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Application of the Orthogonalized Plane-Wave Method to Silicon Crystal*

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Approximate solutions for $\mathbf{k}=0$ of the Hartree-Fock-Slater equations for a perfect silicon crystal have been obtained by the orthogonalized plane-wave method. Estimates of the energy eigenvalues of the valence and conduction states for $\mathbf{k}=0$ are given. A simple method for obtaining a first approximation to the crystal potential and its Fourier coefficients was used. Approximate analytic wave functions and corresponding energy eigenvalues for the $1s$, $2s$, and $2p$ states in the isolated silicon atom were determined by a variational technique.

I. INTRODUCTION

In this paper[1] we describe some of the results and problems which have come from an attempt to solve the one-electron Hartree-Fock-Slater (abbreviated HFS in the following) equations[2] for a perfect silicon crystal by Herring's orthogonalized plane-wave (OPW) method.[3] We have been aided greatly in this investigation by the work of Herman[4–6] and of Herman and Callaway[7] on the energy band structures of diamond and germanium. In his most recent work on germanium,[6] Herman has carried out an ambitious program for the determination of the energy eigenvalues associated with thirteen nonequivalent reduced wave vectors. Our interest is primarily in the methods used for these calculations, and not so much in their results; accordingly, we discuss here the determination of energy eigenvalues and wave functions only for $\mathbf{k}=0$.

Our work on silicon differs from that of Herman on diamond and germanium mainly in two ways:

(1) We have tried to make the whole analysis one degree more rigorous by including the effects of exchange on the core states in the crystal in a way consistent with the way in which we have included these effects on the valence and conduction states. This point is important, because in using the variation procedure to obtain the higher states in a crystal potential by means of a trial function orthogonalized to all of the lower states, as proposed by Herring,[3] it is essential that the functions to which the trial function is orthogonalized should be eigenfunctions of exactly the same Hamiltonian operator used to determine the higher states.[8] The HFS equations were used to determine both the atomic states and the crystal states in order to facilitate this more consistent treatment. We do not believe that the HFS equations are better than or as good as the Hartree-Fock (HF) equations for all kinds of atomic and crystal calculations, but they are convenient to use in the present study.[9]

(2) We have based our determination of a crystal potential for silicon on simpler atomic wave functions than the Hartree or Hartree-Fock wave functions used by Herman.

In Sec. VI of this paper, we discuss the results of our calculations, which are given in Sec. V, and compare them with the corresponding results obtained by Herman. We also point out several of the inadequacies of our work and mention problems connected with it in the hope of encouraging others to improve and extend it.

In Sec. II we give the specifications of a perfect silicon crystal, to which our calculations relate; introduce the HFS equations, which will be assumed to provide a satisfactory description of the electronic states in such a crystal; and refer to the OPW method[3] for solving them. Section III is a description of the determination of the electronic wave functions and associated energy parameters for the isolated silicon atom which are required in the analysis of the silicon crystal problem. The wave functions given in Sec. III are used to provide the Fourier coefficients of crystal potential energy and the orthogonality coefficients which enter into the solution of the electronic energy eigenvalue problem for the crystal; numerical values of these coefficients are listed in Sec. IV.

II. HFS EQUATIONS AND THE OPW METHOD FOR SOLVING THEM

According to current ideas, a real, single, diamond-type crystal of a chemical element of atomic number Z consists at standard temperature and pressure of roughly 10^{22} nuclei of that element per cm^3, most of them oscillating about the points of a space lattice of the type associated with diamond, embedded in a cloud of electrons, Z electrons for each nucleus. There are always impurity atoms present in this system, and

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[1] A preliminary report of some of the results of this work has appeared [Truman O. Woodruff, Phys. Rev. **98**, 1741 (1955)].

[2] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[3] C. Herring, Phys. Rev. **57**, 1169 (1940).

[4] F. Herman, Phys. Rev. **88**, 1210 (1952).

[5] F. Herman, Phys. Rev. **93**, 1214 (1954).

[6] F. Herman, Physica **20**, 801 (1954).

[7] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

[8] J. Callaway, Phys. Rev. **97**, 933 (1955).

