((C')\) is then formed by taking as its columns the \(n\) eigenvectors \((c'_i)\) (or by deleting from \((C'_0)\) the remaining \(\nu - n\) columns or eigenvectors corresponding to the higher eigenvalues). Evidently, from Eqs. (398) and (399),
\[
(C')^\dagger(C') = (I)
\] (400)
where \((I)\) is the \(n \times n\) unit matrix, and
\[
(C')^\dagger(F')(C') = (\varepsilon_i\delta_{ij}),
\] (401)
where \((\varepsilon_i\delta_{ij})\) is the \(n \times n\) diagonal matrix of the algebraically lowest eigenvalues.

The calculation of \((\rho)\), \((F)\), and \((F')\) from the eigenvector matrix \((C')\) has already been discussed. The molecular orbitals \((\phi)\) are
calculated from Eq. (383). Thus it is not necessary at any point in the present procedure to actually use the orthonormal basis functions ($\chi'$) of Eq. (377), although the molecular orbitals ($\phi$) are expressed as linear combinations of the latter functions by Eq. (381). Similarly, if the analogous procedure based on Lowdin's orthogonalized atomic orbitals ($\chi''$) were used (see the discussion following Eq. (378) there would not be any need to actually evaluate the orbitals ($\chi''$) from Eq. (368), or to express the molecular orbitals ($\phi$) in terms of ($\chi''$). This again demonstrates the essential redundancy of the use of Lowdin's orthogonalized orbitals ($\chi''$), involving an additional unitary transformation of the already orthonormal basis functions ($\chi'$) as indicated in Eq. (367). The two procedures are entirely equivalent and will yield identical eigenvalues, $\epsilon_i$, eigenvectors, ($c_i$), and molecular orbitals, $\phi_i$, barring errors of calculation. Since the procedure based on the basis functions ($\chi'$) is simpler it is preferable on the basis of numerical accuracy also.
Chapter 9. Quantum Integrals

9.1 Introduction

As discussed in the preceding chapter, the numerical formulation and solution of the secular equation, Eq. (337), requires the evaluation of the matrix elements, $F_{\alpha\beta}$ and $S_{\alpha\beta}'$, of the Hartree-Fock and overlap matrices, respectively. These matrix elements are in general quantum integrals or linear combinations of quantum integrals which may be classified according to several categories. Thus the integrals may be one-electron quantum integrals of the general type

$$\int \chi^*_{\alpha} (\mathbf{r}_1) G_{1} \chi_{\beta} (\mathbf{r}_1) d\mathbf{r}_1,$$  \hspace{1cm} (402)

where $G_1$ is a one-electron operator and the integration extends over the coordinates of a single electron, or two-electron quantum integrals of the type

$$\int \int \chi^*_{\alpha} (\mathbf{r}_1) \chi^*_{\beta} (\mathbf{r}_2) G_{12} \chi_{\gamma} (\mathbf{r}_1) \chi_{\delta} (\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2,$$  \hspace{1cm} (403)

where $G_{12}$ is a two-electron operator and the integration extends over the coordinates of two electrons. In the preceding chapter atomic orbitals were designated as simply $\chi_{\alpha}$, ($\alpha = 1, \ldots, \nu$), as it was unnecessary for the general formulation of the theory to indicate explicitly the atom on which the orbital was located. However, in the application of the theory to a specific structure as in Chapter 6 or
the present and following chapters it becomes essential to distinguish
the atom upon which an orbital is located. Thus in Eqs. (402) and (403)
\[ \chi_{\alpha} \] indicates the \( \alpha \)th atomic orbital associated with the \( \alpha \)th atom (or
nucleus). (A similar notation was used in Chapter 6 except that the
specific orbitals were indicated by subscripts \( i,j \) rather than \( t \), etc.)
Thus the range of \( \alpha \) now extends only over the relatively small number of
atomic orbitals on the \( \alpha \)th atom which enter into the particular calcula-
tion of interest. In the present application this includes only the 2s\(^{1}\)
(or 2s) and the three 2p orbitals on each boron atom. Atomic orbitals
of principal quantum number greater than 2 are not considered in the
present application, while the effect of the 1s orbital is accounted for
indirectly through the use of an effective nuclear charge taking account
of screening by the 1s electrons and also by using a modified 2s\(^{1}\)
orbital orthogonal to the 1s orbital. For compactness and in accordance
with common practice the atomic orbital \[ \chi_{\alpha} \] will hereafter be
indicated by \( \alpha \)\( (1) \), the 1 representing the three space coordinates of
electron 1. The volume elements indicated in Chapter 8 as \( d\rho_{1} \) and \( d\rho_{2} \)
will be denoted by \( d\tau_{1} \) and \( d\tau_{2} \), respectively, or simply by \( d\tau \)in
one-electron integrals. Furthermore all atomic orbitals to be considered
are real, so that signs indicating complex conjugates may be omitted.
With these simplifications the one-electron integrals appear as
\[ \int \alpha(1)G_{1}\beta(1)d\tau , \] (404)
and the two-electron integrals as
\[ \int \int \alpha(1)A(2)G_{12} \gamma(1)\delta(1)d\tau d\tau , \] (405)
\[ \int \int \alpha(1)\beta(2)G_{12} \gamma(1)\delta(2)d\tau_{1}d\tau_{2} . \]
The quantum integrals may be further classified according to the number of distinct atoms or nuclei represented by the set of indices \( a, b, \ldots \). Thus the one-electron integrals may be one-center integrals,

\[
\int \varphi_a(1) G_1 \psi_a(1) d\tau \tag{406a}
\]

or two-center integrals,

\[
\int \varphi_a(1) G_1 \psi_b(1) d\tau, \quad (a \neq b). \tag{406b}
\]

The two orbitals \( \varphi_a \) and \( \psi_a \) in the one-center integral may be the same orbital or two different orbitals on the same atom, but the orbitals \( \varphi_a \) and \( \psi_b \) in the two-center integral are necessarily distinct. In the case of the nuclear attraction integrals as discussed below, the one-electron operator \( G_1 \) is itself associated with a particular atomic center, say \( c \), so that the integral (406a) be either a one- or two-center integral, and (406b) either a two- or three-center integral. Similarly, the two-electron integrals (405) may be classified as one-, two-, three-, or four-center integrals (the two-electron operator \( G_{12} \) is not associated with an atomic center). Three- and four-center two-electron integrals are extremely difficult to compute and have not been tabulated systematically. As a result they have usually been ignored in molecular orbital calculations, and this approximation will also be adopted here (in naive or semi-empirical molecular orbital theory only one-electron integrals one- and two-center integrals occur). The remaining two-electron integrals are one-center integrals,

\[
\int \int \varphi_a(1) \beta_b(2) G_{12} \gamma_a(1) \delta_b(2) d\tau_1 d\tau_2, \tag{407}
\]

and two-center integrals in which only two of the indices \( a, b, c, \) and \( d \) in the integral (405) are distinct. The one-center integrals are easily evaluated analytically when required and are not given in the
standard tables of quantum integrals. As they are not required for the calculations in the following chapter they will not be considered further. The two-center two-electron integrals are further classified subsequently as Coulomb, exchange, and hybrid type integrals.

The matrix element $S_{\alpha\beta}$ is simply the one-electron overlap integral defined by Eq. (142), or in the present notation

$$S_{\alpha\beta} = \langle \alpha | \beta \rangle = \int \alpha^* (1) \beta^* (1) d\tau$$

(408)

The matrix element $F_{\alpha\beta}$ is given for the closed-shell case by Eq. (284) or in the more explicit notation,

$$F_{\alpha\beta} = H_{\alpha\beta} + \sum_{cd} \sum_{\gamma\delta} \rho_{\gamma\delta} \sum_{\gamma\delta} (2I_{\alpha\beta} \delta_{\gamma\delta} \gamma_{\gamma} - I_{\alpha\beta} \gamma_{\gamma} \delta_{\gamma\delta} \beta_{\delta})$$

(409)

The term $H_{\alpha\beta}$ represents the one-electron part of the matrix element $F_{\alpha\beta}$, and may be further analyzed into a linear combination of one-electron quantum integrals as in Eq. (259), which may be rewritten

$$H_{\alpha\beta} = T_{\alpha\beta} - \sum_{c} Z_c J_{c\alpha\beta}$$

(410)

The kinetic energy integral of Eq. (260) becomes

$$T_{\alpha\beta} = \langle \alpha | -\frac{1}{2} \nabla_1^2 | \beta \rangle = -\frac{1}{2} \int \alpha^* (1) \nabla_1^2 \beta (1) d\tau.$$  

(411)

The nuclear attraction integral of Eq. (261) is rewritten as

$$J_{c\alpha\beta} = \langle \alpha | r_{\alpha,1}^{-1} | \beta \rangle = \int \alpha^* (1) r_{\alpha,1}^{-1} \beta (1) d\tau,$$

(412)

where $r_{\alpha,1}$ (or $r_{c1}$) is the distance of electron 1 from the cth nucleus. The atomic number of the cth nucleus is denoted by $Z_c$ (for the atomic units used the magnitude of the charge e on the electron is \(-1\)). The two-electron integrals in Eq. (409) are given by Eq. (268), or in the
present notation by

\[ I_{\alpha a, \beta b; \gamma c, \delta d} = \int \int \alpha^a_1(1) \beta^b_1(1) r^{-1}_{12} Y(2) \delta^c_2(2) d\sigma_1 d\sigma_2, \quad (413) \]

where \( r_{12} \) (or \( r \)) is the distance between electrons 1 and 2. As discussed in Section 8.62 the preceding notation emphasizes the atomic charge distributions. The more conventional notation and that used for the most part in tabulations of these integrals is that of Eq. (265), or

\[ I_{\alpha a, \beta b; \gamma c, \delta d} = (\alpha^a_{\gamma c} | r^{-1}_{12} Y_0 \delta d \beta^b_{\delta d}). \quad (414) \]

Evidently

\[ I_{\alpha a, \beta b; \gamma c, \delta d} = J_{\alpha a, \gamma c; \beta b, \delta d} = (\alpha^a_{\gamma c} | r^{-1}_{12} \beta^b_{\delta d}). \quad (415) \]

In formulating the secular equation it is necessary that the atomic orbitals, \( \alpha^a, \beta^b \), etc., be some fixed set of basis orbitals, such as the equivalent atomic orbitals for \( \alpha^- \) rhombohedral boron discussed in Sections 6.22-6.24. However, the orientation of these orbitals with respect to vectors or bonds between atom pairs depends on the geometry or configuration of the particular structure considered. It is therefore more convenient to calculate the preceding two-center quantum integrals first with respect to atomic orbitals having simple orientations with respect to the bond or line connecting the pair of atoms. These are the orbitals 2s, 2p\( \alpha \), 2p\( \beta \), and 2p\( \gamma \) defined in Section 6.21, and have in general different orientations in space for each atom pair (except of course in the case of the spherically symmetric 2s orbital). The expressions for the one-electron parts of the matrix elements in terms of integrals between bond oriented orbitals have been obtained in
Chapter 6 by the method of Slater and Koster and are given explicitly in Tables 19 to 22 for the two-center interactions retained. In these expressions the non-vanishing one-electron two-center quantum integrals between bond-oriented orbitals are of four types, denoted by (ssσ), (spσ), (ppσ), and (ppπ), as defined by Eqs. (36) where \( H \) represents the one-electron operator \( G_1 \) of the present discussion. In the present notation these are the integrals \( (2s_a | G_1 | 2s_b) \), \( (2s_a | G_1 | 2p_\sigma_b) \), \( (2p_\sigma_a | G_1 | 2p_\sigma_b) \), and \( (2p_\pi_a | G_1 | 2p_\pi_b) \), respectively, where \( a \neq b \). The corresponding transformations of the two-electron parts of the matrix elements from bond-oriented to equivalent orbitals may be obtained by an obvious extension of the method of Slater and Koster, but were not given in Chapter 6. They are not required for the approximate or zeroth-order calculation of the next chapter in which the two-electron part of the matrix elements \( F_{xa, pb} \) is discarded.

In this chapter all the one-electron one- and two-center and two-electron two-center quantum integrals of the general types listed above are evaluated and tabulated for bond-oriented orbitals 2s, 2pσ, 2pπ, and 2pπ* of the Slater type. The integrals are also evaluated for the 2s' orbital orthogonalized to the Slater 1s orbital by the procedure of Kopineck. The analytical expressions for the 1s, 2s, 2pσ and 2pπ Slater orbitals are given in Eqs. (118a) to (118d) and for the 2s' orbital in Eq. (128) or (131) of Section 7. The effect of the two electrons in the closed 1s subshell are taken into account by appropriately reducing the nuclear charge, and only the 2s' (orthogonalized to 1s) and 2p orbitals are considered for the evaluation of the
integrals. The formulation of the Kopineck orthogonalized 2s' orbital may be summarized as follows. The 1s' orbital appearing in Eq. (131) has the same normalization factor as Slater 1s orbital, the same effective nuclear charge as 2s orbital, and is obtained by substituting $\zeta_2$ for $\zeta_1$ in the exponent of Eq. (118a). The 1s' orbital is denoted by $k$ in agreement with the usage of Preuss and the 2s' orbital becomes

$$2s' = N \left\{ \beta(k) - (2s) \right\}$$

as given earlier in Section 7.42. Thus $\zeta_1$ appears only in the expressions for $N$ and $\beta$ as given in Eqs. (132) and (133) for the 2s' orbital. The orthogonalized 2s orbital of Kopineck has been used rather than that of Roothaan as it leads to considerably simpler formulas for the quantum integrals. The $\zeta$ value appearing in Eq. (116) for the real normalized Slater orbitals is given by $(Z - s)/n^*$ and is assigned the values $\zeta_1 = 4.7$ for 1s and $\zeta_2 = 1.3$ for 2s, 2p orbitals as discussed in Section 7.41. Since orbitals containing the principal quantum number 2 are utilized with greatest frequency, it is convenient to replace the designations 2s, 2s', 2p, 2p', and 2p'' by $s', s^*, \sigma', \pi'$ and $\pi''$ as is the common practice in the molecular integral tabulations. As noted above the 1s' orbital which enters into the orthogonalized 2s' orbital is denoted by $k$. It is not necessary to make any further reference to the Slater 1s orbital to which the 2s' orbital has been orthogonalized.

In so far as possible the values of the quantum integrals have been taken or interpolated from the extensive tabulations of Kotani et al.55 and of Preuss.56 These works also give many auxiliary formulas, some of which have been used in the calculation of integrals not
tabulated. Additional formulas have been developed as required.
Principal reliance was placed on the tables of Preuss because they
tabulate the integrals involving the 1s* or k orbital required for the
calculation of the integrals involving Kopineck's Orthogonalized 2s* orbital. Preuss also gives the formulas necessary for the calculation
of these integrals in Volume 1, Section 2.4. These have been extended
to include the kinetic energy integrals using the general formulation of
the latter given by Roothaan. Preuss does not tabulate the kinetic
ergy integrals, which are expressible as linear combinations of
overlap and nuclear attraction integrals through formulas given by
Kotani et al. and Roothaan. Kotani also tabulates the kinetic
ergy integrals involving 2s, 2pσ, and 2pπ orbitals. The integrals
involving the 1s* or k orbitals were expressed in terms of the corre­
sponding overlap and nuclear attraction integrals tabulated by Preuss by
means of the formulas referred to above.

A given type of two-center quantum integral between bond-oriented
atomic orbitals of assigned types and Z values is a function only of the
distance R between the pair of atoms a and b involved. In the standard
tabulations this distance is represented by the dimensionless
parameter

\[ d = \frac{[(Z - s)/n^2]}{a_o} R/a_o = Z (R/a_o). \]

where \( a_o = 0.5292\text{Å} \) is the atomic unit of length. In the present case
\( Z = Z_2 = 1.3 \). The two-electron two-center integrals have been evaluated
for the values of R corresponding to nearest-neighbor pairs of boron
atoms within an icosahedron, 1.733, 1.777, 1.785, and 1.77Å, as well as
the values of R for the two-center and three-center intericosahedral
bonds, 1.709 and 2.020Å, respectively, as listed in Table 14 and illustrated in Figures 1, 2, and 3. The corresponding values of \( \alpha \) are 4.257, 4.365, 4.385, 4.390, 4.198, and 4.962. The one-electron two-center integrals have been evaluated for these values of \( R \) and also approximately for the next-nearest neighbor pairs of boron within an icosahedron using a mean value \( R = 2.87\text{Å} \) calculated from Table 14. As in the standard tables of quantum integrals, all energies are expressed in the atomic unit, \( e^2/a_0 = 27.210 \text{ electron-volt} = 4.3592 \times 10^{-11} \text{ erg} \), equal to twice the ionization energy of the hydrogen atom in its ground state.

9.2 One-Electron Integrals

In this section the non-vanishing one-electron two-center integrals, including the overlap, nuclear attraction, and kinetic energy integrals are evaluated and tabulated for the values of \( R \) or \( \alpha \) previously indicated (see Eq. (416). Kotani et al. tabulate the one-electron integrals from \( \alpha = 2.00 \) to 11.50 (and two-electron integrals from \( \alpha = 2.00 \) to 8.50) at intervals of 0.25. Preuss tabulates all integrals from \( \alpha = 2.0 \) to 7.0 at intervals of 0.5. For the reason stated earlier all integrals tabulated by Preuss were interpolated from his tables in spite of the greater interval of \( \alpha \). The method of five-point Lagrangian interpolation was used. In the case of the overlap integrals, additional values of the integrals have been calculated at intermediate values of \( \alpha \) and plotted versus \( \alpha \). However, the evaluation of other integrals for intermediate \( \alpha \) from auxiliary functions becomes very involved in some cases. The graphical values agree well with the Lagrangian interpolated values. Although the graphical method provides a better picture of the
functional form of integrals, greater uniformity and accuracy of interpolation is achieved by the Lagrangian method. The Lagrangian interpolated values agree very well with calculated intermediate values as well as those given by Kotani up to the fifth decimal place in several cases tested. Since all the distances involved and energies concerned are accurate only up to the third decimal, the above accuracy is more than adequate. The Lagrangian interpolation of the logarithms of the quantum integrals would undoubtedly be even more accurate but does not appear to be necessary. The appropriate Lagrangian interpolation coefficients are tabulated below.

