ON THE ORTHOGONALIZED PLANE WAVE METHOD FOR CALCULATING ENERGY EIGENVALUES IN A PERIODIC POTENTIAL

Thesis by

Truman Owen Woodruff

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1955

ACKNOWLEDGMENTS

It is a pleasure to thank Professor R. F. Christy for constant advice and encouragement and Professor R. P. Feynman for helpful and stimulating conversations.

This work was carried out while I was a member of the technical staff of the Semiconductor Laboratory in the Semiconductor Division of Hughes Aircraft Company during my tenure of a Howard Hughes Fellowship, for which I should like to express my appreciation. Dr. Harvey Winston of that laboratory helped me generously and patiently in my efforts to understand and use parts of the representation theory of space groups; I am very much indebted to him for this help and for his interest in all of this work. I should like to thank Dr. Maria Steinberg and her associates at the Hughes Aircraft Company for assistance with some of the numerical computations.

I am grateful to Dr. Frank Herman of the R. C. A. Laboratories for his courteous answers to my inquiries about his work on the electronic structure of valence crystals and for sending me several related papers by himself and his associates prior to their publication.

Words could not adequately describe or discharge my debt to my wife for her encouragement and help during every step in the making of this thesis; however, I wish to dedicate it to her.

ABSTRACT

The orthogonalized plane wave (OPW) method is used in the first step towards determination of self-consistent solutions of the Hartree-Fock equations (with Slater's free-electron simplification of the exchange terms) for electrons in a diamond-type crystal. For illustrative purposes, the techniques developed are applied to the determination of energy eigenvalues of the valence and lowest conduction states with zero wave vector in silicon crystal. The initial crystal potential is computed from the charge distribution obtained by placing the atoms forming the crystal on the points of the appropriate space lattice. The atomic charge distributions are determined from simple orthogonalized Slater functions, which can be easily constructed for all atoms, rather than from Hartree or Hartree-Fock atomic functions. A procedure for determining sufficiently good approximations to the wave functions and energy eigenvalues for the core electrons in the initial crystal potential is given. The importance for the convergence and accuracy of the OPW method of using core wave functions which are eigenfunctions of the same operator used to determine the valence and excited states is emphasized. The secular determinant of the OPW method is factored by using appropriate linear combinations of orthogonalized plane waves in the trial function for the valence and excited states. In this connection a detailed exposition is given of a method for obtaining explicit representation matrices for the group of the wave vector, which can then be used to construct basis functions for these representations from sets of orthogonalized plane waves.

TABLE OF CONTENTS

I. INTRODUCTION

In the first few years after the development of quantum mechanics a close connection was shown to exist between many of the most obvious and important properties of crystalline materials and the problem of the interaction of one electron with a potential field periodic in three dimensions. An account of this work with references to the men who pioneered in it is included in the article by Sommerfeld and Bethe in the Handbuch der Physik (1). After it had been established that a solution of the mathematical problem of an electron in a periodic potential would be useful in explaining the physical properties of crystals, efforts were made to refine the mathematical formulation so as to make it a more accurate model of the real physical situation in some specific kind of crystal, and to develop methods which would yield more accurate solutions of the resultant mathematical problem. Some of the methods which have been found useful in dealing with periodic potentials modelled after real crystals are the Wigner-Seitz cellular method (2), a modification of the cellular method by Slater (3), Herring's orthogonalized plane wave method (4), and the augmented plane wave method of Slater and Saffren (5). These and other methods are discussed and compared by G. V. Raynor in a review article (6), and by Frank Herman (7), (8).

One remarkable result of these investigations was to make possible the rise during the last fifteen years of a whole new branch of physics devoted to the study of semiconducting crystals. The theoretical distinction between metals, semiconductors and insulators is based on the idea of a band of energies for which no acceptable solution of the Schrödinger equation for an electron in the crystal potential can exist, and the interpretation of a great many interesting and technically useful electronic phenomena in single crystals of semiconductors has been similarly based on other details of approximate solutions of the periodic potential problem. While the recent rapid growth of semiconductor physics would have been very unlikely without this energy-band theory, it would have been equally unlikely except for the development of techniques for making and purifying large single crystals of germanium and silicon. Single crystals of these materials with less than one part in 10^9 of impurities have been obtained by present techniques. The availability of semiconducting crystals of such a high degree of perfection stimulated extensive calculations by Frank Herman of approximate solutions of the Schrödinger equation for periodic potentials modelled after the diamond (7), (8), (9), and germanium crystals (8), (10), and in turn many experimental efforts have been made to correlate observed electronic effects in these crystals with the results of these predictions of the energy band theory (11), (12), (13).

The present theoretical study is concerned with the orthogonalized plane wave (OPW) method proposed by Herring (4) for the calculation of approximate energy eigenvalues of the Schrödinger equation for a periodic potential. Some preliminary results for the silicon crystal are derived here as an illustration of the use of the method. Briefly, the OPW method is based on the idea that the lowest states in the crystal potential (the core states) are well represented by Bloch sums of the isolated-atom core functions, and that a trial function made up of a sum of terms, each labelled by a wave vector $\underline{k}$, consisting of a plane wave $e^{i\underline{k}\cdot\underline{r}}$ plus a function chosen to make the term orthogonal to all of the core eigenfunctions will lead to rapid convergence of the usual variational process for determining the higher states (the valence and conduction states).

Herman was the first to apply this technique to valence-type crystals and has carried out extensive calculations for the diamond and germanium crystals. He based his work on estimates of crystal potential and core-state wave functions derived from the published solutions of the Hartree-Fock equations for the isolated carbon atom (14), in the case of diamond, and of the Hartree equations for the germanium atom (15), in the case of germanium. He included approximate exchange terms in the diamond calculations, which converged very well. His initial calculation for germanium, which neglected all exchange terms, also converged well, but in his more refined calculations for germanium, his effort to include some of the exchange contribution to this crystal potential resulted in a much less convergent solution.

In this work our principal objectives are: (a) to simplify the application of the OPW method to diamond-type crystals by replacing many of the numerical procedures used by Herman by analytical procedures; (b) to base the estimation of crystal potential and core eigenfunctions on the approximate analytical wave functions which can be constructed for all atoms according to simple rules given by Slater some years ago (16), thus making possible calculations for crystals containing atoms for which the Hartree-Fock equations have not yet been solved; (c) to include a more consistent approximate treatment of the effects of exchange than has previously appeared by basing the calculation of both core and higher states in the crystal on Slater's form of the Hartree-Fock equations with the free-electron approximation for the exchange potential (17); (d) to provide a more complete exposition of the use of group theory in factoring the secular determinant of the OPW method than any which we have been able to find in the literature.

For purposes of experiment and illustration we have calculated the energy eigenvalues of the valence and lowest conduction states of an electron with wave vector $\underline{k} = 0$ in the silicon crystal. Silicon was chosen for this illustration, because as a result of the very intensive investigation of the electronic properties of large silicon crystals during the last few years there is now available a considerable amount of information derived from experiments as to their energy-band structure. Also, because of recent work on silicon-germanium alloys there is currently much interest in comparing the energy band-structures of silicon and germanium crystals (18). Finally, we are not aware of the existence of any solutions of the Hartree-Fock equations for the neutral silicon atom, so that the approximate solutions of Slater's form of these equations which we have obtained in this work (see Section VII) may be of use in other connections.

Perhaps the most interesting general result of this study is the improvement in the rate of convergence of the energy eigenvalues for the silicon crystal calculated by the methods developed here as compared with those calculated by Herman for the germanium and diamond crystals. We attribute this improved convergence to the more consistent treatment of the exchange term in the crystal potential and to the fact that we determined our core functions and their associated energy parameters by approximate solution of the Schrödinger equation constructed with the same potential which we used to describe the valence and excited states.

Another general result which is suggested, but not demonstrated by the present work, is that the solution to the energy band problem in a diamond-type crystal is not very sensitive to the assumed crystal potential, providing both core and higher states are determined in the <u>same</u> potential. These general results, and the numerical results of the silicon crystal calculation are discussed in Section IX.

Section II contains a more mathematical formulation of the crystal energy eigenvalue problem and the OPW method for attacking it. In Sections III, IV, and V, we describe in some detail how to make use of the symmetry of the crystal potential to factor the secular determinants of the OPW method. The factored determinants for approximations of several orders to the energy eigenvalues of the wave functions with zero crystal momentum are given explicitly in Section VI. In Sections VII and VIII we discuss procedures for calculating the three different classes of numbers which must be substituted into the factored secular determinants of Section VI: the energy parameters $E_{n\ell}$, the orthogonality coefficients, $A_{n\ell}(k)$, and the Fourier coefficients of the potential energy of an electron in the crystal field, $v(\underline{h})$. Tables of these numbers for use in our application to silicon are given in these sections. The calculation of $E_{n\ell}$ and $A_{n\ell}(k)$ requires knowledge of the core eigenfunctions, and these are also determined in Section VII. In the process of determining the core eigenfunctions a new method for obtaining approximate solutions in analytical form of Slater's simplified version of the Hartree-Fock equations is described and applied. This method should be useful in connection with many other problems where solutions of these equations are needed, and particularly when an analytical expression for these solutions is more convenient than the usual numerical tabulation.

II. FORMULATION OF THE PROBLEM

According to current ideas, a real single crystal of a chemical element of atomic number Z consists at room temperature of very roughly 10^{22} nuclei of that element per cubic centimeter, most of them oscillating about the points of a space lattice, embedded in a cloud of electrons, Z electrons for each nucleus. There are always impurity atoms present in this system, and imperfections in the array of nuclei, such as vacant lattice sites, interstitial atoms and dislocations. We do not endeavor here to determine the quantum states of such a complicated system. Instead, we abstract from this system the regularity in the disposition of the nuclei and ask for the wave function of all the electrons in the potential field arising from a perfect, rigid array of N' nuclei of the element (where $N' \sim 10^{22}$) on the points of the space lattice which we know from experiment to be appropriate for that element. Next we approximate the many-electron wave function by an antisymmetric combination of products of one-electron wave functions, and for the one-electron wave function of the i-th electron we take a solution of the approximate Schrödinger equation:

$$\left[-\nabla^2 + V(x)\right] u_i(x) = E_i u_i(x), \tag{2.1}$$

where x represents the space coordinate $\underline{r}$ and spin coordinate s of the electron, on which u_i depends. In this equation

$$V(x) = -2Z \sum_{\nu} \frac{1}{|\underline{r} - \underline{R}_\nu|} + 2 \sum_j \int \frac{u_j^*(x') u_j(x')}{|\underline{r} - \underline{r}'|} d\tau' - 6 \left\{ \frac{3}{8\pi} \sum_j u_j^*(x)\; u_j(x) \right\}^{1/3}, \tag{2.2}$$

where $\underline{r}$ is a variable of integration ranging over the volume of the crystal, $\int \ldots d\tau'$ means integration over $\underline{r}$ and summation over s, $\underline{R}_\nu$ is the position vector of the nucleus at the ν-th lattice point, ν runs over all lattice points in the crystal, and j runs over all of the electrons, including the i-th electron. Whenever it is convenient, we shall go to the limit in which our crystal is extended over all space. Atomic units are used throughout this work: distances are measured in units of the first Bohr radius a_0(a_0 = 5.2917×10^{-9} cm.) and energies in terms of rydbergs (one rydberg = 13.6050 electron volts). For a derivation and excellent discussion of Eqs. (2.1) and (2.2), see Slater (17). The last term in Eq. (2.2),

$$-6\left\{\frac{3}{8\pi}\sum_j u_j^*(x)u_j(x)\right\}^{1/3},$$

is called the exchange term in the electron's potential energy; it is an approximation to the exchange potential energy which appears in the Hartree-Fock equations. At least for the case when the crystal is extended over all space, it is clear that a set of solutions for the functions $u_i(x)$ can be found which make the potential V(x) have the same periodicity in $\underline{r}$ as the space lattice on which the nuclei are disposed; it is these solutions which we seek. In Eq. (2.2) it has been assumed that exactly half of the electrons have wave functions corresponding to one spin orientation and the other half to the opposite spin orientation. We look for a set of solutions of this sort, since we know that in the valence bonds in the diamond-type structures the spins of the two electrons forming the bond are balanced;

and hence in the lowest state of the crystal when all valence bonds are perfect, the spins will all be balanced. When one or more electrons are in conduction states, these electrons and their former partners in valence bondage may not continue to have a zero resultant spin, but even in this case, we expect any contributions from spin-dependent terms to the energies of the electrons in these states to be small, inasmuch as the exchange term in Eq. (2.2) is a small part of the total V(x), and a small unbalance in spins would have an extremely small effect on the exchange term. In this study then, for the sake of simplicity, we shall neglect any splitting up of the degenerate states in our solutions for zero crystal momentum which might be caused by the exchange term or the spin-orbit interaction, though these effects should be included in a more refined calculation. Thus, neglecting the dependence of the solutions of (2.1) on spin, and assuming balanced spins, we can replace Eqs. (2.1) and (2.2) by

$$\left[-\nabla^2 + V(\underline{r})\right]\psi_i(\underline{r}) = E_i\psi_i(\underline{r}), \tag{2.3}$$

with

$$V(\underline{r}) = -2Z\sum_{\nu}\frac{1}{|\underline{r}-\underline{R}_\nu|} + 2\sum_j\int\frac{\psi_j^*(\underline{r}')\psi_j(\underline{r}')}{|\underline{r}-\underline{r}'|}\,d\underline{r}' - 6\left\{\frac{3}{8\pi}\sum_j\psi_j^*(\underline{r})\psi_j(\underline{r})\right\}^{1/3}, \tag{2.4}$$

where $\psi_i(\underline{r})$ is the space dependent part of the wave function $u_i(x)$. Note that whereas the u_i were all different functions of x, as required by the Pauli principle, there will generally be two identical functions of $\underline{r}$ in the sequence $\psi_1(\underline{r}), \ldots, \psi_i(r), \ldots, \psi_{N'Z}(\underline{r})$ needed for a complete solution of the problem of the N'Z electrons in the crystal; that is, two electrons can be accommodated in each coordinate wave function, because their spins can be different.

The fact that the equations for the N'Z functions $\psi_i(\underline{r})$ are coupled by the exchange term and the electronic Coulomb term

$$2 \sum_j \int \frac{\psi_j^*(\underline{r}')\psi_j(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}'$$

in $V(\underline{r})$ complicates the problem of solving them. The most promising method for obtaining approximate solutions seems to be the one suggested by Hartree (19): guess a set of solutions $\psi_i^{(0)}(\underline{r})$; use these solutions for the computation of $V(\underline{r})$ in Eq. (2.4); solve Eq. (2.3) with this potential and obtain a second set of solutions $\psi_i^{(1)}(r)$; if $\psi_i^{(1)}(\underline{r}) \cong \psi_i^{(0)}(\underline{r})$, stop; if not, try by comparing $\psi_i^{(1)}(\underline{r})$ and $\psi_i^{(0)}(\underline{r})$ to obtain a better approximate set of solutions to be used in computing $V(\underline{r})$, and repeat the whole procedure. This study is devoted entirely to the first stage in this self-consistent field approach: guessing solutions $\psi_i^{(0)}(\underline{r})$, using them to compute $V(\underline{r})$, and obtaining approximate solutions, including the eigenvalues E_i, of Eq. (2.3) by the OPW method.

For our guess as to the solutions $\psi_i(\underline{r})$ which we shall use to obtain an initial estimate $V^{(0)}(\underline{r})$ of the potential field $V(\underline{r})$ for a diamond-type structure, we follow Herman (8) in using the chemical idea that a crystal of diamond or of one of the similar elements silicon and germanium which form diamond-type crystals can be formed by bringing the atoms in their valence or combining state into proper positions on the points of the appropriate space lattice, and that the electron distributions about the atoms in these states will be little changed by this process of crystal formation. The valence state of carbon is $(1s)^2(2s)(2p)^3, {}^5S$; by chemical analogy, the valence state of silicon should be $(1s)^2(2s)^2(2p)^6(2s)(3p)^3, {}^5S$.

Let $\varphi_{n\ell m}(\underline{r})$ be the wave function in the isolated atom for the electron of total quantum number n, azimuthal quantum number ℓ, and magnetic quantum number m. Then,

$$\varphi_{n\ell m}(r) = Y_{\ell m}(\theta,\varphi)(1/r)P_{n\ell}(r), \tag{2.5}$$

where $Y_{\ell m}(\theta,\varphi)$ is a spherical harmonic normalized so that

$$\int_0^{\pi}\int_0^{2\pi} Y_{\ell m}Y^*_{\ell m}\cos\theta \; d\varphi\, d\theta = 1, \tag{2.6}$$

and $P_{n\ell}(r)$ is the radial wave function multiplied by r and normalized so that

$$\int_0^{\infty}\left[P_{n\ell}(r)\right]^2 dr = 1. \tag{2.7}$$

We determine the radial wave functions $P_{n\ell}(r)$ which go into our initial estimate of $V(\underline{r})$ by very simple methods proposed by Slater (16), (20). The radial wave functions for silicon atom are constructed and given explicitly in Section VII. Using the wave functions $\varphi_{n\ell m}(\underline{r})$ the potential energy function for each of the electrons in the isolated atom can be written

$$V_{\text{atomic}}(\underline{r}) = -\frac{2Z}{|\underline{r}|} + 2\sum_{j=1}^{Z}\int \frac{\varphi_j^*(\underline{r}')\,\varphi_j(\underline{r}')}{|\underline{r}-\underline{r}'|}\,d\underline{r}'$$

$$-\,6\left\{\frac{3}{8\pi}\sum_{j=1}^{Z}\varphi_j^*(r)\,\varphi_j(r)\right\}^{1/3}, \qquad (2.8)$$

where now $\varphi_j(\underline{r})$ means that one of the $\varphi_{n\ell m}(\underline{r})$ functions which refers to the j-th electron, or j can be thought of as an abbreviation for the three quantum numbers n, ℓ, m, and summations over j are over those values of n, ℓ, m which we use in specifying the state of the atom.

We obtain the crystal potential energy function $\overset{(0)}{V}(\underline{r})$ by superposing the atomic potentials $\overset{(0)}{V}_{\text{atomic}}(\underline{r})$:

$$\overset{(0)}{V}(\underline{r}) = \sum_{\nu}\overset{(0)}{V}_{\text{atomic}}(\underline{r}-\underline{R}_\nu). \qquad (2.9)$$

(Here and everywhere in this study, the potential function is the potential energy function of an electron; its sign is the negative of that of the potential usually used in electrostatics.) The assumption on which Eq. (2.9) is based, that the crystal potential can be written as the superposition of atomic potentials, is rigorously correct with respect to the first two terms of $V(\underline{r})$, as given in Eq. (2.4), but the superposition principle would hold for the exchange term only if the atomic charge distributions did not overlap in the crystal. We know that the charge distributions of the valence electrons certainly do overlap, but the error arising from this source, which is given by

$$- 6\left(\frac{3}{8\pi}\right)^{1/3}\left[\left\{\sum_{\nu=1}^{N} \sum_{j=1}^{Z} \varphi_j^*(\underline{r} - \underline{R}_\nu)\,\varphi_j(\underline{r} - \underline{R}_\nu)\right\}^{1/3} - \sum_{\nu=1}^{N} \left\{ \sum_{j=1}^{Z} \varphi_j^*(\underline{r} - \underline{R}_\nu)\,\varphi_j(\underline{r} - \underline{R}_\nu)\right\}^{1/3}\right],$$

should be small compared to the exchange term in the final crystal potential at every point in the crystal, and over the major part of the crystal's volume, it should be much smaller. Since the exchange term itself is much smaller than the other terms in the crystal potential for almost all points in the crystal, we feel that this superposing of exchange potentials is not likely to introduce a major error.

Now we follow Herring's formulation (4) of the orthogonalized plane wave method for obtaining approximate solutions of Eq. (2.3). Assume that our model of the crystal under consideration consists of N identical unit cells, each of volume Ω_0. As already mentioned, we let N become infinite on occasion.

The potential energy of an electron at $\underline{r}$ is $V^{(0)}(\underline{r})$, as given in Eq. (2.9). $V^{(0)}(\underline{r})$ has the full symmetry of the crystal (the precise meaning of this statement will be explained in Section III).

If we imagine the crystal to be formed by bringing together all of its constituent atoms simultaneously, as suggested above, then it can be shown by means of the tight-binding approximation, as discussed in Section 2.6 of the book by Wilson (21), that the electrons occupying closed shells below the valence electrons (the 1s, 2s, and 2p electrons in silicon) will be very little affected by the crystal formation process, and the quantum states in the crystal of these electrons, which we call the core electrons, can all be well represented by

$$\psi_{n\ell;\underline{\not k}}(\underline{r}) = \frac{1}{\sqrt{N}} \sum e^{i\underline{\not k}\cdot\underline{R}_\nu}\, \varphi_{n\ell;\underline{\not k}}(\underline{r} - \underline{R}_\nu) , \tag{2.10}$$

where $\varphi_{n\ell;\underline{\not k}}(\underline{r})$ is the isolated atom wave function for the electron of total quantum number n, azimuthal quantum number ℓ, and magnetic quantum number m = 0 when the axis of magnetic quantization is taken in the direction of $\underline{\not k}$, and where $\underline{\not k}$ is 2π times a wave vector $\underline{k}$ associated with the crystal. (The definition and construction of the wave vectors $\underline{k}$ associated with a crystal are given in Section IV.) An expression like that on the right of Eq. (2.10) is called a Bloch sum of atomic wave functions. The energy eigenvalue $E_{n\ell}(\underline{\not k})$ which is associated with $\psi_{n\ell;\underline{\not k}}(\underline{r})$ by Eq. (2.4) is given to a good approximation by $E_{n\ell}$, the energy eigenvalue associated with $\varphi_{n\ell m}$ in the isolated atom by the equation for an electron in the isolated atom:

$$\left[-\nabla^2 + V_{\text{atomic}}(\underline{r})\right] \varphi_{n\ell m}(\underline{r}) = E_{n\ell}\, \varphi_{n\ell m}(\underline{r}) \tag{2.11}$$

The basis and validity of this approximation are discussed in the section of Wilson's book referred to above.

To obtain the wave functions and energy eigenvalues of the remaining electrons, which are called the valence and conduction electrons, we make use of the variational method with a trial function $\psi_{i;\underline{\not k}}(\underline{r})$ of the form

$$\psi_{i;\underline{\not k}}(\underline{r}) = \sum_{\underline{\not h}} a_{\underline{\not h}}\, \Pi_{\underline{\not k} + \underline{\not h}} , \tag{2.12}$$

where

$$\pi_{\underline{K}}(\underline{r}) = \frac{e^{i\underline{K}\cdot\underline{r}}}{\sqrt{N\Omega_0}} - \frac{1}{\sqrt{N}} \sum_{\nu} \sum_{n\ell} e^{i\underline{K}\cdot\underline{R}_\nu} .$$

$$\cdot A_{n\ell}(K)\, \varphi_{n\ell;\underline{K}}(\underline{r} - \underline{R}_\nu).$$

(2.13)

In Eq. (2.13), ν runs over all lattice sites, as usual, and

$$A_{n\ell}(K) = \int_\infty \frac{e^{i\underline{K}\cdot\underline{r}}}{\sqrt{\Omega_0}}\, \varphi^*_{n\ell;\underline{K}}(\underline{r})\, d\underline{r},$$

(2.14)

where $\int_\infty \ldots\ldots d\underline{r}$ means integration over the region of the crystal, which may fill all space. The numbers $A_{n\ell}(K)$ are called orthogonality coefficients; they are calculated to make each $\pi_{\underline{K}}$ orthogonal to all of the $\varphi_{n\ell m}(\underline{r}-\underline{R}\ )$ when one neglects the very small amount of overlapping between <u>core</u> functions about different atoms.

Varying the coefficients $a_{\underline{\not{h}}}$ so as to minimize the expected value of the energy associated with $\psi_{i;\not{k}}(\underline{r})$ we are led in the usual way (See Pauling and Wilson (22), Section 26d) to the secular equation

$$\det\left[(\pi_{\underline{K}}, H\pi_{\underline{K}'}) - E\,(\pi_{\underline{K}}, \pi_{\underline{K}'})\right] = 0$$

(2.15)

for the energy eigenvalue $E = E_i(\underline{\not{k}})$, where

$$H = -\nabla^2 + V(\underline{r}),$$

(2.16)

$\underline{K} = \underline{\not{k}} + \underline{\not{h}}$, $\underline{K}' = \not{k} + \underline{\not{h}}'$, and $V(r) = V^{(0)}(\underline{r})$, given in Eq. (2.9). Our use of the tight-binding approximation for the core states in the way described is equivalent to the assumption that the functions $\varphi_{n\ell m}(\underline{r}-\underline{R}_\nu)$ are true eigenfunctions in the crystal field $V(\underline{r})$ such that

$$H\varphi_{n\ell;\underline{k}}(\underline{r}) = E_{n\ell}\varphi_{n\ell;\underline{k}}(\underline{r}). \tag{2.17}$$

With this assumption, and again neglecting any overlapping of core functions of different atoms, it can be shown by straightforward manipulation that

$$(\Pi_K, H\Pi_{\underline{K}'}) = K^2\delta_{\underline{KK}'} + v(\underline{K}'-\underline{K})$$

$$- \sum_{n,\ell} E_{n\ell}A_{n\ell}(K)A_{n\ell}(K')P_\ell(\cos\theta_{\underline{K}\,\underline{K}'}) \sum_{\nu}^{\text{cell}} e^{i(\underline{K}'-\underline{K})\cdot\underline{R}_\nu}, \tag{2.18}$$

$$v(K) = \frac{1}{\Omega_0}\int_{\Omega_0} e^{i\underline{K}\cdot\underline{r}}V(\underline{r})\,d\underline{r}, \tag{2.19}$$

if $\underline{K} - \underline{K}'$ is 2π times a reciprocal lattice vector, and $=$ 0 otherwise (reciprocal lattice vectors are defined in Section IV). The summation with respect to ν is over all lattice sites in a single unit cell, and the angle between $\underline{K}$ and $\underline{K}'$ is denoted by $\theta_{\underline{K}\,\underline{K}'}$ in (2.18). Similarly,

$$(\Pi_K, \Pi_{K'}) = \delta_{\underline{K}\,\underline{K}'} - \sum_{n,\ell} A_{n\ell}(K)\,A_{n\ell}(K')\cdot$$

$$\cdot P_\ell(\cos\theta_{\underline{K}\,\underline{K}'}) \sum_{\nu}^{\text{cell}} e^{i(\underline{K}'-\underline{K})\cdot\underline{R}_\nu} \tag{2.20}$$

if $\underline{K} - \underline{K}'$ is 2π times a reciprocal lattice vector, and $=$ 0 otherwise. From Eqs. (2.18) and (2.20) it can be seen that the only

$\Pi_{\underline{k}+\underline{K}}$ functions which need to be included in the sum $\sum_{\underline{K}} a_{\underline{K}} \Pi_{\underline{k}+\underline{K}}$ for a wave function $\psi_{i;\underline{k}}(\underline{r})$ with wave vector $\underline{k}/2\pi$ are those for which $\underline{K}$ is 2π times a reciprocal lattice vector. The more orthogonalized plane waves $\Pi_{\underline{k}+\underline{K}}$ which we include in (2.12), the better value of $E_i(\underline{k})$ we shall obtain.