[9] For critical comments on Slater's free-electron modification of the HF equations, see the papers by G. G. Hall and by S. Raimes, Proceedings of the Malvern Symposium on Band Structure, Malvern, England, 1954 (unpublished).

imperfections in the array of nuclei, such as vacant lattice sites, interstitial atoms and dislocations. We do not indeavor 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 M nuclei of the element (where $M \sim 10^{22}$) 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 ith electron we take a solution $\psi_i(\mathbf{r})$ of the approximate Schrödinger equation

$$[-\nabla^2+V(\mathbf{r})]\psi_i(\mathbf{r})=E_i\psi_i(\mathbf{r}), \tag{2.1}$$

with

$$V(\mathbf{r})=-2Z\sum_\nu \frac{1}{|\mathbf{r}-\mathbf{R}_\nu|}+2\sum_j \int_\infty \frac{\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' -6[(3/8\pi)\sum_j \psi_j^*(\mathbf{r})\psi_j(\mathbf{r})]^{\frac{1}{3}}, \tag{2.2}$$

where the integration is over the volume of the crystal, $\mathbf{R}_\nu$ is the position vector of the nucleus at the νth lattice point, ν runs over all lattice points in the crystal, and j runs over all of the electrons, including the ith 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 ($a_0=5.2917\times10^{-9}$ cm) and energies in terms of Rydbergs (one Rydberg=13.6050 electron volts). Equations (2.1) and (2.2) are obtained from Slater's[2] Eq. (14) for a crystal containing an equal number of electrons of each spin by neglecting any dependence of the one-electron wave functions on the electron spin coordinate. The last term in Eq. (2.2) is called the exchange term in the electron's potential energy; it is an approximation to the exchange potential energy which appears in the HF equations.

The fact that the equations for the MZ functions $\psi_i(\mathbf{r})$ are coupled by the exchange term and the electronic Coulomb term

$$2\sum_j \int_\infty [\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]d\mathbf{r}'$$

in $V(\mathbf{r})$ complicates the problem of solving them. We obtain approximate solutions for them by the self-consistent field method of Hartree.[10] This study is devoted entirely to the first stage in this self-consistent field approach: guessing solutions $\psi_i^{(0)}(\mathbf{r})$, using them to compute $V(\mathbf{r})$, and obtaining approximate solutions, including the eigenvalues E_i, of Eq. (2.1) by the OPW method. For our guess as to the solutions $\psi_i^{(0)}(\mathbf{r})$ which we shall use to obtain an initial estimate $V^{(0)}(\mathbf{r})$ of the potential field $V(\mathbf{r})$ for a diamond-type structure, we follow Herman[5] 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 $(1s)^2(2s)^2(2p)^6(3s)(3p)^3$, ^5S.

Let $\varphi_{nlm}(\mathbf{r})$ 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, $\varphi_{nlm}(\mathbf{r})=Y_{lm}(\theta,\varphi)P_{nl}(r)/r$, where $Y_{lm}(\theta,\varphi)$ is a surface spherical harmonic normalized so that $\int_0^{2\pi}\int_0^{\pi} Y_{lm}Y_{lm}^* \cos\theta d\theta d\varphi=1$, and $P_{nl}(r)$ is the radial wave function multiplied by r and normalized so that $\int_0^\infty [P_{nl}(r)]^2 dr=1$. We determine the radial wave functions $P_{nl}(r)$ which go into our initial estimate of $V(\mathbf{r})$ by very simple methods proposed by Slater.[11,12] The radial wave functions for silicon atom are given explicitly in Sec. III. When one uses the wave functions $\varphi_{nlm}(\mathbf{r})$, the potential energy function for each of the electrons in the isolated atom can be written

$$V_{\text{atomic}}(\mathbf{r})=-\frac{2Z}{|\mathbf{r}|}+2\sum_{j=1}^{Z}\int_\infty \frac{\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' -6[(3/8\pi)\sum_{j=1}^{Z}\varphi_j^*(\mathbf{r})\varphi_j(\mathbf{r})]^{\frac{1}{3}}, \tag{2.3}$$

where now $\varphi_j(\mathbf{r})$ means that one of the $\varphi_{nlm}(\mathbf{r})$ functions which refers to the jth 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 $V^{(0)}(\mathbf{r})$ by superposing the atomic potentials $V_{\text{atomic}}^{(0)}(\mathbf{r})$:

$$V^{(0)}(\mathbf{r})=\sum_\nu V_{\text{atomic}}^{(0)}(\mathbf{r}-\mathbf{R}_\nu). \tag{2.4}$$

(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. (2.4) 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 $V(\mathbf{r})$, as given in Eq. (2.2), but the superposition principle would hold for the exchange term only if the atomic charge distributions did not overlap in the crystal.