**TABLE 35. Lagrangian Interpolation Coefficients**

<table>
<thead>
<tr>
<th>$d = \ell^2 r$</th>
<th>$p = \frac{d - d_e}{\hbar}$</th>
<th>$A_{-2}$</th>
<th>$A_{-1}$</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.198</td>
<td>-.604</td>
<td>-.04163</td>
<td>.58697</td>
<td>.57725</td>
<td>-.14491</td>
<td>.02232</td>
</tr>
<tr>
<td>4.257</td>
<td>-.486</td>
<td>-.03845</td>
<td>.45303</td>
<td>.71870</td>
<td>-.15670</td>
<td>.02342</td>
</tr>
<tr>
<td>4.365</td>
<td>-.269</td>
<td>-.02359</td>
<td>.22346</td>
<td>.91086</td>
<td>-.12872</td>
<td>.01800</td>
</tr>
<tr>
<td>4.385</td>
<td>-.230</td>
<td>-.02024</td>
<td>.18611</td>
<td>.93457</td>
<td>-.11650</td>
<td>.01606</td>
</tr>
<tr>
<td>4.390</td>
<td>-.220</td>
<td>-.01937</td>
<td>.17677</td>
<td>.94009</td>
<td>-.11302</td>
<td>.01553</td>
</tr>
<tr>
<td>4.962</td>
<td>.924</td>
<td>.00606</td>
<td>-.03682</td>
<td>.11501</td>
<td>.93221</td>
<td>-.01646</td>
</tr>
</tbody>
</table>

The Lagrangian interpolation formula approximates a given function by a polynomial and expresses the interpolated value as a sum of products of consecutive tabular entries by suitable coefficients. Considering
one typical case, \( f(\alpha_n) = S_{\sigma\sigma}(\alpha_n) \), \( f(4.198) \) can be calculated from
the equation
\[
f(\alpha) = \sum_{n=-2}^{2} A_n(p) f(\alpha_n)
\]
as follows:

**TABLE 36. Calculation of \( S_{\sigma\sigma}(\alpha) \)**

<table>
<thead>
<tr>
<th>n</th>
<th>( \alpha_n )</th>
<th>( f(\alpha_n) )</th>
<th>( A_n(-.604) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>3.5</td>
<td>.26485</td>
<td>-.04163</td>
</tr>
<tr>
<td>-1</td>
<td>4.0</td>
<td>.31869</td>
<td>.58697</td>
</tr>
<tr>
<td>0</td>
<td>4.5</td>
<td>.33257</td>
<td>.57725</td>
</tr>
<tr>
<td>1</td>
<td>5.0</td>
<td>.31891</td>
<td>-.14491</td>
</tr>
<tr>
<td>2</td>
<td>5.5</td>
<td>.28863</td>
<td>.02232</td>
</tr>
</tbody>
</table>

The functional values of \( \alpha \), starting with 3.5 at intervals of \( h = .5 \)
are tabulated either from tables or by calculation. For the five-point
interpolation the central \( \alpha \) value is taken as \( \alpha_0 = 4.5 \) and the corre­
sponding \( p = -.604 \) is calculated. The Lagrangian interpolation coeffi­
cients \( A_n(-.604) \), as a function of \( p \) are read from the tables as in
Table 35, and the functional value \( f(\alpha) \), at the required \( \alpha \) value
calculated as indicated. This procedure is repeated for all the neces­
sary integrals \( s's', s'_\sigma, \sigma-s', \sigma-\sigma \) and \( \pi\pi \) at all the required \( \alpha \) values.
The weighted average value of all the next-nearest neighbor distances,
\( R = 2.87 \) was calculated from Table 14. The corresponding \( \alpha \) parameter is
calculated as 7.05. The next-nearest neighbor integrals have been
calculated using a rounded value of $\alpha = 7.0$, since they make a smaller contribution than the nearest-neighbor integrals.

9.21 Overlap Integral

Let $\alpha$ designate one of the normalized $k$, $s$, $s'$, $\sigma$, $\pi$ orbitals on nucleus $a$, and let $\beta$ designate any of the same orbitals on nucleus $b$. Then the overlap integral is defined as

$$S_{\alpha \beta} = \langle \alpha_a | \beta_b \rangle = \int \alpha_a \beta_b d\tau$$

(418)

The overlap integral is a dimensionless quantity. In semi-empirical molecular orbital theory the magnitude of the so-called "resonance integrals" is assumed to be proportional to the corresponding overlap integral. However, as the discussion in Chapter 8 shows, the overlap integrals are not directly involved in the Hartree-Fock matrix ($F$), but form the elements of the second or overlap matrix, $(S)$ which enters into the secular equation. The general formulas using Kopineck's 2s orbital are given by Preuss in Sections 2.3 through 2.5:

$$S_{s' s'} = N^2 \left[ \beta^2 S_{kk} - 2 \beta S_{ks} + S_{ss} \right],$$

(419)

with

$$S_{kk} = 3 \alpha^2 / 2 \left[ 3 \lambda_2(\alpha) - A_0(\alpha) \right],$$

$$S_{ks} = 3 \alpha^2 / 2 \left[ 3 \lambda_2(\alpha) - A_0(\alpha) \right],$$

(420a)

$$S_{ks} = \alpha^4 / 12 \left[ 3 \lambda_3(\alpha) - A_1(\alpha) \right],$$

(420b)

$$S_{ss} = \alpha^5 / 24 \left[ A_0(\alpha) / 5 - 2 / 3 \lambda_2(\alpha) + A_1(\alpha) \right];$$

(420c)

$$S_{s' s'} = S_{s' s'} = N \left[ \beta S_{s' s} - S_{ss} \right],$$

(421)

with

$$S_{k \sigma} = \alpha^4 / 12 \left[ A_0(\alpha) - 3 \lambda_2(\alpha) \right],$$

(422a)

$$S_{s \sigma} = \alpha^5 / 12 \left[ - A_1(\alpha) / 5 + A_3(\alpha) \right];$$

(422b)
\[ S_{\sigma\sigma} = \frac{\alpha^5}{6} \left[ -A_0(\alpha) + 6/5 A_2(\alpha) - 1/3 A_4(\alpha) \right] ; \]  

(423)

and

\[ S_{\pi\pi} = \frac{\alpha^5}{24} \left[ A_0(\alpha) + 6/5 A_2(\alpha) + A_4(\alpha) \right] . \]  

(424)

All the above formulas have been derived and checked numerically with the help of the tabulated values for the auxiliary function \( A_m(\lambda) \).

As an illustration of the evaluation of one of the above mentioned integrals, consider the overlap integral between the 2s\(\sigma\)-orbital on atom a and the 2s\(\sigma\)-orbital on atom b,

\[ S_{ss} = \int (2s\sigma)_{a}(l)(2s\sigma)_{b}(l)d\tau(l) \]  

(425)

Substituting for 2s orbitals from Eq. (118b)

\[ S_{ss} = \int \left( \frac{G^5}{3\pi} \right)^{1/2} e^{-\frac{1}{2}r_a r_a} \left( \frac{G^5}{3\pi} \right)^{1/2} e^{-\frac{1}{2}r_b r_b} d\tau \]  

(426)

This integration can be carried on conveniently by using elliptic coordinates \( \lambda, \mu \) and \( \phi \) with

\[ \lambda = 1/R(r_a + r_b) \]  

(427a)

\[ \mu = 1/R(r_a - r_b) \]  

(427b)

and

\[ d\tau = (R/2)^3 (\lambda^2 - \mu^2) d\lambda d\mu d\phi . \]  

(427c)

The range of variation in case of these variables is

\[ 1 \leq \lambda \leq \infty; \quad -1 \leq \mu \leq 1 \text{ and } 0 \leq \phi \leq 2 \]  

(428)

with this change of coordinates one obtains

\[ S_{ss} = \frac{G^5}{3} \int e^{-\frac{1}{2}R(\lambda + \mu)} R/2(\lambda - \mu) R/2(\lambda^2 - \mu^2) R^3 d\lambda d\mu d\phi \]  

(429)

Integration with respect to \( \phi \) gives a constant 2\(\pi\) and the integration with respect to \( \mu \) is elementary and leads to

\[ S_{ss} = \frac{G^5}{2} R^5/48 \int_{1}^{\infty} e^{-\frac{1}{2}R(\lambda^4 + 1/5 - 2\lambda^2/3)} d\lambda . \]  

(430)
Integration with respect to $\lambda$ however requires evaluation of auxiliary functions of the form

$$A_m(\alpha) = \int_1^\infty e^{-\alpha \lambda} \lambda^m d\lambda = m! e^{-\alpha} \sum_{k \geq 0} \frac{\alpha^k}{k!}.$$  \hspace{1cm} (431)

It is convenient to express $S_{ss\sigma}$ in terms of $A_m(\alpha)$ as its numerical values are tabulated by Preuss and Kotani.

$$S_{ss} = \sum_{\alpha} \frac{5}{2} \frac{R^5}{24} \left\{ \frac{1}{5} A_0(\ell_2 R) - \frac{2}{3} A_2(\ell_2 R) + A_4(\ell_2 R) \right\}. \hspace{1cm} (432)$$

This is the same as Eq. (420c) with $\alpha$ replacing $\ell_2 R$.

The corresponding one-electron one-center integral is obtained by taking the limit of Eq. (432) as $R \to 0$,

$$S_{ss}^0 = \text{Limit}_{R \to 0} \left( \sum_{\alpha} \frac{5}{2} \frac{R^5}{24} \left\{ \frac{1}{5} e^{-\ell_2 R} - \frac{2}{3} e^{-\ell_2 R} + e^{-\ell_2 R} \right\} \right) = 1. \hspace{1cm} (433)$$

One can also arrive at the same result from the definition with both the orbitals located on the same atom. The values of auxiliary integrals are given by

$$S_{kk}^0 = 1, \quad S_{ss}^0 = 1, \quad S_{ks}^0 = \sqrt{3}/2 \quad \text{and} \quad S_{ks}^0 = 0, \quad S_{ss}^0 = 0. \hspace{1cm} (434)$$

These auxiliary overlap integrals help to evaluate the necessary final integrals as

$$S_{s's'}^0 = S_{s's'}^0 = S_{s's'}^0 = 1, \hspace{1cm} (435a)$$

and

$$S_{\alpha\beta}^0 = 0, \quad \text{for} \quad \alpha \neq \beta. \hspace{1cm} (435b)$$

These are dimensionless quantities and are found to be independent of $\ell_2$.

The one-electron two-center integrals are listed in Table 37a using Tables 16 and 18 of Preuss. The values of $S_{s's'}$ and $S_{s's'}$ are calculated from Eqs. (419) and (421) using auxiliary integrals and $S_{s's'}$ and $S_{\pi\pi}$ are read directly. Due to the spherical symmetry one obtains
### TABLE 37a. Tabulated and Calculated Overlap Integrals

\[ S_{s' s} = N^2 (\beta^2 S_{kk} - 2\beta S_{ks} + S_{ss}) \]

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( S_{kk} )</th>
<th>( S_{ks} )</th>
<th>( S_{ss} )</th>
<th>( S_{s' s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>0.25919</td>
<td>0.38465</td>
<td>0.54485</td>
<td>0.59224</td>
</tr>
<tr>
<td>4.0</td>
<td>0.18926</td>
<td>0.30490</td>
<td>0.45626</td>
<td>0.51417</td>
</tr>
<tr>
<td>4.5</td>
<td>0.13609</td>
<td>0.23691</td>
<td>0.37479</td>
<td>0.43743</td>
</tr>
<tr>
<td>5.0</td>
<td>0.09658</td>
<td>0.18089</td>
<td>0.30246</td>
<td>0.36488</td>
</tr>
<tr>
<td>5.5</td>
<td>0.06777</td>
<td>0.13602</td>
<td>0.24016</td>
<td>0.29872</td>
</tr>
<tr>
<td>7.0</td>
<td>0.02219</td>
<td>0.05361</td>
<td>0.11056</td>
<td>0.14864</td>
</tr>
</tbody>
</table>

### TABLE 37b. Interpolated Values of Overlap Integrals

\[ S_{s' s} = N (\beta S_{k \sigma} - S_{s \sigma}) \]

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( S_{k \sigma} )</th>
<th>( S_{s \sigma} )</th>
<th>( S_{s' s} )</th>
<th>( S_{s' \sigma} )</th>
<th>( S_{s \tau} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>0.45359</td>
<td>0.48613</td>
<td>-0.44941</td>
<td>0.26485</td>
<td>0.37017</td>
</tr>
<tr>
<td>4.0</td>
<td>0.37852</td>
<td>0.44413</td>
<td>-0.42973</td>
<td>0.31869</td>
<td>0.28694</td>
</tr>
<tr>
<td>4.5</td>
<td>0.30619</td>
<td>0.39108</td>
<td>-0.39287</td>
<td>0.33257</td>
<td>0.21857</td>
</tr>
<tr>
<td>5.0</td>
<td>0.24144</td>
<td>0.33390</td>
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<td>0.04602</td>
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</tbody>
</table>

### TABLE 37c. Interpolated Values of Overlap Integrals

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<th>( S_{s' \sigma} )</th>
<th>( S_{s \sigma} )</th>
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The interpolated overlap integral values at required interatomic distances are tabulated in Table 37b.

9.22 Resonance and Nuclear Attraction Integrals

The two-center nuclear attraction integrals for which the two atomic orbitals involved are on different atoms (or centers) is called a resonance integral, and denoted by

\[
J_{\alpha\beta} = \langle \alpha | r^{-1} | \beta \rangle = \int \alpha(1)r_{ab}^{-1}\beta(1)\,d\tau
\]

and

\[
J_{\beta\alpha} = \langle \beta | r^{-1} | \alpha \rangle = \int \beta(1)r_{ab}^{-1}\alpha(1)\,d\tau
\]

where \(\alpha\) and \(\beta\) denote any one of the chosen orbitals on nucleus a or b. Although simply a special form of nuclear attraction integral it has been given a distinct name because of its fundamental role in the theory of chemical bonding. In general, \(J_{\alpha\beta} \neq J_{\beta\alpha}\) for \(\alpha \neq \beta\) because the operator \(r_{ab}^{-1}\) is not Hermitian. The two-center nuclear attraction integrals for which the two atomic orbitals are on the same atom or center, while the \(r^{-1}\) operator in the integrand represents (except for a constant factor) the potential arising from the other center or nucleus, will be denoted by

\[
K_{\alpha\beta} = \langle \alpha | r_{ab}^{-1} | \beta \rangle = \int \alpha(1)r_{ab}^{-1}\beta(1)\,d\tau
\]

They will be referred to simply as nuclear attraction integrals to distinguish them from the resonance integrals. \(K_{\alpha\beta} = K_{\beta\alpha}\) in this case as the interacting orbitals are located on the same nucleus. These
integrals represent energies and are expressed in terms of $e^2/a_o$ atomic units.

The necessary formulas are again collected from Sections 2.3 and 2.4 of Preuss and given below

$$J_{s's'} = N^2\left\{\beta^2 J_{kk} - \beta(J_{ks} + J_{sk}) + J_{ss}\right\}, \quad (438)$$

where

$$J_{kk} = \alpha^2/2 A_1(\alpha), \quad (439a)$$
$$J_{ks} = \alpha^2/12 \sqrt{3} \left[3A_2(\alpha) + A_o(\alpha)\right], \quad (439b)$$
$$J_{sk} = \alpha^2/12 \sqrt{3} \left[3A_2(\alpha) - A_o(\alpha)\right], \quad (439c)$$
$$J_{ss} = \alpha^4/72 \left[3A_3(\alpha) - A_1(\alpha)\right], \quad (439d)$$
$$J_{s's'} = N(\beta J_{sk} - J_{ss}), \quad (440a)$$

and

$$J_{s't'} = N(\beta J_{sk} - J_{s's'}), \quad (440b)$$

with

$$J_{k\sigma} = \alpha^3/3 A_1(\alpha) \text{ and } J_{\sigma k} = \alpha^3/6 A_1(\alpha), \quad (441a)$$
$$J_{s'\sigma} = (1/24 \sqrt{3})\left[\alpha^4 - A_o(\alpha) + 3A_2(\alpha)\right], \quad (441b)$$
$$J_{s\sigma} = (1/24 \sqrt{3})\left[\alpha^4 - A_1(\alpha) + A_2(\alpha)\right] \quad (441c)$$
$$J_{s\sigma'} = (1/24)\alpha^4 \left[3A_1(\alpha) - A_2(\alpha)\right], \quad (441d)$$

and

$$J_{\pi\pi} = (1/24)\alpha^4 \left[-A_1(\alpha) + A_2(\alpha)\right], \quad (443)$$

The corresponding nuclear attraction integrals are given by

$$K_{s's'} = N^2(\beta^2 K_{kk} - 2\beta K_{ks} + K_{ss}), \quad (444)$$

where

$$K_{kk} = \left[\frac{1}{\alpha^4} - (1+i\alpha) e^{-2\alpha^4/\alpha^4}\right], \quad (445a)$$
$$K_{ks} = (2/\sqrt{3})\alpha^3 \left[6/(2\alpha)^4 + A_2(2\alpha) - A_3(2\alpha)\right], \quad (445b)$$
\[
K_{ss} = (2/3)\alpha^4 \left[ 41/(2\alpha)^5 + A_3(2\alpha) - A_4(2\alpha) \right] ; \quad (445c)
\]

\[
K_{\sigma\sigma} = K_{s\sigma} = N(\beta K_{\sigma k} - K_{\sigma s}) , \quad (446)
\]

with

\[
K_{\sigma k} = (2/3)\alpha^3 \left[ 24/(2\alpha)^5 + A_1(2\alpha) - A_4(2\alpha) \right] , \quad (447a)
\]

\[
K_{\sigma s} = (2/3\sqrt{3})\alpha^3 \left[ 51/(2\alpha)^5 + A_2(2\alpha) - A_5(2\alpha) \right] ; \quad (447b)
\]

\[
K_{\sigma\sigma} = (2/15)\alpha^4 \left[ 51/(2\alpha)^5 + 2*61/(2\alpha)^7 + 2A_1(2\alpha) \right] + 5A_3(2\alpha) - 5A_4(2\alpha) - 2A_6(2\alpha) \] ; \quad (448)

and

\[
K_{\pi\pi} = (2/15)\alpha^4 \left[ 51/(2\alpha)^5 - 61/(2\alpha)^7 - A_1(2\alpha) + 5A_3(2\alpha) \right.
\]

\[
- 5A_4(2\alpha) + A_6(2\alpha) \] . \quad (449)

All these formulas are given for the effective nuclear charge \( Z = 1 \) and we shall hereafter refer to them as reduced values of the integrals.