Our problem, then, is to solve the secular equation (2.15) for the energy eigenvalues as a function of $\underline{k}$. The wave functions associated with these eigenvalues will be those which can be occupied by the valence and conduction electrons. In the next three sections we show how by making use of the crystal's symmetry the secular determinant of Eq. (2.15) can be factored into lower order secular determinants, with a resultant enormous reduction in the labor of computing the solutions $E_i(\underline{k})$. We devote Section VII to showing how to obtain the core eigenfunctions $\varphi_{n\ell m}$ in the separated atom potentials from which we build up the approximate crystal potential $V(\underline{r})$, and from the core eigenfunctions we compute the orthogonality coefficients $A_{n\ell}(K)$ and the energy parameters $E_{n\ell}$ which enter into Eq. (2.18). The Fourier coefficients of potential, $v(\underline{K})$, are determined in Section VIII by means of Eq. (2.19) and the approximate crystal potential of Eq. (2.9) which we have described in this section. We compute actual solutions of Eq. (2.15) for the $\underline{k} = 0$ wave functions in silicon in Section IX.

III. CRYSTAL SYMMETRY

For a careful and complete exposition of the basic concepts arising from the study of crystals and their symmetry, which we cannot include here, the reader is referred to Seitz (23) and Zachariasen (24). For our purposes we need primarily the geometrical concept of an infinite space lattice of points. This is an unbounded set of points in a three-dimensional Euclidean space which are to be identified with the position vectors obtained by the following construction: choose an origin point 0 in the space, three non-coplanar vectors $\underline{a}_i$, $i = 1, 2, 3$, and m other vectors $\underline{d}_j$, $j = 1, 2, \ldots m$, which can be written as linear combinations of the $\underline{a}_i$ with fractional coefficients. Then the infinite space lattice consists of all points $\underline{r}$ given by

$$\underline{r} = \sum_{i=1}^{3} n_i \underline{a}_i + \underline{d}_j. \qquad (3.1)$$

Here and throughout, n_i is an integer. The $\underline{a}_i$ are the basis vectors and the $\underline{d}_j$ will be called the interior vectors of the lattice. An ideal crystal of a pure element can be thought of as formed from the condensation of atoms of that element on a finite set of the points of a space lattice associated with that element consisting of all of the lattice points within some region completely bounded by planes. The types of space lattices associated with crystals of various substances are completely characterized by the vectors $\underline{a}_i$ and $\underline{d}_j$.

For the lattices associated with crystals of diamond, silicon, and germanium (or diamond-type lattices), one possible choice for the

$\underline{a}_i$ and $\underline{d}_j$ is:

$$\underline{a}_1 = (1/2)a(0, 1, 1)$$
$$\underline{a}_2 = (1/2)a(1, 0, 1)$$
$$\underline{a}_3 = (1/2)a(1, 1, 0) \qquad (3.2)$$

$$\underline{d}_1 = (1/8)a(1, 1, 1)$$
$$\underline{d}_2 = -(1/8)a(1, 1, 1), \qquad (3.3)$$

where

$a = 3.5597$ Ang. for diamond (45)

$a = 5.431$ Ang. for silicon (37)

$a = 5.657$ Ang. for germanium (37). (3.4)

As an aid to discussion of the symmetry of a space lattice of points, L, it is convenient to imagine a second identical space lattice, L', in the same space as L and initially in coincidence with it, but in which each point $\underline{r}$ is subject to an arbitrary translation-rotation operation which carries it into a point $\underline{r}'$ as follows:

$$\underline{r}' = \alpha \underline{r} + \underline{t}, \qquad (3.5)$$

where α is a proper or improper rotation operator and $\underline{t}$ is a translation vector, $\underline{t} = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$. In a system of rectangular cartesian coordinates α is represented by a real orthogonal matrix α_{ij}, and $\underline{t}$ has components t_i $(i, j = 1, 2, 3)$. If the x, y, z components of $\underline{r}$ in this system are called r_1, r_2, r_3, respectively, the components of Eq. (3.5), written out, are:

$$\begin{aligned} r_1 &= \alpha_{11} r_1 + \alpha_{12} r_2 + \alpha_{13} r_3 + t_1 \\ r_2 &= \alpha_{21} r_1 + \alpha_{22} r_2 + \alpha_{23} r_3 + t_2 \\ r_3 &= \alpha_{31} r_1 + \alpha_{32} r_2 + \alpha_{33} r_3 + t_3 . \end{aligned} \tag{3.5'}$$

Following Seitz (25), we condense expressions like (3.5) or (3.5') to

$$\underline{r}' = \left\{\alpha \,\middle|\, \underline{t}\right\} \underline{r},$$

where $\{\alpha \mid \underline{t}\}$ is an operator which acts upon a vector $\underline{r}$ as indicated in (3.5); it is easy to see from (3.5) that the product of two such operators is given by the rule

$$\{\alpha \mid \underline{a}\} \; \{\beta \mid \underline{b}\} = \{\alpha\beta \mid \alpha\underline{b} + \underline{a}\}. \tag{3.7}$$

The continuously infinite set of all such operators contains a denumerably infinite subset which change the space lattice L' into another space lattice which coincides with L. The operations of this set are the symmetry operations admitted by a space lattice of the type of L; from what has been said of them it is clear that they form a group, the infinite crystal lattice space group. Zachariasen (24) demonstrates that the number of different space groups, and hence types of space lattices, is limited to 230, and he shows how they can be enumerated and described. A complete specification of the symmetry of a given type of lattice consists simply of a list of all the symmetry operations it admits.

The periodicity of space lattices is an evident consequence of the definition in Eq. (3.1); i. e., a space lattice based on $\underline{a}_i$ and $\underline{d}_j$

admits the infinite set of symmetry operations $\{\epsilon | \underline{R}_n\}$, where

$$\underline{R}_n = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3, \tag{3.8}$$

and ϵ is the identity operator.

These operations form a subgroup of the space group called the infinite translation group. For our purposes it is convenient to replace the infinite space group and its subgroup, the infinite translation group, with groups of finite order, by means of the following convention (26): those operations of the infinite space group which differ in their effect on L' only by a translation of all of its points through $n_1N_1\underline{a}_1 + n_2N_2\underline{a}_2 + n_3N_3\underline{a}_3$, where N_1, N_2, and N_3 are (usually large) fixed positive integers and n_1, n_2, n_3 are any integers, are considered to be the same operations of the finite space group. We call the finite space group $\mathcal{L}$; like the infinite one, it may be regarded as the direct product (in Zachariasen's sense (24)) of an invariant subgroup consisting of the operations corresponding to pure translations, and a factor group. The elements of this factor group are the cosets of the translation group in the finite space group. The order of the finite space group is $N_1N_2N_3 \cdot g$ where g is the order of the factor group. The factor group associated with each one of the 230 space groups is abstractly identical with one of the 32 crystallographic point groups, although factor groups associated with some space groups may include cosets containing other than purely point operations (those of the form $\{\alpha | 0\}$) combined with lattice translations, e. g. , screw rotations or glide reflections. Seitz (23) showed that operations of this more complicated sort can all be represented in the form $\{\epsilon | \underline{R}_n\}\{\alpha | \underline{\tau}_\alpha\}$, where $\underline{\tau}_\alpha$ is a fractional lattice translation depending on α of the form

$$\underline{\tau}_\alpha = f_1\underline{a}_1 + f_2\underline{a}_2 + f_3\underline{a}_3; \qquad (3.9)$$

the f_i are fractional rational numbers which are functions of α.

To describe the symmetry of a diamond-type lattice, then, in addition to specifying the primitive translation vectors in Eq. (3.1), from which all of the operations of the translation subgroup can be constructed, we enumerate a simple set of g operations from which all of the cosets of the translation group belonging to the factor group can be constructed. For brevity we call these g operations the factor-group symmetry operations. In the Schoenflies system the symbol for the diamond-type space group is O_h^7. Because we shall need them later, we give in Table 1 (see pages 26 and 27) explicit descriptions of all of the symmetry operations of the factor group of O_h^7. We describe these operations by specifying for each one α and $\underline{\tau}_\alpha$, and $\underline{r}' = \{\alpha \mid \underline{\tau}_\alpha\}\underline{r}$ for a general vector $\underline{r}$. It is of interest to consider two different possible choices of origin for the position vector $\underline{r}$, with respect to the "center" of the symmetry operation. By the "center" of a symmetry operation we mean any lattice point on the axis of rotation if the operation is a pure rotation, or the center of inversion if it includes an inversion. The origin of $\underline{r}$ may be taken at the center of the symmetry operation, or at a point midway between the center and one of the four nearest lattice points; the latter choice will generally be made, and this origin will be called the "standard origin".

A set of rectangular cartesian coordinates at the standard origin can be uniquely established by assigning the center of the symmetry operation the coordinates $(-a/8, -a/8, -a/8)$ and the three nearest-neighbor lattice sites of the center which are farthest from the standard origin the coordinates $(+a/8, -3a/8, -3a/8)$, $(-3a/8, a/8, -3a/8)$, $(-3a/8, -3a/8, a/8)$. The other nearest neighbor site of the center will, of course, have coordinates $(a/8, a/8, a/8)$. In this system of coordinates a set of primitive translation vectors is given by (3.2). The symbols in the second column of Table 1 are those commonly used to denote the corresponding point-group classes. Operations within a given class are such that any one operation could be made to have the same effect on a general $\underline{r}$ as any other operation in the class by a change in the choice of coordinate frame to which $\underline{r}$ is referred. Of the 48 operations in the factor group, the first 24 listed are simple, being rotations or rotations followed by inversions about the center. The last 24 operations are compound, involving a fractional lattice displacement as well as a rotation-reflection.

The compound operations at a given lattice point are ordered in the table so that the n-th compound operation is derived from the n-th simple operation at that point by left-multiplication with $\{\iota|\tau\}$; where the inversion ι is about the same point, and

$$\underline{\tau} = (1/4)(\underline{a}_1 + \underline{a}_2 + \underline{a}_3) = (a/4)(1, 1, 1).$$

The Seitz symbol for the operation is given in the third column of the table; the notation for the rotation-inversion operators is that used by Herring (27):

δ_{4i}, δ_{4i}^{-1} $(i = x,y,z)$: rotations through ±90° about the x-, y-, and z- axes, respectively;

$\delta_{2i} = \delta_{4i}^{2}$ $(i = x,y,z)$;

$\delta_{3s}, \delta_{3s}^{-1}$(s = xyz, $\bar{x}$yz, x$\bar{y}$z, $\bar{x}\bar{y}$z): rotations through ± 120° about axes along the diagonals of cubes in the various octants:

δ_{2p}(p = xy, yz, zx, $\bar{x}$y, $\bar{y}$z, $\bar{z}$x): rotations through 180° about axes halfway between two coordinate axes;

ι: the inversion;

$\sigma_{4i} = \iota\delta_{4i}, \sigma_{4i}^{-1}$ (i = x,y,z);

$\rho_i = \iota\delta_{2i}$(i = x,y,z);

$\sigma_{6s} = \iota\delta_{3s}, \sigma_{6s}^{-1}$ (s = xyz, etc.);

$\rho_p = \iota\delta_{2p}$(p = xy, etc.);

$\underline{\tau}$ = (a/4)(1, 1, 1).

In the fourth column the vector $\underline{r}' = \{\alpha \mid \underline{\tau}_\alpha\}^{-1}\underline{r}$ is given, with $\underline{r}$ and $\underline{r}'$ referred to the center of the symmetry operation. From this point on, the simple symbol L will be used to stand for a general space-group symmetry operation, $\{\alpha \mid \underline{\tau}_\alpha\}$, and L^{-1} for its inverse. We use the symbol Ls to denote the s-th operation listed in Table 1; the s-numbers labelling these operations run from 1 to 48 and are given in the first column. Column five gives $\underline{r}' = L^{-1}\underline{r}$ when $\underline{r}$ and $\underline{r}'$ are vectors fixed at the standard origin associated with the symmetry operation. It is easy to see how to obtain the entry in column five from the corresponding entry in column four. Let vectors originating at the center of the symmetry operation be $\underline{r}$, $\underline{r}'$, $\underline{r}''$,... , and vectors orignating at the associated standard origin be $\underline{R}$, $\underline{R}'$, $\underline{R}''$, ... , Under the rotation α of L = $\{\alpha \mid \underline{\tau}_\alpha\}$, $\underline{r}$ is transformed into $\underline{r}'$ according to the relation $\underline{r}' = \alpha\underline{r}$. Then, since $\underline{R}' = \underline{r}' - (1/2)\underline{\tau}$,

$\underline{R}' = \alpha\underline{r} - (1/2)\underline{\tau}$;

and since

$$\underline{r} = \underline{R} + (1/2)\underline{\tau},$$

$$\underline{R}' = \alpha\underline{R} + (1/2)\alpha\underline{\tau} - (1/2)\underline{\tau} = \alpha\underline{R} + (1/2)(\alpha - \epsilon)\underline{\tau}.$$

Hence

$$\underline{R}' = L\underline{R} + (1/2)(\alpha - \epsilon).$$

In columns four and five, $L^{-1}\underline{r}$ is tabulated instead of $L\underline{r}$ simply for convenience in later work.

Table 1a: SIMPLE SYMMETRY OPERATIONS OF THE FACTOR GROUP

OF SPACE GROUP O_h^7

s	Class	Operation L	$L^{-1}r$ Center Origin			$L^{-1}\underline{r}$ Standard Origin		
1	E	$\{\epsilon\|0\}$	x	y	z	x	y	z
2	C_4^2	$\{\delta_{2z}\|0\}$	$\bar{x}$	$\bar{y}$	z	$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	z
3		$\{\delta_{2x}\|0\}$	x	$\bar{y}$	$\bar{z}$	x	$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$
4		$\{\delta_{2y}\|0\}$	$\bar{x}$	y	$\bar{z}$	$\bar{x} - \frac{1}{4}a$	y	$\bar{z} - \frac{1}{4}a$
5	JC_4	$\{\sigma_{4z}^{-1}\|0\}$	y	$\bar{x}$	$\bar{z}$	y	$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$
6		$\{\sigma_{4z}\|0\}$	$\bar{y}$	x	$\bar{z}$	$\bar{y} - \frac{1}{4}a$	x	$\bar{z} - \frac{1}{4}a$
7		$\{\sigma_{4x}^{-1}\|0\}$	$\bar{x}$	z	$\bar{y}$	$\bar{x} - \frac{1}{4}a$	z	$\bar{y} - \frac{1}{4}a$
8		$\{\sigma_{4x}\|0\}$	$\bar{x}$	$\bar{z}$	y	$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	y
9		$\{\sigma_{4y}^{-1}\|0\}$	$\bar{z}$	$\bar{y}$	x	$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	x
10		$\{\sigma_{4y}\|0\}$	z	$\bar{y}$	$\bar{x}$	z	$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$
11	JC_2	$\{\rho_{xy}\|0\}$	$\bar{y}$	$\bar{x}$	z	$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	z
12		$\{\rho_{xz}\|0\}$	$\bar{z}$	y	$\bar{x}$	$\bar{z} - \frac{1}{4}a$	y	$\bar{x} - \frac{1}{4}a$
13		$\{\rho_{yz}\|0\}$	x	$\bar{z}$	$\bar{y}$	x	$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$
14		$\{\rho_{x\bar{y}}\|0\}$	y	x	z	y	x	z
15		$\{\rho_{x\bar{z}}\|0\}$	z	y	x	z	y	x
16		$\{\rho_{y\bar{z}}\|0\}$	x	z	y	x	z	y
17	C_3	$\{\delta_{3xyz}^{-1}\|0\}$	z	x	y	z	x	y
18		$\{\delta_{3xyz}\|0\}$	y	z	x	y	z	x
19		$\{\delta_{3x\bar{y}z}^{-1}\|0\}$	z	$\bar{x}$	$\bar{y}$	z	$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$
20		$\{\delta_{3x\bar{y}z}\|0\}$	$\bar{y}$	$\bar{z}$	x	$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	x
21		$\{\delta_{3x\bar{y}\bar{z}}^{-1}\|0\}$	$\bar{z}$	$\bar{x}$	y	$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	y
22		$\{\delta_{3x\bar{y}\bar{z}}\|0\}$	$\bar{y}$	z	$\bar{x}$	$\bar{y} - \frac{1}{4}a$	z	$\bar{x} - \frac{1}{4}a$
23		$\{\delta_{3xy\bar{z}}^{-1}\|0\}$	$\bar{z}$	x	$\bar{y}$	$\bar{z} - \frac{1}{4}a$	x	$\bar{y} - \frac{1}{4}a$
24		$\{\delta_{3xy\bar{z}}\|0\}$	y	$\bar{z}$	$\bar{x}$	y	$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$

Table 1b: COMPOUND SYMMETRY OPERATIONS OF THE FACTOR GROUP

OF SPACE GROUP O_h^7

s	Class	Operation L	$L^{-1}r$ Center Origin			$L^{-1}r$ Standard Origin		
25	J	$\{\iota\|\underline{\tau}\}$	$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$\bar{x}$	$\bar{y}$	$\bar{z}$
26	JC_4^2	$\{\rho_z\|\underline{\tau}\}$	$x - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$x - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{z}$
27		$\{\rho_x\|\underline{\tau}\}$	$\bar{x} - \frac{1}{4}a$	$y - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{x}$	$y - \frac{1}{4}a$	$z - \frac{1}{4}a$
28		$\{\rho_y\|\underline{\tau}\}$	$x - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$z - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{y}$	$z - \frac{1}{4}a$
29	C_4	$\{\delta_{4z}^{-1}\|\underline{\tau}\}$	$\bar{y} - \frac{1}{4}a$	$x - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{y}$	$x - \frac{1}{4}a$	$z - \frac{1}{4}a$
30		$\{\delta_{4z}\|\underline{\tau}\}$	$y - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$z - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{x}$	$z - \frac{1}{4}a$
31		$\{\delta_{4x}^{-1}\|\underline{\tau}\}$	$x - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$y - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{z}$	$y - \frac{1}{4}a$
32		$\{\delta_{4x}\|\underline{\tau}\}$	$x - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$x - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{y}$
33		$\{\delta_{4y}^{-1}\|\underline{\tau}\}$	$z - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$z - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{x}$
34		$\{\delta_{4y}\|\underline{\tau}\}$	$\bar{z} - \frac{1}{4}a$	$y - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{z}$	$y - \frac{1}{4}a$	$x - \frac{1}{4}a$
35	C_2	$\{\delta_{2xy}\|\underline{\tau}\}$	$y - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$y - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{z}$
36		$\{\delta_{2xz}\|\underline{\tau}\}$	$z - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$x - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{y}$	$x - \frac{1}{4}a$
37		$\{\delta_{2yz}\|\underline{\tau}\}$	$\bar{x} - \frac{1}{4}a$	$z - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{x}$	$z - \frac{1}{4}a$	$y - \frac{1}{4}a$
38		$\{\delta_{2x\bar{y}}\|\underline{\tau}\}$	$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$\bar{y}$	$\bar{x}$	$\bar{z}$
39		$\{\delta_{2x\bar{z}}\|\underline{\tau}\}$	$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$\bar{z}$	$\bar{y}$	$\bar{x}$
40		$\{\delta_{2y\bar{z}}\|\underline{\tau}\}$	$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$\bar{x}$	$\bar{z}$	$\bar{y}$
41	JC_3	$\{\sigma_{6xyz}^{-1}\|\underline{\tau}\}$	$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$\bar{z}$	$\bar{x}$	$\bar{y}$
42		$\{\sigma_{6xyz}\|\underline{\tau}\}$	$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$\bar{y}$	$\bar{z}$	$\bar{x}$
43		$\{\sigma_{6x\bar{y}z}^{-1}\|\underline{\tau}\}$	$\bar{z} - \frac{1}{4}a$	$x - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{z}$	$x - \frac{1}{4}a$	$y - \frac{1}{4}a$
44		$\{\sigma_{6x\bar{y}z}\|\underline{\tau}\}$	$y - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$y - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{x}$
45		$\{\sigma_{6x\bar{y}\bar{z}}^{-1}\|\underline{\tau}\}$	$z - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	$z - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{y}$
46		$\{\sigma_{6x\bar{y}\bar{z}}\|\underline{\tau}\}$	$y - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	$x - \frac{1}{4}a$	$y - \frac{1}{4}a$	$\bar{z}$	$x - \frac{1}{4}a$
47		$\{\sigma_{6xy\bar{z}}^{-1}\|\underline{\tau}\}$	$z - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	$y - \frac{1}{4}a$	$z - \frac{1}{4}a$	$\bar{x}$	$y - \frac{1}{4}a$
48		$\{\sigma_{6xy\bar{z}}\|\underline{\tau}\}$	$\bar{y} - \frac{1}{4}a$	$z - \frac{1}{4}a$	$x - \frac{1}{4}a$	$\bar{y}$	$z - \frac{1}{4}a$	$x - \frac{1}{4}a$

IV. SYMMETRY PROPERTIES OF THE CRYSTAL EIGENFUNCTIONS

This section consists of a brief review of the connection between the theory of group representations and quantum mechanics, as given in books by Wigner (28) and by Eyring, Walter, and Kimball (29), and a discussion of the work by Seitz (25) and Bouckaert, Smoluchowski, and Wigner (30) on space-group representations.

A. The Theory of Group Representations and Quantum Mechanics

Let us examine the effect on the crystal eigenfunctions $\psi_i(\underline{r})$ of crystal symmetry operations on the space containing the vector $\underline{r}$. To this end it is convenient to introduce the operator P_L by the following definition:

$$P_L f(\underline{r}) = f(L^{-1}\underline{r}) \tag{4.1}$$

where $L = \{\alpha \mid \underline{a}\}$. The identity (4.1) means that the number associated with the position $\underline{r}$ by the function $P_L f$ is the same as the number associated with the position $\underline{r}' = L^{-1}\underline{r}$ by the function f; $f(\underline{r})$ is an arbitrary scalar complex function of the vector $\underline{r}$. In other words, to find the value of the function f at the position into which $\underline{r}$ is transformed by the symmetry operation L^{-1}, we apply the operator P_L to f and evaluate $P_L f$ at the position $\underline{r}$. The definition (4.1) is based on the inverse symmetry operation L^{-1} instead of the direct operation L in order to simplify some of the following results. In terms of this operator the statement in Section II that $V(\underline{r})$ for the crystal problem has the full symmetry of the crystal becomes: for all of the symmetry operations L of the finite crystal lattice space group,

$$P_L V(\underline{r}) = V(\underline{r}) \tag{4.2}$$

If $\psi_i(\underline{r})$ is an eigenfunction of the Hamiltonian H for one electron in a crystal lattice potential $V(\underline{r})$, then for any of the symmetry operations L, $P_L \psi_i$ will be an eigenfunction of a physically indistinguishable Hamiltonian. That is,

$$H\psi_i = E_i\psi_i \tag{4.3}$$

implies

$$H(P_L\psi_i) = E_i(P_L\psi_i), \tag{4.4}$$

and hence

$$P_L H = HP_L, \tag{4.5}$$

or H commutes with the operator P_L. If $f(\underline{r})$ is an arbitrary function of $\underline{r}$, then according to our definitions, $P_L f(\underline{r}) = f(L^{-1}\underline{r})$, or if La and Lb are any two particular symmetry operations of the set $\mathcal{L}$, $P_{Lb}f(\underline{r}) = f([Lb]^{-1}\underline{r})$, and $P_{La}\cdot P_{Lb}f(\underline{r}) = P_{La}f([Lb]^{-1}\underline{r}) = f([Lb]^{-1}\cdot[La]^{-1}\underline{r}) = f([La\cdot Lb]^{-1}\underline{r})$. But if we denote the product La·Lb by Lc, $P_{Lc}f(r) = f([Lc]^{-1}\underline{r}) = f([La\cdot Lb]^{-1}\underline{r}) = P_{La}\cdot P_{Lb}f(\underline{r})$. Since $f(\underline{r})$ is an arbitrary function, the last equality implies

$$P_{La}\cdot P_{Lb} = P_{La\cdot Lb}, \tag{4.6}$$

so that the group of algebraic operators P_L is isomorphic to the group of geometrical operators L. Note that the isomorphy of these two groups is a consequence of our definition $P_L f(\underline{r}) = f(L^{-1}\underline{r})$; L^{-1} rather than L appears on the right-hand side of the definition in order to insure this isomorphy. The P_L operators are obviously linear.

We now make various assumptions as to the degeneracy of E_i in Eq. (4.4) and discuss the relation between $P_L\psi_i$ and ψ_i. First, assume that E_i is non-degenerate. Then since $P_L\psi_i$ and ψ_i are eigenfunctions of H corresponding to the same energy, E_i,

$$P_L\psi_i = a\psi_i, \tag{4.7}$$

where a is a constant. $P_L\psi_i$ is normalized if and only if $|a| = 1$. Next, consider the possibilities when E_i is ν-fold degenerate. It is then convenient to attach the number i to $\psi(\underline{r})$ as a superscript instead of a subscript, and to let the subscript label the various eigenfunctions associated with the ν-fold degenerate energy E_i. Then any eigenfunction corresponding to E_i can be expressed as a linear combination of the functions $\psi_1^i, \psi_2^i, \dots, \psi_\nu^i$. Since by (4.4) $P_L\psi_n^i$ is such an eigenfunction,

$$P_L\psi_n^i = \sum_{m=1} a_{mn}^i\psi_m^i , \tag{4.8}$$

where the a_{mn}^i are constants.