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[10] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1927).

[11] J. C. Slater, Phys. Rev. 36, 57 (1930).

[12] J. C. Slater, Phys. Rev. 42, 33 (1932).

We know that the charge distributions of the valence electrons certainly do overlap, but the error arising from this source, which is given by

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

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.

The remainder of this paper is devoted to determining energy eigenvalues and wave functions which are approximate solutions of

$$H\psi_i(\mathbf{r})=E_i\psi_i(\mathbf{r}), \tag{2.5}$$

with

$$H=-\nabla^2+V^{(0)}(\mathbf{r}), \tag{2.6}$$

where $V^{(0)}(r)$ is given by Eqs. (2.4) and (2.3) with $\varphi_j^{(0)}$ replacing φ_j for a crystal consisting of N identical unit cells, each of volume Ω_0. (We let N become infinite when convenient.) Since $V^{(0)}(\mathbf{r})$ is periodic in space, the quantum numbers characterizing a solution E, $\psi(\mathbf{r})$ of Eq. (2.5) and symbolized by the subscript i include the three components of the wave vector $\mathbf{k}$.

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[13] 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

$$\psi_{nl;\mathbf{k}}(\mathbf{r})=N^{-\frac{1}{2}}\sum_\nu \exp(i\mathbf{k}\cdot\mathbf{R}_\nu)\varphi_{nl;\mathbf{k}}(\mathbf{r}-\mathbf{R}_\nu), \tag{2.7}$$

where $\varphi_{nl;\mathbf{k}}(\mathbf{r})$ 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 $\mathbf{k}$. The energy eigenvalue $E_{nl;k}$ which is associated with $\psi_{nl;\mathbf{k}}(\mathbf{r})$ by Eq. (2.5) is given to a good approximation by E_{nl}, the energy eigenvalue associated with φ_{nlm} in the isolated atom by the equation for an electron in the isolated atom

$$[-\nabla^2+V_{\text{atomic}}(\mathbf{r})]\varphi_{nlm}(\mathbf{r})=E_{nl}\varphi_{nlm}(\mathbf{r}). \tag{2.8}$$

Applying Herring's work with neglect of any overlap between atomic core wave functions, we find that the energy eigenvalues for the valence and excited states in our crystal are approximated by the roots of

$$\det[(\chi_{\mathbf{K}},H\chi_{\mathbf{K}'})-E(\chi_{\mathbf{K}},\chi_{\mathbf{K}'})]=0, \tag{2.9}$$

where $\mathbf{K}=\mathbf{k}+\mathbf{g}$, $\mathbf{K}'=\mathbf{k}+\mathbf{g}'$, and $\mathbf{g}$, $\mathbf{g}'$ are reciprocal lattice vectors. Expressions for the orthogonalized plane waves $\chi_{\mathbf{K}}$ and the matrix elements $(\chi_{\mathbf{K}},H\chi_{\mathbf{K}'})$ and $(\chi_{\mathbf{K}},\chi_{\mathbf{K}'})$ are given in Herring's paper.[3] The matrix elements depend on orthogonality coefficients $A_{nl}(K)$ and Fourier coefficients of the crystal potential energy, $v(\mathbf{K})$ (written $U[\mathbf{K}]$ in reference 3); numerical values of these coefficients are obtained in Sec. IV. Successively better approximations $E_{\mathbf{k},j}$ are obtained from Eq. (2.9) by increasing the volume about the origin in reciprocal space over which $\mathbf{g}$ and $\mathbf{g}'$ range. By classifying the orthogonalized plane waves and taking symmetric linear combinations of them in accordance with the principles of the representation theory of space groups,[14] it is possible to transform the secular determinant of Eq. (2.9) for trial functions with special reduced wave vectors, such as $\mathbf{k}=0$, into a factored form. Each factor in the determinant is associated with a trial crystal wave function of a particular symmetry type. The roots of Eq. (2.9) can be found by equating each of the factors to zero and solving for E. By means of this symmetry factorization, the order of the determinantal equations which must be solved is greatly reduced, and consequently, the computational effort required to find the solutions $E_{\mathbf{k},j}$ is decreased sufficiently to make their determination with an automatic computing machine practical.