To show the details of a simple example the case of resonance between a 2s orbital on atom \( b \) and a 1s orbital on atom \( a \) (with \( \xi_2 \) as exponent) is considered.

\[
J_{sk} = \int (2s)_b(1)\xi_2^{-1} (k)_a(1)d\xi_1 \quad (450)
\]

substituting the orbital expressions for 2s and \( k \), one has

\[
J_{sk} = \int (2s)_b(1)\xi_2^{-1} (k)_a(1)d\xi_1 \quad (451)
\]

Once again using elliptic coordinates as before and using the additional substitution \( r_a + r_b = R \), one gets

\[
J_{sk} = \xi_2^{4/3} \sqrt{3} \pi \int e^{-\xi_2^{2} r_b} (r_b/r_b) (\xi_2^2) d\xi_1 \quad (452)
\]

Integration with respect to \( \phi \) gives a constant \( 2\pi \) and further integration with respect to \( \lambda \) gives...
\[ J_{sk} = \frac{\xi_2^4 R^3}{\sqrt{3}} \int_1^{\infty} e^{-\frac{\xi_2^2 R}{2}(3\lambda^2 - 1)} d\lambda \]  

(453)

Final integration relative to \( \lambda \) can be seen to yield

\[ J_{sk} = \frac{\xi_2^4 R^3}{\sqrt{3}} \left[ (3A_2(\alpha) - A_0(\alpha)) \right] \]  

(454)

which is the same as Eq. (439c).

Next consider the nuclear attraction integral for \( k \) orbitals centered on the same atom, \( a \), or

\[ K_{kk} = \frac{1}{\pi} \int_{a}^{\infty} \left( \int_{a}^{\infty} \right) \]  

(455)

Substituting the expressions for the Slater orbitals yields

\[ K_{kk} = \frac{\xi_2^3}{\pi} \int_{a}^{\infty} e^{-\frac{\xi_2^2 r_1}{2} r_b^{-1}} d\tau. \]  

(456)

As before, by using elliptical coordinates

\[ K_{kk} = \frac{\xi_2^3 R^2}{4\pi} \int_{a}^{\infty} e^{-\frac{\xi_2^2 (\lambda + \mu)}{2}} \lambda d\lambda d\mu \]  

(457)

Integration with respect to \( \phi \) gives a constant \( 2\pi \), and integration with respect to \( \lambda \) leads to evaluation of an auxiliary function of the form

\[ B_n(\alpha) = \int_{-1}^{1} e^{-\frac{\alpha}{2} \mu^2} d\mu. \]  

(458)

Hence

\[ K_{kk} = \frac{\xi_2^3 R^2}{2} \int_{1}^{\infty} e^{-\frac{\xi_2^2 R}{2}} \left( \lambda B_0 + B_1 \right) d\lambda. \]  

(459)

Integration with respect to \( \lambda \) however leads to evaluation of the auxiliary function \( A_n(\alpha') \) of Eq. (431) so that

\[ K_{kk} = \frac{\xi_2^3 R^2}{2} \left( B_0 A_1 + B_1 A_0 \right). \]  

(460)

Further simplification gives

\[ K_{kk} = (1 - (1 + \alpha) e^{-2\alpha/2}) \]  

(461)

which is the same as the Eq. (445a). The relation between \( B_n(\alpha') \) and
\[ A_n(\alpha) \text{ and several other recursion relations among } A_n(\alpha)'s \text{ and } B_n(\alpha)'s \text{ alone are listed in section 1.4 of Preuss.} \]

The one-electron one-center nuclear attraction integral can be found either from the definition

\[ J_{\alpha\beta}^0 = (\alpha_a | R_a^{-1} | \beta_a), \quad (462) \]

or by taking the limit as \( R \to 0 \) for the corresponding resonance integral or two-center nuclear attraction integral. For the case already worked out

\[ J_{sk}^0 = \text{Limit } \frac{\hbar^2 R^3}{6} \sqrt{3} \left[ (3A_2(\alpha) - A_0(\alpha)| = \frac{1}{2} \sqrt{3} \quad (463) \right. \]

The values of auxiliary integrals are found to be

\[ J_{kk}^0 = 1/2, \quad J_{ss}^0 = 1/4, \quad J_{ks}^0 = 1/2 \sqrt{3}, \quad J_{sk}^0 = 1/ \sqrt{3} \quad (464a) \]

\[ J_{k\sigma}^0 = 0, \quad J_{\sigma k}^0 = 0, \quad J_{s\sigma}^0 = 0, \quad J_{\sigma s}^0 = 0 \quad (464b) \]

and the final needed integrals are

\[ J_{s' s}^0 = .21, \quad J_{\sigma \sigma}^0 = J_{\pi \pi}^0 = .25 \quad (465a) \]

and

\[ J_{\alpha \beta}^0 = 0, \text{ for } \alpha \neq \beta \quad (465b) \]

All the above integrals are given in atomic units for \( Z = 1 \), and will be called reduced integrals.

The reduced values of the resonance and nuclear attraction integrals are given in Tables 38a and 39a. \( J_{s' s}^0, J_{\sigma \sigma}^0 \) and \( J_{s' \sigma}^0 \) are calculated from Eqs. (438) and (440a and b). \( K_{s' s}^1, K_{\sigma \sigma}^1, K_{s' \sigma}^1 \) are obtained from Eqs. (444) and (446) by using various auxiliary integrals. Integrals involving \( \sigma \sigma, \pi \pi \) are read directly from the tables. It may be shown that Kotani's \( J_{\alpha \beta}^0 \) is equivalent to Preuss' \( J_{\beta \alpha}^0 \) whenever \( \alpha \neq \beta \). Another difference is that the positive lobe of Kotani's \( \sigma \) orbitals is
### TABLE 38a. Tabulated and Calculated Values of Reduced Resonance Integrals

\[ J_{s's'/Z} = \frac{N^2}{Z^2} \left( J_{kk} - \beta (J_{ks} + J_{sk}) + J_{ss} \right) \]

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<th>( J_{kk}/Z )</th>
<th>( J_{ks}/Z )</th>
<th>( J_{sk}/Z )</th>
<th>( J_{ss}/Z )</th>
<th>( J_{s's'/Z} )</th>
<th>( J_{\sigma \pi}/Z )</th>
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</tbody>
</table>

\[ (J_{s's'/Z} = \frac{N}{Z} (J_{\sigma \sigma}) - (J_{s's'}) \]

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( J_{kr}/Z )</th>
<th>( J_{\sigma s}/Z )</th>
<th>( J_{\sigma's'}/Z )</th>
<th>( J_{kr}/Z )</th>
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### TABLE 38b. Interpolated Values of Reduced Resonance Integrals

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<th>( J_{s's'/Z} )</th>
<th>( J_{s's'/Z} )</th>
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</table>
TABLE 39a. Tabulated and Calculated Values of Reduced Nuclear Attraction Integrals

\[ K_{S'S}/Z = \left( \frac{N}{Z} \right) \left( \frac{Z}{N} \right)^2 \left( K_{kk} - 2K_{ks} + K_{ss} \right) \]

<table>
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<th>( \alpha )</th>
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\[ K_{\pi'S}/Z = K_{S'S}/Z = \left( \frac{N}{Z} \right) \left( \frac{Z}{N} \right)^2 \left( K_{\pi k} - K_{\pi s} \right) \]

<table>
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TABLE 39b. Interpolated Values of Reduced Nuclear Attraction Integrals

\[ K_{S'S}/Z = K_{S'S}/Z = \left( \frac{N}{Z} \right) \left( \frac{Z}{N} \right)^2 \left( K_{\pi k} - K_{\pi s} \right) \]

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<td>-.01548</td>
<td>.07577</td>
<td>.06924</td>
</tr>
</tbody>
</table>
always directed in the positive $x$ direction, whereas in Preuss and the present work the positive lobe is always directed at the other atom of the pair (for two center integrals). Hence the type $J_{\alpha\sigma} (all \alpha)$ of Kotani, having the $\sigma$ orbital on the right-hand atom, are equal in value but opposite in sign to the corresponding integral of Preuss. In addition Kotani tabulates these integrals in terms of $Z/2$ times the atomic energy unit, whereas Preuss uses $Z$ times the atomic energy unit. We have tabulated the integrals in atomic energy units for $Z = 1$ and designated them as **reduced integrals**. Thus the numerical values given in Tables 38 and 39 agree with those given by Preuss and are half those of Kotani.

### 9.23 Kinetic Energy Integral

The kinetic energy integral for a pair of atomic orbitals is

$$ T_{\alpha\beta} = \langle a_\alpha | -\frac{1}{2} \nabla^2 | b_\beta \rangle = \int \rho_a(1)(-\frac{1}{2} \nabla^2_1) \rho_b(1) d^2 \tau \quad (466) $$

In this case $T_{\alpha\beta} = T_{\beta\alpha}$ for all $\alpha$ and $\beta$, because of the Hermitian property of the kinetic energy operator $-\frac{1}{2} \nabla^2$. These integrals are not mentioned by Preuss and Kotani et al. present the final compact formation and tabulate the numerical values of $ss$, $s\sigma$, $\sigma\sigma$ and $\pi\pi$ integrals. Roothaan shows how the kinetic energy integral can be expressed in general in terms of overlap and resonance integrals and also presents the general formulation. Since the tables do not give the details of the calculations it seems profitable to consider the major steps involved in the derivation of the kinetic energy integral.

From the definition, the Slater orbital is denoted by

$$ (n, l, m) = (2S)^{\frac{1}{2}} [2n)]^\frac{-\frac{3}{2}n-1}{1} e^{-\frac{\pi r^2}{\ell}} S_{l, m} (\theta, \phi) \quad (467) $$
where

\[ S_{\ell,m}(\theta, \phi) = \theta(\phi) \bar{q}(\phi) \quad (468a) \]

\[ \Theta(\phi) = \frac{\sqrt{2l + 1}}{2} \frac{(l - |m|)!}{(l + |m|)!} P^{|m|}_l \cos \theta, \quad (468b) \]

and

\[ \bar{q}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}. \quad (468c) \]

In order to obtain the result of operating with the kinetic energy operator, \(-(1/2)\nabla^2\), on \((n, l, m)\) it is convenient to separate the Laplacian operator in spherical polar coordinates into a part \(\Delta_r = (\partial^2/\partial r^2) + (2/r)(\partial/\partial r)\) and a remainder \(\Delta_{\theta, \phi} = \nabla^2 - \Delta_r\). It is then found that

\[ \Delta_r(n, l, m) = l^2 \left\{ (n, l, m) - 2\left(\frac{2n}{2n - 1}\right)^{\frac{3}{2}} (n - 1, l, m) \right. \]

\[ + \left. \frac{4n(n - 1)(n - 2, l, m)}{[(2n)(2n - 1)(2n - 2)(2n - 3)]^{\frac{1}{2}}} \right\} S_{\ell,m}(\theta, \phi) \quad (469) \]

is operation on \((n, l, m)\) and

\[ \Delta_{\theta, \phi}(n, l, m) = l^2 \left\{ \frac{4l(l + 1)(n - 2, l, m)}{[(2n)(2n - 1)(2n - 2)(2n - 3)]^{\frac{1}{2}}} \right\} S_{\ell,m}(\theta, \phi) \quad (470) \]

can be directly added to the above expression to give the result

\[ -1/2 \nabla^2(n, l, m) = -l^2/2 \left\{ (n, l, m) - 2\left(\frac{2n}{2n - 1}\right)^{\frac{3}{2}} (n - 1, l, m) \right\} \]

\[ + \frac{4(n + l)(n - l - 1)}{[(2n)(2n - 1)(2n - 2)(2n - 3)]^{\frac{1}{2}}} \] \(S_{\ell,m}(\theta, \phi) \quad (471) \]

Also, the terms in \((2/r)(n, l, m)\) can be regrouped to give

\[ 2/r(n, l, m) = 2l \zeta \left[ \frac{(2n)(2n - 1)}{(2n - 2)(2n - 3)} \right]^{\frac{1}{2}} (n - 1, l, m). \quad (472) \]
Applying equations (471) and (472) to the case of \((n, l', m) \rightarrow (n, l, m)_a\), \(\xi \rightarrow \xi_a\), and \(r \rightarrow r_a\), and using the relations
\[
\xi_a = (1 + \tau)\xi, \quad \xi_b = (1 - \tau)\xi, \quad R = \rho/\xi
\]
(473)
one obtains the more general relations of Roothaan,\(^6\)
\[
\{(n, l, m)_a | -1/2 \nabla^2 | (n', l', m)_b\} = \left\{ -1/2 \nabla^2 (n, l, m)_a \right\} (n', l', m)_b
\]
\[
= -1/2 \xi^2 (1 + \tau)^2 \left[ \{(n, l, m)_a | (n', l', m)_b\} - 2 \left[ (2n)(2n - 1) \right] \frac{1}{2} \{(n - 1, l, m)_a | (n', l', m)_b\} \right]
\]
\[
+ \frac{4(n + 1)(n - 3 - 1)}{2n(2n - 1)(2n - 2)(2n - 3)} x \left\{ (n - 2, l, m)_a | (n', l', m)_b\right\}. \quad (474)
\]
and
\[
\{(n, l, m)_a | Z | r_a | (n', l', m)_b\}
\]
\[
= 2\xi(1 + \tau)\left[ (2n)(2n - 1) \right]^{1/2} \left\{ (n - 1, l, m)_a | (n', l', m)_b\right\}. \quad (475)
\]

These general equations can be applied to 1s, 2s, and 2p atomic orbitals to obtain explicit formulas. As an illustration, one can consider the kinetic energy integral between a 1s orbital centered on atom "a" and a 1s orbital on atom b. By definition

\[
T_{1s,1s} = (1s_a | -\frac{1}{2} \nabla^2 | 1s_b) = \int (1s_a | -\frac{1}{2} \nabla^2 | 1s_b) d\tau \quad (476)
\]
and as can be easily seen to follow from Eq. (474)
\[
(1s_a | -\frac{1}{2} \nabla^2 | 1s_b) = -\frac{1}{2} \xi^2 (1 + \tau)^2 \left\{ (1s_a | 1s_b) - 2 \sqrt{\xi} (0s_a | 1s_b) \right\}. \quad (477)
\]
The integral \((0s_a | 1s_b)\) follows directly from Eq. (474),
\[
(1s_a | \frac{1}{r_a} | 1s_b) = \sqrt{\xi} \xi_a (0s_a | 1s_b) \quad (478)
\]
(In Roothaan’s formulas \(0s\) represents a fictitious "atomic" orbital obtained by setting \(n = m = 0\) in Eq. (467).) Thus, the kinetic energy relation reduces to

\[
T_{ls,ls} = -\frac{1}{2} \zeta_2^2 \langle 1s_a | 1s_b \rangle - 2 \zeta_a \langle 1s_a | 1/r_a | 1s_b \rangle
\]

\[ (479) \]

If in this formula \(\zeta_2\) is set equal to \(\zeta_2\), the \(1s\) orbital are in effect replaced by \(1s'\) or \(K\) orbitals and one obtains the integral

\[
T_{kk} = \left\{ -\frac{1}{2} \zeta_2^2 \langle K_a | K_b \rangle + \zeta_2 \langle K_a | 1/r_a | K_b \rangle \right\}
\]

\[ (480) \]

required for the calculation of \(T_{s's'}\). From the basic definitions, it is easy to see that the kinetic energy integral is the algebraic sum of the overlap and resonance integrals.

\[
T_{kk} = \frac{\zeta_2^2}{2} (-\frac{1}{2} S_{kk} + J_{kk}/\zeta_2).
\]

\[ (481) \]

All the necessary kinetic energy integrals can now be put in the following useful forms:

\[
T_{s's'} = N^2 \left[ \frac{\beta^2 T_{kk}}{2} - 2 \beta T_{ks} + T_{ss} \right],
\]

\[ (482) \]

with

\[
T_{ks} = \frac{\zeta_2^2}{2} (-\frac{1}{2} S_{ks} + J_{sk}/\zeta_2),
\]

\[ (483) \]

\[
T_{ss} = \frac{\zeta_2^2}{2} \left\{ -\frac{1}{2} S_{ss} + 2 \zeta_2 J_{ss} - \frac{1}{4} (2\alpha^2 + 3\alpha + 3)e^{-\alpha} \right\},
\]

\[ (484) \]

and \(T_{kk}\) as given by Eq. (480).

Also,

\[
T_{s'\sigma} = T_{\sigma s'} = N \left\{ \beta T_{k\sigma} - T_{s\sigma} \right\},
\]

\[ (485) \]

where

\[
T_{k\sigma} = \frac{\zeta_2^2}{2} (-\frac{1}{2} S_{k\sigma} + 2 \zeta_2 J_{k\sigma}),
\]

\[ (486) \]

and

\[
T_{s\sigma} = \frac{\zeta_2^2}{2} (-\frac{1}{2} S_{s\sigma} + 2 \zeta_2 J_{s\sigma});
\]

\[ (487) \]

\[
T_{\sigma\sigma} = \frac{\zeta_2^2}{2} \left\{ -\frac{1}{2} S_{\sigma \sigma} + 2 \zeta_2 J_{\sigma \sigma} \right\};
\]

\[ (488) \]

and

\[
T_{\pi\pi} = \frac{\zeta_2^2}{2} \left\{ -\frac{1}{2} S_{\pi \pi} + 2 \zeta_2 J_{\pi \pi} \right\}.
\]

\[ (489) \]
All these specific formulas are in agreement with Roothaan's general formula and can be readily applied. Here again the formulas are given for $Z = 1$ and for any $Z$, one obtains the actual kinetic energy in atomic units by multiplying reduced $T$ by $Z^2$.

The one-electron one-center kinetic energy integrals are not evaluated by Preuss or Kotani but are readily evaluated analytically. The values of these integrals may also be obtained by letting the internuclear distance $R$ approach zero in the general formula of Eq. (474).