Now consider the effect of two successive operations, P_{La} and P_{Lb}, corresponding to La and Lb, two different symmetry operations of the space group. All summations are from 1 to ν.

$$P_{Lb}\psi_n^i = \sum_m b_{mn}^i\psi_m^i , \tag{4.9}$$

$$P_{La}\psi_s^i = \sum_{\ell} a_{\ell s}^i \psi_{\ell}^i . \tag{4.10}$$

Applying P_{La} to both sides of Eq. (4.9) and making use of the linearity and group property of the P_L operator:

$$P_{La\cdot Lb}\psi_n^i = P_{La}P_{Lb}\psi_n^i = \sum_m b_{mn}^i P_{La}\psi_m^i$$

$$= \sum_m b_{mn}^i \sum_{\ell} a_{\ell m}^i \psi_{\ell}^i = \sum_{\ell,m} a_{\ell m}^i b_{mn}^i \psi_{\ell}^i . \tag{4.11}$$

Now the product of La and Lb, La·Lb, is likewise a symmetry operation of the crystal space group which may be called Lc, so that $P_{Lc}\psi_n^i$ is also an eigenfunction of H, and we have seen that

$$P_{Lc}\psi_n^i = \sum_{\ell} c_{\ell n}^i \psi_{\ell}^i , \tag{4.12}$$

where

$$c_{\ell n}^i = \sum_m a_{\ell m}^i b_{mn}^i . \tag{4.13}$$

Thus the product of the matrix a^i of the coefficients $a_{\ell m}^i$ and of the matrix b^i of the coefficients b_{mn}^i is equal to the matrix c^i of the coefficients $c_{\ell n}^i$. In other words, the matrices obtained from the coefficients in the expansion of $P_{La}\psi_n^i$, etc., form a representation of the group $\mathcal{L}$ of the operations (the crystal lattice space-group symmetry operations) which leave the Hamiltonian unchanged. The set of eigenfunctions $\psi_1^i , \ldots , \psi_\nu^i$ form a basis for the representation of the group, since the representation is generated by the application of the operations P_L

to these functions. If the crystal eigenfunctions ψ^i_n are normalized, the representation matrices are unitary. Usually the degenerate eigenfunctions of a given Hamiltonian associated with a particular energy value E_i form a basis for one irreducible representation; the case when they can be chosen to form bases for several irreducible representations is called accidental degeneracy. In general discussions the possibility of accidental degeneracy is not considered. Then we can say that the dimension of the irreducible representation equals ν, the degeneracy of the corresponding eigenvalue. The n-th function in the basis set, ψ^i_n, belongs to the n-th row of the i-th irreducible representation of $\mathcal{L}$, as does any function f_n, with ν-1 partners $f_1, \dots, f_{n-1}, f_{n+1}, \dots, f_\nu$ such that

$$P_{La} f_n = \sum_m a^i_{mn} f^i_n \tag{4.14}$$

for all La in $\mathcal{L}$.

Wigner proves that functions belonging to different rows of the same representation, or to different representations, are orthogonal; more than that, he shows that

$$(f^i_n, g^{i'}_{n'}) = \frac{1}{\ell_i} \delta_{ii'} \delta_{nn'} \sum_m (f^i_m, g^i_m), \tag{4.15}$$

where ℓ_i is the dimensionality of the i-th representation and

$$(f, g) \equiv \int f^*(\underline{r}_1, \dots, \underline{r}_n) \cdot g(\underline{r}_i, \dots, \underline{r}_n) .\, d\tau_1, \dots, d\tau_n. \tag{4.16}$$

That is, given 2 sets of functions belonging to the i-th representation, the scalar products of functions belonging to the same row are equal, independent of which row is considered. Using this result, and the fact that $HP_L = P_LH$, which implies that Hf^i_n belongs to the n-th row of the i-th representation if f^i_n does, we have that

$$(f^i_n, Hg^{i'}_{n'}) = \delta_{ii'}\,\delta_{nn'}(f^i_n , Hg^i_n). \tag{4.17}$$

This is the fundamental result which we shall use to reduce the order of the OPW secular equation, Eq. (2.15).

B. Representations of the Finite Crystal Lattice Space Group

We have seen that $HP_L = P_L H$, where H is the Hamiltonian for one electron in a crystal lattice potential and L is any of the space group symmetry operations of the lattice. In particular L can be a translation,

$$\{\epsilon \mid \underline{R}_n\}, \quad \underline{R}_n \equiv \underline{R}_{n_1 n_2 n_3} \equiv n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3, \tag{4.18}$$

and hence any eigenfunction of H must belong to a set of functions which form a basis for an irreducible representation of the finite translation group associated with the lattice. Since this group is Abelian, its representations are one-dimensional, and since they are also unitary, they can be chosen to be of the form $(e^{-2\pi i \underline{k}\cdot\underline{R}_n})$, where

$$\underline{k} = \frac{n_1}{N_1}\underline{b}_1 + \frac{n_2}{N_2}\underline{b}_2 + \frac{n_3}{N_3}\underline{b}_3, \tag{4.19}$$

and the $\underline{b}_j$ are solutions of

$$\underline{a}_i \cdot \underline{b}_j = \delta_{ij}, \quad i, j \text{ -- } 1, 2, 3. \tag{4.20}$$

Hence we can say that every crystal eigenfunction ψ can be labeled with a "wave vector" $\underline{k}$, and

$$\psi_{\underline{k}}(\underline{r} + \underline{R}_n) = e^{2\pi i \underline{k}\cdot\underline{R}_n}\psi_{\underline{k}}(\underline{r}). \tag{4.21}$$

The vectors $\underline{b}_j$ introduced in (4.20) are called the vectors reciprocal to the set $\underline{a}_i$. It is easy to see that the equations in (4.20) are satisfied by

$$\underline{b}_1 = \frac{\underline{a}_2 \times \underline{a}_3}{(\underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3)}, \quad \underline{b}_2 = \frac{\underline{a}_3 \times \underline{a}_1}{(\underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3)}, \quad \underline{b}_3 = \frac{\underline{a}_1 \times \underline{a}_2}{(\underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3)}. \tag{4.22}$$

The three-dimensional space spanned by the $\underline{b}_i$ vectors is the reciprocal space; it contains $\underline{k}$, according to Eq. (4.19). Shockley (31) calls the vector $h\underline{k}$, where h is Planck's constant, the crystal momentum vector; it plays a large role in the quantum mechanical discussion of crystal phenomena.

The wave vector $\underline{k}$ of a given representation is uniquely determined only to within a vector $\underline{h}_n$ of the reciprocal lattice, where

$$\underline{h}_n \equiv \underline{h}_{n_1 n_2 n_3} \equiv n_1\underline{b}_1 + n_2\underline{b}_2 + n_3\underline{b}_3. \tag{4.23}$$

For this reason it is often convenient to restrict attention to a symmetrical region around the origin in reciprocal space such that no two points within it are separated by a distance greater than the length of any reciprocal lattice vector. This region is called the (first) Brillouin Zone. In later work we shall need to make use of basis functions for representations which have wave vectors $\underline{k}$ lying outside the first Brillouin Zone. These vectors can always be written in the form

$$\underline{k} = \underline{k}' + \underline{h}$$

where $\underline{h}$ is a reciprocal lattice vector and $\underline{k}'$ is a wave vector lying in the first Brillouin Zone; $\underline{k}' = \underline{k}'(\underline{k})$ is called a reduced wave vector of the basis function of wave vector $\underline{k}$.

Now we examine the effect on the crystal wave function, and particularly on its wave vector $\underline{k}$, of the operation P_L, where L is any factor group symmetry operation.

For a diamond-type crystal potential, for example, P_L would be one of the operations in Table 1. From Eq. (4.4) we know that $P_L\psi_{\underline{k}}(\underline{r})$ is a crystal eigenfunction with the same energy as $\psi_{\underline{k}}(\underline{r})$. We write

$$P_L\psi_{\underline{k}}(\underline{r}) = \psi_{\underline{k}}(L^{-1}\underline{r}) \equiv \varphi(\underline{r}); \tag{4.24}$$

and investigate the nature of the function $\varphi(\underline{r})$ in the following steps:

$$P_L\psi_{\underline{k}}(\underline{r} + \underline{R}_n) = \psi_{\underline{k}}(L^{-1}\underline{r} + \underline{R}_n); \tag{4.25}$$

since

$$P_L\left[Cf(\underline{r})\right] = CP_Lf(\underline{r})$$

for constant C,

$$P_L\left[e^{2\pi i\underline{k}\cdot\underline{R}_n}\psi_{\underline{k}}(\underline{r})\right] = e^{2\pi i\underline{k}\cdot\underline{R}_n}\psi_{\underline{k}}(L^{-1}\underline{r}). \tag{4.26}$$

Now, applying P_L to both sides of (4.21) and using (4.25), (4.26):

$$\psi_{\underline{k}}(L^{-1}\underline{r} + \underline{R}_n) = e^{2\pi i\underline{k}\cdot\underline{R}_n}\psi_{\underline{k}}(L^{-1}\underline{r}). \tag{4.27}$$

From Eq. (3.7),

$$L^{-1} = \left\{\alpha^{-1} \middle| -\alpha^{-1}\underline{\tau}_\alpha\right\}, \tag{4.28}$$

$$\begin{aligned} L^{-1}\underline{r} + \underline{R}_n &= \alpha^{-1}\underline{r} - \alpha^{-1}\underline{\tau}_\alpha + \underline{R}_n \\ &= \alpha^{-1}\underline{r} - \alpha^{-1}\underline{\tau}_\alpha + \alpha^{-1}\underline{R}_{n'}, \end{aligned} \tag{4.29}$$

where

$$\underline{R}_{n'} = \alpha\underline{R}_n, \text{ or } \underline{R}_n = \alpha^{-1}\underline{R}_{n'}.$$

Thus (4.27) becomes

$$\psi_{\underline{k}}\left[L^{-1}(\underline{r} + \underline{R}_{n'})\right] = e^{2\pi i\underline{k}\cdot\alpha^{-1}\underline{R}_{n'}}\psi_{\underline{k}}(L^{-1}\underline{r})$$

$$= e^{2\pi i\alpha\underline{k}\cdot\underline{R}_{n'}}\psi_{\underline{k}}(L^{-1}\underline{r}), \tag{4.30}$$

where the last step is justified by the observation that α is a real orthogonal matrix. Thus the behavior of $\varphi(\underline{r}) = \psi_{\underline{k}}(L^{-1}\underline{r})$ under translation is given by

$$\varphi(\underline{r} + \underline{R}_n) = e^{2\pi i\alpha\underline{k}\cdot\underline{R}_n}\varphi(\underline{r}), \tag{4.31}$$

and hence $\varphi(\underline{r})$ is a crystal wave function with wave vector $\alpha\underline{k}$:

$$P_{\{\alpha|\underline{\tau}_\alpha\}}\psi_{\underline{k}}(\underline{r}) = \varphi(\underline{r}) = \psi_{\alpha\underline{k}}(\underline{r}). \tag{4.32}$$

This very useful relation shows us that the effect of applying to $\psi_{\underline{k}}(\underline{r})$ a symmetry operation P_L, where L includes a rotation-reflection matrix α is to produce another wave function of the same degenerate set, with wave vector $\alpha\underline{k}$. Note that $\alpha\underline{k}$ may in some cases be equal to $\underline{k}$ or may differ from $\underline{k}$ by a vector of the reciprocal lattice, in which case we say that $\alpha\underline{k}$ is equivalent to $\underline{k}$. Crystal wave functions with equivalent wave vectors have exactly the same behavior under translations. To illustrate the possibility $\alpha\underline{k} = \underline{k}$, we can choose $\underline{k}$ so that it lies along the axis of a space group rotation α. In the next section further illustrations of $\alpha\underline{k}$ equal to or equivalent to $\underline{k}$ will appear.

Having considered the effect on crystal wave functions of the application of P_L when L is one of the pure translations and when L is one of the factor group operations of the space group, we now allow L to run through all operations of the whole space group $\mathcal{L}$. The set of crystal symmetry operations L such that P_L takes any crystal wave function $\psi_{\underline{k}}$ into one with the same or an equivalent wave vector is a sub-group of $\mathcal{L}$ which is called the group of the wave vector $\underline{k}$, and symbolized by $G^{\underline{k}}$. Seitz showed (25) that all of the irreducible representations of $\mathcal{L}$ can be obtained by finding for each wave vector $\underline{k}$ in the first Brillouin Zone irreducible representations of $G^{\underline{k}}$ of wave vector $\underline{k}$. A representation of $G^{\underline{k}}$ is said to be of wave vector $\underline{k}$ if a pure translation $\underline{R}_n$ of $G^{\underline{k}}$ is represented by $e^{-2\pi i\underline{k}\cdot\underline{R}_n}$ times a unit matrix of the dimensionality of the representation. If there exist any elements $T_n = \{\epsilon \mid \underline{R}_n\}$ of the translation sub-group of $\mathcal{L}$ such that $\underline{k}\cdot\underline{R}_n$ is an integer, then for any L in $G^{\underline{k}}$, $T_n \cdot L$ will be represented by the same matrix as L. This means that once we have found representation matrices for all the elements of the factor group $G^{\underline{k}}/T^{\underline{k}}$, where $T^{\underline{k}}$ is the group of all translations T_n for which $\underline{k}\cdot\underline{R}_n$ is an integer, it is easy to find all of the remaining representation matrices of the group of the wave vector, $G^{\underline{k}}$. In the next section we shall show how to obtain representation matrices for $G^{\underline{k}}/T^{\underline{k}}$ from the character tables for the space group. Character tables for the O_h^7, or diamond-type space group, have been published by C. Herring (27); these tables can be used to obtain explicitly the representations of the groups of some special wave vectors for the O_h^7 space group, and these representation matrices can then be used to obtain linear combinations of plane waves belonging to the different rows of the representations. These symmetrized sets are called (O_h^7-type) crystal symmetry combinations of plane waves, CSCPW; they are of great importance in the setting up of appropriate trial functions for the variational determination of crystal energy eigenvalues and wave functions, as in the OPW method.

V. CONSTRUCTION OF CRYSTAL SYMMETRY COMBINATIONS OF PLANE WAVES AND REPRESENTATION MATRICES FOR THE GROUP OF THE WAVE VECTOR

Consider any point, (k_1, k_2, k_3), in the reciprocal space of a given lattice. We associate with this point a set of plane waves consisting of $e^{2\pi i\underline{k}\cdot\underline{r}}$ and those members of the set $P_{Lj}e^{2\pi i\underline{k}\cdot\underline{r}}$, $j = 1, 2, \ldots, g(\underline{k}')$, which have a wave vector different from $\underline{k}$. Here Lj is one of the $g(\underline{k}')$ symmetry operations of the factor group $G^{\underline{k}'}/T^{\underline{k}'}$, where $G^{\underline{k}'}$ is the group of the reduced wave vector $\underline{k}'(\underline{k})$. Thus, for all j, $P_{Lj}e^{2\pi i\underline{k}\cdot\underline{r}}$ has for its wave vector either $\underline{k}$ or a vector equivalent to $\underline{k}$. Herman's (7) abbreviations $\left[k_1k_2k_3\right]$ for $e^{2\pi i\underline{k}\cdot\underline{r}}$ and $\langle k_1k_2k_3\rangle$ for the set $P_{Lj}e^{2\pi i\underline{k}\cdot\underline{r}}$ will be adopted. For a general point $\underline{k}$, $g(\underline{k}')$ is unity, and the set $\langle k_1k_2k_3\rangle$ will consist of only one plane wave, $\left[k_1k_2k_3\right]$, but for certain special points in the reciprocal space, called points of symmetry, $g(\underline{k}') > 1$, and the set $\langle k_1k_2k_3\rangle$ may contain several different plane waves with equivalent wave vectors. Let the total number of such different plane waves with wave vectors equivalent to $\underline{k}$ be $m(\underline{k})$. At a general point, $(k_1k_2k_3)$, $g(\underline{k}') = 1$, $m(\underline{k}) = 1$, the crystal symmetry combination of plane waves reduces to one plane wave, $\left[k_1k_2k_3\right]$, and the representation matrices for the group of $\underline{k}$, which in this case is the translation sub-group of the crystal space group, are one-dimensional matrices of the form $(e^{-2\pi i\underline{k}\cdot\underline{R}_\nu})$, where $\underline{R}_\nu$ is a lattice translation. At a point of symmetry, $(k_1k_2k_3)$, $g(\underline{k}') > 1$, and the group $G^{\underline{k}'}/T^{\underline{k}'}$ has in general several, say $c(\underline{k}')$, irreducible representations (i. r.), which will be denoted by $\mathcal{D}_1(\underline{k}')$, $\mathcal{D}_2(\underline{k}')$, $\ldots$, $\mathcal{D}_{c(\underline{k}')}(\underline{k}')$. Let the dimensionality of the j-th representation be ℓ_j. As shown on page 123 of Wigner's book (28),

$$\sum_{j=1}^{c(\underline{k}')} \ell_j^2 = g(\underline{k}'). \tag{5.1}$$

From the $m(\underline{k})$ plane waves $\langle k_1k_2k_3\rangle$ we shall show how to form $m(\underline{k})$ linear combinations which can be grouped into sets of basis functions for some of the $\mathcal{D}_j(\underline{k}')$. These functions, which are all mutually orthogonal, are the crystal symmetry combinations of plane waves (CSCPW) associated with $\underline{k}$; the set of them will be symbolized by $\{k_1k_2k_3\}$. We denote the set of j-indices of those representations $\mathcal{D}_j(\underline{k}')$ for which $\{k_1k_2k_3\}$ provide basis sets by $j\{\underline{k}\}$; this set may include the same index j' more than once, because the set $\{k_1k_2k_3\}$ may provide several sets of basis functions for $\mathcal{D}_{j'}(\underline{k}')$. But in any case, since the dimensionality of the representation sub-space associated with $\underline{k}$ is unchanged by the transformation from the basis set $\langle k_1k_2k_3\rangle$ to the basis set $\{k_1k_2k_3\}$,

$$\sum_{j \text{ in } j\{\underline{k}\}} \ell_j = m(\underline{k}). \tag{5.2}$$

In this section we discuss:

(A) given the character table for $G^{\underline{k}'}/T^{\underline{k}'}$, how to find the set of indices $j\{\underline{k}\}$, from which we learn the number of sets of basis functions for each i. r. $\mathcal{D}_j(\underline{k}')$ which can be obtained from the set $\langle k_1k_2k_3\rangle$;

(B) how to obtain the set of CSCPW, $\{k_1k_2k_3\}$, from the character table for $G^{\underline{k}'}/T^{\underline{k}'}$ when the explicit matrices of the representations $\mathcal{D}_j(\underline{k}')$ of $G^{\underline{k}'}/T^{\underline{k}'}$ are not known;

(C) how to obtain the explicit representation matrices of all of the representations $\mathcal{D}_j(\underline{k}')$ for which j is in $j\{\underline{k}\}$ (the $\mathcal{D}_j(\underline{k}')$ associated with $\underline{k}$) when the CSCPW associated with $\underline{k}$ are known; and

(D) how to obtain the combinations in $\{k_1k_2k_3\}$ from $\langle k_1k_2k_3\rangle$ with the aid of the sets of matrices of the $\mathcal{D}_j(\underline{k}')$ associated with $\underline{k}$. As an illustration, and to prepare material necessary for the OPW calculations to follow, these procedures will be applied to a diamond-type crystal lattice. The most important result of this section will be to establish an efficient, easily mechanized system for obtaining the CSCPW for any symmetry point $\underline{k}$ in the reciprocal space of a crystal lattice from the known matrices of the representations of $G^{\underline{k}'}/T^{\underline{k}'}$. This system makes it easy to obtain a CSCPW belonging to a specified row of a specified representation $\mathcal{D}_j(\underline{k}')$ of the group $G^{\underline{k}'}/T^{\underline{k}'}$ from any set $\langle k_1k_2k_3\rangle$ (which spans a space in which a sub-space is transformed irreducibly according to $\mathcal{D}_j(\underline{k}')$ under $G^{\underline{k}'}/T^{\underline{k}'}$) once the matrices of $\mathcal{D}_j(\underline{k}')$ are known. These matrices will be determined and tabulated for the point of highest symmetry, $\underline{k}' = (0, 0, 0)$, in the Brillouin Zone for a diamond-type lattice.

A. Character Analysis of $\langle k_1k_2k_3\rangle$

Given the set of plane waves $\langle k_1k_2k_3\rangle$, we determine how many linearly independent sets of basis functions for each of the representations $\mathcal{D}_j(\underline{k}')$ can be formed from them, or, in geometrical language, how many sub-spaces of the space of $\langle k_1k_2k_3\rangle$ transform irreducibly according to $\mathcal{D}_j(\underline{k}')$ under $G^{\underline{k}'}/T^{\underline{k}'}$. Let this number be a(j), a positive integer or zero. To find a(j) we make use of a table of the characters for each operation in each irreducible representation $\mathcal{D}_j(\underline{k}')$ of the group $G^{\underline{k}'}/T^{\underline{k}'}$. Let the character of operation Ls in representation $\mathcal{D}_j(\underline{k}')$ be $\chi_j(Ls)$; the character is by definition the trace of the matrix in $\mathcal{D}_j(\underline{k}')$ which represents Ls. We recall that $1 \leq s \leq g(\underline{k}')$ and that $1 \leq j \leq c(\underline{k}')$.

By virtue of the way in which the set $\langle k_1k_2k_3\rangle$ is formed, it is clear that the plane waves belonging to it are basis functions for a representation of the group $G^{\underline{k}'}/T^{\underline{k}'}$. In general this representation is reducible; the matrices of irreducible representation $\mathcal{D}_j(\underline{k}')$ occur a(j) times in the reduced matrices of this representation, and because of the invariance of the trace of a matrix under a similarity transformation,

$$\chi(Ls) = \sum_{j=1}^{c(\underline{k}')} a(j)\,\chi_j(Ls)\,, \tag{5.3}$$

where $\chi(Ls)$ is the character of the operation Ls in the reducible representation with basis set $\langle k_1k_2k_3\rangle$. Eq. (5.3) can be solved for the a(j) by means of a theorem proved just below:

$$\sum_{s} \chi_i(Ls)\chi_j(Ls)^* = g\,\delta_{ij}, \tag{5.4}$$

where δ_{ij} is the usual Kronecker delta.

This relation is true for the characters of the irreducible matrix representations of any group of order g consisting of the elements Ls, s = 1, ... , g. Multiplying both sides of Eq. (5.3) by $\chi_i(Ls)^*$ and summing over s, we obtain:

$$\sum_{s=1}^{g(\underline{k}')} \chi(Ls)\chi_i(Ls)^* = \sum_{s=1}^{g(\underline{k}')} \sum_{j=1}^{c(\underline{k}')} a(j) \quad {}_j(Ls)\chi_i(Ls)^*$$

$$= \sum_{j} g a(j)\delta_{ij} = g a(i),$$

or

$$a(i) = \frac{1}{g} \sum_{s=1}^{g(\underline{k}')} \chi_i(Ls)\chi(Ls)^*. \tag{5.5}$$

The proof of Eq. (5.4) depends on the very important and useful set of orthogonality relations between the irreducible matrix representations of any group of order g:

$$\sum_{s=1}^{g} D_j(Ls)_{mn}\sqrt{\frac{\ell_j}{g}}\, D_{j'}(Ls)^*_{m'n'}\sqrt{\frac{\ell_{j'}}{g}} = \delta_{jj'}\delta_{mm'}\delta_{nn'}\ , \tag{5.6}$$

where $D_j(Ls)_{mn}$ is the element in the m-th row and n-th column of the matrix representing the group operation Ls in the j-th irreducible representation, which is of dimensionality ℓ_j. The proof of this set of fundamental relations, which is too long to be included here, is given in Chapter IX of Wigner's book (28). One of the consequences of Eq. (5.6) is

$$\sum_{s=1}^{g} D_j(Ls)_{mm} D_{j'}(Ls)^*_{m'm'} = \frac{g}{\ell_j} \delta_{jj'} \delta_{mm'};$$

summing over m from 1 to ℓ_j and over m' from 1 to $\ell_{j'}$, we obtain

$$\sum_{s=1}^{g} \chi_j(Ls) \chi^*_{j'}(Ls) = \frac{g}{\ell_j} \delta_{jj'} \sum_{m=1}^{\ell_j} \sum_{m'=1}^{\ell_{j'}} \delta_{mm'}$$

$$= \frac{g}{\ell_j} \delta_{jj'} \ell_j = g\, \delta_{jj'},$$

which is Eq. (5.4)

In order to use Eq. (5.5) we must have a table of the characters $\chi(Ls)$ in the reducible representation for which $\langle k_1 k_2 k_3 \rangle$ is a basis set. We indicate how to construct such a table. Let the $m(\underline{k})$ plane waves in the set $\langle k_1 k_2 k_3 \rangle$ be represented by $W_1, W_2, \cdots, W_{m(\underline{k})}$. The order in which the plane waves are numbered is not important. Then for any operations Ls in the group $G^{\underline{k}'}/T^{\underline{k}'}$,

$$P_{Ls} W_j = \sum_{i=1}^{m(\underline{k})} D(Ls)_{ij} W_i, \tag{5.7}$$

where $D(Ls)$ is the matrix representing Ls in the $m(\underline{k})$ dimensional representation for which the W_j are basis functions. Because of the way in which the W_j were determined, $D(Ls)_{ij}$ for fixed j will vanish for all except one values of i. To determine $\chi(Ls)$, write (5.7) for each value of j from 1 to $m(\underline{k})$ and sum all of the numbers $D(Ls)_{jj}$, or diagonal matrix elements, which appear in the whole set of equations. ($\chi(Ls) = \sum_j D(Ls)_{jj}$.) To obtain (5.7) for a particular plane wave $W_j = e^{2\pi i\underline{k}'\cdot\underline{r}}$ and for group element $Ls = \{\alpha|\underline{\tau}_\alpha\}$, recall from (4.1) and (4.28) that

$$P_{Ls}W_j = P_{Ls}e^{2\pi i\underline{k}'\cdot\underline{r}} = e^{2\pi i\alpha\underline{k}'\cdot(\underline{r} - \underline{\tau}_\alpha)} = e^{-2\pi i\alpha\underline{k}'\cdot\underline{\tau}_\alpha}\cdot W_{i'}, \tag{5.8}$$

where $W_{i'} = e^{2\pi i\alpha\underline{k}'\cdot\underline{r}}$, and hence $D(Ls)_{i'j}$, the only non-vanishing matrix element in the j-th column, is $e^{-2\pi i\alpha\underline{k}'\cdot\underline{\tau}_\alpha}$. This whole procedure for determining $\chi(Ls)$ is easier to perform than it is to describe, and can be done mentally after one has made up a table giving $P_{Ls}W_j$ for each symmetry operation P_{Ls} in $G^{\underline{k}'}/T^{\underline{k}'}$ and for each plane wave W_j in $\langle k_1k_2k_3\rangle$. The construction of this table, which we call an "operation table" for the group $G^{\underline{k}'}/T^{\underline{k}'}$ and the plane waves $\langle k_1k_2k_3\rangle$ is the first thing to be done in the complete process of forming $\{k_1k_2k_3\}$ from $\langle k_1k_2k_3\rangle$. In making such a table we have found it convenient to represent each plane wave W_j simply by the integer j. We number the columns in the operation table from 1 up to $m(\underline{k})$ and label the rows by the symmetry operations Ls, or simply by the integers s. Then, for the case given in (5.8), $P_{Ls}W_j = e^{-2\pi i\alpha\underline{k}'\cdot\underline{\tau}_\alpha}\cdot W_{i'}$, under column j and in row s we enter the number i' of the plane wave W_i multiplied by $e^{-2\pi i\alpha\underline{k}'\cdot\underline{\tau}_\alpha}$

(which in our applications is usually ± 1 or $\pm \sqrt{-1}$). It should be noticed that the character is a function only of the class of an operation Ls, and if the classes of operations in $G^{\underline{k}'}/T^{\underline{k}'}$ have been determined, it is sufficient to find $\chi(Ls)$ for one Ls in each class.