III. ELECTRONIC STATES IN THE SILICON ATOM

From Eq. (2.8) we obtain for $P_{nl}(r)$, the radial part of $\varphi_{nlm}(\mathbf{r})$,

$$d^2P_{nl}(r)/dr^2+\{E_{nl}-V_{\text{atomic}}^{(0)}(r)-l(l+1)/r^2\}P_{nl}(r)=0, \tag{3.1}$$

where $V_{\text{atomic}}^{(0)}(r)$ is the same as $V_{\text{atomic}}^{(0)}(\mathbf{r})$ [Eq. (2.3)] in the cases of interest to us, for which $V_{\text{atomic}}^{(0)}(\mathbf{r})$ is a spherically symmetric function of $\mathbf{r}$. The studies of Slater[2] and Pratt[15] have established the fact that the solutions $P_{nl}(r)$ of Eq. (3.1) provide reasonably accurate radial one-electron atomic wave functions. Using Slater's empirical rules[11,12] we constructed the following approximate radial one-electron atomic wave functions $P_{nl}^{(0)}(r)$ on which all of the calculations for

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[13] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1953), second edition, pp. 38–41.

[14] For details of this theory and its application to factoring the secular determinant of Eq. (2.9) see T. O. Woodruff, Ph.D. thesis, California Institute of Technology, 1955 (unpublished), and references given there.

[15] G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).

the silicon crystal are based:

$$P_{1s}^{(0)}=101.41702r\exp(-13.70000r), \tag{3.2}$$

$$P_{2s}^{(0)}=65.474552r^2\exp(-4.925000r) \\ -33.578420r\exp(-13.70000r), \tag{3.3}$$

$$P_{2p}^{(0)}=62.156271r^2\exp(-4.925000r), \tag{3.4}$$

$$P_{3s}^{(0)}=1.3304028r^3\exp(-1.383333r) \\ -10.769874r^2\exp(-4.925000r) \\ +5.1026382r\exp(-13.70000r), \tag{3.5}$$

$$P_{3p}^{(0)}=1.3288878_4r^3\exp(-1.383333r) \\ -9.7757812r^2\exp(-4.925000r). \tag{3.6}$$

To the extent that they are accurate, they should resemble solutions of Eq. (3.1).

We could now use for the zero-order approximation to E_{nl}, $E_{nl}^{(0)}$, the quantum-mechanical expectation value of H_{atomic} for the state $\varphi_{nlm}^{(0)}$:

$$E_{nl}^{(0)}=\int_\infty \varphi_{nlm}^{(0)*}(\mathbf{r})H_{\text{atomic}}\varphi_{nlm}^{(0)}(\mathbf{r})d\mathbf{r},$$

with

$$H_{\text{atomic}}=-\nabla^2+V_{\text{atomic}}^{(0)}(\mathbf{r}).$$

Also we could compute the required functions $A_{nl}(K)$ from the functions $\varphi_{nlm}^{(0)}(\mathbf{r})$ and then proceed to the solution of the secular equations of Sec. II for $E_j(\mathbf{k})\equiv E_{\mathbf{k},j}$ in the valence and conduction states. In a previous effort to reproduce Herman's results for the diamond crystal,[4] we did carry through just this program; however, our results for $E_j(000)$ 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 $[A_{nl}(K)]^2$ which we used, and $A_{nl}(K)$ in turn was very sensitive to the behavior of $P_{nl}(r)$, the radial part of the wave function $\varphi_{nlm}(\mathbf{r})$ in its tail region (the region $r>r_0$, where r_0 is the largest number such that $dP_{nl}(r)/dr=0$). Hence, we concluded, $\varphi_{nlm}^{(0)}(\mathbf{r})$ and $E_{nl}^{(0)}$ are not sufficiently good solutions of the eigenfunction-eigenvalue problem of Eq. (2.8). We then developed and used a method for obtaining eigenfunctions $\varphi_{nlm}^{(1)}(\mathbf{r})$ and eigenvalues $E_{nl}^{(1)}$ which are better approximations to the solutions of (2.8) with $V_{\text{atomic}}^{(0)}(\mathbf{r})$ still given by the substitution of $\varphi_{nlm}^{(0)}(\mathbf{r})$ in Eq. (2.3). When we had applied this method in a rough way to carbon and repeated the calculations of $E_j(000)$ for diamond, using $E_{nl}^{(1)}$ and values of $A_{nl}(K)$ computed from $\varphi_{nlm}^{(1)}(\mathbf{r})$, we obtained agreement with Herman's values of $E_j(000)$ to within the accuracy of our calculation at each of the stages of the approximation which we attempted.