This yields the auxiliary integrals

$$T_{kk}^0 = 1/8, \quad T_{ks}^0 = 1/16\sqrt{3}, \quad T_{ss}^0 = 1/24.$$  \hspace{1cm} (490a)

and

$$T_{k\sigma}^0 = 0, \quad T_{s\sigma}^0 = 0.$$  \hspace{1cm} (490b)

The final values are obtained as

$$T_{s's'}^0 = .065, \quad T_{\sigma\tau}^0 = T_{\pi\pi}^0 = .125.$$  \hspace{1cm} (491a)

and

$$T_{\alpha\beta}^0 = 0, \text{ for } \alpha \neq \beta.$$  \hspace{1cm} (491b)

All the formulas of Kotani have been checked numerically and his tabulations of $ss, \sigma\sigma, \pi\pi$ in his Table 22 have been used. However $T_{s's'}^0$ and $T_{s's'}^0$ of Eqs. (482) and (485) have been computed using the auxiliary table of integrals of Preuss and tabulated in Table 40a. The interpolated values are listed in Table 40b.

### 9.3 Two-Electron Integrals

As discussed earlier, the two-electron integrals enter the matrix elements of the secular equation through the general Eq. (284). In general a two-electron integral is defined by Eq. (265) and can have four distinct orbitals on as many as four atomic centers. $\chi_\alpha, \chi_\beta, \chi_\gamma$ and $\chi_\delta$ are abbreviated by $\alpha, \beta, \gamma, \delta$ and the subscript indicates the
TABLE 40a. Tabulated and Calculated Values of Reduced Kinetic Energy Integrals

\[ T_{kk}/z^2 = -(S_{kk}/\alpha) + (J_{kk}/2z^2), \quad T_{ks}/z^2 = -(S_{ks}/\alpha) + (J_{sk}/2z), \]

\[ T_{s1}/z^2 = (N/z^2)(\beta^2T_{kk} - 2\beta T_{ks} + T_{ss}) \]

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>(T_{kk}/z^2)</th>
<th>(T_{ks}/z^2)</th>
<th>(T_{ss}/z^2)</th>
<th>(T_{s1}/z^2)</th>
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</tr>
</tbody>
</table>

\[ T_{k\sigma}/z^2 = -(S_{k\sigma}/\alpha) + (J_{k\sigma}/z), \quad T_{s1\sigma}/z^2 = (N/z^2)(\beta T_{k\sigma} - T_{s\sigma}) \]

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>(T_{k\sigma}/z^2)</th>
<th>(T_{s\sigma}/z^2)</th>
<th>(T_{s1\sigma}/z^2)</th>
<th>(T_{r\sigma\sigma})</th>
<th>(T_{s1\sigma})</th>
</tr>
</thead>
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TABLE 40b. Interpolated Values of Reduced Kinetic Energy Integrals

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>(T_{s1}/s1)</th>
<th>(T_{s1}\sigma)</th>
<th>(T_{\sigma\sigma})</th>
<th>(T_{\pi\pi})</th>
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<td>.03120</td>
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</tr>
<tr>
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</tr>
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<td>-.00021</td>
</tr>
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</table>
atom considered. Thus a general two-center integral is of the form

\[ \int \int \alpha_a(1)\beta_b(1) r^{-1}_{12} \gamma_c(2) \delta_d(2) d\tau_1 d\tau_2 \quad (492) \]

and can be written compactly as \((\alpha_a^\dagger \beta_b | r^{-1} | \gamma_c \delta_d \rangle \). As in the preceding part of this section the orbitals are bond-oriented orbitals, 2s' (or 2s), 2p\sigma, 2p\pi and 2p\pi'. However, in the present calculation only the two-center integrals are considered (all of these which do not vanish are tabulated). The general expressions for the distinct two-electron two-center integrals are given below. The Coulomb integral is defined as

\[ J_{\alpha \beta \gamma \delta} = (\alpha_a(1) | \beta_b(2) | r^{-1}_{12} | \gamma_c(1) \delta_d(2) \rangle, \quad (493) \]

the exchange integral as

\[ K_{\alpha \beta \gamma \delta} = (\beta_b(1) | \alpha_a(2) | r^{-1}_{12} | \gamma_c(1) \delta_d(2) \rangle, \quad (494) \]

and the ionic or hybrid integral is given by

\[ L_{\alpha \beta \gamma \delta} = (\alpha_a(1) | \beta_b(2) | r^{-1}_{12} | \gamma_c(1) \delta_d(2) \rangle \quad (495) \]

The bar on S in L indicates that the S orbital is located on a different atom than the \(\alpha, \beta,\) and \(\gamma, \delta\) orbitals. Preuss denotes the Coulomb and exchange integrals by \(C_{\alpha \beta \gamma \delta} \) and \(A_{\alpha \beta \gamma \delta'} \) respectively, but defines them as above.

As pointed out in Section 8.62, it is more meaningful to rearrange the integrand so that the mean electron charge distribution is brought out. From this viewpoint one considers the two-center integrals of form \((\alpha_a^\dagger \beta_b | r^{-1} | \gamma \delta \rangle \) where \( \neq b, \) and \( \gamma, \delta = \alpha_a \) or \( \beta_b \). This gives for the Coulomb integral

\[ (\alpha_a(1)\beta_a(1) | r^{-1} | \gamma_b(2)\beta_b(2) \rangle, \quad (496) \]
for the exchange integral

\[ (a(1)\beta(1)|r^{-1}|a(2)\beta(2)) , \tag{497} \]

and for the ionic or hybrid integral

\[ (a(1)\beta(1)|r^{-1}|\beta(2)\beta(2)) . \tag{498} \]

Here \( a \) can be any one of the s', p\( \sigma \), or p\( \pi \) orbitals, and \( \beta \) is one of the s', p\( \sigma \), p\( \pi \) or p\( \pi' \) orbitals. The relation between these and the conventional representations are shown in Eq. (415)

The symmetry relations among these various integrals are given by

(see Eqs. (270a,b)):

\[ J_{\alpha\beta\gamma\delta} = J_{\gamma\beta\delta\alpha} = J_{\delta\gamma\alpha\beta} = J_{\delta\gamma\beta\alpha} = J_{\beta\gamma\delta\alpha} = J_{\beta\gamma\alpha\delta} \tag{499} \]

\[ K_{\alpha\beta\gamma\delta} = K_{\beta\alpha\delta\gamma} = K_{\gamma\delta\alpha\beta} = K_{\delta\gamma\beta\alpha} \tag{500} \]

and

\[ L_{\alpha\beta\gamma\delta} = L_{\gamma\beta\alpha\delta} \tag{501} \]

Additional relations which exist for real atomic orbitals make it necessary to evaluate only a few non-vanishing integrals of each type. The relations using the orthogonalized 2s' orbital in terms of auxiliary integrals are given in Section 2.4 of Preuss and these are made use of in evaluating these integrals. It is rather cumbersome to evaluate these integrals numerically from fundamentals. However it is convenient to use spheroidal coordinates and integrate successively over the electron coordinates one at a time. The formulas for Coulomb integrals using Kopineck's 2s' orbital in Preuss have been checked and evaluated by means of Roothaan's tables.\(^{91}\)

The numerical values of all the necessary auxiliary functions are obtained from Tables 16, 17 and 18 of Preuss, Vol. I. The final values
of all non-vanishing two-center Coulomb, exchange, and ionic or hybrid involving the orbitals 2s', 2pσ, 2pπ, and 2pπ' are tabulated in Tables 41, 42, and 43, respectively. The method of three-point Lagrangian interpolation was used to obtain the values of the integrals at the necessary internuclear distances. These values are not required for the calculation in the zeroth approximation given in the next chapter, but would be required for higher approximations. They enter into the evaluation of the Hartree-Fock matrix elements of Eq. (284) as multipliers of the first-order density matrix elements and many could be neglected in the present calculation. However, their utilization must await further extension of the present investigation.
TABLE 41. Calculated and Interpolated Values of Reduced Coulomb Integrals

<table>
<thead>
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TABLE 42. Calculated and Interpolated Values of Reduced Exchange Integrals

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TABLE 43. Calculated and Interpolated Values of Reduced Hybrid Integrals

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Chapter 10. Density Matrix Formulation of Hartree-Fock

Self-Consistent Field Theory for a Crystal

in the LCAO Approximation

10.1 Form of the Secular Equation for a Crystal
Prior to the Bloch Transformation

The density-matrix formulation of Hartree-Fock self-consistent
field theory in the molecular orbital and LCAO approximations developed
in detail in Chapter 8 is applicable to a system of any size, and is
therefore applicable to a crystal as well as to a molecule. The treat­
ment in Chapter 8 was limited to the case in which the wave function of
the system has the form of a single antisymmetrized Slater determinand
of the form given in Eq. (151), that is to the case of a single config­
uration. The development was also carried furthest for the so-called
closed-shell case in which each one-electron function or molecular
orbital is occupied by a pair of electrons with opposed spins, leading
to a singlet wave function for the entire system of the form $\Psi$ of Eq.
(153). It is likely that the ground-state of most crystals not showing
ferro- or anti-ferromagnetism is a singlet state of this type (or that
the effect of any unpaired electron spin which may exist is of negligible
importance). The present discussion is restricted to the application of
the singlet or closed-shell single-configuration theory to a crystal in
the LCAO approximation. This appears likely to be a reasonably adequate
formulation for crystals (including semiconductors) in which the bonding
between the atoms of the lattice is primarily of the covalent type, and should thus be applicable to the $\alpha$-rhombohedral boron structure which is of interest. It may also be adequate for the valence states of metals, but an orthogonalized or augmented wave type theory is obviously more suited to conduction states than an LCAO theory. On the other hand the relatively low mobility of an electron in the conduction band of a valence-type semiconductor compared to that in a metal may well be due to the partial LCAO character of the wave functions even in the conduction bands.

The formal application of the secular equation of Eq. (333) or (337) to a large system such as a crystal is straightforward. The only difficulty is a practical one connected with the very high degree of the secular equation, but it will be seen that even this may be overcome by means of the Bloch and other symmetry transformations. In order to formulate the secular equation and wave functions for a crystal it is essential to modify the notation to take account of the enormous number of atoms and atomic orbitals in a crystal. A suitable notation has already been presented in Section 6.11, but will be modified to be more consistent with that of Chapters 8 and 9. A given unit cell will be designated by the triple of integers $n_1n_2n_3$; particular atoms within a cell will be designated by $a$, $b$, $c$, and $d$ (rather than $i$ and $j$); and particular atomic orbitals on a given atom by $\alpha$, $\beta$, $\gamma$, and $\delta$ (rather than $a$ and $b$). Thus $\chi_{a\alpha}(n_1n_2n_3; \mathbf{f})$ or simply $\alpha_{a}\mathbf{f}(n_1n_2n_3; \mathbf{f})$ represents the $\alpha$th atomic orbital on the $a$th atom in the $n_1n_2n_3$th unit cell, and $\chi_{a\alpha}(\mathbf{f})$ or simply $\alpha_{a}(\mathbf{f})$ represents any one of the translationally equivalent set of $\alpha$th orbitals on the $a$th atoms for all values of $n_1n_2n_3$. 

The secular equation, Eq. (337), then becomes

\[
\begin{vmatrix}
F_{ab}(n_1^1 n_2^1; n_1^{n_2}; n_1^{n_2}) - \epsilon S_{ab}(n_1^1 n_2^1; n_1^{n_2}; n_1^{n_2})
\end{vmatrix} = 0,
\]

(502)

where from Eq. (142) the overlap integral is

\[
S_{ab}(n_1^1 n_2^1; n_1^{n_2}; n_1^{n_2}) = \int \alpha^*(n_1^1 n_2^1; \mathbf{r}_1) \beta(n_1^{n_2}; \mathbf{r}_1) \, d\mathbf{r}_1.
\]

(503)

Similarly, from Eq. (284), the elements of the Hartree-Fock Hamiltonian matrix are

\[
F_{ab}(n_1^1 n_2^1; n_1^{n_2}; n_1^{n_2}) = H_{ab}(n_1^1 n_2^1; n_1^{n_2}; n_1^{n_2}) + \sum_{m_1^1 m_2^1 m_3^1} \sum_{m_1^2 m_2^2 m_3^2} \sum_{r \delta} \rho_{\delta r} \delta(m_1^1 m_2^1 m_3^1; m_1^2 m_2^2 m_3^2) \times \left[ 2I_{ab}(n_1^1 n_2^1; n_1^{n_2}; m_1^1 m_2^1 m_3^1, m_1^2 m_2^1 m_3^2, m_1^1 m_2^2 m_3^1) - I_{aca} \delta_{ab}(n_1^1 n_2^1; m_1^1 m_2^1 m_3^1, m_1^2 m_2^1 m_3^2, m_1^1 m_2^2 m_3^1) \right].
\]

(504)

Here

\[
H_{ab}(n_1^1 n_2^1; n_1^{n_2}; n_1^{n_2}) = \int \alpha^*(n_1^1 n_2^1; \mathbf{r}_1) H_1 \beta(n_1^{n_2}; \mathbf{r}_1) \, d\mathbf{r}_1,
\]

(505)

with \(H_1\) the one-electron Hamiltonian for the entire crystal, which from Eq. (156) is

\[
H_1 = -(1/2) \nabla^2 - \sum_c z_c \sum_{m_1^1 m_2^1 m_3^1} r_{c1}^{-1}(m_1^1 m_2^1 m_3^1) \tag{506}
\]

with

\[
r_{c1}(m_1^1 m_2^1 m_3^1) = |\mathbf{r}_{c1} - \mathbf{r}_c(m_1^1 m_2^1 m_3^1)|.
\]

(507)

the distance from the \(c\)th atom in the \(m_1^1 m_2^1 m_3^1\)th unit cell to electron 1.

The two-electron integrals within the square brackets in Eq. (504) are seen by comparison with Eq. (268) to be given by

\[
I_{aca} \delta_{ab}(n_1^1 n_2^1; m_1^1 m_2^1 m_3^1, m_1^2 m_2^1 m_3^2, m_1^1 m_2^2 m_3^1) = \int \alpha^*(n_1^1 n_2^1; \mathbf{r}_1) \beta(n_1^{n_2}; \mathbf{r}_1) r_{12}^{-1} \gamma_{c1}(m_1^1 m_2^1 m_3^1; \mathbf{r}_2) \delta_d(m_1^1 m_2^1 m_3^1; \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2,
\]

(508)

where \(r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|\) is the distance between electrons 1 and 2.
It follows from the translational symmetry of the lattice that
the one-electron integrals (503) and (505) depend only on the separa-
tions, \( n_i = n_i'' - n_i' \), (i = 1, 2, 3,), of the pair of unit cells involved,
and not on their absolute locations in the crystal, \( n_i' \) and \( n_i'' \)
individually. They may therefore be rewritten as

\[
S_{\alpha \alpha, \beta \beta}(n_1 n_2 n_3) = \int d^{*}(000; r_1) \rho_b(n_1 n_2 n_3; r_1) dr_1, \tag{509}
\]

\[
H_{\alpha \alpha, \beta \beta}(n_1 n_2 n_3) = \int d^{*}(000; r_1) H_1 \rho_b(n_1 n_2 n_3; r_1) dr_1. \tag{510}
\]

From Eqs. (506) and (510),

\[
H_{\alpha \alpha, \beta \beta}(n_1 n_2 n_3) = T_{\alpha \alpha, \beta \beta}(n_1 n_2 n_3)
- \sum_c 2c \sum_{m_1 m_2 m_3} J_{c; \alpha \alpha, \beta \beta}(m_1 m_2 m_3; n_1 n_2 n_3), \tag{511}
\]

where

\[
T_{\alpha \alpha, \beta \beta}(n_1 n_2 n_3) = -(1/2) \int d^{*}(000; r_1) \nabla^2 \rho_b(n_1 n_2 n_3; r_1) dr_1 \tag{512}
\]

is the kinetic energy integral, and

\[
J_{c; \alpha \alpha, \beta \beta}(m_1 m_2 m_3; n_1 n_2 n_3)
= \int d^{*}(000; r_1) r_1^{-1}(m_1 m_2 m_3) \rho_b(n_1 n_2 n_3; r_1) dr_1 \tag{513}
\]

is the nuclear attraction integral. Similarly the two-electron integral
(508) depends only on the locations of the last three cells relative to
the first, say, or on \( n_i = n_i'' - n_i' \), \( p_i = m_i' - n_i' \), and \( q_i = m_i'' - n_i' \),
(i = 1, 2, 3). It may therefore be written as

\[
I_{\alpha \beta, \gamma \delta}(n_1 n_2 n_3; p_1 p_2 p_3, q_1 q_2 q_3)
= \int \int \int d^{*}(000; r_1) \rho_b(n_1 n_2 n_3; r_1) r_1^{-1} \rho_b(n_1 n_2 n_3; r_2) \delta_d(q_1 q_2 q_3; r_2) dr_1 dr_2. \tag{514}
\]
The mean electron density in the crystal in the LCAO approximation is obtained from Eq. (248) as

\[
\rho(\mathbf{r}) = 2 \sum_{p_1p_2p_3} \sum_{q_1q_2q_3} \sum_{\alpha\beta} \sum_{\gamma\delta} \rho_{\gamma\delta}(p_1p_2p_3; q_1q_2q_3)
\]

\[
x \gamma_{\alpha}(p_1p_2p_3; \mathbf{r}) \delta_{\gamma}(q_1q_2q_3; \mathbf{r}).
\]

It is easily shown that the translational symmetry of \(\rho(\mathbf{r})\) requires that the LCAO first-order density-matrix elements on the right-hand side of Eq. (515) depend only on the separations of the two cells indicated or on \(q_i - p_i = n_i^d - n_i^a\), \((i = 1, 2, 3;\) see the preceding paragraph). From Eqs. (504), (510), (514), and (515),

\[
\begin{align*}
F_{\alpha\beta}(n_1n_2n_3; n_1n_2n_3) &= H_{\alpha\beta}(n_1n_2n_3) \\
&+ \sum_{p_1p_2p_3} \sum_{q_1q_2q_3} \sum_{\alpha\beta} \sum_{\gamma\delta} \rho_{\gamma\delta}(q_1 - p_1, q_2 - p_2, q_3 - p_3) \\
&\times \left[ 2 I_{\alpha\beta\gamma\delta}(n_1n_2n_3; p_1p_2p_3, q_1q_2q_3) \\
&- I_{\alpha\beta\gamma\delta}(p_1p_2p_3; q_1q_2q_3, n_1n_2n_3) \right] \\
&= F_{\alpha\beta}(n_1n_2n_3),
\end{align*}
\]

showing that the elements of the Hartree-Fock matrix also depend only on \(n_i = n_i^a - n_i^d\), \((i = 1, 2, 3)\).