Also required in Eq. (5.5) are the characters $\chi_i(Ls)$ in the irreducible representation $\mathcal{D}_i(\underline{k}')$; for the diamond-type space group (O_h^7), we obtain these from the work of Herring (27) and Bouckaert, Smoluchowski, and Wigner (30). In the tables which follow we exhibit the characters $\chi_i(Ls)$ for each of the irreducible representations of the group $G^{(000)}/T^{(000)}$ in O_h^7, and also, as typical examples, the operation table for the set $\langle 111 \rangle$ and the characters $\chi(Ls)$ in the reducible representation spanned by the set $\langle 111 \rangle$. From these tables and Eq. (5.5) we then find the numbers a(i) for the set $\langle 111 \rangle$.

Table 2, giving the characters of the i. r. of the group $G^{(000)}/T^{(000)}$ (usually called Γ), is taken from Table 1 in the paper by Bouckaert, Smoluchowski, and Wigner (30), except for slight changes in arrangement. Each column is labelled by the symbol $\mathcal{D}_i(000)$ for one of the representations of Γ and contains the characters of all of the classes of symmetry operations of the group Γ. The 48 symmetry operations of Γ and their classes are given in Table 1. The row designation at the left gives the class, and in a parenthesis to the left, the number of operations of Γ in that class. Thus, in the column under $\mathcal{D}_6(000) = \Gamma_{12}$ and in the row to the right of $(3)C_4^2$ we find 2, which is the character $\chi_6(C_4^2)$, where in the last symbol C_4^2 may be replaced by any one of the (3) symbols $L2 = \{\delta_{2z}|0\}$, $L3 = \{\delta_{2x}|0\}$, or $L4 = \{\delta_{2y}|0\}$, which belong to class C_4^2. The character of the identity E in a

Table 2: CHARACTERS OF THE IRREDUCIBLE REPRESENTATIONS OF $G^{(000)}/T^{(000)}$ IN O_h^7

	$\Gamma_1 =$ $\mathcal{D}_1$	$\Gamma_2' =$ $\mathcal{D}_2$	$\Gamma_{25}' =$ $\mathcal{D}_3$	$\Gamma_{15} =$ $\mathcal{D}_4$	$\Gamma_{12}' =$ $\mathcal{D}_5$	$\Gamma_{12} =$ $\mathcal{D}_6$	$\Gamma_{25} =$ $\mathcal{D}_7$	$\Gamma_{15}' =$ $\mathcal{D}_8$	$\Gamma_1' =$ $\mathcal{D}_9$	$\Gamma_2 =$ $\mathcal{D}_{10}$
(1)E	1	1	3	3	2	2	3	3	1	1
(3)C_4^2	1	1	−1	−1	2	2	−1	−1	1	1
(6)JC_4	1	1	−1	−1	0	0	1	1	−1	−1
(6)JC_2	1	1	1	1	0	0	−1	−1	−1	−1
(8)C_3	1	1	0	0	−1	−1	0	0	1	1
(1)J	1	−1	3	−3	−2	2	−3	3	−1	1
(3)JC_4^2	1	−1	−1	1	−2	2	1	−1	−1	1
(6)C_4	1	−1	−1	1	0	0	−1	1	1	−1
(6)C_2	1	−1	1	−1	0	0	1	−1	1	−1
(8)JC_3	1	−1	0	0	1	−1	0	0	−1	1

Note: In the column headings, $\mathcal{D}_i$ stands for $\mathcal{D}_i(000)$.

particular representation is the dimensionality of the representation. Note that we have labelled the various representations of Γ with the standard symbols, as given in Wigner, of the type Γ_{ij}, and also the symbols $\mathcal{O}_i(000)$.

Table 3 is the operation table which we have described above for the set $\langle 111 \rangle$. In it, the 48 operations are denoted by the numbers given in Table 1. The plane waves W_r are labelled by r:

$$
\begin{aligned}
W_1 &= [1\ 1\ 1] \\
W_2 &= [1\ \bar{1}\ \bar{1}] \\
W_3 &= [\bar{1}\ 1\ \bar{1}] \\
W_4 &= [\bar{1}\ \bar{1}\ 1] \\
W_5 &= [\bar{1}\ \bar{1}\ \bar{1}] \\
W_6 &= [\bar{1}\ 1\ 1] \\
W_7 &= [1\ \bar{1}\ 1] \\
W_8 &= [1\ 1\ \bar{1}].
\end{aligned}
\tag{5.9}
$$

Then for the set $\langle 111 \rangle$, using the procedure described, we find:

$$
\begin{aligned}
\chi(E) &= 8 \\
\chi(C_4^2) &= 0 \\
\chi(JC_4) &= 0 \\
\chi(JC_2) &= 4 \\
\chi(C_3) &= 2 \\
\chi(J) &= 0 \\
\chi(JC_4^2) &= 0 \\
\chi(C_4) &= 0
\end{aligned}
$$

$$\chi(C_2) = 0$$

$$\chi(JC_3) = 0. \tag{5.10}$$

Finally, substituting $\chi(Ls)$ from (5.10) and $\chi_i(Ls)$ from Table 2 in Eq. (5.5) we obtain:

$$\begin{aligned}
a(1) &= 1 \\
a(2) &= 1 \\
a(3) &= 1 \\
a(4) &= 1 \\
a(5) &= 0 \\
a(6) &= 0 \\
a(7) &= 0 \\
a(8) &= 0 \\
a(9) &= 0 \\
a(10) &= 0.
\end{aligned} \tag{5.11}$$

Table 3: OPERATION TABLE FOR THE GROUP $G^{(000)}/T^{(000)}$ IN O_h^7 AND THE PLANE WAVES $\langle 111 \rangle$

s in P_{Ls}	r (in W_r) 1	2	3	4	5	6	7	8
1	1	2	3	4	5	6	7	8
2	−4	3	2	−1	−8	7	6	−5
3	−2	−1	4	3	−6	−5	8	7
4	−3	4	−1	2	−7	8	−5	6
5	−3	−1	4	2	−7	−5	8	6
6	−2	4	−1	3	−6	8	−5	7
7	−4	3	−1	2	−8	7	−5	6
8	−3	4	2	−1	−7	8	6	−5
9	−2	3	4	−1	−6	7	8	−5
10	−4	−1	2	3	−8	−5	6	7
11	−4	2	3	−1	−8	6	7	−5
12	−3	2	−1	4	−7	6	−5	8
13	−2	−1	3	4	−6	−5	7	8
14	1	3	2	4	5	7	6	8
15	1	4	3	2	5	8	7	6
16	1	2	4	3	5	6	8	7
17	1	4	2	3	5	8	6	7
18	1	3	4	2	5	7	8	6
19	−4	−1	3	2	−8	−5	7	6
20	−2	4	3	−1	−6	8	7	−5
21	−3	2	4	−1	−7	6	8	−5
22	−4	2	−1	3	−8	6	−5	7
23	−2	3	−1	4	−6	7	−5	8
24	−3	−1	2	4	−7	−5	6	8

Table 3: OPERATION TABLE FOR THE GROUP $G^{(000)}/T^{(000)}$ IN O_h^7 AND THE PLANE WAVES $\langle 111 \rangle$ (CONT.)

s in P_{Ls}	r (in W_r) 1	2	3	4	5	6	7	8
25	5	6	7	8	1	2	3	4
26	−8	7	6	−5	−4	3	2	−1
27	−6	−5	8	7	−2	−1	4	3
28	−7	8	−5	6	−3	4	−1	2
29	−7	−5	8	6	−3	−1	4	2
30	−6	8	−5	7	−2	4	−1	3
31	−8	7	−5	6	−4	3	−1	2
32	−7	8	6	−5	−3	4	2	−1
33	−6	7	8	−5	−2	3	4	−1
34	−8	−5	6	7	−4	−1	2	3
35	−8	6	7	−5	−4	2	3	−1
36	−7	6	−5	8	−3	2	−1	4
37	−6	−5	7	8	−2	−1	3	4
38	5	7	6	8	1	3	2	4
39	5	8	7	6	1	4	3	2
40	5	6	8	7	1	2	4	3
41	5	8	6	7	1	4	2	3
42	5	7	8	6	1	3	4	2
43	−8	−5	7	6	−4	−1	3	2
44	−6	8	7	−5	−2	4	3	−1
45	−7	6	8	−5	−3	2	4	−1
46	−8	6	−5	7	−4	2	−1	3
47	−6	7	−5	8	−2	3	−1	4
48	−7	−5	6	8	−3	−1	2	4

Table 4: OPERATION TABLE FOR THE GROUP $G^{(000)}/T^{(000)}$ IN O_h^7 AND THE PLANE WAVES $\langle 200 \rangle$

s in P_{Ls}	r (in W_r)					
	1	2	3	4	5	6
1	1	2	3	4	5	6
2	−4	−5	3	−1	−2	6
3	1	−5	−6	4	−2	−3
4	−4	2	−6	−1	5	−3
5	2	−4	−6	5	−1	−3
6	−5	1	−6	−2	4	−3
7	−4	3	−5	−1	6	−2
8	−4	−6	2	−1	−3	5
9	−6	−5	1	−3	−2	4
10	3	−5	−4	6	−2	−1
11	−5	−4	3	−2	−1	6
12	−6	2	−4	−3	5	−1
13	1	−6	−5	4	−3	−2
14	2	1	3	5	4	6
15	3	2	1	6	5	4
16	1	3	2	4	6	5
17	3	1	2	6	4	5
18	2	3	1	5	6	4
19	3	−4	−5	6	−1	−2
20	−5	−6	1	−2	−3	4
21	−6	−4	2	−3	−1	5
22	−5	3	−4	−2	6	−1
23	−6	1	−5	−3	4	−2
24	2	−6	−4	5	−3	−1

Table 4: OPERATION TABLE FOR THE GROUP $G^{(000)}/T^{(000)}$ IN O_h^7 AND THE PLANE WAVES $\langle 200 \rangle$ (CONT.)

s in P_{Ls}	r (in W_r)					
	1	2	3	4	5	6
25	4	5	6	1	2	3
26	-1	-2	6	-4	-5	3
27	4	-2	-3	1	-5	-6
28	-1	5	-3	-4	2	-6
29	5	-1	-3	2	-4	-6
30	-2	4	-3	-5	1	-6
31	-1	6	-2	-4	3	-5
32	-1	-3	5	-4	-6	2
33	-3	-2	4	-6	-5	1
34	6	-2	-1	3	-5	-4
35	-2	-1	6	-5	-4	3
36	-3	5	-1	-6	2	-4
37	4	-3	-2	1	-6	-5
38	5	4	6	2	1	3
39	6	5	4	3	2	1
40	4	6	5	1	3	2
41	6	4	5	3	1	2
42	5	6	4	2	3	1
43	6	-1	-2	3	-4	-5
44	-2	-3	4	-5	-6	1
45	-3	-1	5	-6	-4	2
46	-2	6	-1	-5	3	-4
47	-3	4	-2	-6	1	-5
48	5	-3	-1	2	-6	-4

B. Determination of Crystal Symmetry Combinations of Plane Waves from the Character Table

The results of the preceding sub-section will be used in the process we now describe for assembling from a set of plane waves $\langle k_1k_2k_3\rangle$ linear combinations $\{k_1k_2k_3\}$ which transform under the operations of $G^{\underline{k}'}/T^{\underline{k}'}$ according to some of the irreducible representations $\mathcal{D}_1(\underline{k}')$, ... , $\mathcal{D}_{c(k')}(\underline{k}')$. We know that we must be able to find a(1) sets of basis functions for $\mathcal{D}_1(\underline{k}')$, a(2) sets for $\mathcal{D}_2(\underline{k}')$, etc., where the a(i) depend on $\underline{k}$, of course. Let W_r denote one of the original plane waves $[k_1k_2k_3]$ (as in the last section) and S^i_{pm} the p-th symmetrized plane wave combination belonging to the m-th row of $\mathcal{D}_i(\underline{k}')$, $1 \leq i \leq c(\underline{k}')$, which can be made up out of $\langle k_1k_2k_3\rangle$. Since the symmetrized plane waves are to be obtained by a non-singular transformation from $\langle k_1k_2k_3\rangle$, any particular plane wave W_r can be written as a linear combination of S^i_{pm}, i. e.,

$$W_r = \sum_{i=i}^{c(\underline{k}')} \sum_{p=1}^{a(i)} \sum_{m=1}^{\ell_i} b_{ipm} S^i_{pm} . \tag{5.12}$$

From Eq. (5.7) we obtain, for any operation Ls of the group $G^{\underline{k}'}/T^{\underline{k}'}$:

$$P_{Ls}W_r = \sum_{i=1}^{c(\underline{k}')} \sum_{p=1}^{a(i)} \sum_{m=1}^{\ell_i} b_{ipm} \sum_{n=1}^{\ell_i} D^i(Ls)_{nm} S^i_{pm}.$$

Now multiply each side of this equation by $\chi_j(Ls) = \sum_{t=1}^{\ell_j} D^j(Ls)_{tt}$ and sum over s from 1 to g ($\underline{k}'$):

$$\sum_{s=1}^{g(\underline{k}')} \chi_j(Ls)P_{Ls}W_r = \sum_{i=1}^{c(\underline{k}')} \sum_{p=1}^{a(i)} \sum_{m=1}^{\ell_i} b_{ipm}\cdot$$

$$\sum_{n=1}^{\ell_i} \sum_{t=1}^{\ell_j} \sum_{s=1}^{g(\underline{k}')} D^j(Ls)_{tt}D^i(Ls)_{nm}\, S^i_{pn}$$

$$= \sum_{p=1}^{a(j)} \sum_{m=1}^{\ell_j} b_{jpm} \frac{g(\underline{k}')}{\ell_j} \sum_{n=1}^{\ell_j} \sum_{t=1}^{\ell_j} \delta_{tn}\delta_{tm}S^j_{pn}$$

$$= \sum_{p=1}^{a(j)} \sum_{t=1}^{\ell_j} \frac{g(\underline{k}')}{\ell_j}\, b_{jpt}S^j_{pt}. \tag{5.13}$$

The last two forms of this equality are obtained by making use of the orthogonality relations (5.6). The equality of the first and last terms means that the effect of the operation

$$\sum_{s=1}^{g(\underline{k}')} \chi_j(Ls)P_{Ls}$$

on W_r is to produce a symmetrized plane wave combination, S^j_{11}, if σ_j is one-dimensional and a(j) is unity; the sum of several such combinations, each belonging to different rows of σ_j,

$$c_1S^j_{11} + c_2S^j_{12} + \dots + c_{\ell_j}S^j_{1\ell_j}, \tag{5.14}$$

if $\mathcal{O}_j$ has dimensionality ℓ_j and a(j) is unity; and the sum of several sums like (5.14), each consisting of a sum of basis functions for $\mathcal{O}_j$, including one from each row, if $\mathcal{O}_j$ has dimensionality ℓ_j and $a(j) > 1$. In practice, after applying the operation

$$\sum_{s=1}^{g(\underline{k}')} \chi_j(Ls)P_{Ls}$$

to several different plane waves in the set $\langle k_1k_2k_3\rangle$ one sees which of the resulting combinations are partners in a representation of $\mathcal{O}_j$, or can be linearly combined in some simple manner to form such partners, although we can give no exact general prescription for this procedure. In the following typical example we use the set $\langle 111\rangle$ to illustrate how easily we can disentangle and classify these various combinations of symmetrized plane waves.

From the results of the sub-section A, we know that in the set $\langle 111\rangle$ consisting of eight plane waves it is possible to find one linear combination belonging to Γ_1, one belonging to Γ_2', three belonging to Γ_{25}'(one three-dimensional basis set), and three belonging to Γ_{15}. To find the Γ_1 linear combination we apply the operation

$$\sum_{s=1}^{48} \chi_1(Ls)P_{Ls}$$

to $W_1 = [111]$:

$$\sum_{s=1}^{48} \chi_1(Ls)P_{Ls}W_1 =$$

$$\begin{aligned}
&1\cdot(1 - 4 - 2 - 3 - 3 - 2 - 4 - 3 - 2 - 4 - 4 - 3\\
&- 2 + 1 + 1 + 1 + 1 + 1 - 4 - 2 - 3 - 4 - 2 - 3\\
&+ 5 - 8 - 6 - 7 - 7 - 6 - 8 - 7 - 6 - 8 - 8 - 7\\
&- 6 + 5 + 5 + 5 + 5 + 5 - 8 - 6 - 7 - 8 - 6 - 7\\
&= 6\cdot(1 - 2 - 3 - 4 + 5 - 6 - 7 - 8),
\end{aligned} \tag{5.15}$$

where in a product like 6·4 the first number, 6, has its usual meaning, but the second number, 4, stands for $W_4 = [\bar{1}\bar{1}1]$. In writing (5.15), we used the operation table, Table 3, and the character table, Table 2. The application of

$$\sum_{s=1}^{48} \chi_1(Ls)P_{Ls}$$

to any other plane wave in the set $\langle 111 \rangle$ gives the same result. Normalized, the linear combination given by Eq. (5.15) becomes

$$S_{11}^{1} = (1/\sqrt{8})(1 - 2 - 3 - 4 + 5 - 6 - 7 - 8). \tag{5.16}$$

Proceeding in the same way, but replacing $\chi_1(Ls)$ by $\chi_2(Ls)$, we obtain

$$S_{11}^{2} = (1/\sqrt{8})(1 - 2 - 3 - 4 - 5 + 6 + 7 + 8). \tag{5.17}$$

Next, we find the Γ'_{25} linear combinations. Using Eq. (5.13), Table 2, and Table 3, we get:

$$\sum_{s=1}^{48} \chi_3(Ls)P_{Ls}W_1 = 6\cdot1 + 2\cdot2 + 2\cdot3 + 2\cdot4 + 6\cdot5 + 2\cdot6 + 2\cdot7 + 2\cdot8$$

$$\equiv Q_1$$

$$\sum_{s=1}^{48} \chi_3(Ls)P_{Ls}W_2 = 2\cdot1 + 6\cdot2 - 2\cdot3 - 2\cdot4 + 2\cdot5 + 6\cdot6 - 2\cdot7 - 2\cdot8$$

$$\equiv Q_2$$

$$\sum_{s=1}^{48} \chi_3(Ls)P_{Ls}W_3 = 2\cdot1 - 2\cdot2 + 6\cdot3 - 2\cdot4 + 2\cdot5 - 2\cdot6 + 6\cdot7 - 2\cdot8$$

$$\equiv Q_3$$

$$\sum_{s=1}^{48} \chi_3(Ls)P_{Ls}W_4 = 2\cdot1 - 2\cdot2 - 2\cdot3 + 6\cdot4 + 2\cdot5 - 2\cdot6 - 2\cdot7 + 6\cdot8$$

$$\equiv Q_4$$

$$\sum_{s=1}^{48} \chi_3(Ls)P_{Ls}W_{j+4} = Q_j, \quad j = 1, 2, 3, 4. \tag{5.18}$$

It is easy to see that $Q_1 = Q_2 + Q_3 + Q_4$, so that Q_2, Q_3, and Q_4 must be linearly independent; however, they are not mutually orthogonal, as our basis functions must be. After trying several simple combinations of the Q_i's, we observe that $(Q_1 - Q_4)$, $(Q_1 - Q_3)$, and $(Q_1 - Q_2)$ are mutually orthogonal. Normalizing these combinations we have, finally,

$$s^3_{11} = (1/\sqrt{8})(1 + 2 + 3 - 4 + 5 + 6 + 7 - 8)$$

$$s^3_{12} = (1/\sqrt{8})(1 + 2 - 3 + 4 + 5 + 6 - 7 + 8)$$

$$s^3_{13} = (1/\sqrt{8})(1 - 2 + 3 + 4 + 5 - 6 + 7 + 8).$$

(5.19)

For Γ_{15}, the procedure is similar:

$$\sum_{s=1}^{48} \chi_4(Ls)P_{Ls}W_1 = 6\cdot1 + 2\cdot2 + 2\cdot3 + 2\cdot4 - 6\cdot5 - 2\cdot6 - 2\cdot7 - 2\cdot8$$

$$\equiv Q_1'$$

$$\sum_{s=1}^{48} \chi_4(Ls)P_{Ls}W_2 = 2\cdot1 + 6\cdot2 - 2\cdot3 - 2\cdot4 - 2\cdot5 - 6\cdot6 + 2\cdot7 + 2\cdot8$$

$$\equiv Q_2'$$

$$\sum_{s=1}^{48} \chi_4(Ls)P_{Ls}W_3 = 2\cdot1 - 2\cdot2 + 6\cdot3 - 2\cdot4 - 2\cdot5 + 2\cdot6 - 6\cdot7 + 2\cdot8$$

$$\equiv Q_3'$$

$$\sum_{s - 1}^{48} \chi_4(Ls)P_{Ls}W_4 = 2\cdot1 - 2\cdot2 - 2\cdot3 + 6\cdot4 - 2\cdot5 + 2\cdot6 + 2\cdot7 - 6\cdot8$$

$$\equiv Q_4' \;;$$

(5.20)

the orthogonal combinations are $(Q_1' - Q_4')$, $(Q_1' - Q_3')$, and $(Q_1' - Q_2')$, and the final results are:

$$S^4_{11} = (1/\sqrt{8})(1 + 2 + 3 - 4 - 5 - 6 - 7 + 8)$$

$$S^4_{12} = (1/\sqrt{8})(1 + 2 - 3 + 4 - 5 - 6 + 7 - 8)$$

$$S^4_{13} = (1/\sqrt{8})(1 - 2 + 3 + 4 - 5 + 6 - 7 - 8). \tag{5.21}$$

C. Construction of the Representation Matrices of $\mathcal{D}_j(\underline{k}')$ from the Crystal Symmetry Combinations of Plane Waves

Once we have found a single set of ℓ_j CSCPW's which form a basis set for the representation $\mathcal{D}_j(\underline{k}')$, we can easily determine all of the matrices in the representation $\mathcal{D}_j(\underline{k}')$ by means of the fundamental relation

$$P_{Ls}S^j_{pm}(\underline{r}) = \sum_{n=1}^{\ell_j} D^j(Ls)_{nm}S^j_{pn}(\underline{r}). \tag{5.22}$$

(See Eq. (23), Ch. XI, in Wigner's book (28).)

Thus, to find the m-th column of the matrix representing Ls in the representation $\mathcal{D}_j(\underline{k}')$, we operate with P_{Ls} on the known symmetry combination $S^j_{pm}(\underline{r})$ (the m-th combination in the set $S^j_{pn}(\underline{r})$, $n = 1, \ldots, \ell_j$, which is known to form a basis set for $\mathcal{D}_j(\underline{k}')$), using the definition

$$P_{Ls}S^j_{pm}(\underline{r}) = S^j_{pm}(Ls^{-1}\underline{r}) \tag{5.23}$$

and Table 1 to simplify the left-hand side of Eq. (5.22). The resulting combination of plane waves must be a linear combination of the set $S^j_{pn}(\underline{r})$:

$$P_{Ls}S^j_{pm}(\underline{r}) = S^j_{pm}(Ls^{-1}\underline{r}) = \sum_{n=1}^{\ell_j} \gamma_n S^j_{pn}(\underline{r}). \tag{5.24}$$

We determine the γ_n by inspection, or if need be, by using the relation

$$\gamma_n = (S^j_{pm}(Ls^{-1}\underline{r}),\ S^j_{pn}(\underline{r})), \tag{5.25}$$

which is a consequence of Eq. (4.17) applied to the set of functions $S^j_{pn}(\underline{r})$. Comparing Eqs. (5.22) and (5.24), we see that $\gamma_n = D^j(Ls)_{nm}$, one of the desired elements of the m-th column of $D^j(Ls)$.

As an illustration of this procedure we work out the matrices representing several symmetry operations Ls in $\mathcal{O}_3(000)$, using S^3_{11}, S^3_{12}, S^3_{13}, CSCPW constructed from $\langle 111 \rangle$ in B of this Section. In this example alone, to simplify the notation, we write S_1 for S^3_{11}, S_2 for S^3_{12}, and S_3 for S^3_{13}, since we deal only with one representation.

Let us obtain the matrix representing $L2 = \{\delta_{2z}|0\}$ in $\mathcal{O}_3(000)$:

$$P_{L2}S_1 = (1/\sqrt{8})(-4+3+2+1-8+7+6+5) = S_1$$

$$P_{L2}S_2 = (1/\sqrt{8})(-4+3-2-1-8+7-6-5) = -S_2$$

$$P_{L2}S_3 = (1/\sqrt{8})(-4-3+2-1-8-7+6-5) = -S_3. \tag{5.26}$$

Thus, the matrix representing L2 in $\mathcal{O}_3(000)$ is

$$D^3(L2) = \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix} . \tag{5.27}$$

As a second example, we find for L45:

$$P_{L45}S_1 = (1/\sqrt{8})(-7+6+8+5-3+2+4+1) = S_2$$

$$P_{L45}S_2 = (1/\sqrt{8})(-7+6-8-5-3+2-4-1) = -S_3$$

$$P_{L45}S_3 = (1/\sqrt{8})(-7-6+8-5-3-2+4-1) = -S_1; \tag{5.28}$$

thus,

$$D^3(I45) = \begin{matrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{matrix} . \tag{5.29}$$

Proceeding in this way we have determined matrices representing all 48 of the elements in Γ for the representation $\mathscr{D}_3(000)$; these are given in Table 5. The representation $\mathscr{D}_4(000) = \Gamma_{15}$ can also be obtained from Table 5 by means of the following relations:

$$D^4(In) = D^3(In),\ n = 1, 2, \ldots, 24$$
$$D^4(In) = -D^3(In),\ n = 25, 26, \ldots, 48 . \tag{5.30}$$

In the representation $\mathscr{D}_1(000) = \Gamma_1$, all of the symmetry operations in Γ are represented by (1); in $\mathscr{D}_2(000) = \Gamma_2'$, the first 24 operations are represented by (1), and the last 24 by (−1).