TABLE I. Approximate energy eigenvalues (in Rydbergs) of the Hartree-Fock-Slater (HFS) equations for the core electrons in the isolated silicon atom.

nl	$E_{nl}^{(1)}$
1s	−134.597
2s	−11.1237
2p	−8.17697

We made use of analytical rather than numerical methods for obtaining $\varphi_{nlm}^{(1)}(\mathbf{r})$ and $E_{nl}^{(1)}$ because when that work was performed, we did not have access to automatic computing machinery. Using linear trial functions for $P_{nl}(r)$ of a form suggested by the work of Löwdin[16] and well-known quantum-mechanical variational procedures, we were able to determine the eigenvalues $E_{nl}^{(1)}$ given in Table I and the following normalized analytical forms for $P_{nl}^{(1)}(r)$, without numerical integration:

$$P_{1s}^{(1)}(r)=P_{1s}^{(0)}(r)=101.41702r\exp(-13.70000r). \tag{3.7}$$

$$P_{2s}^{(1)}=41.2929r^2\exp(-4.20r) \\ +12.9072r^2\exp(-7.96r) \\ -28.4408r\exp(-13.70r). \tag{3.8}$$

$$P_{2p}^{(1)}=r^2[32.3954\exp(-4.20r) \\ +55.6008\exp(-7.96r)]. \tag{3.9}$$

It should be observed that with these methods it was necessary in order to obtain (3.8)–(3.9) to carry out lengthy, though straightforward, algebraic manipulations and several hundred hours of computation with a desk-type multiplying, dividing, and adding machine. Also, better solutions of Eq. (3.1) than (3.7)–(3.9) could be obtained in numerical form by direct numerical integration. Note that in the computation of the crystal potential $V(\mathbf{r})$ (Sec. IV), we used the *same* estimate of $V_{\text{atomic}}(\mathbf{r})$ as we used in determining the atomic core functions $\varphi_{nlm}^{(1)}(\mathbf{r})$ upon which the computation of the orthogonality coefficients $A_{nl}(K)$ was based.

IV. ORTHOGONALITY COEFFICIENTS AND FOURIER COEFFICIENTS OF CRYSTAL POTENTIAL ENERGY

A. Orthogonality Coefficients for the Core States

The orthogonality coefficient $A_{nl}(K)$ is given by

$$A_{nl}(K)=\Omega_0^{-\frac{1}{2}}\int_\infty \exp(i\mathbf{K}\cdot\mathbf{r})\varphi_{nl;\mathbf{K}}^*(\mathbf{r})d\mathbf{r}. \tag{4.1}$$

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

$$A_{nl}(K)=\Omega_0^{-\frac{1}{2}}\int_\infty \exp(iKr\cos\theta)\varphi_{nl0}^*(\mathbf{r})d\mathbf{r}, \tag{4.2}$$

where

$$\varphi_{nl0}(\mathbf{r})=r^{-1}P_{nl}(r)Y_{l0}(\theta,\varphi). \tag{4.3}$$

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[16] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

TABLE II. Orthogonality coefficients $A_{nl}(K)$.

h^2	$A_{1s}(2\pi h/a)$	$A_{2s}(2\pi h/a)$	$-iA_{2p}(2\pi h/a)$
0	0.0170094	0.171077	0.0000000
3	0.0168074	0.138815	0.0704738
4	0.0167409	0.129765	0.0769323
8	0.0164787	0.100072_2	0.0879129
11	0.0162861	0.0831092	0.0888203
12	0.0162226	0.0782396	0.0884426
16	0.0159724	0.0618685	0.0850910
19	0.0157886	0.0522041	0.0815371

Using Eq. (4.3) and Eq. (19.9) of Schiff[17] in (4.2), we obtain

$$A_{nl}(K)=\left[\frac{4\pi(2l+1)}{\Omega_0}\right]^{\frac{1}{2}} i^l\int_0^\infty rP_{nl}(r)j_l(Kr)dr. \quad (4.4)$$

Substituting the functions $P_{nl}^{(1)}(r)$ from (3.7)–(3.9), together with the appropriate n, l, values and $\Omega_0=a^3/4$, where $a=5.431\times10^{-8}$ cm is the lattice constant of silicon,[18] we obtain the values of $A_{nl}(K)$ given in Table II.