10.2 Transformation from Atomic Orbitals to Bloch Wave Functions

The secular equation for a crystal, Eq. (502), is of very high degree prior to its reduction by utilization of the translational (and possibly also the point or factor group) symmetry of the lattice. If the Born-von Karman cyclic boundary conditions for the one-electron
crystal wave functions are assumed, attention may be restricted to a parallelepipedal crystal block of the crystal having \( N_1 \), \( N_2 \), and \( N_3 \) unit cells, respectively, along its three edges, or a total of \( N = N_1 N_2 N_3 \) unit cells. The three translation vectors of the lattice are denoted by \( \vec{a}_1, \vec{a}_2, \) and \( \vec{a}_3 \), having magnitudes \( a_1, a_2, \) and \( a_3 \), respectively, so that the lengths of the three edges of the block are \( N_1 a_1, N_2 a_2, \) and \( N_3 a_3 \), respectively. If the total number of atomic orbitals considered in each unit cell (including each orbital on each atom in the cell) is \( \omega \), the total number of orbitals to be considered in the entire crystal block and the degree of the secular equation prior to its reduction is \( N \) (the total number of atomic orbitals in the entire system was denoted simply by \( \omega \) in Chapter 8).

The translation vectors of the reciprocal lattice (defined in Section 5.1) are \( \vec{b}_1, \vec{b}_2, \) and \( \vec{b}_3 \). From Eqs. (5) and (6) it follows that

\[
\vec{a}_i \cdot \vec{b}_j = \delta_{ij} \tag{517}
\]

The wave vector \( \vec{k} \) in the first or reduced Brillouin zone of the crystal which has been discussed in Section 5.2 may be represented more explicitly as

\[
\vec{k} = (k_1/N_1)\vec{b}_1 + (k_2/N_2)\vec{b}_2 + (k_3/N_3)\vec{b}_3 \tag{518}
\]

where \( k_1, k_2, \) and \( k_3 \) take integral values (positive, negative, or zero). Since \( N_1, N_2, \) and \( N_3 \) are assumed to be very large positive integers the Eq. (518) represents a quasi-continuous vector \( \vec{k} \). Instead of restricting \( \vec{k} \) to the first Brillouin zone, however, it will be more convenient to require that

\[
-N_i/2 \leq k_i \leq (N_i/2) - 1, \quad (i = 1, 2, 3) \tag{519}
\]

which restricts \( k_i \) to \( N_i \) integral values (assuming \( N_i \) is an even
integer). The total number of values of the vector \( \mathbf{k} \) permitted by (519) is \( N \). The region of wave vector space thus included is a parallelepiped with edges parallel to \( \mathbf{b}_1, \mathbf{b}_2, \) and \( \mathbf{b}_3 \), and lengths \( b_1, b_2, \) and \( b_3 \), respectively (\( b_1 \) is the magnitude of \( \mathbf{b}_1 \)). From Eq. (9) the volume of this region equals the volume of the unit cell in reciprocal space and therefore the volume of the first Brillouin zone. As is well known the Brillouin zone can be cut and rearranged to give such a parallelepiped, so that a one-to-one correspondence exists between the values of \( \mathbf{k} \) in the two regions based on the equivalence (16). The vector from the origin of the reference cell \( (n_1 = n_2 = n_3 = 0) \) to the origin of the \( n_1n_2n_3 \text{th} \) cell of the direct or crystal lattice is
\[
\mathbf{r}_0(n_1n_2n_3) = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,
\] (520)
where \( n_1 \) takes \( N_1 \) integral values (within the crystal block) which may conveniently be restricted to the same range as \( k_1 \) in (519). From Eqs. (517), (518), and (520),
\[
\mathbf{k} \cdot \mathbf{r}_0(n_1n_2n_3) = (k_1n_1/N_1) + (k_2n_2/N_2) + (k_3n_3/N_3).
\] (521)

Bloch one-electron wave functions for the crystal may now be defined as
\[
\Psi_a(k, \mathbf{r}) = \sqrt{\frac{1}{N}} \sum_{n_1n_2n_3} \alpha_a(n_1n_2n_3; \mathbf{r}) \exp \left[ 2\pi i \mathbf{k} \cdot \mathbf{r}_0(n_1n_2n_3) \right].
\] (522)
Since \( \mathbf{k} \) assumes \( N \) values, there is a set of \( N \) Bloch functions for each of the \( \nu \) atomic orbitals \( \alpha_a \) in a single unit cell of the crystal, and a total of \( N\nu \) Bloch functions precisely equal to the number of atomic orbitals. Equation (522) represents the Bloch function of Eq. (29) in the present notation, and clearly satisfies the Bloch condition, Eq. (30),
under translation by a lattice vector $\mathbf{r}_0(m_1m_2m_3)$. From Eq. (521) and (522),

\[
N^{-1} \sum_{k_1,k_2,k_3} \varphi_{\alpha}(\mathbf{r}, \mathbf{r}) \exp[-2ik_1 \cdot \mathbf{r}_0(n_1n_2n_3)] \\
= N^{-1} \sum_{m_1m_2m_3} \alpha_a(m_1m_2m_3; \mathbf{r}) \sum_{k_1,k_2,k_3} \exp\left[2ik_1 \cdot \left(\mathbf{r}_0(m_1m_2m_3) - \mathbf{r}_0(n_1n_2n_3)\right)\right] \\
= N^{-1} \sum_{m_1m_2m_3} \alpha_a(m_1m_2m_3; \mathbf{r}) \prod_{i=1,2,3} N_{i} \left\{ \sum_{k_i} \exp\left[2ik_1(m_i - n_i)/N_i\right] \right\} \\
= N^{-1} \sum_{m_1m_2m_3} \alpha_a(m_1m_2m_3; \mathbf{r}) \prod_{i=1,2,3} N_i \left( \sum_{m_1n_i} \right) \\
= \alpha_a(n_1n_2n_3; \mathbf{r}),
\]

(523)

which represents the inverse transformation to Eq. (522), and expresses the $N$ atomic orbitals in terms of the Bloch functions. In obtaining Eq. (523) the following well known result has been used. Let $k, n,$ and $N$ be integers with $N$ an even positive integer; then

\[
\sum_{k=-(N/2)}^{(N/2)-1} \exp(2\pi ikn/N) = \sum_{k=0}^{N-1} \exp\left[2\pi ikn/N\right] \\
= \frac{1 - \exp(2\pi in)}{1 - \exp(2\pi in/N)} = 0, \quad (n \neq 0) \\
= N, \quad (n = 0),
\]

(524)

provided

\[-(N/2) \leq n \leq (N/2) - 1,
\]

(525)

since the numerator of the expression in square brackets on the second line of Eq. (524) vanishes for all integral $n$ while the denominator vanishes only for $n = 0$ (in which case the value of the sum is clearly $N$).
The transformations (522) and (523) may be represented as
\[ \psi_{\alpha}(k_1k_2k_3; \mathbf{r}) = \sum_{n_1n_2n_3} a_{\alpha}(n_1n_2n_3; \mathbf{r}) B(n_1n_2n_3; k_1k_2k_3), \] (526)
(using a more explicit notation for \( \psi_{\alpha}(k, \mathbf{r}) \)) and
\[ a_{\alpha}(n_1n_2n_3; \mathbf{r}) = \sum_{k_1k_2k_3} \psi_{\alpha}(k_1k_2k_3) B^{-1}(k_1k_2k_3; n_1n_2n_3), \] (527)
respectively, where \( B \) is the matrix of the Bloch transformation and \( B^{-1} \) is its inverse. Comparison of Eqs. (522) and (523) with (526) and (527), and use of Eq. (521) shows that
\[ B(n_1n_2n_3; k_1k_2k_3) = N^{-\frac{3}{2}} \exp \left\{ 2\pi i \left[ \left( n_1k_1/N_1 \right) + \left( n_2k_2/N_2 \right) + \left( n_3k_3/N_3 \right) \right] \right\} \] (528a)
\[ B^{-1}(k_1k_2k_3; n_1n_2n_3) = N^{-\frac{3}{2}} \exp \left\{ -2\pi i \left[ \left( k_1n_1/N_1 \right) + \left( k_2n_2/N_2 \right) + \left( k_3n_3/N_3 \right) \right] \right\} \]
\[ = B^*(n_1n_2n_3; k_1k_2k_3), \] (528b)
proving that the Bloch transformation is unitary, or that
\[ (B)^{-1} = (B)^*; \quad (B)^{\dagger}B = B(B)^{\dagger} = (I), \] (529)
where \( (I) \) is the \( N \times N \) unit matrix. It should be noted in particular that the Bloch matrix \( B \) is the same unitary matrix for each of the sets of Bloch functions (that is, \( B \) does not depend on the set of translationally equivalent atomic orbitals \( a_{\alpha} \) from which the Bloch functions are formed). The transformations (526) and (527) may be written still more compactly as
\[ (\psi_{\alpha}) = (a_{\alpha})(B), \] (530)
\[ (a_{\alpha}) = (\psi_{\alpha})(B)^{\dagger}, \] (531)
where \( (a_{\alpha}) \) is a \( 1 \times N \) row matrix having as the (single) element in its \( n_1n_2n_3 \)th column \( a_{\alpha}(n_1n_2n_3; \mathbf{r}) \), and \( (\psi_{\alpha}) \) is a \( 1 \times N \) row matrix having \( \psi_{\alpha}(k_1k_2k_3; \mathbf{r}) \) as the element in its \( k_1k_2k_3 \)th column. The Bloch wave
functions form a useful set of basis functions for the formulation of
the secular equation, because as shown in the next section there are no
non-vanishing matrix elements (e.g., of the matrices \((S)\) and \((F)\)) between
two Bloch functions corresponding to different values of \(\mathbf{k}\), or different
points in the Brillouin zone. The explanation of this on the basis of
group theory as applied to the translation group of the crystal has been
discussed in Section 6.12. The importance of this result is that
following the Bloch transformation the original secular equation of
degree \(Nz\) (see Eq. (502)) factors into \(N\) equations, each of degree \(z\)
and corresponding to one of the \(N\) values of \(\mathbf{k}\).

10.3 Transformation of the Secular Equation
to the Basis of Bloch Wave Functions

In the formulation of the secular equation in Chapter 8, the
atomic orbitals were represented as a row matrix \((\chi)\). Since in the
notation of this chapter there are \(Nz\) orbitals in the crystal block,
\((\chi)\) will be a \(1 \times Nz\) matrix. We now assume that \((\chi)\) is formed by
arranging in a row the \(z\)' distinct \(1 \times N\) row matrices \((\alpha_a)\) of Eqs. (530)
and (531) in some definite order (e.g., ordered first with respect to
the atom \(a\) and second with respect to the orbital \(\alpha\) on that atom).
That is,

\[
(\chi) = (\alpha_1) (\beta_1) \ldots (\alpha_z) (\beta_z) \ldots \quad \text{.} \tag{532}
\]

(compare Eq. (326), where \(z\) is now replaced by \(Nz\)). In a similar way
let \((\gamma)\) be the \(1 \times Nz\) row matrix formed from all the Bloch wave
functions by arranging in a row the \(z\) distinct \(1 \times N\) row matrices
Introduce also a super-Bloch matrix \( B \) of dimension \( N \times N \) formed by repeating \( \nu \) times as minors or blocks on the principal diagonal the \( N \times N \) Bloch matrix \( B \), and setting equal to zero all elements outside these blocks. The \( \nu \) matrices \( B \) are identical and have elements as given by Eq. (528a); therefore the elements of \( B \) are

\[
B_{\alpha \beta}(n; k) = \delta_{\alpha \beta} \delta_{\alpha \beta} B(n; k) \quad (534)
\]

(in this section the triples of numbers \( n_1, n_2, n_3 \), \( k_1 k_2 k_3 \), etc., will usually be indicated simply by \( n, k \), etc., and similarly \( n'' n' \) will denote the triple \( n''_1 n_1', n''_2 n_2', n''_3 n_3' \)). The matrix \( B \) is unitary, since from Eqs. (528) and (531)

\[
B^{-1}_{\alpha \alpha', \beta \beta'}(k; n) = \delta_{\alpha \alpha'} \delta_{\beta \beta'} B^{-1}(k; n) \\
= \delta_{\alpha \alpha'} \delta_{\beta \beta'} B^*(n; k) \\
= B^*_{\alpha \alpha', \beta \beta'}(n; k) \quad (535)
\]

and

\[
(B)^{-1} = (B)^+; (B)^+(B) = (B)(B)^+ = (I), \quad (536)
\]

where \((I)\) is the \( N \times N \) unit matrix.

The complete transformation from the entire set of \( N' \) atomic orbitals \( \{\chi\} \) to the \( N' \) Bloch wave functions may now be represented as (compare Eqs. (530) and (531)),

\[
(\psi) = (\chi)(B) \quad (537)
\]

and the inverse transformation as

\[
(\chi) = (\psi)^{(B)^+} \quad (538)
\]
In Chapter 8 the \( n \) molecular orbitals were represented by the \( 1 \times n \) row matrix \( (\phi) \) of Eq. (325). For a closed-shell configuration these \( n \) molecular orbitals were occupied by \( 2n \) electrons, one pair with opposed spins occupying each molecular orbital. It is now convenient to let \( 2n \) represent the number of electrons per unit cell of the crystal, so that the total number of electrons to be considered in the entire crystal block is \( 2Nn \), and the number of occupied one-electron crystal wave functions for a closed-shell configuration of the crystal is \( Nn \). That is, at the absolute zero of temperature the Fermi surface will enclose \( Nn \) one-electron wave functions. It will be convenient to represent these as a \( 1 \times Nn \) row matrix \( (\phi) \). The transformation from the \( N^N \) atomic orbitals \( (\chi) \) to the \( Nn \) one-electron crystal wave functions \( (\phi) \) may be represented by

\[
(\phi) = (\chi)(C), \tag{539}
\]

where the \( N^N \times Nn \) matrix of LCAO coefficients \( (C) \) replaces the \( z \times n \) matrix \( (C) \) of Eq. (379). Substitution of Eq. (538) in (539) yields

\[
(\phi) = (\psi)(\mathcal{P})^\dagger(C). \tag{540}
\]

On the other hand the transformation from Bloch functions \( (\psi) \) to the wave functions \( (\phi) \) may be represented directly as

\[
(\phi) = (\psi)(C) \tag{541}
\]

where from Eq. (540) \( (C) \) is the \( N^N \times Nn \) matrix

\[
(C) = (\mathcal{P})^\dagger(C). \tag{542}
\]

Also, from Eq. (536),

\[
(C) = (\mathcal{P})(C). \tag{543}
\]

Equation (541) represents the one-electron crystal wave functions \( (\phi) \) as
linear combinations of Bloch functions (LCBF), whereas in Eq. (539) the same wave functions ($\Psi$) are represented as linear combinations of atomic orbitals (LCAO).

The secular equation of the crystal relative to the $N^a$ atomic orbitals as a basis is

$$ (F)(C) = (S)(C)(\epsilon) , $$

(544)

where the elements of the $N^a \times N^a$ matrix $(S)$ are given by Eqs. (503) or (509), those of the $N^a \times N^a$ matrix $(F)$ by Eqs. (504) or (516), and $(\epsilon)$ is a diagonal matrix having the $N^a$ eigenvalues as its diagonal elements (compare Eq. (324)). Substitution of Eq. (543) for $(C)$ in Eq. (544), and premultiplication of both sides of the resulting equation by $(B)^\dagger$ yields the secular equation relative to the Bloch functions as a basis,

$$ (F)(C) = (S)(C)(\epsilon) , $$

(545)

where

$$ (F) = (B)^\dagger(F)(B) $$

(546)

and

$$ (S) = (B)^\dagger(S)(B) $$

(547)

are the Hartree-Fock and overlap matrices, respectively, for the Bloch functions ($\Psi$). The eigenvalues and eigenvalue matrix $(\epsilon)$ are unaffected by this unitary transformation. It was shown in Section 10.1 that the matrices $(F)$ and $(S)$ both have the property

$$ A_{aa', bb'}(n'; n") = A_{aa', bb'}(n) $$

(548)

where $n = n" - n'$ (see Eqs. (509), (516), and the comment following Eq. (534)). The unitary transformations indicated in Eqs. (546) and (547) may be dealt with simultaneously by considering the unitary transformation

$$ (A) = (B)^\dagger(A)(B) , $$

(549)
where \((A)\) has the property stated in Eq. (548). Substitution of Eq. (534) for \((B)\) in Eq. (549) yields

\[
A_{a\alpha, b\beta}(k; k') = \sum_{\alpha \beta} \sum_{n''} \sum_{n'''} \langle B \rangle^\dagger_{a\alpha, c\gamma}(k; n') \times A_{c\gamma, d\delta(n'\prime; n'')} \delta_{d\delta, b\beta(n'''; k')}
\]

\[
= \sum_{\alpha \beta} \sum_{n''} \sum_{n'''} \delta_{a\alpha, c\gamma} \delta_{b\beta, d\delta} \langle B \rangle^\dagger_{a\alpha, c\gamma}(k; n') \times \delta_{d\delta, b\beta}(n'''; k')
\]

\[
= \sum_{n''} \langle B \rangle^\dagger_{a\alpha, b\beta}(n'; k) \times A_{a\alpha, b\beta}(n''; k')
\]

\[
= \sum_{n''} \langle B \rangle^\dagger_{a\alpha, b\beta}(n'; k) B(n''; k') A_{a\alpha, b\beta}(n''; n''')
\]

where Eqs. (534), (535), 536), and (548) have been utilized, and \(n = n'' - n'\).