We have now given explicitly the matrices of the representations Γ_1, Γ_2', Γ_{25}', and Γ_{15}; these are the representations which are needed in determining the wave functions for the valence and conduction states in a diamond-type crystal.

Table 5: MATRICES REPRESENTING $\Gamma_{25}' = \mathcal{D}_3(000)$

$$D(1) = \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad D(9) = \begin{matrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{matrix} \qquad D(17) = \begin{matrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{matrix}$$

$$D(2) = \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix} \qquad D(10) = \begin{matrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{matrix} \qquad D(18) = \begin{matrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{matrix}$$

$$D(3) = \begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad D(11) = \begin{matrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{matrix} \qquad D(19) = \begin{matrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{matrix}$$

$$D(4) = \begin{matrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix} \qquad D(12) = \begin{matrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{matrix} \qquad D(20) = \begin{matrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{matrix}$$

$$D(5) = \begin{matrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{matrix} \qquad D(13) = \begin{matrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad D(21) = \begin{matrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{matrix}$$

$$D(6) = \begin{matrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{matrix} \qquad D(14) = \begin{matrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{matrix} \qquad D(22) = \begin{matrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{matrix}$$

$$D(7) = \begin{matrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{matrix} \qquad D(15) = \begin{matrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{matrix} \qquad D(23) = \begin{matrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{matrix}$$

$$D(8) = \begin{matrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{matrix} \qquad D(16) = \begin{matrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad D(24) = \begin{matrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{matrix}$$

$$D(n + 24) = D(n), \quad n = 1, 2, \ldots, 24$$

Note: In this table, $D(n)$ means $D^3(In)$.

D. Use of the Representation Matrices in the Production of Crystal Symmetry Combinations of Plane Waves

With the aid of the representation matrices for $\mathcal{D}_j(\underline{k}')$, which we have shown how to construct in sub-section C, it is easy to obtain a CSCPW belonging to a specified row of a specified representation $\mathcal{D}_j(\underline{k}')$ of the group $G^{\underline{k}'}/T^{\underline{k}'}$ from any set $\langle k_1k_2k_3\rangle$ which spans a space in which a subspace is transformed according to $\mathcal{D}_j(\underline{k}')$. We learn which representations $\mathcal{D}_j(\underline{k}')$ describe the ways in which the subspaces of the space spanned by $\langle k_1k_2k_3\rangle$ transform under $G^{\underline{k}'}/T^{\underline{k}'}$ from the character analysis of sub-section A. Then, to obtain a CSCPW belonging to the n-th row of a particular representation $\mathcal{D}_j(\underline{k}')$ from the set $\langle k_1k_2k_3\rangle$, we choose any one of the plane waves in $\langle k_1k_2k_3\rangle$, say $W_r(\underline{r})$ and use the fact that

$$\sum_s D^j(Ls)_{nn}P_{Ls}W_r = \lambda_r S^j_n \tag{5.31}$$

where λ_r is a proportionality constant which may be zero. (See Eq. 6 of Ch. XII in Wigner (28)). If λ_r is zero for a particular choice of W_r, then we choose other plane waves from the set $\langle k_1k_2k_3\rangle$ and use them in Eq. (5.16) until we find one for which λ_r does not vanish. Then by normalizing the plane wave combination

$$\sum_s D^j(Ls)_{nn}P_{Ls}W_r\ , \tag{5.32}$$

we obtain a CSCPW S^j_n belonging to the n-th row of the representation $\mathcal{D}_j(\underline{k}')$. The operations in (5.32) can be carried out easily and efficiently by making use of the operating table for $P_{Ls}W_r$ and a long thin slip of paper on which the numbers $D^j(Ls)_{nn}$ are entered in a column, for s ranging from 1 to 48, with the same spacing between entries as between the rows in the operating table. When this "column slip" is placed beside the column in the operating table which gives the results of applying the various operations P_{Ls} to the particular plane wave W_r, the sum

$$\sum_s D^j(Ls)_{nn}P_{Ls}W_r$$

can be read off very rapidly.

For example, let us build the CSCPW's which transform according to Γ'_{25} from the set $\langle 200 \rangle$; the operation table for this set is given in Table 4, with

$$\begin{aligned} W_1 &= [200] \\ W_2 &= [020] \\ W_3 &= [002] \\ W_4 &= [\bar{2}00] \\ W_5 &= [0\bar{2}0] \\ W_6 &= [00\bar{2}]. \end{aligned} \tag{5.33}$$

The three column slips are made up from Table 6. Using Tables 4 and 6, we obtain:

$$\sum_{s=1}^{48} D^3(Ls)_{11}P_{Ls}W_1 =$$

$$= 1\cdot 1 - 1\cdot 4 - 1\cdot 1 + 1\cdot 4 - 1\cdot 2 + 1\cdot 5 - 1\cdot 5 + 1\cdot 2 = 0,$$

$$\sum_{s=1}^{48} D^{3}(Ls)_{11}P_{Ls}W_{2}$$

$$= 1\cdot 2 - 1\cdot 5 + 1\cdot 5 - 1\cdot 2 + 1\cdot 4 - 1\cdot 1 - 1\cdot 4 + 1\cdot 1 = 0,$$

$$\sum_{s=1}^{48} D^{3}(Ls)_{11}P_{Ls}W_{3}$$

$$= 1\cdot 3 + 1\cdot 3 + 1\cdot 6 + 1\cdot 6 + 1\cdot 6 + 1\cdot 6 + 1\cdot 3 + 1\cdot 3 = 4\cdot 3 + 4\cdot 6 \; ;$$

(5.34)

and

$$\sum_{s=1}^{48} D^{3}(Ls)_{11}P_{Ls}W_{4} = 0,$$

$$\sum_{s=1}^{48} D^{3}(Ls)_{11}P_{Ls}W_{5} = 0,$$

$$\sum_{s=1}^{48} D^{3}(Ls)_{11}P_{Ls}W_{6} = 4\cdot 3 + 4\cdot 6.$$

(5.35)

Thus the CSCPW belonging to the first row of $\mathcal{D}_{3}(000)$ which can be made up from $\langle 200 \rangle$ is of the form

$$S^3_{11} = N\,(1\cdot 3 + 1\cdot 6),$$

where N can be taken equal to $1/\sqrt{2}$ so that the combination is normalized:

$$S^3_{11} = (1/\sqrt{2})(0\cdot 1 + 0\cdot 2 + 1\cdot 3 + 0\cdot 4 + 0\cdot 5 + 1\cdot 6). \tag{5.36}$$

Similarly, we obtain for the CSCPW belonging to the second row of $\mathcal{D}_3(000)$:

$$S^3_{12} = (1/\sqrt{2})(0\cdot 1 + 1\cdot 2 + 0\cdot 3 + 0\cdot 4 + 1\cdot 5 + 0\cdot 6), \tag{5.37}$$

and for the CSCPW belonging to the third row of $\mathcal{D}_3(000)$:

$$S^3_{13} = (1/\sqrt{2})(1\cdot 1 + 0\cdot 2 + 0\cdot 3 + 1\cdot 4 + 0\cdot 5 + 0\cdot 6). \tag{5.38}$$

By these methods, and with the aid of the representation matrices given in sub-section C, all of the CSCPW's given in Table 7 can be determined. The OPW calculations for silicon which follow are based on those symmetry combinations and those alone. As given in Table 7, the CSCPW's are not normalized, but it requires only simple mental arithmetic to determine the normalization constant for each combination.

Table 6: COLUMNS DERIVED FROM $\Gamma_{25}' = \mathcal{D}_3(000)$

s	$D^3(Ls)_{11}$	$D^3(Ls)_{22}$	$D^3(Ls)_{33}$
1	1	1	1
2	1	−1	−1
3	−1	−1	1
4	−1	1	−1
5	−1	0	0
6	−1	0	0
7	0	0	−1
8	0	0	−1
9	0	−1	0
10	0	−1	0
11	1	0	0
12	0	1	0
13	0	0	1
14	1	0	0
15	0	1	0
16	0	0	1
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0
21	0	0	0
22	0	0	0
23	0	0	0
24	0	0	0

$D^3(L[n + 24]) = D^3(Ln), \quad n = 1, 2, \ldots, 24$

Table 7: SOME CRYSTAL SYMMETRY COMBINATIONS OF PLANE WAVES ASSOCIATED WITH $G^{(000)}/T^{(000)}$ IN O_h^7

	$\Gamma_1 = \mathcal{D}_1(000)$	$\Gamma_2' = \mathcal{D}_2(000)$	$\Gamma_{25}' = \mathcal{D}_3(000)$			$\Gamma_{15} = \mathcal{D}_4(000)$		
	s^1_{11}	s^2_{11}	s^3_{11}	s^3_{12}	s^3_{13}	s^4_{11}	s^4_{12}	s^4_{13}
0 0 0	1							
1 1 1	1	1	1	1	1	1	1	1
$1\ \bar{1}\ \bar{1}$	−1	−1	1	1	−1	1	1	−1
$\bar{1}\ 1\ \bar{1}$	−1	−1	1	−1	1	1	−1	1
$\bar{1}\ \bar{1}\ 1$	−1	−1	−1	1	1	−1	1	1
$\bar{1}\ \bar{1}\ \bar{1}$	1	−1	1	1	1	−1	−1	−1
$\bar{1}\ 1\ 1$	−1	1	1	1	−1	−1	−1	1
$1\ \bar{1}\ 1$	−1	1	1	−1	1	−1	1	−1
$1\ 1\ \bar{1}$	−1	1	−1	1	1	1	−1	−1
2 0 0		1	0	0	1			
0 2 0		1	0	1	0			
0 0 2		1	1	0	0			
$\bar{2}\ 0\ 0$		−1	0	0	1			
$0\ \bar{2}\ 0$		−1	0	1	0			
$0\ 0\ \bar{2}$		−1	1	0	0			
2 2 0	1		1	0	0	0	1	1
2 0 2	1		0	1	0	1	0	1
0 2 2	1		0	0	1	1	1	0
$\bar{2}\ 2\ 0$	−1		1	0	0	0	−1	1
$\bar{2}\ 0\ 2$	−1		0	1	0	−1	0	1
$0\ \bar{2}\ 2$	−1		0	0	1	−1	1	0
$\bar{2}\ \bar{2}\ 0$	1		1	0	0	0	−1	−1
$\bar{2}\ 0\ \bar{2}$	1		0	1	0	−1	0	−1
$0\ \bar{2}\ \bar{2}$	1		0	0	1	−1	−1	0
$2\ \bar{2}\ 0$	−1		1	0	0	0	1	−1
$2\ 0\ \bar{2}$	−1		0	1	0	1	0	−1
$0\ 2\ \bar{2}$	−1		0	0	1	1	−1	0

VI. THE FACTORIZED SECULAR DETERMINANT

To make use of the results of the preceding three sections we return to Eq. (2.12) and write for the trial function for a valence or conduction state in the crystal:

$$\psi_{i,\underline{k}}(\underline{r}) = \sum_{i,p,m} \sum_{\underline{K}} a^{i}_{pm}(\underline{k} + \underline{K}) S^{i}_{pm}(\Pi_{\underline{k}} + \underline{K}), \qquad (6.1)$$

where $S^{i}_{pm}(\Pi_{\underline{k}} + \underline{K})$ is our symbol for the p-th crystal symmetry combination of planes waves belonging to the m-th row of the i-th irreducible representation of $G^{\underline{k}}{}'/T^{\underline{k}}{}'$, but with the plane wave $e^{i(\underline{k} + \underline{K})\cdot\underline{r}}$ replaced by the orthogonalized plane wave $\Pi_{\underline{k} + \underline{K}}(\underline{r})$. The summation over $\underline{K}$ is over reciprocal lattice vectors (multiplied by 2π) which we specify in advance for each trial function, and the summations over i, p, and m are over all the positive integers characterizing those CSCPW's which can be built up from the set

$$P_{L_j} e^{i(\underline{k} + \underline{K})\cdot\underline{r}}, \; j = 1, 2, \ldots , g(\underline{k}).$$

For example, in silicon we use as a trial function for the crystal wave function having $\underline{k} = 0$, Eq. (6.1) with $\underline{K} = (2\pi/a)(0,0,0)$, $(2\pi/a)(1,1,1)$, $(2\pi/a)(2,0,0)$, and $(2\pi/a)(2,2,0)$. For $\underline{K} = (2\pi/a)(0,0,0)$: (p = 1, m = 1); for $\underline{K} = (2\pi/a)(1,1,1)$: i = 1 (p = 1, m = 1), i = 2 (p = 1, m = 1), i = 3 (p = 1, m = 1,2,3), i = 4 (p = 1, m = 1,2,3); for $\underline{K} = (2\pi/a)(2,0,0)$: i = 2 (p = 1, m = 1), i = 3 (p = 1, m = 1,2,3), i = 5 (p = 1, m = 1,2); for $\underline{K} = (2\pi/a)(2,2,0)$: i = 1 (p = 1, m = 1), i = 3 (p = 1, m = 1,2,3), i = 4 (p = 1,

$m = 1,2,3$), $i = 6$ ($p = 1$, $m = 1,2$), $i = 7$ ($p = 1$, $m = 1,2,3$). The linear transformation of the trial function in going from Eq. (2.12) to Eq. (6.1) effects a similarity transformation of the matrix

$$\left(\Pi_{\underline{K}}, H\Pi_{\underline{K}'}\right) - E\left(\Pi_{\underline{K}}, \Pi_{\underline{K}'}\right) \tag{6.2}$$

appearing in Eq.(2.15), so that after rearrangement of rows and columns, this matrix consists entirely of zero elements except for blocks which are symmetrical about the principal diagonal. This transformation of the matrix (6.2) simplifies or factors the determinant in Eq. (2.15) into a product of determinants of lower order; some of these determinants may be identical. In fact, it is easy to see that the use of the trial function (6.1) will lead to a secular equation

$$\det\left[\left(S^{i}_{pm}(\Pi_{\underline{K}}), HS^{i'}_{p'm'}(\Pi_{\underline{K}'})\right) - E\left(S^{i}_{pm}(\Pi_{\underline{K}}), S^{i'}_{p'm'}(\Pi_{\underline{K}'})\right)\right] = 0; \tag{6.3}$$

from Eqs. (2.19), (2.20), and (4.28) we know that an element will vanish unless $\underline{K} - \underline{K}'$ is 2π times a reciprocal lattice vector $\underline{h}/a$, and also $i = i'$, and $m = m'$; if these conditions are satisfied, then elements which differ only by having different $m = m'$ will be the same.

Below we give explicitly the four determinants appearing as factors in the determinant of (6.3) which lead to the four lowest energy values for the valence and excited states of electrons in silicon crystal. These explicit forms have been obtained with the help of the table of CSCPW's (Table 7) and Eqs. (2.18) and (2.20). Each determinant is labelled with the symbol for the irreducible representation characterizing the functions $S^{i}_{pm}(\Pi_{\underline{K}})$ from which its elements are formed. These symbols are all different, so that each of the four determinants is associated with a crystal wave function of different symmetry. For the n × n determinant associated with a crystal wave function of wave vector $\underline{k} = (0,0,0)$ and symmetry type Γ, we write

$$\Delta^{\Gamma}_{n}(000) = \det\left[M^{\Gamma}_{ij}(000)\right],\ i,\ j = 1,2,\ \ldots\ , n. \tag{6.4}$$

In the following four determinants for silicon crystal we have suppressed the $\underline{k}$ label, which is $\underline{k} = (0,0,0)$ in each case:

$$\Delta^{\Gamma_1}_{3}$$

$$M^{\Gamma_1}_{11} = -|V_{000}| + K^2_{000} + (0,0)_{1s,2s} - E$$

$$M^{\Gamma_1}_{12} = M^{\Gamma_1}_{21} = 2\sqrt{2}|V_{111}| - 2(3,0)_{1s,2s}$$

$$M^{\Gamma_1}_{22} = -|V_{000}| - 3|V_{220}| + K^2_{111} + 4(3,3)_{1s,2s} - E$$

$$M^{\Gamma_1}_{13} = M^{\Gamma_1}_{31} = -2\sqrt{3}(-|V_{220}| + (8,0)_{1s,2s})$$

$$M^{\Gamma_1}_{23} = M^{\Gamma_1}_{32} = -\sqrt{6}(|V_{111}| + 2|V_{311}| + |V_{331}|) + 4\sqrt{3}(8,3)_{1s,2s}$$

$$M^{\Gamma_1}_{33} = -|V_{000}| - 4|V_{220}| - 2|V_{400}| - 4|V_{422}|$$

$$-|V_{440}| + K^2_{220} + 12(8,8)_{1s,2s} - E$$

$$\Delta^{\Gamma_2'}_{2}$$

$$M^{\Gamma_2'}_{11} = -|V_{000}| - 3|V_{220}| + K^2_{111} - 4(3,3)_{1s,2s} - E$$

$$M^{\Gamma_2'}_{12} -- M^{\Gamma_2'}_{21} = 2\sqrt{3}(-|V_{111}| - |V_{311}| + \sqrt{2}(4,3)_{1s,2s})$$

$$M_{22}^{\Gamma_2'} = -|V_{000}| - 4|V_{220}| - |V_{400}| + \not{k}^2_{200}$$

$$+ 6(4,4)_{1s,2s} - E$$

$\Delta_3^{\Gamma_{25}'}$

$$M_{11}^{\Gamma_{25}'} = -|V_{000}| + |V_{220}| + \not{k}^2_{111} + \frac{4}{3}(3,3)_{2p} - E$$

$$M_{12}^{\Gamma_{25}'} = -2|V_{111}| + 2|V_{311}| + \frac{4}{\sqrt{6}}(4,3)_{2p}$$

$$M_{22}^{\Gamma_{25}'} = -|V_{000}| + |V_{400}| + \not{k}^2_{200} + 2(4,4)_{2p} - E$$

$$M_{13}^{\Gamma_{25}'} = M_{31}^{\Gamma_{25}'} = -\sqrt{2}(|V_{111}| + |V_{331}| - 2|V_{311}|)$$

$$M_{23}^{\Gamma_{25}'} = M_{32}^{\Gamma_{25}'} = 0$$

$$M_{33}^{\Gamma_{25}'} = -|V_{000}| - |V_{440}| + 2|V_{400}| + \not{k}^2_{220} - E$$

$\Delta_2^{\Gamma_{15}}$

$$M_{11}^{\Gamma_{15}} = -|V_{000}| + |V_{220}| + \not{k}^2_{111} + \frac{4}{3}(3,3)_{2p} - E$$

$$M_{12}^{\Gamma_{15}} = M_{21}^{\Gamma_{15}} = -2|V_{111}| + 2|V_{331}| + \frac{4}{\sqrt{3}}(8,3)_{2p}$$

$$M_{22}^{\Gamma_{15}} = -|V_{000}| - 2|V_{220}| + |V_{440}| + 2|V_{422}| + \not{k}^2_{220} + 4(8,8)_{2p} - E.$$

In writing the elements M_{ij}^{Γ} we have used the following notations, in addition to those previously introduced:

$$(h^2, h'^2)_{n\ell,n'\ell'}, \ldots \equiv 2(E - E_{n\ell})A^*_{n\ell}(2\pi h/a)A_{n\ell}(2\pi h/a)$$

$$+ 2(E - E_{n'\ell'})A_{n'\ell'}(2\pi h/a)A_{n'\ell'}(2\pi h/a)$$

$$+ \ldots \qquad (6.5)$$

$$k_{\underline{h}} \equiv (2\pi/a)(h_1^2 + h_2^2 + h_3^2)^{\frac{1}{2}}. \tag{6.6}$$

The determinants given are all based on the trial function built up from the sets of plane waves $\langle 000\rangle$, $\langle 111\rangle$, $\langle 200\rangle$, and $\langle 220\rangle$. If we had included in the trial function only the set $\langle 000\rangle$ we should have obtained only $\Delta_1^{\Gamma_1}$ with $M_{11}^{\Gamma_1}$ as given above; if we had used only $\langle 000\rangle$ and $\langle 111\rangle$, we should have obtained

$$\Delta_2^{\Gamma_1} = \begin{vmatrix} M_{11}^{\Gamma_1} & M_{12}^{\Gamma_1} \\ M_{21}^{\Gamma_1} & M_{22}^{\Gamma_1} \end{vmatrix}$$

with $M_{ij}^{\Gamma_1}$ as given above, and

$$\Delta_1^{\Gamma_2'} = \left|M_{11}^{\Gamma_2'}\right|, \quad \Delta_1^{\Gamma_{25}'} = \left|M_{11}^{\Gamma_{25}'}\right|, \quad \Delta_1^{\Gamma_{15}} = \left|M_{11}^{\Gamma_{15}}\right|;$$

the addition of $\langle 200\rangle$ to the trial function borders the determinant $\Delta_1^{\Gamma_2'}$ with $M_{12}^{\Gamma_2'}$, $M_{22}^{\Gamma_2'}$, and $M_{21}^{\Gamma_2'}$; and $\Delta_1^{\Gamma_{25}'}$ with $M_{12}^{\Gamma_{25}'}$, $M_{22}^{\Gamma_{25}'}$, $M_{21}^{\Gamma_{25}'}$.

Similarly, the addition of each set $\langle k_1 + h_1, k_2 + h_2, k_3 + h_3\rangle$ to the trial function results in the addition of a border to some or all of the four determinants. Thus, we obtain successive approximations to the energy eigenvalues of the two valence states and the two lowest conduction states in the silicon crystal by adding successive sets of crystal symmetry combinations of orthogonalized plane waves (CSCOPW) to the trial function. The lowest solution of the secular equation $\Delta_n^{\Gamma} = 0$ (Γ stands for any one of the four symbols Γ_1, Γ_2',

Γ_{25}', Γ_{15}) we call E_n^{Γ}; from the variational principle we know that

$$E_{n+1}^{\Gamma} \leq E_n^{\Gamma} . \tag{6.7}$$

In Sections VII and VIII, which follow, we obtain explicit formulas for the various functions which enter into the matrix elements M_{ij}^{Γ} given above, and apply them to the case of silicon crystal.

VII. WAVE FUNCTIONS AND ASSOCIATED ENERGY PARAMETERS AND ORTHOGONALITY COEFFICIENTS FOR THE CORE STATES

In Section II, the problem of finding wave functions for the core electrons in the crystal was reduced by means of the tight-binding approximation to the problem of finding wave functions $\varphi_{n\ell m}(\underline{r})$ for the core electrons in the isolated atoms forming the crystal.

The equation for the determination of $\varphi_{n\ell m}(\underline{r})$ and the associated energy eigenvalue $E_{n\ell}$ was (2.11), or:

$$H_{atomic}\,\varphi_{n\ell m}(\underline{r}) = E_{n\ell}\,\varphi_{n\ell m}(\underline{r}) \tag{7.1}$$

with

$$H_{atomic} = -\nabla^2 + V_{atomic}(\underline{r}) \tag{7.2}$$

and

$$V_{atomic}(\underline{r}) = -\frac{2Z}{|\underline{r}|} + 2\sum_{j=1}^{Z}\int_{\infty}\frac{\varphi_j^*(\underline{r}')\,\varphi_j(\underline{r}')}{|\underline{r}-\underline{r}'|}\,d\underline{r}' - 6\left\{(3/8\pi)\sum_{j=1}^{Z}\varphi_j^*(\underline{r})\varphi_j(\underline{r})\right\}^{1/3}. \tag{7.3}$$

In this section we discuss methods for obtaining approximate solutions of Eq. (7.1). When the wave functions $\varphi_{n\ell m}(\underline{r})$ have been determined, they can be used in Eq. (2.10) to give the wave functions of the core electrons in the crystal, and in Eq. (2.14) to provide us with the values of $A_{n\ell}(K)$ which are required in the secular equations of Sections VI for the energy eigenvalues of valence and conduction electrons. Also required in setting up these secular determinants are values of $E_{n\ell}$ from Eq. (7.1) for the core states, and the Fourier coefficients $v(\underline{K})$ of the potential energy function of an electron in the crystal. From Eqs. (2.19), (2.9), and (7.3) we see that $v(\underline{K})$ can be determined from the wave functions $\varphi_{n\ell m}(\underline{r})$ for the core and valence electrons in the isolated atom in the valence state.

Our first step in this section (sub-section A) is to determine very approximate wave functions $\varphi^{(0)}_{n\ell m}$ for all the electrons in the isolated atom from Slater's empirical rules (16). Using these functions we compute the potential energy function in the free atom from Eq. (7.3), the crystal potential from Eq. (2.9), and then the Fourier coefficients of the crystal potential from Eq. (2.19). Once computed these functions are used without any alteration throughout the reminder of this work.

We could then use for the zero-order approximation to $E_{n\ell}$, $E^{(0)}_{n\ell}$, the quantum-mechanical expectation value of H_{atomic} for the state $\varphi_{n\ell m}$:

$$E^{(0)}_{n\ell} = \int_{\infty} \varphi^{*}_{n\ell m}(\underline{r}) H_{\text{atomic}} \varphi_{n\ell m}(\underline{r}) d\underline{r}$$

Also we could compute the required functions $A_{n\ell}(K)$ from the functions $\varphi^{(0)}_{n\ell m}(\underline{r})$ and then proceed to the solution of the final secular equations of Section VII for $E_i(\underline{k})$ in the valence and conduction states. In a previous effort to reproduce Herman's results for the diamond crystal (9), we did carry through just this program; however, our results for E_i (000) did not converge as well as Herman's and there was a serious disagreement between our results so calculated, and those of Herman, in that we found $E^{\Gamma_2'}(000) < E^{\Gamma_{15}}(000)$, as far as we carried the calculation. We observed that our results for diamond were very sensitive to the values of $\left[A_{n\ell}(K)\right]^2$ which we used, and $A_{n\ell}(K)$ in turn was very sensitive to the behavior of $P_{n\ell}(r)$, the radial part of the wave function $\varphi_{n\ell m}(\underline{r})$, in its tail region (the region $r > r_0$, where r_0 is the largest number such that $dP_{n\ell}(r)/dr = 0$). Hence, we concluded, $\varphi^{(0)}_{n\ell m}(\underline{r})$ and $E^{(0)}_{n\ell}$ are not sufficiently good solutions of the eigenfunction-eigenvalue problem of Eq. (7.1). We then devised a method for obtaining eigenfunctions $\varphi^{(1)}_{n\ell m}(\underline{r})$ and eigenvalues $E^{(1)}_{n\ell}$ which are better approximations to the solutions of (7.1) with $V_{\text{atomic}}(\underline{r})$ still given by the substitution of $\varphi^{(0)}_{n\ell m}(\underline{r})$ in Eq. (7.3).