B. Fourier Coefficients of the Potential Energy Function

The only quantities entering into the secular equations of Sec. II which remain to be computed are the Fourier coefficients of the potential energy of an electron, $v(\mathbf{g})$.

Our crystal potential energy function is given by Eq. (2.4), with

$$V_{\text{atomic}}^{(0)}(\mathbf{r})=-\frac{2Z}{r}+\left(\frac{2}{r}\right)\int_0^r 4\pi r'^2\rho(r')dr' +2\int_r^\infty\left[\frac{4\pi r'^2\rho(r')}{r'}\right]dr'-6\left[\frac{3\rho(r)}{8\pi}\right]^{\frac{1}{3}}, \quad (4.5)$$

where

$$\rho(r)=(4\pi r^2)^{-1}\{2[P_{1s}(r)]^2+2[P_{2s}(r)]^2+6[P_{2p}(r)]^2 +[P_{3s}(r)]^2+3[P_{3p}(r)]^2\}. \quad (4.6)$$

It is convenient to write

$$V_{\text{atomic}}^{(0)\ \text{Coulomb}}\equiv-\frac{2Z}{r}+\left(\frac{2}{r}\right)\int_0^r 4\pi r'^2\rho(r')dr' +2\int_r^\infty\left[\frac{4\pi r'^2\rho(r')}{r'}\right]dr', \quad (4.7)$$

$$V_{\text{atomic}}^{(0)\ \text{exchange}}\equiv-6[3\rho(r)/8\pi]^{\frac{1}{3}}, \quad (4.8)$$

$$V^{(0)}(\mathbf{r})=V^{(0)\ \text{Coulomb}}(\mathbf{r})+V^{(0)\ \text{exchange}}(\mathbf{r}), \quad (4.9)$$

with

$$V^{(0)\ \text{Coulomb}}(\mathbf{r})=\textstyle\sum_\nu V_{\text{atomic}}^{(0)\ \text{Coulomb}}(\mathbf{r}-\mathbf{R}_\nu) =\sum_{\mathbf{g}} v^{(0)}(\mathbf{g})^{\text{Coulomb}}\exp(-i\mathbf{g}\cdot\mathbf{r}), \quad (4.10)$$

$$V^{(0)\ \text{exchange}}(\mathbf{r})=\textstyle\sum_\nu V_{\text{atomic}}^{(0)\text{exchange}}(\mathbf{r}-\mathbf{R}_\nu) =\sum_{\mathbf{g}} v^{(0)}(\mathbf{g})^{\text{exchange}}\exp(-i\mathbf{g}\cdot\mathbf{r}). \quad (4.11)$$

Then

$$v^{(0)}(\mathbf{g})=v^{(0)}(\mathbf{g})^{\text{Coulomb}}+v^{(0)}(\mathbf{g})^{\text{exchange}}. \quad (4.12)$$

The Fourier coefficients $v^{(0)}(\mathbf{g})^{\text{Coulomb}}$ are related to the Fourier coefficients of the charge distribution, $\rho(r)$, and are easily computed by means of this relation.[5] Thus, for $\mathbf{g}\neq0$,

$$v^{(0)}(\mathbf{g})^{\text{Coulomb}}=-(4a^2/\pi\Omega_0g^2)\cos[\tfrac{1}{4}\pi(h_1+h_2+h_3)] \times\left[Z-\int_0^\infty 4\pi r^2\rho(r)\frac{\sin(2\pi hr/a)}{2\pi hr/a}dr\right], \quad (4.13)$$

where $\mathbf{h}=(a/2\pi)\mathbf{g}$. For the coefficients $v^{(0)}(\mathbf{g})^{\text{exchange}}$, it follows from Eqs. (4.11) and (4.8) that

$$v^{(0)}(\mathbf{g})^{\text{exchange}}=-\left(\frac{6}{N\Omega_0}\right)\int_\infty \exp(i\mathbf{g}\cdot\mathbf{r}) \times\sum_\nu\left[\frac{3\rho(|\mathbf{r}-\mathbf{R}_\nu|)}{8\pi}\right]^{\frac{1}{3}}d\mathbf{r}$$

$$=-\left(\frac{24a}{\Omega_0h}\right)\cos[\tfrac{1}{4}\pi(h_1+h_2+h_3)] \times\int_0^\infty\left[\frac{3\rho(r)}{8\pi}\right]^{\frac{1}{3}} r\sin\left(\frac{2\pi hr}{a}\right)dr. \quad (4.14)$$

For $h\neq0$, then, $v^{(0)}(\mathbf{g})$ is given by Eqs. (4.12), (4.13), (4.6), and (4.14).