Substitution of Eq. (528) in (550) yields on using also Eq. (524),

\[
A_{a\alpha, b\beta}(k_1 k_2 k_3; k_1' k_2' k_3') = \sum_{n_1 n_2 n_3} A_{a\alpha, b\beta}(n_1 n_2 n_3) \exp\left\{2\pi i \left[\left(n_1 k_1 / N_1\right) + \left(n_2 k_2 / N_2\right) + \left(n_3 k_3 / N_3\right)\right]\right\}
\]

\[
\times \sum_{n_1 n_2 n_3} \exp\left\{2\pi i \left[\left(n_1' k_1' - k_1\right) / N_1 + \left(n_2' k_2' - k_2\right) / N_2 + \left(n_3' k_3' - k_3\right) / N_3\right]\right\}
\]

\[
= \delta_{k_1 k_1'} \delta_{k_2 k_2'} \delta_{k_3 k_3'} \sum_{n_1 n_2 n_3} A_{a\alpha, b\beta}(n_1 n_2 n_3) \exp\left\{2\pi i \left[\left(n_1 k_1 / N_1\right) + \left(n_2 k_2 / N_2\right) + \left(n_3 k_3 / N_3\right)\right]\right\}
\]

The elements of \((F)\) and \((S)\) are obtained by replacing \(A\) by \(F\) and \(S\), respectively, in Eq. (551). It follows that there are non-vanishing matrix elements in \((F)\) and \((S)\) between Bloch functions \(\Psi_{a\alpha}(k)\) and \(\Psi_{b\beta}(k')\) only for \(k = k'\), or for Bloch functions corresponding to the same wave vector. The secular equation (545) of degree \(N\) is therefore factored into \(N\) equations each of degree \(\nu\), one such equation corresponding to each value of the wave vector \(k\). A typical equation is

\[
(E_{\alpha k} - \epsilon_{\alpha k}) = (S_{\alpha k} - \epsilon_{\alpha k})(E_{\alpha k} - \epsilon_{\alpha k})
\]
where from Eqs. (521) and (551),
\[
E_{k;a_{\alpha},b_{\beta}} = \sum_{n_1n_2n_3} F_{\alpha_{\alpha},b_{\beta}}(n_1n_2n_3) \exp \left[ 2\pi i k \cdot r_0(n_1n_2n_3) \right],
\]
\[
S_{k;a_{\alpha},b_{\beta}} = \sum_{n_1n_2n_3} S_{\alpha_{\alpha},b_{\beta}}(n_1n_2n_3) \exp \left[ 2\pi i k \cdot r_0(n_1n_2n_3) \right].
\]

Here $F_{\alpha_{\alpha},b_{\beta}}(n_1n_2n_3)$ and $S_{\alpha_{\alpha},b_{\beta}}(n_1n_2n_3)$ are defined by Eqs. (516) and (509), respectively. It will be noted that Eqs. (553) and (554) are of the same form as Eq. (33) which was derived for a general one-electron operator $H$ possessing the translational symmetry of the crystal. Equation (554) is simply a special case of Eq. (33). However, Eq. (553) shows that the same result applies to the self-consistent field Hartree-Fock matrix in the LCAO approximation.

For each of the $N$ values of $k$ in the first Brillouin zone, Eq. (552) yields the following determinantal or secular equation for the determination of $\nu$ roots $\epsilon_{k_1}, \epsilon_{k_2}, \ldots, \epsilon_{k}$:
\[
\left| \begin{array}{c}
E_{k_1; \alpha_{\alpha},b_{\beta}} - \epsilon_{k_1} S_{k_1; \alpha_{\alpha},b_{\beta}} \\
E_{k_2; \alpha_{\alpha},b_{\beta}} - \epsilon_{k_2} S_{k_2; \alpha_{\alpha},b_{\beta}} \\
\vdots \\
E_{k_\nu; \alpha_{\alpha},b_{\beta}} - \epsilon_{k_\nu} S_{k_\nu; \alpha_{\alpha},b_{\beta}} \\
\end{array} \right| = 0.
\]

Since $k$ is a quasi-continuous vector, this equation may be solved at selected points in the first Brillouin zone, for example at the special points discussed in Section 5.4 for the case of $\alpha$-rhombohedral boron. The solution may be obtained by successive diagonalizations of $(S_k)$ and $(F_k)$ as discussed in Section 8.63(a) for the analogous Eq. (337). Each root $\epsilon_{k_i}$, $(i = 1, \ldots, \nu)$, will then be a quasi-continuous function of $k$ in the first Brillouin zone, and may be represented by an energy surface in this zone. The set of $N$ eigenvalues or energies $\epsilon_{k_i}$ for fixed $i$ represents the $i$th energy band of the crystal, and becomes a continuous
band of permitted energies for $N \rightarrow \infty$. This representation of the $\nu$ energy surfaces or bands within the first Brillouin zone corresponds to the reduced zone scheme (in the extended zone scheme each of the $\nu$ energy surfaces would be represented in a different Brillouin zone and there would in general be discontinuities in the energies at the faces of the Brillouin zones). For general values of $\vec{k}$ in the reduced zone scheme the $\nu$ eigenvalues or energies $\varepsilon_{\vec{k}_1}$ will be separated by finite intervals corresponding to a discrete energy spectrum. However, at special positions or in special directions in the Brillouin zone for a crystal with non-trivial symmetry degeneracies may occur and two or more of the eigenvalues may coincide (see Section 5.4). Such degeneracies correspond to touching or osculation of the energy surfaces in the first Brillouin zone and have been extensively discussed in the literature. In this case there will of course be no gap or region of forbidden energies between the two corresponding energy bands. Even though two successive energy surfaces do not touch for any $\vec{k}$ in the first Brillouin zone, the maximum and minimum energies on one surface may be above and below, respectively, the maximum energy on the other surface in which case the two bands are said to overlap one another (since the maxima and minima occur at different $\vec{k}$ in general, this does not require that the two bands touch at any point in $\vec{k}$ space).

Following the solution of Eq. (555) for the $\nu$ eigenvalues $\varepsilon_{\vec{k}_1}$ for given $\vec{k}$, the corresponding eigenvectors $(\zeta_{\vec{k}_1})$ are obtained by substitution of each eigenvalue in turn into the equation

$$\left| (P_{\vec{k}} - \varepsilon_{\vec{k}_1}) (\zeta_{\vec{k}_1}) \right| = 0 ,$$

(556)
which is equivalent to the following set of \( \nu \) simultaneous homogeneous linear equations for the elements \( \alpha_{k1,b\beta} \) of the \( \nu \times 1 \) column matrix \( (\alpha_{k1}) \),

\[
\sum_{b\beta} (E_{k1;\alpha_a,b\beta} - \varepsilon_{k1;\alpha_a,b\beta}) \alpha_{k1,b\beta} = 0.
\] (557)

In view of Eq. (541) the crystal wave function corresponding to the eigenvalue \( \varepsilon_{k1} \) is

\[
\phi_{\alpha}(k; \vec{r}) = \sum_{b\beta} \psi_{b\beta}(k; \vec{r}) \alpha_{k1,b\beta},
\] (558)

where \( \psi_{b\beta}(k; \vec{r}) \) is the Bloch function defined by Eq. (522) or (526).

The occupied states at the absolute temperature will be those \( N_n \) states \( \phi_{\alpha}(k; \vec{r}) \) associated with the \( N_n \) algebraically lowest of the total of \( N \nu \) eigenvalues \( \varepsilon_{k1} \), and will be separated from the occupied states by the Fermi energy surface. The states of each band which are occupied will be those corresponding to \( k \) values or points on the corresponding energy surface which have energies lower than the Fermi surface. Bands may be entirely below, partially below, or entirely above the Fermi surface, corresponding to completely filled, partially filled, and vacant bands, respectively. If the uppermost filled band is completely filled and there is a gap (as opposed to contact or overlapping) between it and the first vacant band, the crystal will be an insulator or intrinsic semiconductor. If the uppermost filled band is only partially filled, or two overlapping bands are both partially filled (or more rarely if the first vacant band contacts the uppermost filled band) the crystal will exhibit metallic conduction.
Although the Bloch transformation factors the Hartree-Fock self-consistent field LCAO secular equation of degree $N\nu$, Eq. (502), into $N$ equations of degree $\nu$ (one for each $k$) as in Eq. (555), these equations are not entirely independent as they may appear to be superficially. This is because the matrix elements for given $k$, $F_{\alpha \beta, a_r b_s}$, depend through Eq. (553) on the LCAO matrix elements $F_{\alpha, b}(n_1 n_2 n_3)$, and the latter depend through Eq. (516) on the first-order LCAO density matrix elements $\rho_{\alpha, b}(n_1 n_2 n_3)$. To determine the latter it is necessary first to express the crystal wave function $\phi_1(k; \vec{r})$ in LCAO form. Substitution of Eq. (522) into Eq. (558) gives

$$
\phi_1(k; \vec{r}) = \sum_{\alpha, \beta} \sum_{n \lesssim n_2 n_3} c_{\alpha}(n_1 n_2 n_3) \alpha_{\alpha}(n_1 n_2 n_3; \vec{r}),
$$

(559)

where

$$
c_{\alpha}(n_1 n_2 n_3) = N^{-\frac{1}{2}} \xi_{k_1, \alpha} \exp\left[2\pi ik \cdot r_0(n_1 n_2 n_3)\right].
$$

(560)

Equation (559) is equivalent to Eq. (139), except that there are $N\nu$ rather than $\nu$ distinct atomic orbitals in the sum on the right-hand side of Eq. (559). The LCAO density matrix for a closed-shell crystal configuration is given by the analog of Eq. (245) with $c_{x_1}$ replaced by $c_{\alpha}(n_1 n_2 n_3)$ of Eqs. (559) and (560). Therefore,

$$
\rho_{\alpha, \beta}(n_1 n_2 n_3; n_2 n_2 n_2) = \sum_{k} \sum_{i} c_{\alpha}(n_1 n_2 n_3) c_{\beta}(n_1 n_2 n_3),
$$

(561)

where

$$
\rho_{\alpha, \beta}(k) = \sum_{i} c_{\alpha}(k) c_{\beta}(k).
$$

(562)
Equation (521) and (561) confirm the result stated in connection with Eqs. (515) and (516) that $P_{\alpha \beta}(n_1 n_2 n_3; n_1' n_2' n_3')$ is a function only of $n_1 = n_1' - n_1$, $n_2 = n_2' - n_2$, and $n_3 = n_3' - n_3$, so that it may be written in the form

$$P_{\alpha \beta}(n_1 n_2 n_3) = N^{-1} \sum_k P_{\alpha \beta}(k) \exp \left\{ -2 \pi i \left[ (k_1 n_1 / N_1) + (k_2 n_2 / N_2) + (k_3 n_3 / N_3) \right] \right\}$$

(563)

It is important to note that in Eqs. (561) to (563) the summations over $k$ and $i$ are restricted to the states $\phi_i(k; r)$ which are occupied by a pair of electrons, and therefore to those states for which $E_{i(k)}$ is less than or equal to the Fermi energy. Therefore the summations over two summations are not independent. Thus for given $k$ in the summand of Eq. (563), $P_{\alpha \beta}(k)$ is to be calculated from Eq. (562) with the summation extending only over those values of $i$ corresponding to bands occupied for that $k$. In the limit $N \to \infty$ the summations over $k$ are replaced by integrations over $k$ space. In the reduced zone scheme considered here the range of integration never exceeds that of the first Brillouin zone. In conclusion, the fact that $P_{\alpha \beta}(n_1 n_2 n_3)$ in Eq. (516) depends on sums over all occupied states shows that the $N$ secular equations of degree $\nu$, Eqs. (555), obtained as a result of the Bloch transformation are a coupled set of eigenvalue-eigenvector equations. This is of course simply a reflection of the self-consistent feature of the Hartree-Fock theory, as discussed in Section 8.63(e), so that an accurate solution must be obtained by iterative methods. It seems to be generally assumed that the difficulties involved in a self-consistent field treatment of a crystal are insuperable in practice. The relatively simple form of Eqs. (562) and (563)
suggests that this is not the case if high-speed computers are available. Once the eigenvalues, $\epsilon_{k1}$, and eigenvectors, $(\varphi_{k1})$, are calculated at a number of points in the first Brillouin zone the problem of calculation of the density matrix is reduced to one of numerical integration over regions of the zone corresponding to occupied states. The practicality of this is a subject for future investigation.

10.4 Approximate Calculation for $\alpha$-Rhombohedral Boron with Neglect of Electron Interaction

10.41 Evaluation of One-Electron Contributions to Matrix Elements

As indicated at the end of the preceding section (see also Section 8.63(e)) an accurate solution of the secular equation, Eq. (555), requires an iterative procedure in which (1) the elements $F_{k1;aa,b\beta}$ defined by Eqs. (516) and (553) are calculated with some initial approximation to the density matrix elements $\rho_{aa,b\beta}(n_1n_2n_3)$; (2) the eigenvalues $\epsilon_{k1}$ and eigenvectors $(\varphi_{k1})$ are calculated for several or a number of values of $\mathbf{k}$ from Eqs. (555) and (557); (3) a better approximation to the density matrix elements is calculated from Eqs. (562) and (563); and (4) the cycle is repeated using the improved values of the density matrix. In order to obtain an initial approximation to the density matrix a solution of the secular equation for $\alpha$-rhombohedral boron was undertaken based on several well-defined approximations:

1. All two-electron terms corresponding to electron-electron repulsion and depending on the elements of the density matrix were ignored. In this approximation, from Eqs. (516) and (553),

$$F_{k1;aa,b\beta} \approx \sum_{n_1n_2n_3} H_{aa,b\beta}(n_1n_2n_3)e^{2\pi \mathbf{k} \cdot \mathbf{r}_{0}(n_1n_2n_3)},$$

(564)
where $H_{\alpha \beta}(\mathbf{n}_1 \mathbf{n}_2 \mathbf{n}_3)$ is the one-electron part of the matrix element given in terms of one-electron kinetic and nuclear attraction integrals by Eqs. (511), (512), and (513). The overlap integrals $S_{\alpha \beta}$ were calculated from Eqs. (509) and (554).

2. Only one-center and certain two-center nuclear attraction resonance integrals are considered, so that for $a \neq b$,

$$H_{\alpha \beta}(\mathbf{n}_1 \mathbf{n}_2 \mathbf{n}_3) = T_{\alpha \beta}(\mathbf{n}_1 \mathbf{n}_2 \mathbf{n}_3) - Z_a J_{\alpha \alpha} - Z_b J_{\beta \beta}.$$

In this case the nuclear attraction integrals are the resonance integrals of Section 9.22. For $a = b$ only one-center nuclear attraction integrals were retained, so that

$$H_{\alpha \alpha}(000) = T_{\alpha \alpha} - Z_a J_{\alpha \alpha},$$

(565)

In this case the orthogonalized $2s^1$, $2px$, $2py$, and $2pz$ equivalent Slater atomic orbitals on a given boron atom (see Sections 6.23 and 7.4) diagonalize separately the kinetic energy operator and nuclear potential arising from that atom.

3. In Eqs. (565) and (566) the atomic numbers of the nuclei, $Z_a$, $Z_b$, etc., occur as coefficients of the resonance and one-center nuclear attraction integrals (the electronic charge does not appear because it equals unity in atomic units). If all the atomic electrons were included in the calculation these parameters would be set equal to the true atomic numbers (or $Z = 5$ in the case of boron). Because of the great complexity of the present problem the reasonable approximation has been made of omitting the tightly-bound $1s$ electrons from the detailed LCAO
calculations. As discussed in Section 7.4 $Z_a$, $Z_b$, etc., for all the boron atoms are set equal to the effective atomic number, $Z - s$, for the electrons of principal quantum number $n = 2$ retained in the calculation. Here $s$ is the screening constant which has the value $2.4$ for $n = 2$ according to the early rules of Slater which have been verified with remarkable accuracy by subsequent calculations (Section 7.42). This value of $s$ for each $n = 2$ electron in the 5-electron boron atom is computed as the sum of a screening constant $1.7$ due to the two $1s$ electrons and a screening constant $0.7$ due to the other two $n = 2$ electrons. Thus in this sense electron-electron repulsion is accounted for in the present approximate calculation even though the explicit two-electron terms of the Hartree-Fock theory are neglected. The effective $Z$ for boron as utilized in the present calculation is thus $2.6$. On the other hand the parameter occurring in the exponent of the Slater orbitals for $n = 2$ is $\beta_2 = (Z - s)/n = 1.3$ (see Section 7.4 and Chapter 9). It should also be recalled that the original Slater $2s$ orbital is replaced by a $2s'$ orbital orthogonal to the $1s$ orbital.

4. The quantum integrals of the type $A_{\alpha\alpha',\beta\beta'}(n_1 n_2 n_3)$, where $A$ represents $S$, $J$, $T$, or $H$, are matrix elements of the appropriate operator between the $\alpha$th atomic orbital on the $a$th atom in the reference cell ($n_1 = n_2 = n_3 = 0$), and the $\beta$th orbital on the $b$th atom in the $n_1 n_2 n_3$th cell. If in the case of the second orbital also, $n_1 = n_2 = n_3 = 0$, the integrals are intracellular integrals or matrix elements; otherwise they are intercellular integrals or matrix elements. In the present case a symmetrical unit cell containing a (distorted) icosahedron of boron atoms has been chosen, so that these two classes of integrals or matrix
elements are also designated as intra- and intericosahedral, respectively (in the present connection see the extensive discussion, tables, and figures in Chapter 4). Additional approximations made in the present calculation are the retention of only those intraicosahedral two-center integrals designated as nearest-neighbor interactions in Chapter 4 (see particularly Fig. 1 and Table 14). As will be seen the numerical calculations indicate that this approximation is not entirely adequate in the case of the overlap integrals because of their relatively slow rate of decrease with internuclear distance. In the case of the intericosahedral integrals only those are retained which correspond to the two-center bonds of Table 12 and Fig. 3, and the three-center bonds of Table 11 and Fig. 2 (more accurately in the latter case to the two two-center bonds of each three-center bond which connect an atom in the reference cell to an atom in an adjacent cell since no three-center integrals are retained).