When we had applied this method in a rough way to carbon and repeated the calculations of $E_i(000)$ for diamond, using $E^{(1)}_{n\ell}$ and values of $A_{n\ell}(K)$ computed from $\varphi^{(1)}_{n\ell m}(r)$, we obtained agreement with Herman's values of $E_i(000)$ to within the accuracy of our calculation at each of the stages of the approximation which we attempted. The method for obtaining $\varphi^{(1)}_{n\ell m}(\underline{r})$ and $E^{(1)}_{n\ell}$ is described and applied to silicon in the second part of this section (sub-section B).

In sub-section C, formulas are given for the computation of the necessary values of $A_{n\ell}(K)$.

A. Orthogonalized and Normalized Slater Functions: $\varphi^{(0)}_{n\ell m}(\underline{r})$

By substituting Eq. (2.5) in Eq. (7.1) and separating in the usual way we obtain the following equation for $P_{n\ell}(r)$, the radial part of $\varphi_{n\ell m}(\underline{r})$:

$$\frac{d^2P_{n\ell}(r)}{dr^2} + \left[E_{n\ell} - V_{\text{atomic}}(r) - \frac{\ell(\ell+1)}{r^2}\right] P_{n\ell}(r) = 0, \tag{7.4}$$

where $V_{\text{atomic}}(r)$ is the same as $V_{\text{atomic}}(\underline{r})$ (Eq. 7.3) in the cases of interest to us, for which $V_{\text{atomic}}(\underline{r})$ is a spherically symmetric function of $\underline{r}$. The studies of Slater (17) and Pratt (32) have established the fact that the solutions $P_{n\ell}(r)$ of Eq. (7.4) represent the radial one-electron atomic wave functions to a very good approximation. Now by means of Slater's empirical rules we construct radial one-electron atomic wave functions $P^{(0)}_{n\ell}(r)$; insofar as they are good approximations, they should satisfy Eq. (7.4).

For a neutral atom with Z electrons, the radial functions which we construct according to Slater's simplest rules (16) are of the type

$$P^{(S)}_{n\ell}(r) = N_n(Z)r^{n^*}e^{-(Z-s)r/n^*} \tag{7.5}$$

where n^* depends on n, and s depends on n and ℓ, according to the rules given by Slater (16), and $N_n(Z)$ is a normalization constant, which is chosen so that $P_{n\ell}(r)$ satisfies Eq. (2.7). In general, these functions approximate only the tails of the one-electron atomic wave functions. But if, using ideas developed in a later paper by Slater (20), we use (7.5) to obtain the functions $P_{n\ell}(r)$ for electronic states with n and ℓ such that $n-\ell = 1$, and orthogonalize the functions given by (7.5) for the states with n and ℓ such that $n - \ell = 2,3,4$, to all of the functions (previously obtained) for the states with smaller n and the same ℓ, we obtain functions which everywhere resemble the Hartree or Hartree-Fock one-electron radial atomic wave functions. For example, in the case of the silicon atom, $Z = 14$, for all states arising from the configuration $(1s)^2(2s)^2(2p)^6 3s(3p)^3$ using Eq. (7.5) we get

$$P_{1s}^{(S)}(r) = N_1(14)\, r e^{-\lambda_1 r}$$

$$P_{2s}^{(S)}(r) = P_{2s}^{(S)}(r) = N_2(14)\, r^2 e^{-\lambda_2 r}$$

$$P_{3s}^{(S)}(r) = P_{3p}^{(S)}(r) = N_3(14)\, r^3 e^{-\lambda_3 r},$$

where (7.6)

$$\lambda_1 = \frac{14 - 0.30}{1} = 13.70$$

$$\lambda_2 = \frac{14 - 7 \times 0.35 - 2 \times 0.85}{2} = \frac{9.85}{2} = 4.925$$

$$\lambda_3 = \frac{14 - 3 \times 0.35 - 8 \times 0.85 - 2 \times 1.00}{3} = \frac{4.15}{3} = 1.38333\ldots$$

For our $P^{(0)}$ and $P_{2p}^{(0)}$ we use $P_{1s}^{(S)}$ and $P_{2p}^{(S)}$ as given in (7.6). For $P_{2s}^{(0)}$, we take

$$P_{2s}^{(0)} = N_{2s}(14)\left[P_{2p}^{(S)} - (P_{2p}^{(S)}, P_{1s}^{(0)})P_{1s}^{(0)}\right], \tag{7.7}$$

which is orthogonal to $P_{1s}^{(0)}$; for $P_{3s}^{(0)}$ we take

$$P_{3s}^{(0)} = N_{3s}(14)\left[P_{3p}^{(S)} - (P_{3p}^{(S)}, P_{1s}^{(0)})P_{1s}^{(0)} - (P_{3p}^{(S)}, P_{2s}^{(0)})P_{2s}^{(0)}\right], \tag{7.8}$$

which is orthogonal to $P_{1s}^{(0)}$ and $P_{2s}^{(0)}$; and for $P_{3p}^{(0)}$ we take

$$P_{3p}^{(0)} = N_{3p}(14)\left[P_{3p}^{(S)} - (P_{3p}^{(S)}, P_{2p}^{(0)})P_{2p}^{(0)}\right], \tag{7.9}$$

which is orthogonal to $P_{2p}^{(0)}$. The constants $N_{n\ell}(14)$ are determined so that

$$\int_0^\infty \left[P_{n\ell}^{(0)}\right]^2 dr = 1. \tag{7.10}$$

In explicit form the functions $P_{n\ell}^{(0)}(\underline{r})$ on which all of the calculations for silicon are based are as follows:

$$P_{1s}^{(0)} = 101.41702 \; r \, e^{-13.70000r} \tag{7.11}$$

$$P_{2s}^{(0)} = 65.474552 \; r^2 e^{-4.925000r} - 33.578420 \; r \, e^{-13.70000r} \tag{7.12}$$

$$P_{2p}^{(0)} = 62.156271 \; r^2 e^{-4.925000r} \tag{7.13}$$

$$P_{3s}^{(0)} = 1.3304028 \; r^3 e^{-1.383333r} - 10.769874 \; r^2 e^{-4.925000r} + 5.1026382 \; r \, e^{-13.70000r} \tag{7.14}$$

$$P_{3p}^{(0)} = 1.3288878_4 \; r^3 e^{-1.383333r} - 9.7757812 \; r^2 e^{-4.925000r} \tag{7.15}$$

As can be seen from Eqs. (7.6)-(7.10), the constants in these functions depend only on λ_1, λ_2, and λ_3; they are given to seven significant figures (with a doubtful eighth figure carried, to avoid rounding off) because that many significant figures are needed in some of the work to follow. Our final results for the silicon crystal do not depend on what figures we write in these constants in the fourth through the eighth places of each, but we must make some choice for them and adhere to that choice thoughout the following calculations. We could have put zeros in all of these places, but we preferred to assume that λ_1, λ_2, λ_3 are given to seven figures, and carry the consequences of that assumption in the computing. For the seven-figure values of the λ's we used

$$\begin{aligned} \lambda_1 &= 13.70000 \\ \lambda_2 &= 4.925000 \\ \lambda_3 &= 1.38333 . \end{aligned} \tag{7.16}$$

B. Determination of $\varphi^{(1)}_{n\ell m}(\underline{r})$ and $E^{(1)}_{n\ell}$, the Refined Atomic Wave Functions and Energy Eigenvalues

For the reasons indicated in sub-section A, the functions $\varphi^{(0)}_{n\ell m}(\underline{r})$ can be expected to provide rough solutions of Eq. (7.4) with $V_{\text{atomic}}(r)$ replaced by $V^{(0)}_{\text{atomic}}(r)$ as given in Eq. (7.3) with $\varphi^{(0)}_{n\ell m}(\underline{r})$ substituted for $\varphi_j(\underline{r})$. If they were exact solutions of this equation, the energy eigenvalue $E^{(0)}_{n\ell}$ associated with $\varphi^{(0)}_{n\ell m}(\underline{r})$ would be given exactly by

$$W^{(0)}\left[P^{(0)}_{n\ell}(r)\right] = \int_0^\infty P^{(0)*}_{n\ell}\left[-d^2/dr^2 + V_{\text{atomic}}(r) + \ell(\ell+1)/r^2\right]P^{(0)}_{n\ell}\,dr; \tag{7.17}$$

if $\varphi^{(0)}_{n\ell m}(r)$ is not very different from the the exact solution of Eq. (7.4) then $W^{(0)}$ should give a good estimate of the energy eigenvalue for the state labelled by n and ℓ.

In any case, we know from the variational principle that

$$W^{(0)}\left[P^{(i)}_{1\ell}(r)\right] \geq E^{(0)}_{1\ell} \tag{7.18}$$

where $P^{(i)}_{1\ell}(\underline{r})$ is any trial function and $E^{(0)}_{1\ell}$ is the lowest eigenvalue of the radial part of the atomic Hamiltonian operator

$$\mathcal{H}^{(0)}(\ell) = -d^2/dr^2 + V^{(0)}_{\text{atomic}}(r) + \ell(\ell+1)/r^2. \tag{7.19}$$

Likewise, if $P^{(i)}_{n\ell}(r)$ is a trial function which is orthogonal to all of the true eigenfunctions of $\mathcal{H}^{(0)}(\ell)$ with smaller total quantum numbers n and the same azimuthal quantum number ℓ, then

$$W^{(0)}\left[P^{(i)}_{n\ell}(r)\right] \geq E^{(0)}_{n\ell},$$

where $E^{(0)}_{n\ell}$ is the energy eigenvalue associated with the true eigenfunction of $\mathcal{H}^{(0)}(\ell)$. Obviously, we can make use of these consequences of the variational principle to obtain approximate solutions of Eq. (7.4) with $V_{\text{atomic}}(r) = V^{(0)}_{\text{atomic}}(r)$ which are better than the functions $P^{(0)}_{n\ell}$ given in (7.11)-(7.15). An appropriate form for the trial functions $P^{(1)}_{n\ell}(r)$ is suggested by the work of Löwdin (33) who was able to fit the numerical solutions of the Hartree-Fock equations for several different atoms by expressions of the form

$$P_{1s}(r) = r\sum_j A_j e^{-a_j r}$$

$$P_{2s}(r) = r\sum_j A_j e^{-a_j r} - r^2\sum_j B_j e^{-b_j r}$$

$$P_{2p}(r) = r^2\sum_j B_j e^{-b_j r}$$

$$P_{3s}(r) = r\sum_j A_j e^{-a_j r} - r^2\sum_j B_j e^{-b_j r} + r^3\sum_j C_j e^{-c_j r} \tag{7.20}$$

$$P_{3p}(r) = r^2\sum_j B_j e^{-b_j r} - r^3\sum_j C_j e^{-c_j r}$$

......, etc.,

where the exponents a_j, b_j, ... , and the coefficients A_j, B_j, ... , may be different in each radial function. Our procedure for obtaining refined (radial) atomic wave functions $P^{(1)}_{n\ell}(r)$ is to determine the coefficients A_j, B_j, ... , in trial functions of the form (7.20) with judiciously chosen exponents so as to minimize $W^{(0)}\left[P^{(1)}_{n\ell}(r)\right]$; $E^{(1)}_{n\ell}$ is the resulting minimum value of $W^{(0)}\left[P_{n\ell}^{(1)}(r)\right]$. The function $P_{n\ell}^{(1)}(r)$ is considered a better or more refined solution of (7.4) with $V(r) = V^{(0)}(r)$ than $P_{n\ell}^{(0)}(r)$ if $E_{n\ell}^{(1)} < W^{(0)}\left[P_{n\ell}^{(0)}(r)\right]$. There can be no unique choice for the exponents in expressions like (7.20). The extent to which $P_{n\ell}^{(1)}(r)$ is a better solution of Eq. (7.4) than $P_{n\ell}^{(0)}(r)$ depends on the number of terms included in the summation over j in the trial functions $P_{n\ell}^{(1)}(r)$ and the skill with which the exponents a_j, b_j, ... , are chosen. The choice of the exponents is discussed in connection with the illustrative calculations for silicon which follow.

It should be clear that the method outlined could be used to obtain atomic wave functions in the analytical form of (7.20) which are (to any desired degree) self-consistent solutions of Eq. (7.4).

Thus the (first-)refined functions $P_{n\ell}^{(1)}(r)$ could be used to obtain a (first-)refined estimate of $V_{\text{atomic}}(r)$, call it $V_{\text{atomic}}^{(1)}(r)$; this (first-)refined potential could be used in place of $V_{\text{atomic}}^{(0)}(r)$ in Eq. (7.4); and (second-)refined solutions could be obtained by the same methods used to determine $P_{n\ell}^{(1)}$ in $V^{(0)}(r)$. The cycle could be repeated until the desired degree of self-consistency had been attained. We have not proved that this process is convergent, but if the functions used for $P_{n\ell}^{(0)}(r)$ are well chosen it seems to us not unreasonable to expect it to converge. Since the study of this process for obtaining solutions of Eq. (7.4) is not the object of this investigation, we have not tried to improve our initial estimate of $V_{\text{atomic}}(r)$ by using the solutions $P_{n\ell}^{(1)}(r)$ in Eq. (7.3). Instead, as already mentioned, we use our initial estimate, $V_{\text{atomic}}^{(0)}(r)$, of $V_{\text{atomic}}(r)$ in all that follows. The important point is that we use the <u>same</u> estimate of $V_{\text{atomic}}(r)$ in computing the crystal potential V(r) (see Section VIII) and in determining the atomic core functions $\varphi_{n\ell m}(\underline{r})$ and hence the crystal core functions (see Eq. 2.10).

For the sake of convenience in computation we take for the trial function $P^{(1)}_{n\ell}(r)$:

$$P^{(1)}_{n\ell}(r) = \sum_{j=1}^{t_{n\ell}} A_{n\ell;j}\,\xi_{n\ell;j}(r) \tag{7.21}$$

where $\xi_{.j}(r)$ is normalized:

$$\int_0^\infty \left[\xi_{n\ell;j}(r)\right]^2 dr = 1,$$

and orthogonalized to all of the (previously determined) functions $P^{(1)}_{n\ell}(r)$ with the same ℓ quantum number and a smaller n quantum number:

$$\int_0^\infty \xi_{n\ell;j}(r) P^{(1)}_{n'\ell}(r)\,dr = 0$$

for $n' < n$ and all j.

The functions $\xi_{n\ell;j}(r)$ are given by

$$\xi_{1s;j}(r) = \eta_1(r;\, a_j)$$

$$\xi_{2s;j}(r) = N_{2s,j}\left[\eta_2(r;\, b_j) - \left(\eta_2(r;\, b_j)\middle| P^{(1)}_{1s}(r)\right) P^{(1)}_{1s}(r)\right]$$

$$\xi_{2p;j}(r) = \eta_2(r;\, b_j)$$

$$\xi_{3s;j}(r) = N_{3s;j}\left[\eta_3(r;\, c_j) - \left(\eta_3(r;\, c_j)\middle| P^{(1)}_{2s}(r)\right) P^{(1)}_{2s}(r) - \left(\eta_3(r;\, c_j)\middle| P^{(1)}_{1s}(r)\right) P^{(1)}_{1s}(r)\right]$$

$$\xi_{3p;j}(r) = N_{3p;j}\left[\eta_3(r;\, c_j) - \left(\eta_3(r;\, c_j)\middle|P^{(1)}_{2p}(r)\right)P^{(1)}_{2p}(r)\right]$$

... etc.,

(7.22)

where

$$\eta_m(r;\, a) = N_{ma}r^m e^{-ar}$$

(7.23)

and N_{ma} is chosen so that

$$\int_0^\infty \left[\eta_m(r;\, a)\right]^2 dr = 1,$$

(7.24)

i. e.,

$$N_{ma} = (a^{m+1}/\Gamma(m+1))^{\frac{1}{2}}.$$

(7.25)

Note that the exponents b_j, c_j, ... , which appear explicitly in (7.22) as they are written may be different in different ξ functions. Starting with the functions $\xi_{1s;j}$ all of the functions $\xi_{n\ell;j}$ (and $P^{(1)}_{n\ell}$) can be constructed in succession by means of (7.22). The expressions (7.22) can then be seen to be of the same form as those in (7.20), but with the additional property

$$\int_0^\infty P^{(1)}_{n\ell}(r)P_{n'\ell'}(r)dr = \delta_{nn'}.$$

(7.26)

The equations determining the values of $A_{n\ell;j}$ which minimize $W^{(0)}\left[P^{(1)}_{n\ell}(r)\right]$ are (see Pauling and Wilson (22), Section 26d):

$$\sum_{i=1}^{t_{n\ell}} A_{n\ell;i}\left[(\xi_{n\ell;i}|\mathcal{H}^{(0)}(\ell)|\xi_{n\ell;j}) - E(\xi_{n\ell;i}|\xi_{n\ell;j})\right] = 0, \tag{7.27}$$

$j = 1, \ldots, t_{n\ell}$.

These equations have a non-trivial solution if and only if

$$\det\left[(\xi_{n\ell;i}|\mathcal{H}^{(0)}(\ell)|\xi_{n\ell;j}) - E(\xi_{n\ell;i}|\xi_{n\ell;j})\right] = 0. \tag{7.28}$$

The lowest root of Eq. (7.27) is $E = W^{(0)}\left[P^{(1)}_{n\ell}(r)\right] = E^{(1)}_{n\ell}$. When this root has been found and substituted into the equations (7.27) they can be solved for $A_{n\ell;2}, \ldots, A_{n\ell;t_{n\ell}}$ in terms of $A_{n\ell;1}$, which is then adjusted so that $P^{(1)}_{n\ell}(r)$ is normalized.

From Eqs. (7.22), we see that the evaluation of the matrix elements $(\xi_{n\ell;i}|\mathcal{H}^{(0)}(\ell)|\xi_{n\ell;j})$ can be reduced to the evaluation of matrix elements:

$$(\eta_p(r;\, b)|\mathcal{H}^{(0)}(\ell)|\eta_q(r;\, c)), \tag{7.29}$$

and we now work out explicit expressions for these matrix elements in the case of silicon. The first step is to obtain $\mathcal{H}^{(0)}(\ell)$, and hence $V^{(0)}_{\text{atomic}}$, as given by Eq. (7.3), in a form with which we can compute.

We note that for the valence state of silicon

$$\rho(r) = \sum_{j=1}^{Z} \varphi^*_j(\underline{r})\varphi_j(\underline{r}) = 2\left|\varphi_{1,0,0}(\underline{r})\right|^2$$

$$+\ 2\left|\varphi_{2,0,0}(\underline{r})\right|^2 + 2\left|\varphi_{2,1,-1}(\underline{r})\right|^2 + 2\left|\varphi_{2,1,0}(\underline{r})\right|^2$$

$$+ 2\left|\varphi_{2,1,1}(\underline{r})\right|^2 + \left|\varphi_{3,0,0}(\underline{r})\right|^2 + \left|\varphi_{3,1,-1}(\underline{r})\right|^2$$

$$+\left|\varphi_{3,1,0}(\underline{r})\right|^2 + \left|\varphi_{3,1,1}(\underline{r})\right|^2$$

$$= (1/4\pi r^2)(2\left[P_{1s}(r)\right]^2 + 2\left[P_{2s}(r)\right]^2 + 6\left[P_{2p}(r)\right]^2$$

$$+ \left[P_{3s}(r)\right]^2 + 3\left[P_{3p}(r)\right]^2), \tag{7.30}$$

where we have used Eq. (2.5) and

$$\begin{aligned} Y_{0,0} &= (1/4\pi)^{\frac{1}{2}} \\ Y_{1,-1} &= (3/8\pi)^{\frac{1}{2}} \sin\theta\ e^{i\varphi} \\ Y_{1,0} &= (3/4\pi)^{\frac{1}{2}} \cos\theta \\ Y_{1,-1} &= (3/8\pi)^{\frac{1}{2}} \sin\theta\ e^{-i\varphi}. \end{aligned} \tag{7.31}$$

The electronic charge density in the isolated atom, called $\rho(r)$ in Eq. (7.30), is seen to be a function of r alone. For silicon, substituting $\varphi^{(1)}_{n\ell m}(\underline{r})$ for $\varphi_j(\underline{r})$ in (7.30), we obtain

$$\rho(r) = (1/4\pi r^2) \sum_{i=1}^{6} f_i r^{n_i} e^{-\alpha_i r}, \tag{7.32}$$

where

$$\begin{aligned} f_1 &= 7.0678003 & n_1 &= 6 \\ f_2 &= -106.60204 & n_2 &= 5 \\ f_3 &= 32156.934 & n_3 &= 4 \\ f_4 &= 13.577128 & n_4 &= 4 \\ f_5 &= -8904.0375 & n_5 &= 3 \\ f_6 &= 22851.882 & n_6 &= 2 \end{aligned}$$

$$\begin{aligned} \alpha_1 &= 2.766666 \\ \alpha_2 &= 6.308333 \\ \alpha_3 &= 9.850000 \\ \alpha_4 &= 15.08333 \\ \alpha_5 &= 18.62500 \\ \alpha_6 &= 27.40000. \end{aligned} \tag{7.33}$$

The electronic Coulomb term is

$$\begin{aligned} 2\sum_{j=1}^{Z}\int_{\infty}\frac{\varphi_j^*(\underline{r}')\varphi_j(\underline{r}')}{|\underline{r}-\underline{r}'|}\,d\underline{r}' &= 2\int_{\infty}\frac{\sum_{j=1}^{Z}\varphi_j^*(\underline{r}')\varphi_j(\underline{r}')}{|\underline{r}-\underline{r}'|}\,d\underline{r}' \\ = 2\int_{\infty}\frac{\rho(r')}{|\underline{r}-\underline{r}'|}\,d\underline{r}' &= (2/r)\int_0^r\rho(r')dr' + 2\int_r^{\infty}\frac{\rho(r')}{r'}\,dr', \end{aligned} \tag{7.34}$$

where in writing the last of the equalities in (7.34) use has been made of well-known results from potential theory on the potential function in a spherically symmetric medium of varying density. Thus, the atomic potential energy function can be written

$$V_{\text{atomic}}(r) = -\frac{2Z}{r} + \frac{2}{r}\int_0^r\rho(r')dr'$$

$$+ \; 2\int_{r}^{\infty} \frac{\rho(r')}{r'}\,dr' \; - \; 6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3}, \tag{7.35}$$

with $\rho(r)$ given by (7.30). The integrals in Eq. (7.35) are easily evaluated when $\rho(r)$ is replaced by the expression given in Eq. (7.32), with the result (for silicon):

$$\frac{2}{r}\int_{0}^{r} \rho(r')\,dr' \; + \; 2\int_{r}^{\infty} \frac{\rho(r')}{r'}\,dr' \; = \; \frac{2}{r}\sum_{j=1}^{6} f_j F(r;\, n_j,\, \alpha_j), \tag{7.36}$$

where

$$F(r;\, n_1, \alpha_1) \; = \; (1/\alpha_1^7)\Big[720 - e^{-\alpha_1 r}\big(720 + 600\,\alpha_1 r + 240(\alpha_1 r)^2 + 60(\alpha_1 r)^3 + 10(\alpha_1 r)^4 + (\alpha_1 r)^5\big)\Big]$$

$$F(r;\, n_2, \alpha_2) \; = \; (1/\alpha_2^6)\Big[120 - e^{-\alpha_2 r}\big(120 + 96\,\alpha_2 r + 36(\alpha_2 r)^2 + 8(\alpha_2 r)^3 + (\alpha_2 r)^4\big)\Big]$$

$$F(r;\, n_3, \alpha_3) \; = \; (1/\alpha_3^5)\Big[24 - e^{-\alpha_3 r}\big(24 + 18\,\alpha_3 r + 6(\alpha_3 r)^2 + (\alpha_3 r)^3\big)\Big]$$

$$F(r;\, n_4, \alpha_4) \; = \; (1/\alpha_4^5)\Big[24 - e^{-\alpha_4 r}\big(24 + 18\,\alpha_4 r + 6(\alpha_4 r)^2 + (\alpha_4 r)^3\big)\Big]$$

$$F(r;\, n_5, \alpha_5) \; = \; (1/\alpha_5^4)\Big[6 - e^{-\alpha_5 r}\big(6 + 4\alpha_5 r + (\alpha_5 r)^2\big)\Big]$$

$$F(r;\, n_6, \alpha_6) \; = \; (1/\alpha_6^3)\Big[2 - e^{-\alpha_6 r}\big(2 + \alpha_6 r\big)\Big]. \tag{7.37}$$

The exchange term in Eq. (7.3), which we call $\frac{-z(r)}{r}$, following Pratt (32), can now be written

$$-\frac{z(r)}{r} \equiv -6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3} = -6\left\{\frac{3}{32\pi^2}\sum_{i=1}^{6} f_i r^{n_i-2} e^{-\alpha_i r}\right\}^{1/3}. \tag{7.38}$$

With the exchange term in this form, the many integrations involving this term which must be performed to obtain the matrix elements (7.29) and the Fourier coefficients of potential (see Section VIII) could only be carried out numerically. To avoid these numerical integrations we evaluted (7.38) at 65 appropriately-spaced points in the interval $0 < r \leq 25$ where $z(r)/r$ differs significantly from zero, and then by empirical curve-fitting procedures we constructed the following function, $\not{z}(r)/r$, which reproduces very well the values of $z(r)/r$ at all of the 65 points and has the additional virtue of rendering easy the evaluation of the integrals involving $z(r)/r$ which are needed in computing the matrix elements (7.29) and the Fourier coefficients of potential:

$$\frac{\not{z}(r)}{r} \equiv \sum_{j=1}^{8} g_j r^{\nu_j} e^{-\beta_j r} \cong \frac{z(r)}{r}, \tag{7.39}$$

with

$\log_e g_1 = 3.5851613$ $\quad$ sign $g_1 = +$

$\log_e g_2 = 0.89141478$ $\quad$ sign $g_2 = +$

$\log_e g_3 = 8.6695650$ $\quad$ sign $g_3 = +$

$\log_e |g_4| = 7.6897000$ $\quad$ sign $g_4 = -$

$\log_e g_5 = 42.300400$ $\quad$ sign $g_5 = +$

$$\begin{array}{lll} \log_e|g_6| = 61.999900 & \qquad & \text{sign } g_6 = - \\ \log_e g_7 = 58.545900 & & \text{sign } g_7 = + \\ \log_e|g_8| = 27.354900 & & \text{sign } g_8 = - \end{array} \tag{7.40}$$

$$\begin{array}{lll} \nu_1 = 0 & \qquad & \beta_1 = 9.1333330 \\ \nu_2 = 1.3333330 & & \beta_2 = 0.9222220 \\ \nu_3 = 3.8150000 & & \beta_3 = 9.2190000 \\ \nu_4 = 8.7038000 & & \beta_4 = 9.8810000 \\ \nu_5 = 39.0000000 & & \beta_5 = 44.2150000 \\ \nu_6 = 38.0000000 & & \beta_6 = 75.0000000 \\ \nu_7 = 27.0000000 & & \beta_7 = 90.8700000 \\ \nu_8 = 9.0000000 & & \beta_8 = 72.0000000\ . \end{array}$$

The expression for $z(r)/r$ in (7.39) reproduces the values computed from (7.38) with a maximum error of 0.005% for $r \geq 3$, 0.025% for $1.4 \leq r \leq 3$, 0.6% for $0.22 \leq r \leq 1.4$, and 1% for $0 < r \leq 0.22$. Thus $\not{z}(r)/r$ was designed to reproduce $z(r)/r$ with considerable precision for $r \gtrsim 2$ because in this range $z(r)/r$ is a large part of $V_{\text{atomic}}(r)$ and isolated atom wave functions for silicon centered about points of the silicon lattice would overlap in this region. (Half of the distance between nearest neighbor nuclei in silicon crystal at room temperature is about $2.2a_o$.)

The final explicit expression for $V^{(0)}_{\text{atomic}}(r)$ is given by

$$V^{(0)}_{\text{atomic}}(r) = -(2Z/r) + (2/r)\sum_{j=1}^{6} f_j F_j(r;\, n_j, \alpha_j)$$

$$-\sum_{j=1}^{8} g_j r^{\nu_j} e^{-\beta_j r},$$

(7.41)

together with (7.33), (7.37), and (7.40). Using (7.41) we now evaluate (7.29); we make a slight simplification in the notation of (7.29) by writing

$$\eta_{pb} \equiv \eta_p(r;\, b), \qquad \eta_{qc} \equiv \eta_q(r;\, c).$$

It is also convenient to introduce

$$m \equiv \frac{p+q}{2}, \qquad a \equiv \frac{b+c}{2}.$$

(7.42)

By simple analysis, including the use of formula (861.2) in Dwight (34), we obtain

$$(\eta_{pb}|\mathcal{H}^{(0)}(\ell)|\eta_{qc}) = (\eta_{pb}|\eta_{qc})\cdot$$

$$\cdot\left[\frac{p(p-1)c^2 - 2pqbc - q(q-1)b^2}{(p+q)(p+q-1)} - 2Z(\eta_{ma}|\frac{1}{r}|\eta_{ma})\right.$$

$$+ 2\sum_{j=1}^{6} f_j(\eta_{ma}|\frac{F_j}{r}|\eta_{ma}) - \sum_{j=1}^{8} g_j(\eta_{ma}|r^{\nu_j} e^{-\beta_j r}|\eta_{ma})$$

$$\left. + \ell(\ell+1)(\eta_{ma}|\frac{1}{r^2}|\eta_{ma})\right],$$

(7.43)

where

$$F_j = F(r;\, n_j, \alpha_j),$$

$$(\eta_{pb}|\eta_{qc}) = N_{pb}N_{qc}\int_0^\infty r^{p+q}e^{-(b+c)r}dr = \frac{N_{pb}N_{qc}}{(N_{ma})^2}, \tag{7.44}$$

$$(\eta_{ma}|\frac{1}{r}|\eta_{ma}) = N_{ma}^2\,\frac{\Gamma(2m)}{(2a)^{2m}}, \tag{7.45}$$

$$\begin{aligned}(\eta_{ma}|\frac{F_1}{r}|\eta_{ma}) = (N_{ma}^2/\alpha_1^7)\Bigg[720\,\frac{\Gamma(2m)}{(2a)^{2m}} - \frac{\Gamma(2m)}{(\alpha_1+2a)^{2m}}\,\cdot\\ \cdot\Bigg(720 + 600(2m)\,\frac{\alpha_1}{\alpha_1+2a} + 240(2m)(2m+1)\left(\frac{\alpha_1}{\alpha_1+2a}\right)^2\\ + 60(2m)(2m+1)(2m+2)\left(\frac{\alpha_1}{\alpha_1+2a}\right)^3\\ + 10(2m)(2m+1)(2m+2)(2m+3)\left(\frac{\alpha_1}{\alpha_1+2a}\right)^4\\ + (2m)(2m+1)(2m+2)(2m+3)(2m+4)\left(\frac{\alpha_1}{\alpha_1+2a}\right)^5\Bigg)\Bigg],\end{aligned} \tag{7.46.1}$$

$$\begin{aligned}(\eta_{ma}|\frac{F_2}{r}|\eta_{ma}) = (N_{ma}^2/\alpha_2^6)\Bigg[120\,\frac{\Gamma(2m)}{(2a)^{2m}} - \frac{\Gamma(2m)}{(\alpha_2+2a)^{2m}}\,\cdot\\ \cdot\Bigg(120 + 96(2m)\,\frac{\alpha_2}{\alpha_2+2a} + 36(2m)(2m+1)\left(\frac{\alpha_2}{\alpha_2+2a}\right)^2\\ + 8(2m)(2m+1)(2m+2)\left(\frac{\alpha_2}{\alpha_2+2a}\right)^3\\ + (2m)(2m+1)(2m+2)(2m+3)\left(\frac{\alpha_2}{\alpha_2+2a}\right)^4\Bigg)\Bigg],\end{aligned} \tag{7.46.2}$$

$$(\eta_{ma}|\frac{F_3}{r}|\eta_{ma}) = (N_{ma}^2/\alpha_3^5)\left[24\,\frac{\Gamma(2m)}{(2a)^{2m}} - \frac{\Gamma(2m)}{(\alpha_3+2a)^{2m}}\cdot\right.$$

$$\cdot\left(24 + 18(2m)\,\frac{\alpha_3}{\alpha_3+2a} + 6(2m)(2m+1)\left(\frac{\alpha_3}{\alpha_3+2a}\right)^2\right.$$

$$\left.\left.+ (2m)(2m+1)(2m+2)\left(\frac{\alpha_3}{\alpha + 2a}\right)^3\right)\right], \tag{7.46.3}$$

$$(\eta_{ma}|\frac{F_4}{r}|\eta_{ma}) = (N_{ma}^2/\alpha_4^5)\left[24\,\frac{\Gamma(2m)}{(2a)^{2m}} - \frac{\Gamma(2m)}{(\alpha_4+2a)^{2m}}\cdot\right.$$

$$\cdot\left(24 + 18(2m)\,\frac{\alpha_4}{\alpha_4+2a} + 6(2m)(2m+1)\left(\frac{\alpha_4}{\alpha_4+2a}\right)^2\right.$$

$$\left.\left.+ (2m)(2m+1)(2m+2)\left(\frac{\alpha_4}{\alpha_4+2a}\right)^3\right)\right], \tag{7.46.4}$$

$$(\eta_{ma}|\frac{F_5}{r}|\eta_{ma}) = (N_{ma}^2/\alpha_5^4)\left[6\,\frac{\Gamma(2m)}{(2a)^{2m}} - \frac{\Gamma(2m)}{(\alpha_5+2a)^{2m}}\cdot\right.$$

$$\left.\cdot\left(6 + 4(2m)\,\frac{\alpha_5}{\alpha_5+2a} + (2m)(2m+1)\left(\frac{\alpha_5}{\alpha_5+2a}\right)^2\right)\right], \tag{7.46.5}$$

$$(\eta_{ma}|\frac{F_6}{r}|\eta_{ma}) = (N_{ma}^2/\alpha_6^3)\left[2\,\frac{\Gamma(2m)}{(2a)^{2m}} - \frac{\Gamma(2m)}{(\alpha_6+2a)^{2m}}\right.$$

$$\left.\cdot\left(2 + 2m\,\frac{\alpha_6}{\alpha_6+2a}\right)\right], \tag{7.46.6}$$

$$(\eta_{ma}|r^{\nu_j}e^{-\beta_j r}|\eta_{ma}) = N_{ma}^2\Gamma(2m+\nu_j+1)/(2a+\beta_j)^{2m+\nu_j+1} \tag{7.47}$$

$$(\eta_{ma}|\frac{1}{r^2}|\eta_{ma}) = N_{ma}^2\Gamma(2m-1)/(2a)^{2m-1}\ . \tag{7.48}$$

From the preceding equations it is clear that the computation of the matrix elements $(\xi_{n\ell;i}|\mathcal{H}^{(0)}(\ell)|\xi_{n\ell;j})$, while perfectly straightforward, is a rather lengthy task, particularly since they must often be determined to many significant figures (8 or 9) in order to make possible the determination of the $A_{n\ell;i}$ in Eq. (7.27) to 4 or 5 significant figures. If many such matrix elements were required, it might be advisable to call upon automatic computing machinery for assistance. In the course of our silicon computations we computed seven matrix elements of this type with an ordinary 10-column Marchant desk computer in about eight days; to provide a check, these computations were then repeated, also by hand, by the computing service department of the Hughes Aircraft Company, with the expenditure of about eight more man-days.

For our silicon calculation we worked out, by the techniques described, refined wave functions and energy eigenvalues for the 2s and 2p atomic core states. We did not go to the trouble of refining the 1s wave function, partly because we felt that it would not be significantly changed by the refinement procedure, but mainly because of the fact that in the secular equations determining the energies of valence and conduction states in the silicon crystal, the 1s wave function and energy eigenvalue enter <u>only</u> through combinations of the type

$$\left(\left[A_{1s}(K)\right]^2 + \left[A_{2s}(K)\right]^2\right) \tag{7.49}$$

and

$$\left(E_{1s}\left[A_{1s}(K)\right]^2 + E_{2s}\left[A_{2s}(K)\right]^2\right); \tag{7.50}$$

it turns out, when the computations are performed, that

$$\left[A_{2s}(K)\right]^2 \sim 50\left[A_{1s}(K)\right]^2,$$

and

$$E_{2s}\left[A_{2s}(K)\right]^2 \sim 6E_{1s}\left[A_{1s}(K)\right]^2;$$

consequently we feel that errors arising from the unrefined functions and energy eigenvalues for the 1s state are likely to be no more significant in the calculation than those coming from the (first-)refined functions and energy eigenvalues for the 2s state.

Thus we take

$$P_{1s}^{(1)}(r) = P_{1s}^{(0)}(r) = 101.41702\ re^{-13.70000r} \tag{7.51}$$

As a trial function for the 2p state we use

$$\begin{aligned} P_{2p}^{(1)} &= A_{2p,1}\xi_{2p;1}(r) + A_{2p,2}\xi_{2p;2}(r) \\ &= A_{2p,1}\eta_2(r;\ 4.20) + A_{2p,2}\eta_2(r;\ 7.96) \\ &= A_{2p,1}N_{2,4.20}r^2e^{-4.20r} + A_{2p,2}N_{2,7.96}r^2e^{-7.96r}. \end{aligned} \tag{7.52}$$

The choice of the exponents 4.20 and 7.96 in this trial function was suggested by substituting

$$P_{2p}^{(1)}(r) = Nr^2(e^{-a_1r} + \alpha_2e^{-a_2r}),\ a_1 < a_2,$$

for $P_{n\ell}(r)$ in Eq. (7.4), along with $E_{2p}^{(0)}$ for E_{2p} and 1 for ℓ, and trying by successive approximations to adjust a_1, a_2, and α_2 so that (7.4) is satisfied or very nearly satisfied for a number of values of r. As indicated earlier, the choice of the smallest exponent a_1, which mainly governs the behavior of the tail of the function $P_{2p}(r)$, is especially important; it is convenient to fix a_1 first so that Eq. (7.4) can be approximately satisfied for large values of r; a_2 and α_2 are then adjusted so that the equation is satisfied for two smaller r values. Admittedly, the procedure outlined does not give an exact prescription for fixing "best" values of a_1 and a_2. However, it is perhaps more profitable to add an extra term to the trial function than to try to define "best" values for the exponents and then to set up an exact program for the determination of those "best" values. Using trial function (7.52), and evaluating the necessary matrix elements by Eq. (7.43), we find from Eq. (7.28) $E_{2p}^{(1)} = -8.17697$ and from Eq. (7.27),

$$P_{2p}^{(1)} = r^2(32.3954e^{-4.20r} + 55.6008e^{-7.96r}). \tag{7.53}$$

for the 2s state we take as a trial function

$$P_{2s}^{(1)}(r) = A_{2s,1}\xi_{2s;\,1}(r) + A_{2s,2}\xi_{2s,2}(r) \tag{7.54}$$

with

$$\xi_{2s;1} = N_{2s;1}\left[\eta_2(r;\,4.20) - \left(\eta_2(r;\,4.20)\middle|P_{1s}^{(1)}(r)\right)P_{1s}^{(1)}(r)\right]$$

$$\xi_{2s;2} = N_{2s;2}\left[\eta_2(r;\,7.96) - \left(\eta_2(r;\,7.96)\middle|P_{1s}^{(1)}(r)\right)P_{1s}^{(1)}(r)\right]. \tag{7.55}$$

Here we used the same η_2 functions as in Eq. (7.52) simply to economize the labor of evaluating the matrix elements in Eq. (7.28). By slightly altering the exponents 4.20 and 7.96 in these functions it might be possible to obtain a better $P_{2s}^{(1)}$ function than the one which we find by using (7.55), but we would not expect the improvement to be large. With trial function (7.54) we get $E_{2s} = -11.1237$ and

$$P_{2s}^{(1)} = 41.2929r^2e^{-4.20r} + 12.9072r^2e^{-7.96r} - 28.4408r\,e^{-13.70r} . \tag{7.56}$$

C. Orthogonality Coefficients for the Core States

According to Eq. (2.14), the orthogonality coefficient $A_{n\ell}(K)$ is given by

$$A_{n\ell}(K) = \frac{1}{(\Omega_0)^{\frac{1}{2}}} \int_{\infty} e^{i\underline{K}\cdot\underline{r}} \varphi_{n\ell;\underline{K}}(r)\,d\underline{r}. \tag{7.57}$$

In carrying out the integration we choose the z axis in the direction of $\underline{K}$; then, by the definition of $\varphi_{n\ell;\underline{K}}(\underline{r})$,

$$A_{n\ell}(K) = \frac{1}{(\Omega_0)^{\frac{1}{2}}} \int_{\infty} e^{iKr\cos\theta} \varphi^{*}_{n\ell 0}(\underline{r})\,d\underline{r}. \tag{7.58}$$

From Eq. (2.5),

$$\varphi_{n\ell 0}(\underline{r}) = \frac{1}{r} P_{n\ell}(r)\, Y_{\ell 0}(\theta,\varphi), \tag{7.59}$$

and from Eq. (19.9) of Schiff (35),

$$e^{iKr\cos\theta} = \sum_{\ell=0}^{\infty} (2\ell+1)\, i^{\ell}\, j_{\ell}(Kr)\, P_{\ell}(\cos\theta)$$

$$= \sum_{\ell=0}^{\infty} \left[4\pi(2\ell+1)\right]^{\frac{1}{2}} i^{\ell} j_{\ell}(Kr)\, Y_{\ell 0}(\theta,\varphi), \tag{7.60}$$

where $j_{\ell}(x)$ is the spherical Bessel function defined in Eq. (15.5) of Schiff (35); substituting (7.59) and (7.60) in (7.58), we obtain

$$A_{n\ell}(K) = \frac{1}{(\Omega_0)^{\frac{1}{2}}} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \frac{1}{r} P_{n\ell}(r)\, Y^*_{\ell 0} \cdot$$

$$\cdot \sum_{s=0}^{\infty} \left[4\pi(2s+1)\right]^{\frac{1}{2}} i^s j_s(Kr)\, Y_{s0}(\theta,\varphi) .\quad r^2 \cos\theta \, d\varphi \, d\theta \, dr$$

$$= \left[\frac{4\pi(2\ell+1)}{\Omega_0}\right]^{\frac{1}{2}} i^{\ell} \int_0^{\infty} r\, P_{n\ell}(r) \cdot j_{\ell}(Kr)\, dr, \tag{7.61}$$

since

$$\int_0^{\pi}\int_0^{2\pi} Y^*_{\ell m}\, Y_{\ell' m'} \cos\theta \, d\varphi \, d\theta = \delta_{\ell\ell'}\, \delta_{mm'} . \tag{7.62}$$

We now make appropriate substitutions for $P_{n\ell}(r)$, ℓ, and $j_{\ell}(Kr)$ in Eq. (7.61) in order to compute the values of $A_{n\ell}(K)$ needed in the secular equations of Section VI. It is convenient to write the atomic core functions $P^{(1)}_{n\ell}(r)$ which we obtained in sub-section B as follows:

$$P^{(1)}_{1s}(r) = B_{1s}\, r\, e^{-b_3 r}$$

$$P^{(1)}_{2s}(r) = \sum_{j=1}^{3} B_{2s,j}\, r^{m_j} e^{-b_j r}$$

$$P^{(1)}_{2p}(r) = \sum_{j=1}^{2} B_{2p,j}\, r^{m_j} e^{-b_j r} \tag{7.63}$$

with

$$\begin{array}{llll} B_{1s} = 2b_1^{3/2} & = 101.41702 & m_1 & = 2 \\ B_{2s,1} & = 41.2929 & m_2 & = 2 \\ B_{2s,2} & = 12.9072 & m_3 & = 1 \\ B_{2s,3} & = -28.4408 & & \\ B_{2p,1} & = 32.3954 & & \\ B_{2p,2} & = 55.6008 & & \end{array}$$

$$\begin{aligned} b_1 &= 4.20 \\ b_2 &= 7.96 \\ b_3 &= 13.70\,. \end{aligned} \qquad (7.64)$$

Thus

$$\begin{aligned} A_{1s}(K) &= \left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}} \int_0^\infty r\, P_{1s}^{(1)}(r)\left(\frac{\sin Kr}{Kr}\right) dr \\ &= \left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}} \frac{B_{1s}}{K} \int_0^\infty r\, e^{-b_3 r} \sin Kr\, dr \\ &= \left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}} \frac{4\, b_3^{\ 5/2}}{(b_3^2 + K^2)}, \end{aligned} \qquad (7.65)$$

$$A_{2s}(K) = \left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}} \int_0^\infty r\, P_{2s}^{(1)}(r)\left(\frac{\sin Kr}{Kr}\right)dr$$

$$= \left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}} \frac{1}{K} \int_0^\infty \sum_{j=1}^{3} B_{2s,j}\, r^{m_j} e^{-b_j r} \sin Kr)\,dr$$

$$= \left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}} \frac{1}{K} \sum_{j=1}^{3} B_{2s,j} \int_0^\infty r^{m_j} e^{-b_j r} \sin Kr\, dr$$

$$= 2\left(\frac{4\pi}{\Omega_0}\right)^{\frac{1}{2}} \left[B_{2s,1}\frac{(3b_1^2 - K^2)}{(b_1^2 + K^2)^3} + B_{2s,2}\frac{(3b_2^2 - K^2)}{(b_2^2 + K^2)^3} \right.$$

$$\left. + B_{2s,3}\frac{b_3}{(b_3^2 + K^2)^2} \right], \qquad (7.66)$$

$$A_{2p}(K) = i\left(\frac{12}{\Omega_0}\right)^{\frac{1}{2}} \int_0^\infty r\, P_{2p}^{(1)}(r) \left[\frac{\sin Kr}{(Kr)^2} - \frac{\cos Kr}{Kr}\right] dr$$

$$= i\left(\frac{12\pi}{\Omega_0}\right)^{\frac{1}{2}} \sum_{j=1}^{2} B_{2p,j} \int_0^\infty r^3 e^{-b_j r} \left[\frac{\sin Kr}{(Kr)^2} - \frac{\cos Kr}{Kr}\right] dr$$

$$= i\left(\frac{12\pi}{\Omega_0}\right)^{\frac{1}{2}} \sum_{j=1}^{2} B_{2p,j}\, \frac{2b_j}{K} \left[\frac{1}{(b_j^2 + K^2)^2} - \frac{(b_j^2 - 3K^2)}{(b_j^2 + K^2)^3}\right]$$

$$= i\left(\frac{12\pi}{\Omega_0}\right)^{\frac{1}{2}} 8K \left[\frac{B_{2p,1} b_1}{(b_1^2 + K^2)^3} + \frac{B_{2p,2} b_2}{(b_2^2 + K^2)^3}\right]; \qquad (7.67)$$

where we have used the integration formulas

$$\int_0^\infty r\, e^{-br} \sin(Kr)\, dr = \frac{2bK}{(b^2 + K^2)^2}$$

$$\int_0^\infty r^2 e^{-br} \sin(Kr)\, dr = \frac{2K(3b^2 - K^2)}{(b^2 + K^2)^3}$$

$$\int_0^\infty r^2 e^{-br} \cos(Kr)\, dr = \frac{2b(b^2 - 3K^2)}{(b^2 + K^2)^3}, \tag{7.68}$$

which are easily derived by differentiation with respect to a parameter from (577.1) and (577.2) of Dwight (34), and

$$j_1(x) = \frac{\sin x}{x}$$

$$j_2(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}, \tag{7.69}$$

from (15.6) of Schiff (35).

We recall that Ω_0 is the volume of the unit cell; for a diamond-type crystal with our choice of unit cell, $\Omega_0 = \frac{a^3}{4}$, where a is the lattice constant. The value of the lattice constant for silicon given in Eq. (3.4), which we use throughout this work is

$$a = 5.43100 \times 10^{-8} \text{ cm.} = 10.2632_2 a_0; \tag{7.70}$$

we took this value from a paper by Conwell (36) which is very commonly used as a source of numerical constants in semiconductor calculations. The value as quoted by Conwell was obtained by rounding off the lattice constant reported by Straumanis and Aka (37) for 99.97% pure silicon at 20°C; according to their data the rounded-off value is equal to the lattice constant in this impure material at about 27°C--a common temperature in California laboratories. For our approximate calculations it would be sufficient to know the lattice constant to three figures, but at various stages in this work we felt that it might be useful to carry out the calculations as if our input numbers were more accurately known, and for this reason we used the lattice constant given in (7.70) throughout. We include this information for the benefit of anyone who may wish to repeat these calculations.

The values of $A_{n\ell}(K)$ needed in the secular equations of Section VI, computed from Eqs. (7.65)-(7.67), are as follows:

h^2	$A_{1s}(2\pi h/a)$	$A_{2s}(2\pi h/a)$	$-iA_{2p}(2\pi h/a)$
0	$0.017009\underline{4}$	$0.17107\underline{7}$	0.0000000
3	$0.016807\underline{5}$	$0.13881\underline{5}$	$0.070474\underline{0}$
4	$0.016740\underline{9}$	$0.12976\underline{4}$	$0.076932\underline{6}$
8	$0.016478\underline{8}$	$0.10007\underline{1}_{\underline{3}}$	$0.087912\underline{4}$

VIII. FOURIER COEFFICIENTS OF THE POTENTIAL ENERGY FUNCTION.

The only quantities entering into the secular equations of Section VI which remain to be computed are the Fourier coefficients of the potential energy of an electron, $v(\underline{K})$.

Our crystal potential energy function is given by

$$V^{(0)}(\underline{r}) = \sum_{\nu} V_{atomic}(\underline{r} - \underline{R}_{\nu}) \tag{8.1}$$

where

$$V^{(0)}_{atomic}(\underline{r}) = -\frac{2Z}{r} + \frac{2}{r}\int_{0}^{r} \rho(r')dr' + 2\int_{r}^{\infty} \frac{\rho(r')}{r'}dr' - 6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3}. \tag{8.2}$$

The Fourier coefficients of the contribution to the potential arising from the first two terms (the Coulomb terms) can be easily computed by obtaining the Fourier coefficients of the charge distribution, which are related to the Coulomb terms through Poisson's equation. It is convenient to write

$$V^{(0)\,Coulomb}_{atomic} = -\frac{2Z}{r} + \frac{2}{r}\int_{0}^{r} \rho(r')dr' + 2\int_{r}^{\infty} \frac{\rho(r')}{r'}dr' \tag{8.3}$$

$$V^{(0)\,exchange}_{atomic} \equiv -6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3}. \tag{8.4}$$

In atomic units, and with $V^{(0)\,Coulomb}_{atomic}$ representing the Coulombic potential energy of an electron in the field of the atom, Poisson's equation is

$$\nabla^2 \overset{(0)}{V}{}^{\text{Coulomb}}_{\text{atomic}} = 8\pi \rho^{\text{total}}_{\text{atomic}} ,$$

(8.5)

where $\rho^{\text{total}}_{\text{atomic}}$ is the total number of positive charges of the magnitude of the charge on an electron per cm^3. Let

$$\overset{(0)}{V}{}^{\text{Coulomb}}(\underline{r}) = \sum_{\nu} \overset{(0)}{V}{}^{\text{Coulomb}}_{\text{atomic}}(\underline{r} - \underline{R}_{\nu}) = \sum_{\underline{h}} \overset{(0)}{V}{}^{\text{Coulomb}}_{\underline{h}} e^{-\frac{2\pi i}{a} \underline{h}\cdot\underline{r}} ,$$

(8.6)

where $\underline{h}/a$ is a reciprocal lattice vector and $V_{\underline{h}} = v(\frac{2\pi}{a}\underline{h})$,

$$\rho^{\text{nuclear}}_{\text{crystal}}(\underline{r}) = Z \sum \delta(\underline{r} - \underline{R}_{\nu}) = \sum_{\underline{h}} \rho^{\text{nuclear}}_{\underline{h}} e^{-\frac{2\pi i}{a} \underline{h}\cdot\underline{r}} ,$$

(8.7)

and

$$\rho^{\text{electronic}}_{\text{crystal}}(\underline{r}) = - \sum \rho^{\text{electronic}}_{\text{atomic}}(|\underline{r} - \underline{R}_{\nu}|)$$

$$= - \sum_{\underline{h}} \rho^{\text{electronic}}_{\underline{h}} e^{-\frac{2\pi i}{a} \underline{h}\cdot\underline{r}}$$

(8.8)

($\rho^{\text{electronic}}_{\text{atomic}}(r)$ is called $\rho(r)$ in Section VII).