As discussed in Chapter 6 the basis atomic orbitals for the present calculation are the equivalent atomic orbitals defined in Section 6.22 which transform simply under the operations of the point or factor group of the crystal. However, the quantum integrals (particularly the two-center integrals) as tabulated in the standard tables and also in Chapter 9 are conveniently expressed only in terms of the bond-oriented orbitals 2s, 2p\(\sigma\), 2p\(\pi\), and 2p\(\rho\) introduced in Section 6.21. The method of Slater and Koster and its matrix extension discussed in Section 6.21 is a procedure for expressing the matrix elements between equivalent orbitals (or other fixed orbitals) in terms of tabulated integrals between bond-oriented orbitals and the direction
cosines of the "bond" or line joining the two centers. As developed by 
Slater and Koster and extended in Section 6.21 it is applicable only to 
matrix elements of an operator possessing axial symmetry (invariant to 
rotation about the bond) and between two s or p atomic orbitals. This 
is essentially because the s and p orbitals transform under rotation as 
tensors of the zeroth and first orders, respectively, so that matrix 
elements connecting two such orbitals transform as zeroth, first, or 
symmetric second-order tensors. The matrix element may transform as a 
symmetric tensor of order higher than the second if (i) atomic orbitals 
of higher azimuthal quantum number are included (e.g., d or f orbitals); 
or (ii) if the matrix element depends on two-electron integrals contain­
ing four atomic orbitals such as the integrals \( I_{\alpha\beta; \gamma\delta} \) which occur 
in Eq. (516) for the matrix element \( F_{\alpha\beta; \gamma\delta} \) of the Hartree-Fock 
matrix. Thus a generalization of the Slater-Koster method would be 
required for the transformation from fixed to bond-oriented orbitals of 
the complete Hartree-Fock matrix elements \( F_{\alpha\beta; \gamma\delta} \) of Eq. (553) in spite 
of their formal resemblance following the Bloch transformation to the 
one-electron two-orbital matrix elements of Eq. (33) considered in 
Chapter 6. The required generalization is straight-forward but will not 
be given here. However, Eqs. (509) and (554) for \( S_{\alpha\beta; \gamma\delta} \) and Eqs. (553) 
and Eq. (564) for the one-electron contribution to \( F_{\alpha\beta; \gamma\delta} \) have the 
form required for the validity of the Slater-Koster method as utilized 
in Chapter 6.

In view of the preceding discussion the scheme for the calculation 
of the \( \nu \times \nu \) (or in the present case \( 48 \times 48 \)) matrices \( S_{\alpha\beta; \gamma\delta} \) and (one-electron
part of \( (E_K) \) developed in Chapter 6 may be applied without change. The intraicosahedral contributions to the matrix elements of these matrices are the single terms \( S_{a\alpha, b\beta}(000) \) and \( H_{a\alpha, b\beta}(000) \) in Eqs. (554) and (564), respectively. For these terms \( r^0(000) = 0 \) and the exponential terms reduce to unity regardless of the value of \( k \). These parts of the matrices are calculated from the partitioned matrix in Table 20 in which the row and column indices represent the atoms \( a \) and \( b \) within the reference cell, respectively. Each off-diagonal block in this partitioned matrix represents one of the nine \( 4 \times 4 \) matrices in Table 19 in which the row indices represent the atomic orbital \( \alpha \) on atom \( a \), and the column index represents the orbital \( \beta \) on atom \( b \) (in Chapter 6 the atoms \( a, b \) were denoted by \( i, j \) and the orbitals \( \alpha, \beta \) by \( a, b \)). The \( 4 \times 4 \) blocks \((aa)\) on the principal diagonal of the partitioned matrix in Table 20 have as their matrix elements

\[
S_{a\alpha, a\beta}(000) = \delta_{\alpha\beta}
\]

(since the atomic orbitals on a single atom are orthonormal), and

\[
H_{a\alpha, a\beta}(000) \text{ of Eq. (566), respectively.}
\]

Because only nearest-neighbor two-center integrals are retained in the present approximation (see item (4) above) all off-diagonal blocks \((ab)\) in Table 20 are set equal to the \( 4 \times 4 \) null matrix except the following four which were computed from Table 19: \((12), (11'), (1\overline{2}'), \) and \( (1'2') \) (see also Fig. 1). The reduced overlap, resonance, and kinetic energy integrals are tabulated in Tables 37b, 38b, and 40b, respectively. The actual values of the resonance and kinetic energy integrals as used here are obtained by multiplying the reduced resonance integrals by \( Z_{\text{eff}} = 2.6 \) and the reduced kinetic energy integrals by
$z_{eff}^2 = 6.76$. The matrices computed in this way are listed in Tables 44a, 45a, and 46a, respectively, of Appendix I. In view of Eqs. (565) and (566), and the discussion of the effective nuclear charge, $z_{eff} = 2.6$, under item (3) above,

$$H_{\alpha, \beta}(n_1 n_2 n_3) = T_{\alpha, \beta}(n_1 n_2 n_3)$$

$$- z_{eff} J_{\alpha; \beta}(n_1 n_2 n_3) + J_{\beta; \alpha}(n_1 n_2 n_3)$$

(568)

for $\alpha \neq \beta$, and

$$H_{\alpha, \beta}(000) = \left[ T_{\alpha, \beta}(000) - z_{eff} J_{\alpha; \beta}(000) \right] S_{\alpha, \beta}$$

(569)

The off-diagonal elements in Table 45a represent the sum of the two resonance integrals within the square brackets in Eq. (568) (with $n_1 = n_2 = n_3 = 0$ and exclusive of the factor $-z_{eff}$).

The diagonal elements represent $J_{\alpha; \beta}(000)$ of Eq. (569). The elements in Tables 44a and 46a represent simply $S_{\alpha, \beta}(000)$ and $T_{\alpha, \beta}(000)$, respectively.

The relatively small number of intericosahedral contributions to the matrix elements which were retained were computed in a similar manner from the 48 x 48 matrix in Table 22, each non-null element of which is one of the two 4 x 4 matrices listed in Table 21. The first of these corresponds to the two-center intericosahedral bonds illustrated in Fig. 3, and the second to the three-center intericosahedral bonds illustrated in Fig. 2. Since these represent intericosahedral contributions to the matrix elements in Eqs. (554) and (564) the exponential factors multiplying them do not reduce to unity in general, but are functions of $k$. This is of course the fundamental basis for the
dependence of the eigenvalues of the secular equation on \( \mathbf{k} \), and thus for the existence of energy bands rather than discrete energy levels in crystals. However, attention is restricted in the present preliminary calculation to the two positions of highest symmetry in the first Brillouin zone of \( \alpha \)-rhombohedral boron. As discussed in Section 5.4 these are the center of the zone, \( \mathbf{k} = 0 \), for which the exponential factors reduce to \(+1\) for all \( \mathbf{r}_0(n_1n_2n_3) \), and the centers of the 111 and \( \overline{111} \) (upper and lower) faces of the zone (which are equivalent and count as only one position) for which the exponential factors are \(-1\) for the two-center bonds and \(+1\) for the three-center bonds (upper left and lower right quadrants, respectively, of the matrix in Table 22), as described in Section 6.33. For the intericosahedral matrix elements \( \mathbf{r}_0(n_1n_2n_3) \neq 0 \), and \( n_1, n_2, \) and \( n_3 \) cannot all vanish. Therefore Eq. (568) applies in all cases, and the matrix elements in Table 45b represent the sum of the two resonance integrals within the square brackets in Eq. (568) (exclusive of the factor \(-Z_{\text{eff}}\)). The matrix elements in Tables 44b and 46b represent simply \( S_{\alpha\beta}(n_1n_2n_3) \) and \( T_{\alpha\beta}(n_1n_2n_3) \).

10.42 Reduction of the Degree of the Secular Equation by Utilization of the Symmetry of the Point Group of the Crystal

In the preceding section the numerical form of the matrices \( F_k \) and \( S_k \) of the eigenvalue equation, Eq. (552), and corresponding secular equation, Eq. (555), have been obtained for two values of \( \mathbf{k} \) to a certain degree of approximation. As the result of the Bloch transformation made possible by the translational symmetry of the crystal the
degree of the secular equation for each \( k \) has been reduced to \( \nu = 46 \).

At general points in the Brillouin zone no further reduction is possible.

However, in a crystal possessing non-trivial symmetry further factorization by utilization of the point or factor group symmetry of the crystal is possible at special points in the Brillouin zone. The further factorization possible in the case of the \( \overline{R}3m \) space group of \( \alpha \)-rhombohedral boron, with point group \( D_{3d} \) has been discussed in Section 5.2 and 5.4. At two inequivalent positions in the Brillouin zone, \( \vec{k} = 0 \) or \( k_1 = k_2 = k_3 = 0 \) in Eq. (518), and \( (k_1/N_1) = (k_2/N_2) = (k_3/N_3) = \pm 1/2 \) (which represents two equivalent positions at the centers of the 111 and \( \overline{111} \) faces and will be denoted for brevity by \( \vec{k} = \vec{k}(\pm 1/2) \)), (the group of operations other than translations which have the wave vector invariant) is the full point group \( D_{3d} \) of the crystal. The 48 atomic orbitals \( \phi_a(\vec{r}) \) under consideration in a given cell or icosahedron, where \( a \) ranges over the 12 boron atoms and \( \phi = 2s, 2p_x, 2p_y, \) and \( 2p_z \), provide a reducible representation of the point group of dimension \( \nu = 48 \). For these two special values of \( \vec{k} \) (which are invariant under all operations of the point group) the corresponding Bloch functions \( \psi_{a\nu}(\vec{k}, \vec{r}) \) of Eq. (522) also provide reducible representations related to those provided by the atomic orbitals by the unitary Bloch transformation, and therefore forming equivalent representations.

As is well known, a reducible representation of a group can be represented as a weighted "sum" of irreducible representations of the group, the number of times each of the latter occurs (a positive integer or zero) being readily determined by means of the orthogonality theorem.
for group characters. The irreducible representations of $D_{3d}$ are denoted by $A_{1g}, A_{1u}, A_{2g}, A_{2u}, E_g,$ and $E_u$, the first four being of dimension unity (non-degenerate) and the last two of dimension 2 (doubly-degenerate). Subscripts g and u indicate representations which are symmetric and antisymmetric, respectively, to the inversion operation; symmetry with respect to dihedral rotation is denoted by subscript 1 and antisymmetry by 2. Under threefold rotation the two "rows" of the doubly-degenerate representations are transformed into linear combinations of themselves, so that further reduction of these representations is not possible. The reduced form of the reducible representations of dimension 48 provided by the atomic orbitals or Bloch functions is found to be

$$6A_{1g} + 2A_{1u} + 2A_{2g} + 6A_{2u} + 8E_g + 8E_u. \quad (570)$$

The analysis can be carried further to yield the reduced form of the eight 6-dimensional reducible representations provided by each of the eight sets of 6 equivalent orbitals of types $s$, $p_x$, $p_y$, $p_z$, $s'$, $p_x'$, $p_y'$, and $p_z'$ defined in Section 6.22. Here the unprimed orbitals are located on the set of 6 equivalent unprimed atoms, and the primed orbitals on the set of 6 equivalent primed atoms in Figure 1. An equivalent set of atoms or orbitals is transformed into itself under the operations of the point group. Thus each of the six sets of 6 equivalent orbitals of types $s$, $p_y$, $p_z$, $s'$, $p_y'$, and $p_z'$ provides the reduced representation

$$A_{1g} + A_{2u} + E_g + E_u, \quad (571a)$$
while the two sets $p_x$ and $-p_x$ provide

$$A_{2g} + A_{1u} + E_g + E_u.$$  \hspace{1cm} (571b)

The weighted sum of (571a) and (571b) of course yields (570). The reduction of the corresponding sets of equivalent Bloch functions is identical at the two special points $\mathbf{k} = 0, \mathbf{k}(\pi/2)$.

From the factorization of the secular equation of the entire crystal, Eq. (502), into separate secular equations for each $\mathbf{k}$ as in Eqs. (556) or (557), it follows that the one-electron crystal wave functions of given $\mathbf{k}$ are linear combinations of Bloch functions of the same $\mathbf{k}$ as in Eq. (558). It will be convenient to represent the $\mathbf{z}$ Bloch functions $\psi_{\beta}(\mathbf{k}, \mathbf{r})$ of given $\mathbf{k}$ as the elements of a $1 \times \mathbf{z}$ row matrix $(\psi_\mathbf{k})$, and similarly the $n_{\mathbf{k}}$ occupied one-electron crystal wave functions $\phi_1(\mathbf{k}, \mathbf{r})$ for given $\mathbf{k}$ occupied one-electron crystal wave functions $\phi_1(\mathbf{k}, \mathbf{r})$ for given $\mathbf{k}$ as the elements of the $1 \times n_{\mathbf{k}}$ matrix $(\phi_\mathbf{k})$.

Equations (558), ($i = 1, \ldots, n_{\mathbf{k}}$), may then be represented compactly as

$$(\phi_\mathbf{k}) = (\psi_\mathbf{k})(C_\mathbf{k}),$$  \hspace{1cm} (572)

where the element in the $b$th row and $i$th column of the $\mathbf{z} \times n_{\mathbf{k}}$ matrix $(C_\mathbf{k})$ is $C_{\mathbf{k}b}^i$ (hereafter the previous underscoring which indicated a formulation in terms of Bloch functions will be omitted as the presence of $\mathbf{k}$ is sufficient). Equation (572) is the analog of Eq. (541) but restricted now to Bloch and wave functions of the special value of $\mathbf{k}$ under consideration. Now consider a general unitary transformation of the Bloch functions $(\psi_\mathbf{k})$,

$$\psi_\mathbf{k}' = (\psi_\mathbf{k})(U_\mathbf{k}),$$  \hspace{1cm} (573)
where \((U^\text{T}_K)\) is a \(w \times w\) unitary matrix. From Eqs. (572) and (573),
\[
(\phi_{jK}) = (\psi^\text{T}_K)(U^\text{T}_K)(C_{jK})
\]
\[
= (\psi^\text{T}_K)(C_{jK}),
\]
say, with
\[
(C_{jK}) = (U^\text{T}_K)(C_{jK}); \quad (C_{jK}) = (U^\text{T}_K)(C_{jK}).
\] (575)
Next substitute Eq. (575) for \((C_{jK})\) into the secular equation for \(\kappa\), Eq. (552) and premultiply both sides of the resulting equation by \((U^\text{T}_K)\) to obtain
\[
(F^\text{T}_K)(C_{jK}) = (S^\text{T}_K)(C_{jK})(\epsilon_{jK}),
\]
where
\[
(F^\text{T}_K) = (U^\text{T}_K)^\text{T}(F^\text{T}_K)(U^\text{T}_K),
\] (577a)
\[
(S^\text{T}_K) = (U^\text{T}_K)^\text{T}(S^\text{T}_K)(U^\text{T}_K),
\] (577b)
and \((\epsilon_{jK})\) is the \(w \times w\) diagonal matrix of eigenvalues \(\epsilon_{jK}\). Equation (576) is the form the eigenvalue-eigenvector equation takes expressed in terms of the transformed Bloch functions \((\psi^\text{T}_K)\) as a basis. If the transformation \((U^\text{T}_K)\), which can always be made unitary, is chosen to give a set of functions \((\psi^\text{T}_K)\) each of which transforms according to an irreducible representation of the group of the wave vector \(\kappa\), then according to a well known result based on the orthogonality theorem for group representations, all matrix elements in \((F^\text{T}_K)\) and \((S^\text{T}_K)\) between members of the set \((\psi^\text{T}_K)\) which transform according to different irreducible representations or different rows of the same irreducible representation (assuming identical representation matrices) will vanish identically. Thus \((F^\text{T}_K)\) and \((S^\text{T}_K)\) will be reduced to a form in which square blocks or minors occur (in identical patterns) on their principal
diagonals with all elements outside these blocks identically zero. The dimensions the block corresponding to a given irreducible representation, and the degree of the corresponding factor in the secular equation, will equal the number of members of the set \( \{ \psi^T \} \) belonging to that representation. If the irreducible representation is of dimension \( d \), \( d \) identical (or equivalent) blocks will occur on the diagonal, and \( d \) identical factors of degree equal to the dimensions of the blocks will occur in the secular equation. It is necessary to solve only one of these \( d \) factors for the corresponding eigenvalues and eigenvectors.

Although general methods for the construction of the matrix \( (U_j^\tau)^T \) which reduces the representation of the \( (\psi^T) \) exist, based for example on the orthogonality theorem for group representations or the theory \(^{92,93}\) of projection operators, the present case is so simple that it is not necessary to use them. Consider the set of three atoms \((123)\) in Figure 1. Under the subgroup \( C_{3v} \) of the point group \( D_{3d} \) these three atoms form an equivalent set, and so also do a set of three equivalent atomic orbitals \( \alpha_a \), \((a = 1,2,3)\), as defined in Section 6.22. It is obvious that the sum \( \alpha_1 + \alpha_2 + \alpha_3 \) is transformed into itself or its negative by each operation of \( C_{3v} \), and thus belongs to a one dimensional representation of \( C_{3v} \). Whether this is the totally symmetric representation \( A_1 \), or \( A_2 \), depends upon whether \( \alpha_a \) for example, belongs to the symmetric representation \( A' \) or antisymmetric representation \( A'' \), respectively, of the subgroup \( C_s \) which leaves the position of atom \( a \) invariant. Thus the sets for which \( \alpha = s \), \( p_y \), or \( p_z \) belong to \( A' \) of \( C_s \) and \( A_1 \) of \( C_{3v} \), while the set \( \alpha = p_x \) belongs to \( A'' \) of \( C_s \) and \( A_2 \) of \( C_{3v} \). Two additional linear combinations which are orthogonal to \( \alpha_1 + \alpha_2 + \alpha_3 \)
and also to one another are $\alpha_2 - \alpha_3$ and $2\alpha_1 - \alpha_2 - \alpha_3$. It is easily established that the latter two transform into linear combinations of one another under the operations $C_3$ and $C_3^2$, and that no further transformation will remove this property. Therefore the latter two must transform according to the two rows of the 2-dimensional irreducible representation $E$ of $C_{3v}$. These results can of course be confirmed by more general methods. The preceding three mutually orthogonal linear (or symmetry) combinations of atomic orbitals correspond to the linear transformation,

$$(a_1, a_2, a_3) \begin{pmatrix} 1 & 0 & 2 \\ 1 & 1 & -1 \\ 1 & -1 & -1 \end{pmatrix}$$  \hspace{1cm} (578)

It is desirable to normalize the sums of the squares of the elements in each column of the transformation matrix to unity, which yields the transformation matrix

$$(w) = \begin{pmatrix} 1/\sqrt{3} & 0 & 2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{2} & -1/\sqrt{6} \\ 1/\sqrt{3} & -1/\sqrt{2} & -1/\sqrt{6} \end{pmatrix}$$  \hspace{1cm} (579)

It will be noted that not only the columns, but also the rows of $(w)$ are now mutually orthogonal and normalized, so that $(w)$ is an orthogonal (real unitary) matrix, $(w)^{-1} = (w)^\dagger$.