Then

$$\nabla^2 V^{(0)\text{Coulomb}} = -\left(\frac{2\pi}{a}\right)^2 \sum_{\underline{h}} V_{\underline{h}}\, h^2 e^{-\frac{2\pi i}{a}\underline{h}\,\underline{r}}$$

$$= 8\pi \rho^{\text{total}}_{\text{atomic}}$$

$$= 8\pi \sum_{\underline{h}} \left[\rho^{\text{nuclear}}_{\underline{h}} - \rho^{\text{electronic}}_{\underline{h}}\right] e^{-\frac{2\pi i}{a}\underline{h}\cdot\underline{r}}. \qquad (8.9)$$

Thus

$$V^{(0)\text{Coulomb}}_{\underline{h}} = -\frac{2a^2}{\pi h^2}\left[\rho^{\text{nuclear}}_{\underline{h}} - \rho^{\text{electronic}}_{\underline{h}}\right] \qquad (8.10)$$

for $h^2 \neq 0$.

We now determine $\rho^{\text{nuclear}}_{\underline{h}}$ and $\rho^{\text{electronic}}_{\underline{h}}$, making use of the fact that for a diamond-type crystal with our choice of unit cell, origin, and reference frame (see Section III), and with appropriate numbering of the lattice points,

$$\underline{R}_\nu = \underline{R}_{\underline{n}(\nu)} + \underline{d}_1, \quad \nu = 1, 2, \ldots, N, \qquad (8.11)$$

and for the other half of the lattice points,

$$\underline{R}_\nu = \underline{R}_{\underline{n}(\nu)} + \underline{d}_2, \quad \nu = N+1, N+2, \ldots, 2N, \qquad (8.12)$$

where

$$\underline{R}_{\underline{n}(\nu)} = \underline{R}_{n_1(\nu)n_2(\nu)n_3(\nu)} = n_1(\nu)\underline{a}_1 + n_2(\nu)\underline{a}_2 + n_3(\nu)\underline{a}_3,$$

$\underline{n}(\nu) = n(\nu + N)$, and the $\underline{a}_i$ and $\underline{d}_j$

vectors are given in Eqs. (3.2), (3.3):

$$\rho_{\underline{h}}^{\text{nuclear}} = \frac{1}{(N\Omega_o)} \int e^{\frac{2\pi i}{a}\,\underline{h}\cdot\underline{r}} \left[Z \sum_{\nu} \delta(\underline{r} - \underline{R}_{\nu})\right] d\underline{r}$$

$$= \frac{Z}{(N\Omega_o)} \sum_{\nu} e^{\frac{2\pi i}{a}\,\underline{h}\cdot\underline{R}_{\nu}} \int_{\infty} e^{\frac{2\pi i}{a}\,\underline{h}\cdot(\underline{r} - \underline{R}_{\nu})} \delta(\underline{r} - \underline{R}_{\nu})\, d\underline{r}$$

$$= \frac{Z}{\Omega_o} \sum_{j=1}^{2} e^{\frac{2\pi i}{a}\,\underline{h}\cdot\underline{d}_j} = \frac{2Z}{\Omega_o} \cos \frac{\pi}{4}\,(h_1 + h_2 + h_3)\,, \tag{8.13}$$

$$\rho_{\underline{h}}^{\text{electronic}} = \frac{1}{N\Omega_o} \int_{\infty} e^{\frac{2\pi i}{a}\,\underline{h}\cdot\underline{r}} \sum_{\nu} \rho_{\text{atomic}}^{\text{electronic}}(|\underline{r} - \underline{R}_{\nu}|)$$

$$= \frac{1}{N\Omega_o} \sum_{\nu} e^{\frac{2\pi i}{a}\,\underline{h}\cdot\underline{R}_{\nu}} \int_{\infty} e^{\frac{2\pi i}{a}\,\underline{h}\cdot(\underline{r} - \underline{R}_{\nu})} \rho_{\text{atomic}}^{\text{electronic}}(|\underline{r} - \underline{R}_{\nu}|)\, d\underline{r}$$

$$= \frac{1}{\Omega_o} \sum_{j=1}^{2} e^{\frac{2\pi i}{a}\,\underline{h}\cdot\underline{d}_j} \int_{\infty} e^{\frac{2\pi i}{a}\,\underline{h}\cdot(\underline{r} - \underline{R}_{\nu})} \rho_{\text{atomic}}^{\text{electronic}}(|\underline{r} - \underline{R}_{\nu}|)\, d\underline{r}$$

$$= \frac{2}{\Omega_o} \cos\left[\frac{\pi}{4}\,(h_1 + h_2 + h_3)\right] \int_{\infty} e^{\frac{2\pi i}{a}\,\underline{h}\cdot\underline{r}} \rho_{\text{atomic}}^{\text{electronic}}(r)\, d\underline{r}$$

$$= \frac{2}{\Omega_o} \cos\left[\frac{\pi}{4}\,(h_1 + h_2 + h_3)\right] \int_{0}^{\infty} \rho_{\text{atomic}}^{\text{electronic}}(r)\, \frac{\sin(2\pi hr/a)}{2\pi hr/a}\, r^2 dr. \tag{8.14}$$

Hence,

$$V_{\underline{h}}^{(0)\text{Coulomb}} = -\frac{4a^2}{\pi\,\Omega_0 h^2}\cos\left[\frac{\pi}{4}(h_1+h_2+h_3)\right]\cdot$$

$$\cdot\left[Z - \int_0^\infty 4\pi r^2 \rho^{\text{electronic}}_{\text{atomic}}(r)\,\frac{\sin(2\pi hr/a)}{2\pi hr/a}\,dr\right]. \tag{8.15}$$

For the exchange term we have:

$$V^{(0)\text{exchange}}_{\text{atomic}} = \sum_{\nu} V^{(0)\text{exchange}}_{\text{atomic}}(|\underline{r} - \underline{R}_\nu|) = \sum_{\underline{h}} V_{\underline{h}}^{(0)\text{exchange}}\, e^{-\frac{2\pi i}{a}\underline{h}\cdot\underline{r}}, \tag{8.16}$$

where the equality of the first two terms is a consequence of the approximation in Eq. (2.9). From Eqs. (7.38) and (8.4) we see that

$$V^{(0)\text{exchange}}_{\text{atomic}}(r) = -6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3} = -\frac{z(r)}{r} \cong -\frac{\not{z}(r)}{r}; \tag{8.17}$$

it follows that

$$V_{\underline{h}}^{(0)\text{exchange}} = -\frac{1}{N\Omega_0}\int_\infty e^{\frac{2\pi i}{a}\underline{h}\cdot\underline{r}}\sum_{\nu}\frac{\not{z}(|\underline{r} - \underline{R}_\nu|)}{|\underline{r} - \underline{R}_\nu|}\,d\underline{r}$$

$$= -\frac{1}{N\Omega_0}\sum e^{\frac{2\pi i}{a}\underline{h}\cdot\underline{R}_\nu}\int_\infty e^{\frac{2\pi i}{a}\underline{h}\cdot(\underline{r} - \underline{R}_\nu)}\,\frac{\not{z}(|\underline{r} - \underline{R}_\nu|)}{|\underline{r} - \underline{R}_\nu|}\,d\underline{r}$$

$$= -\frac{2}{\Omega_0}\cos\left[\frac{\pi}{4}(h_1+h_2+h_3)\right]4\pi\int_0^\infty \not{z}(r)\,\frac{\sin(2\pi hr/a)}{2\pi hr/a}\,r\,dr. \tag{8.18}$$

$$= -\frac{4a}{\Omega_0 h}\cos\left[\frac{\pi}{4}(h_1+h_2+h_3)\right]\int_0^\infty \not{z}(r)\sin(2\pi hr/a)\,dr.$$

For h $\neq$ 0 then,

$$V_{\underline{h}}^{(0)} = -\frac{4a^2}{\pi\Omega_0}\,\frac{\cos\left[(\pi/4)(h_1+h_2+h_3)\right]}{h^2}\Bigg[Z$$

$$-\int_0^\infty 4\pi r^2\rho^{\text{electronic}}_{\text{atomic}}(r)\,\frac{\sin(2\pi hr/a)}{2\pi hr/a}\,dr + \frac{\pi h}{a}\int_0^\infty \not{z}(r)\sin(2\pi hr/a)\,dr\Bigg]$$

$$= -\frac{16}{\pi ah^2}\cos\left[(\pi/4)(h_1+h_2+h_3)\right]\Bigg[Z$$

$$-\frac{a}{2\pi h}\sum_{j=1}^{6} f_j\int_0^\infty r^{n_j-1}\,e^{-\alpha_j r}\sin(2\pi hr/a)\,dr$$

$$+\frac{\pi h}{a}\sum_{j=1}^{8} g_j\int_0^\infty r^{\nu_j+1}\,e^{-\beta_j r}\sin(2\pi hr/a)\,dr\Bigg]$$

$$= -\frac{16}{\pi ah^2}\cos\left[(\pi/4)(h_1+h_2+h_3)\right]\Bigg\{Z$$

$$-\frac{a}{2\pi h}\sum_{j=1}^{6}\frac{f_j\,\Gamma(n_j)}{\left[\left(\frac{2\pi h}{a}\right)^2+\alpha_j^2\right]^{n_j/2}}\sin\left[n_j\tan^{-1}\frac{2\pi h}{a\alpha_j}\right]$$

$$+\frac{\pi h}{a}\sum_{j=1}^{8}\frac{g'_j\,\Gamma(\nu_j+2)}{\left[\left(\frac{2\pi h}{a}\right)^2+\beta_j^2\right]^{(\nu_j+2)/2}}\sin\left[(\nu_j+2)\tan^{-1}\frac{2\pi h}{a\beta_j}\right]\Bigg\}, \tag{8.19}$$

where we have used $\Omega_0 = a^3/4$,

$$4\pi r^2\rho^{\text{electronic}}_{\text{atomic}}(r) = \sum_{j=1}^{6} f_j r^{n_j} e^{-\alpha_j r}, \tag{8.20}$$

$$\frac{\not{z}(r)}{r} = \sum_{j=1}^{8} g_j r^{\nu_j} e^{-\beta_j r}, \tag{8.21}$$

and the integration formula

$$\int_0^\infty r^p e^{-qr} \sin(\gamma r)\,dr = \frac{\Gamma(p+1)}{(\gamma^2+q^2)^{(p+1)/2}} \sin\left[(p+1)\tan^{-1}\frac{\gamma}{q}\right] \tag{8.22}$$

which may be derived from Exercise 2, Ch. IX, page 227 of Copson (38).

The following values of $\left|V_{\underline{h}}^{(0)}\right|$ for the silicon crystal were computed from Eq. (8.19):

$\underline{h}$	$\left\lvert V_{\underline{h}}^{(0)}\right\rvert$
(1,1,1)	0.50758
(2,2,0)	$0.37196\underline{8}$
(3,1,1)	$0.21261\underline{3}$
(4,0,0)	$0.23366\underline{6}$
(3,3,1)	$0.14705\underline{8}$
(4,2,2)	$0.17707\underline{4}$
(4,4,0)	$0.14411\underline{8}$.

(8.23)

$V_{\underline{h}}^{(0)}$ is obtained from this table by means of the relation

$$V_{\underline{h}}^{(0)} = -\frac{\cos\left[(\pi/4)(h_1+h_2+h_3)\right]}{\left|\cos\left[(\pi/4)(h_1+h_2+h_3)\right]\right|}\left|V_{\underline{h}}^{(0)}\right| . \tag{8.24}$$

In computing $V_{000}^{(0)}$ we follow Herman (8) in using

$$\overset{(o)}{V}{}^{\text{Coulomb}}_{000} \doteq -\frac{16\pi^2}{3\,\Omega_s}\int_0^{\infty} r^4 \rho^{\text{electronic}}_{\text{atomic}}(r)\,dr \,, \tag{8.25}$$

with $\Omega_s = \Omega_o/s$, where s is the number of atoms in the unit cell of volume Ω_o, to obtain the Coulomb contribution. This relation is derived in the article by Sommerfeld and Bethe previously cited (1). From it we obtain for silicon

$$\overset{(o)}{V}{}^{\text{Coulomb}}_{000} = -\,1.00353 \text{ ryd.} \tag{8.26}$$

For the exchange contribution to $\overset{(o)}{V}_{000}$ we use Eq. (8.18), which for the limiting case $\underline{h} = 0$ becomes

$$\overset{(o)}{V}{}^{\text{exchange}}_{000} = -\frac{8\pi}{\Omega_o}\int_0^{\infty} \underline{r}^2 \frac{\not{z}(r)}{r}\,dr. \tag{8.27}$$

However, in deriving (8.18) we assumed that the exchange contribution to the crystal potential could be written as the superposition of the atomic exchange potentials:

$$V^{\text{exchange}}(\underline{r}) = \sum V^{\text{exchange}}_{\text{atomic}}(\underline{r} - \underline{R}) \,. \tag{8.28}$$

While this approximation is useful in computing the higher Fourier coefficients of the exchange potential which are sensitive mainly to the behavior of the function $\not{z}(r)$ near $r = 0$, it breaks down completely for V_{000}, where the integral is sensitive to the behavior of $\not{z}(r)$ for larger r values. Although (8.28) is not true, Parmenter has shown in Appendix A of his paper (39) that functions V' can be found such that

$$V^{\text{exchange}}(\underline{r}) = \sum_{\nu} V'(\underline{r} - \underline{R}_{\nu}). \tag{8.29}$$

We expect these functions $V'(\underline{r})$ to resemble $V^{\text{exchange}}_{\text{atomic}}(\underline{r})$ for values of r less than half the smallest spacing of lattice points in the crystal, but for larger values of r we expect $V'(\underline{r}) < V^{\text{exchange}}_{\text{atomic}}(\underline{r})$, since the superposition of the functions $V^{\text{exchange}}_{\text{atomic}}(\underline{r})$ makes the computed value of $V^{\text{exchange}}(\underline{r})$ too large in the regions of overlap. With these considerations in mind we have replaced $\not{z}(r)/r$ in Eq. (8.27) by a different estimate of $6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3}$:

$$6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3} = 6\left\{\frac{3}{32\pi^2 r^2}\sum_{n,\ell}^{\text{core}} 2(2\ell+1)P^2_{n\ell} + \frac{3X}{8\pi\Omega_s}\right\}^{1/3} \tag{8.30.1}$$

for $r \leq r_s$,

$$6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3} = 0 \tag{8.30.2}$$

for $r > r_s$,

where $\Omega_s = \Omega_0/s$, with s the number of atoms in the unit cell of volume Ω_0, r_s is defined by $\Omega_s = (4/3)(\pi r_s^3)$, X is the number of valence electrons per atom (those outside of closed shells), and $\sum_{n,\ell}^{\text{core}}$ means summation over the values of n and ℓ associated with the core electrons in the atom (those in closed shells). This estimate is based on the assumptions that the density distributions of core electrons on neighboring atoms do not overlap and that

$$\sum_{n,\ell}^{\text{core}} 2(2\ell+1)P_{n\ell}^2 = 0 \text{ for } r > r_s$$

(both good assumptions for silicon), and that the valence electrons can be thought of as uniformly distributed inside a spherical box of volume Ω_s, centered on the nucleus, in computing the average potential. The last assumption is suggested by the feeling that for the valence electrons the result of averaging the charge distribution over the Ω_s-sphere and then computing its exchange potential should not greatly differ from the result of computing the exchange potential with the true valence electron distribution and averaging that over the Ω_s-sphere. Replacing $\not{z}(r)/r$ in Eq. (8.27) with expression (8.30) for $6\left\{\frac{3}{8\pi}\rho(r)\right\}^{1/3}$ and carrying out the integration numerically, we obtain for the silicon crystal

$$V_{000}^{(0)\text{exchange}} = -0.99551 \text{ ryd.} \tag{8.31}$$

Thus

$$V_{000} = V_{000}^{(0)\text{Coulomb}} + V_{000}^{\text{exchange}} = -1.99904. \tag{8.32}$$

In all calculations for the silicon crystal we used a rounded-off value of $V_{000}^{(0)}$:

$$V_{000}^{(0)} = -1.99900 .$$

IX. RESULTS FOR THE SILICON CRYSTAL AND DISCUSSION.

In Sections VII and VIII we have shown how to compute the quantities

$$V_{\underline{h}}^{(0)},\ A_{n\ell}(\frac{2\pi\ h}{a}),\ \text{and}\ E_{n\ell}$$

which are required in the secular determinants of Section VI. To establish the feasibility of the methods proposed, we have applied them to the case of silicon crystal and have computed the core state energy parameters $E_{n\ell}$ and the values of $V_{\underline{h}}^{(0)}$ and $A_{n\ell}(\frac{2\pi}{a}\ h)$ which are needed in constructing the determinants

$$\Delta_1^{\Gamma_1},\ \Delta_2^{\Gamma_1},\ \Delta_3^{\Gamma_1},\ \Delta_1^{\Gamma_2'},\ \Delta_2^{\Gamma_2'},\ \Delta_1^{\Gamma_{25}'},\ \Delta_2^{\Gamma_{25}'},\ \Delta_3^{\Gamma_{25}'},\ \Delta_1^{\Gamma_{15}},\ \text{and}\ \Delta_2^{\Gamma_{15}}$$

from which we can obtain the first few successive approximations to the energies of the valence and lowest conduction states with wave vector $\underline{k} = (0,0,0)$ in that crystal.

The results obtained by solving these secular equations are as follows:

$$\begin{array}{llll}
E_1^{\Gamma_1} = -1.3498 & & E_1^{\Gamma_{25}'} = -0.3996 \\
E_2^{\Gamma_1} = -1.4624 & & E_2^{\Gamma_{25}'} = -0.7312 \\
E_3^{\Gamma_1} = -1.4629 & & E_3^{\Gamma_{25}'} = -0.7663 \\
 & & \\
E_1^{\Gamma_2'} = 0.0338 & & E_1^{\Gamma_{15}} = -0.3996 \\
E_2^{\Gamma_2'} = -0.0310 & & E_2^{\Gamma_{15}} = -0.5443\ ,
\end{array} \tag{9.1}$$

where, as explained in Section VI, E_n^{Γ}, the n-th approximation to the energy of the Γ-type state, is the lowest root of an n-th order equation.

A comparison of these results with those given in Herman's convergence diagram for his diamond calculations (9), taking into account the differences in scale of the two sets of results, indicates that the present calculations converge as well as or better than those for diamond at each stage. Also, it seems reasonable to expect that in the higher approximations the energy eigenvalues for the Γ_{25}' and Γ_{15} states should converge better than those for diamond, because the secular equations for these states in silicon include orthogonality terms coming from the 2s and 2p atomic core functions which are not present in the equations for these states in diamond. All previous calculations indicate that such orthogonality terms improve the convergence.

Everything that we have learned in the calculations for silicon described here and in other preliminary calculations which we carried out for diamond emphsizes the importance of the requirement that the trial function (2.12) be orthogonal to the core states in the <u>same</u> crystal potential which is used in Eq. (2.16). If the states to which (2.12) is orthogonalized are not eigenfunctions of

$$H = -\nabla^2 + V^{(0)}(\underline{r}),$$

to a very good approximation, then the successive approximations to the energy eigenvalues of the valence and conduction states will not converge well, and these estimates of the energy eigenvalues may even be wrong as to the order of the solutions of the four different symmetry types. The sensitivity of the results of these calculations to the core functions which are used appears directly in the calculations as a strong sensitivity to the values $E_{n\ell}$ and $A_{n\ell}(K)$ which enter into Eqs. (2.18) and (2.20). Herman in his paper delivered at Amsterdam (40) has emphasized the necessity of using good estimates of $E_{n\ell}$; we share his opinion that the loss of convergence which he noted in his work on germanium in going from a solution neglecting exchange to one including an exchange potential is connected with the difficulty of obtaining good estimates of $E_{n\ell}$--and the related quantities $A_{n\ell}(K)$. While we were preparing the first draft of this work, Dr. Joseph Callaway of the Bell Telephone Laboratories very kindly sent us a copy of his unpublished manuscript on Some Features of the Orthogonalized Plane Wave Method (41) in which he too emphasizes the importance of using good approximations for the core states in the crystal potential in OPW calculations.

In this connection it should be noticed that we used the approximation (7.39) for the exchange potential $V^{(0)\,\text{exchange}}(\underline{r})$ in computing both the total crystal potential and the core eigenfunctions $\varphi^{(1)}_{n\ell m}(\underline{r})$ and eigenvalues $E^{(1)}_{n\ell}$. Thus the small error which the use of (7.39) introduces does not affect the degree to which $\varphi^{(1)}_{n\ell m}(r)$ and $E^{(1)}_{n\ell}$ approximate true eigenfunctions and eigenvalues of the assumed crystal potential $V^{(0)}(\underline{r})$.

From our best approximations for the energy eigenvalues of the valence and conduction states as given in (9.1) we obtain as an estimate of the difference between the highest valence state energy, $E^{\Gamma'_{25}}$, and the lowest conduction state energy, $E^{\Gamma_{15}}$:

$$\begin{aligned} E_2^{\Gamma_{15}} - E_2^{\Gamma'_{25}} &= -0.5443 \text{ ryd.} + 0.7312 \text{ ryd.} \\ &= 0.1869 \text{ ryd.} \\ &= 2.54 \text{ electron-volts.} \qquad (9.2) \end{aligned}$$

While the higher approximations will yield lower estimates of both $E^{\Gamma_{15}}$ and $E^{\Gamma'_{25}}$, the close resemblance between the results of our calculations, as far as we have carried them, and those of Herman for diamond suggests that the higher approximations will also agree with Herman's diamond results in not effecting a large change in the energy difference computed in (9.2). It is interesting to note that a value of about 2.5 electron-volts is consistent with the energy band structure for silicon postulated by Herman (18) in his recently proposed explanation of the variation of energy gap with fraction of silicon in silicon-germanium alloys. Our value of about 2.5 electron-volts for the energy gap in silicon should be compared with the value 1.3 electron volts obtained by Bell, Hensman, Jenkins, and Pincherle (42) in their recent calculations for silicon based on an adaptation of Kohn's variational formulation of the cellular method (43). Both of these calculations for silicon agree in fixing the Γ_{15} state at a lower energy than the Γ'_2 state, in contrast to the results of Yamaka and Sugita (44) which make the lowest conduction state non-degenerate.

One of the most interesting aspects of the present work is that the use of a very crude estimate of the crystal potential in silicon based on the Slater-type functions introduced in Section VII, in our formulation of the OPW method led us to the rather reasonable results given in (9.1) and (9.2). The connection between assumed potential and results is a complicated one, and it might depend on a fortuitous cancellation of errors. However, it seems to us more probable that it does not, in which case this work suggests that the results of calculations of the energy band structure of silicon by the OPW method are not very sensitive to the assumed crystal potential, providing the same potential is used in computing the core states and the valence and conduction states.

REFERENCES

1. Sommerfeld, A., and Bethe, H., Handbuch der Physik XXIV/2 (Springer Verlag, Berlin, Germany, 1933).
2. Wigner, E., and Seitz, F., Phys. Rev. 43, 804 (1933).
3. Slater, J. C., Phys. Rev. 51, 846 (1937).
4. Herring, C., Phys. Rev. 57, 1169 (1940).
5. Saffren, M. M., and Slater, J. C., Phys. Rev. 92, 1126 (1953).
6. Raynor, G. V., Reports on Progress in Physics, The Physical Society, London, England, 15, 173 (1952).
7. Herman, F., Ph. D. thesis, Columbia University, January, 1953 (unpublished); available on microfilm through University Microfilms, University of Michigan, Ann Arbor, Michigan.
8. Herman, F., Phys. Rev. 93, 1214 (1954).
9. Herman, F., Phys. Rev. 88, 1210 (1952).
10. Herman, F., and Callaway, J., Phys. Rev. 89, 518 (1953).
11. Dresselhaus, G., Kip, A. F., Kittel, C., Phys. Rev. 92, 827 (1953).
12. Lax, B., Zeiger, H. J., Dexter, R. N., and Rosenblum, E. S., Phys. Rev. 93, 1418 (1954); Dexter, R. N., et al., Phys. Rev. (to be published).
13. Smith, C., Phys. Rev. 94, 42 (1954).
14. Jucys, A., Jour. Phys. U.S.S.R. 11, 49 (1947).
15. Hartree, W., and Hartree, D. R., Phys. Rev. 59, 306 (1941).
16. Slater, J. C., Phys. Rev. 36, 57 (1930).
17. Slater, J. C., Phys. Rev. 81, 385 (1951).
18. Herman, F., Phys. Rev. 95, 847 (1954).
19. Hartree, D. R., Proc. Camb. Phil. Soc. 24, 89 (1927).

20. Slater, J. C., Phys. Rev. **42**, 33 (1932).

21. Wilson, A. H., *The Theory of Metals* (Cambridge University Press, Cambridge, England, second Edition, 1953).

22. Pauling, L., and Wilson, E. B., Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, N. Y., 1935).

23. Seitz, F., Zeit. f. Kristallographie (A) **88**, 433 (1934); **90**, 289 (1935); **91**, 336 (1935); **94**, 100 (1936).

24. Zachariasen, W. H., *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, N. Y., 1945).

25. Seitz, F., Ann. of Math. **37**, 17 (1936).

26. Winston, H., and Halford, R. S., Jour. Chem. Phys. **17**, 607 (1949).

27. Herring, C., Jour. Franklin Inst. **233**, 525 (1942).

28. Wigner, E., *Gruppentheorie und ihre anwendung auf die Quantenmechanik der Atomspektren* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1944).

29. Eyring, H., Walter, J., and Kimball, G. E., *Quantum Chemistry* (John Wiley and Sons, Inc., New York, N. Y., 1944).

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

31. Shockley, W., *Electrons and Holes in Semiconductors with Applications to Transistor Electronics* (D. Van Nostrand Company, Inc., New York, N. Y., 1950).

32. Pratt, G. W., Jr., Phys. Rev. **88**, 1217 (1952).

33. Löwdin, P. O., Phys. Rev. **90**, 120 (1953).

34. Dwight, H. B., Tables of Integrals and other Mathematical Data (The Macmillan Company, New York, N. Y., 1949).

35. Schiff, L. I., Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, N. Y., 1949).

36. Conwell, E. M., Proc. Inst. Radio Engrs. 40, 1327 (1952).

37. Straumanis, M. E., and Aka, E. J., Jour. App. Phys. 23, 330 (1952).

38. Copson, E. T., An Introduction to the Theory of Functions of a Complex Variable (Oxford University Press, London, England, 1946).

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

40. Herman, F., Physica (to be published in 1955).

41. Callaway, J., (unpublished).

42. Bell, D. G., Hensman, R., Jenkins, D. P., and Pincherle, L., Proc. Phys. Soc. London (A) 67, 562 (1954).

43. Kohn, W., Phys. Rev. 87, 472 (1952).

44. Yamaka, E., and Sugita, T., Phys. Rev. 90, 992 (1953).

45. Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, Ohio, thirty-fourth edition, 1952-53).