Consider next the enlarged set of orbitals obtained by applying the inversion group $C_1 = (E, i)$ to $\alpha_a$, ($a = 1, 2, 3$). According to Section 6.22 this yields the set $\alpha_a (a = 1, 2, 3, 1, 2, 3)$. Furthermore this forms an equivalent set of orbitals under the direct product group $D_{3d} = C_{3v} \times C_1$. It is easily established that an orthogonal matrix
which reduces the representation of $D_{3d}$ provided by the set of 6 equivalent atomic orbitals is the direct product matrix

$$
(W) = (w) \times \begin{bmatrix}
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\
\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}}
\end{bmatrix}
$$

$$
= \begin{bmatrix}
\frac{1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{3}} \\
\frac{1}{\sqrt{6}} & 1/2 & -1/2 \sqrt{3} & \frac{1}{\sqrt{6}} & 1/2 & -1/2 \sqrt{3} \\
\frac{1}{\sqrt{6}} & -1/2 & -1/2 \sqrt{3} & \frac{1}{\sqrt{6}} & -1/2 & -1/2 \sqrt{3} \\
\frac{1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{3}} & -1/2 \sqrt{6} & 0 & -1/2 \sqrt{3} \\
\frac{1}{\sqrt{6}} & 1/2 & -1/2 \sqrt{3} & -1/2 \sqrt{6} & -1/2 & 1/2 \sqrt{3} \\
\frac{1}{\sqrt{6}} & -1/2 & -1/2 \sqrt{3} & -1/2 \sqrt{6} & 1/2 & 1/2 \sqrt{3}
\end{bmatrix}
$$

(580)

The matrix $(W)$ is also orthogonal or real unitary, $(W)^{-1} = (W)^\dagger$. The transformation matrix $(W)$ yields symmetry atomic orbitals belonging to irreducible representations of $D_{3d}$ as follows:

$$
(A_{1g}, E_{g1}, E_{g2}, A_{2u}, E_{u1}, E_{u2}) = (\alpha_1, \alpha_2, \alpha_3, \alpha_1^+, \alpha_2^+, \alpha_3^+)(W)
$$

(581)

for $\alpha = s, p_y, p_z, s^\dagger, p_y^\dagger$, or $p_z^\dagger$, and

$$
(A_{2g}, E_{g2}, E_{g1}, A_{1u}, E_{u2}, E_{u1}) = (\alpha_1, \alpha_2, \alpha_3, \alpha_1^+, \alpha_2^+, \alpha_3^+)(W)
$$

(582)

for $\alpha = p_x$ or $p_x^\dagger$.

Similar symmetry Bloch functions are obtained for the two special values $k = 0, k(\pi/2)$, when the transformation $(W)$ is applied to the corresponding Bloch functions $\psi_{a\alpha}(\vec{k}; \vec{r})$, $(a = 1, 2, 3, 1, 2, 3)$. It is therefore clear that the $48 \times 48$ transformation matrix $(U_k)$ of Eqs. (573-577) which carries the set of Bloch functions $(\psi^a_{k})$ into the set
(ψ_k) transforming according to irreducible representations of D_{3d} can be taken to be the direct product matrix

\[(U_k) = (W) \times (I_8),\]

(583)

where \((I_8)\) is the 8 x 8 unit matrix. That is, \((W)\) is repeated 8 times on the principal diagonal of \((U_k)\) and all other elements of \((U_k)\) vanish.

Each column of \((U_k)\) is labeled with one of the 8 atomic orbital types, and the irreducible representation of \(D_{3d}\) according to which it transforms as indicated by Eqs. (581) and (582). The columns were first rearranged to place the six \(A_{1g}\) columns first, the two \(A_{1u}\) columns second, etc., as indicated by the reduced representation (570). In arranging the 16 \(E_g\) columns the 8 \(E_{g1}\) columns (first row of representation) were placed together and similarly for the 8 \(E_{g2}\) columns; the \(E_{u1}\) and \(E_{u2}\) columns were arranged in the same manner. The rows of \((U_k)\) are labeled initially according to the 4 orbital types \(4^* \text{s}, \text{p}_x, \text{p}_y, \text{p}_z\), and for each \(\alpha\) according to the set of six equivalent positions, \(a = 1, 2, 3, 1, 2, 3\), and the similar primed set.

The rows were rearranged to accord with the order of rows and columns in the partitioned matrices \((S_R)\) and \((P_R)\) as indicated by Table 20; that is, first according to the 12 kinds of positions, 1, 2, ..., 31, and then according to the four orbital types. When this rearranged matrix was used to carry out the unitary transformations of the 48 x 48 matrices \((S_R)\) and \((P_R)\) described in Section 10.41, as indicated in Eqs. (577a,b) they were found to factor or reduce to the block form as anticipated. In Appendix II, the reduced matrices for each symmetry species for overlap, nuclear attraction, kinetic energy and one-electron
Hamiltonian matrices are given in Tables 47a,b; 48a,b; 49a,b; and 50, respectively. Tables containing a denote the symmetry reduction of intraicosahedral matrices and tables with b denote the reduction of intericosahedral matrices. The matrix multiplications were carried out on the IBM 7090 Digital Computer of the Numerical Computation Laboratory of The Ohio State University.

As a first step toward the solution of the factored secular equations for each symmetry species by the method described in Section 8.63(e), the overlap matrices for each symmetry species were diagonalized on the IBM 1620 Digital Computer by the Jacobi method of repeated two-dimensional orthogonal transformations. Unfortunately, as shown in Table 47a, a few of the eigenvalues of the overlap matrices were found to be negative. These values are given right below each sub order matrices and show the location of this negative root. These negative values made it impossible to complete the solution of the secular equations for the energies because the Hermitian square root of an overlap matrix with negative roots is complex. On the other hand, Eq. (143) shows that the exact overlap matrices must be positive-definite. The difficulty seems to be due to the relatively slow rate of decrease of the overlap integrals between atomic orbitals with distance, so that it is probably necessary to include next-nearest as well as nearest-neighbor overlap integrals to obtain a positive-definite overlap matrix. The kinetic energy and resonance integrals fall off more rapidly with distance. Also, the one-electron Hamiltonian at the
center of the Brillouin zone is given by Table 50. This gives an idea of the relative magnitudes of kinetic energy and nuclear attraction matrices as indicated by the "sign" of the particular element appearing in the table.
APPENDIX I

Values of Matrix Elements between Equivalent Atomic Orbitals as Given in Tables 19 and 21

**TABLE 44a. Numerical Values of Two-Center Overlap Integrals between Boron Atoms in the Same Icosahedron**

<table>
<thead>
<tr>
<th>From 1 to 2: $r = 1.7333$</th>
<th>From 1 to 1': $r = 1.785$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4744 0.2062 0.3572 0</td>
<td>0.4548 0 0.1502 -0.3734</td>
</tr>
<tr>
<td>-0.2062 -0.2700 -0.0346 0</td>
<td>0 0.2330 0 0 0</td>
</tr>
<tr>
<td>0.3572 0.0346 0.3100 0</td>
<td>-0.1502 0 0.1542 0.1957</td>
</tr>
<tr>
<td>0 0 0 0.2500 0.3734 0 0.1957 -0.2534</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>From 1 to 2': $r = 1.787$</th>
<th>From 1': to 2'': $r = 1.777$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4540 -0.1950 0.2625 0.2341</td>
<td>0.4578 -0.3283 0.1895 -0.1401</td>
</tr>
<tr>
<td>0.3248 -0.1049 0.0965 0.2648</td>
<td>0.3283 -0.2568 0.0122 -0.1598</td>
</tr>
<tr>
<td>0.0376 0.1763 0.1536 0.0307</td>
<td>0.1895 -0.0122 0.2426 -0.0923</td>
</tr>
<tr>
<td>0.2341 -0.1590 0.2140 -0.0411</td>
<td>-0.1401 0.1598 -0.0923 -0.1674</td>
</tr>
</tbody>
</table>

**TABLE 44b. Numerical Values of Two-Center Overlap Integrals between Boron Atoms in Neighboring Icosahedra**

<table>
<thead>
<tr>
<th>From 1'000 to 1'000: $r = 1.709$</th>
<th>From 1'000 to 2'O10: $r = 2.02$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4834 0 -0.2031 -0.3640</td>
<td>0.3702 -0.1750 -0.3030 0</td>
</tr>
<tr>
<td>0 -0.2581 0 0</td>
<td>0.1750 -0.2059 -0.0663 0</td>
</tr>
<tr>
<td>-0.2031 0 -0.1189 0.2495</td>
<td>-0.3030 0.0663 0.2825 0</td>
</tr>
<tr>
<td>-0.3640 0 0.2495 0.1890</td>
<td>0 0 0 0.1676</td>
</tr>
</tbody>
</table>

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TABLE 45a. Numerical Values of Two-Center Nuclear Attraction
Integrals between Boron Atoms in the Same Icosahedron

<table>
<thead>
<tr>
<th>From 1 to 2:  $r = 1.733$</th>
<th>From 1 to 1':  $r = 1.785$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.4082  .1973  .3422  0</td>
<td>.3874  0  .1417  -.3520</td>
</tr>
<tr>
<td>-.1973  -.2501  -.0731  0</td>
<td>0  .1908  0  0</td>
</tr>
<tr>
<td>.3422  .0731  .3344  0</td>
<td>-.1417  0  .1128  .1934</td>
</tr>
<tr>
<td>0  0  0  .2080</td>
<td>.3520  0  .1934  -.2893</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>From 1 to 1':  $r = 1.785$</th>
<th>From 1' to 1':  $r = 1.777$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.3869  -.1838  .2475  .2207</td>
<td>.3905  -.3102  .1789  -.1323</td>
</tr>
<tr>
<td>.3063  -.1235  .1292  .2616</td>
<td>.3102  -.2748  .4706  -.1586</td>
</tr>
<tr>
<td>.0354  .1404  .1326  .3016</td>
<td>.1789  -.4706  .2207  -.0915</td>
</tr>
<tr>
<td>.2207  -.1570  .2114  -.0013</td>
<td>.1323  .1586  -.0915  -.1258</td>
</tr>
</tbody>
</table>

TABLE 45b. Numerical Values of Two-Center Nuclear Attraction
Integrals between Boron Atoms in the Neighboring
Icosahedron

<table>
<thead>
<tr>
<th>From 1_{000} to 1_{000}:  $r = 1.709$</th>
<th>From 1'<em>{000} to 2</em>{010}:  $r = 2.02$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.4181  0  -.1958  -.3507</td>
<td>.3006  -.1503  -.2668  0</td>
</tr>
<tr>
<td>0  -.2163  0  0</td>
<td>.1503  -.1758  -.0809  0</td>
</tr>
<tr>
<td>-.1958  0  -.0746  .2538</td>
<td>-.2668  .0809  .2694  0</td>
</tr>
<tr>
<td>-.3507  0  .2538  .2387</td>
<td>0  0  0  .1290</td>
</tr>
</tbody>
</table>
### TABLE 46a. Numerical Values of Two-Center Kinetic Energy Integrals between Boron Atoms in the Same Icosahedron

<table>
<thead>
<tr>
<th>From 1 to 2: ( r = 1.733 )</th>
<th>From 1 to 1': ( r = 1.785 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( .0500 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( -0.0398 )</td>
<td>( -0.0971 )</td>
</tr>
<tr>
<td>( 0.0689 )</td>
<td>( 0.0657 )</td>
</tr>
<tr>
<td>( 0 )</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>From 1 to 2': ( r = 1.785 )</th>
<th>From 1' to 2': ( r = 1.777 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0.0460 )</td>
<td>( -0.0358 )</td>
</tr>
<tr>
<td>( 0.0596 )</td>
<td>( -0.0717 )</td>
</tr>
<tr>
<td>( 0.0069 )</td>
<td>( 0.0335 )</td>
</tr>
<tr>
<td>( 0.0429 )</td>
<td>( -0.0700 )</td>
</tr>
</tbody>
</table>

### TABLE 46b. Numerical Values of Two-Center Kinetic Energy Integrals between Boron Atoms on the Neighboring Icosahedron

<table>
<thead>
<tr>
<th>From ( 1000 ) to ( 1000' ): ( r = 1.709 )</th>
<th>From ( 1000' ) to ( 2010' ): ( r = 2.02 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0.0530 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( 0 )</td>
<td>( -0.0631 )</td>
</tr>
<tr>
<td>( -0.0400 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( -0.0716 )</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>
APPENDIX II

Form of the Overlap, Nuclear Attraction, Kinetic Energy and One-Electron Hamiltonian Matrices Following Transformation to Symmetry Orbitals

TABLE 47a. Intraicosahedral Overlap Matrices

<table>
<thead>
<tr>
<th>S(A_{1g})</th>
<th>P_y(A_{1g})</th>
<th>P_z(A_{1g})</th>
<th>S'(A_{1g})</th>
<th>P_y'(A_{1g})</th>
<th>P_z'(A_{1g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9483</td>
<td>.7142</td>
<td>0</td>
<td>1.3625</td>
<td>.6750</td>
<td>.0948</td>
</tr>
<tr>
<td>1.6196</td>
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<td>.4612</td>
<td>.2570</td>
<td></td>
</tr>
<tr>
<td>1.4996</td>
<td>.8414</td>
<td>.6235</td>
<td>-.3355</td>
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<td></td>
</tr>
<tr>
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<td>-.2801</td>
<td>.1845</td>
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<td></td>
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<td>.6650</td>
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<td>1.6350</td>
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<tr>
<td>P_x(A_{2g})</td>
<td>P_x(A_{2g})</td>
<td>P_x'(A_{2g})</td>
<td>P_x'(A_{2g})</td>
<td></td>
<td></td>
</tr>
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<td>.4427</td>
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<td></td>
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</tr>
<tr>
<td>1.5132</td>
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<td></td>
<td>.4863</td>
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<tr>
<td>S(A_{2u})</td>
<td>P_y(A_{2u})</td>
<td>P_z(A_{2u})</td>
<td>S'(A_{2u})</td>
<td>P_y'(A_{2u})</td>
<td>P_z'(A_{2u})</td>
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<td>( S(E_{gl}) )</td>
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<td>( P_y(E_{gl}) )</td>
<td>( P_z(E_{gl}) )</td>
<td>( S'(E_{gl}) )</td>
<td>( P_x'(E_{gl}) )</td>
</tr>
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<td>----------------</td>
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</tr>
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<td>-.1878</td>
<td>-.3054</td>
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<tr>
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<td>.2754</td>
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<tr>
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<td>.8049</td>
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</tr>
<tr>
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<td>( P_x(E_{ul}) )</td>
<td>( P_y(E_{ul}) )</td>
<td>( P_z(E_{ul}) )</td>
<td>( S'(E_{ul}) )</td>
<td>( P_x'(E_{ul}) )</td>
</tr>
<tr>
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<td>-.3572</td>
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</table>
### TABLE 47b. Intericosahedral Overlap Matrices

<table>
<thead>
<tr>
<th>S(A_{1g})</th>
<th>P_x(A_{1g})</th>
<th>P_y(A_{1g})</th>
<th>P_z(A_{1g})</th>
<th>S'(A_{1g})</th>
<th>P_x'(A_{1g})</th>
<th>P_y'(A_{1g})</th>
<th>P_z'(A_{1g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>.4833</td>
<td>-.2031</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-.1189</td>
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<td>.1890</td>
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<td>-.6059</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P_x(A_{1u})</th>
<th>P_x'(A_{1u})</th>
<th>P_x(A_{2g})</th>
<th>P_x'(A_{2g})</th>
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<td>-.4117</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>S(A_{2u})</th>
<th>P_y(A_{2u})</th>
<th>P_z(A_{2u})</th>
<th>S'(A_{2u})</th>
<th>P_y'(A_{2u})</th>
<th>P_z'(A_{2u})</th>
</tr>
</thead>
<tbody>
<tr>
<td>.4833</td>
<td>.2031</td>
<td>-.3639</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>-.1189</td>
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<td>.1890</td>
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<td>-.6059</td>
<td>.5649</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S(E_{g1})</th>
<th>P_x(E_{g1})</th>
<th>P_y(E_{g1})</th>
<th>P_z(E_{g1})</th>
<th>S'(E_{g1})</th>
<th>P_x'(E_{g1})</th>
<th>P_y'(E_{g1})</th>
<th>P_z'(E_{g1})</th>
</tr>
</thead>
<tbody>
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<td>.4834</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>S(E_{ul})</th>
<th>P_x(E_{ul})</th>
<th>P_y(E_{ul})</th>
<th>P_z(E_{ul})</th>
<th>S'(E_{ul})</th>
<th>P_x'(E_{ul})</th>
<th>P_y'(E_{ul})</th>
<th>P_z'(E_{ul})</th>
</tr>
</thead>
<tbody>
<tr>
<td>.4834</td>
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<td>0</td>
</tr>
<tr>
<td>-.2581</td>
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<td>.3030</td>
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</table>

-1.676
TABLE 48a. Intraicosahedral Nuclear Attraction Matrices

<table>
<thead>
<tr>
<th></th>
<th>S(A_{1g})</th>
<th>P_y(A_{1g})</th>
<th>P_z(A_{1g})</th>
<th>S'(A_{1g})</th>
<th>P_y'(A_{1g})</th>
<th>P_z'(A_{1g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3621</td>
<td>0.6842</td>
<td>0</td>
<td>1.1609</td>
<td>0.6365</td>
<td>0.0894</td>
<td></td>
</tr>
<tr>
<td>1.3185</td>
<td>0</td>
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TABLE 48b. Intericosahedral Nuclear Attraction Matrices

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### TABLE 49b. Intericosahedral Kinetic Energy Matrices

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TABLE 50. One-Electron Hamiltonian Matrices at the Center of the Brillouin Zone, $\mathbf{K} = 0$

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<th>$P_y(A_{1g})$</th>
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<th>$P_x'(A_{1g})$</th>
<th>$P_y'(A_{1g})$</th>
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I, Rama Bai Chintakindi, was born at Vishakapatnam, India on September 3, 1930. I had my secondary school education from Municipal High School, Vizianagaram and obtained the Bachelor of Science degree in Physics, Mathematics, and Chemistry from the Mysore University in 1950. From 1950 to 1953 I studied at the Indian Institute of Science, Bangalore and graduated with a Diploma in Electrical Communication Engineering. I worked as a research assistant at the same place till I joined the Graduate School of The Ohio State University in 1954. I obtained the Master's degree in Electrical Engineering in 1956. While a graduate student at The Ohio State University, I held the positions of Research Assistant, Research Fellow, and Research Associate in the Department of Electrical Engineering.