The values of $|v^{(0)}(\mathbf{g})|$ for the silicon crystal given in Table III were computed from these equations. The

TABLE III. Absolute values (in Rydbergs) of Fourier coefficients of the potential energy of an electron in the silicon crystal.

h	$\lvert v^{(0)}(\mathbf{g})\rvert=\lvert v^{(0)}(2\pi\mathbf{h}/a)\rvert$
1,1,1	0.50758
2,2,0	0.37197
3,1,1	0.21261
4,0,0	0.23367
3,3,1	0.14706
4,2,2	0.17707
4,4,0	0.14412
3,3,3	0.11524
5,1,1	0.11524
5,3,1	0.095326
6,2,0	0.12171
5,3,3	0.081308
4,4,4	0.10526
7,1,1	0.070819
8,0,0	0.082694

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[17] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, New York, 1949).

[18] E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).

integration indicated in Eq. (4.14) must be carried out numerically; to facilitate this integration, which had to be repeated for each entry in Table III, we used numerical methods to find a function closely approximating $[3\rho(r)/8\pi]$ which could be integrated analytically. From Table III, we obtain $v^{(0)}(\mathbf{g})$ by means of the relation

$$v^{(0)}(\mathbf{g})=v^{(0)}\left(\frac{2\pi\mathbf{h}}{a}\right)=-\frac{\cos[\frac{1}{4}\pi(h_1+h_2+h_3)]}{|\cos[\frac{1}{4}\pi(h_1+h_2+h_3)]|}\left|v^{(0)}\left(\frac{2\pi\mathbf{h}}{a}\right)\right|. \quad (4.15)$$

In computing $v^{(0)}(000)$, we again follow Herman[5] in using

$$v^{(0)}(000)^{\text{Coulomb}}=-\left(\frac{16\pi^2}{3\Omega_s}\right)\int_0^\infty r^4\rho(r)dr, \quad (4.16)$$

with $\Omega_s=\Omega_0/s$, where s is the number of atoms in the unit cell of volume Ω_0, to obtain the Coulomb contribution. The derivation of this relation is given by Bethe and Sommerfeld.[19] From it, we obtain for silicon

$$v^{(0)}(000)^{\text{Coulomb}}=-1.00353 \text{ ry}. \quad (4.17)$$

For the exchange contribution to $v^{(0)}(000)$ we use Eq. (4.14), which for the limiting case $\mathbf{h}=0$ becomes

$$v^{(0)}(000)^{\text{exchange}}=-\left(\frac{8\pi}{\Omega_0}\right)\int_0^\infty \left[\frac{r^2z(r)}{r}\right]dr, \quad (4.18)$$

where $z(r)/r=-6[3\rho(r)/8\pi]^{\frac{1}{3}}$. However, in deriving (4.14) we assumed that the exchange contribution to the crystal potential could be written as the superposition of the atomic exchange potentials [Eq. (4.11)]. 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 $z(r)$ near $r=0$, it breaks down completely for $v(000)$, where the integral is very sensitive to the behavior of $z(r)$ for larger r values. Although the first part of Eq. (4.11) is not true, Parmenter has shown in Appendix A of his paper[20] that functions V' can be found such that

$$V^{\text{exchange}}(\mathbf{r})=\textstyle\sum_\nu V'(\mathbf{r}-\mathbf{R}_\nu). \quad (4.19)$$

We expect these functions $V'(\mathbf{r})$ to resemble

$$V_{\text{atomic}}{}^{\text{exchange}}(\mathbf{r})$$

for values of r less than half the smallest spacing of lattice points in the crystal, but for larger values of r we expect $|V'(\mathbf{r})|<|V_{\text{atomic}}{}^{\text{exchange}}(\mathbf{r})|$, since the superposition of the functions $V_{\text{atomic}}{}^{\text{exchange}}(\mathbf{r})$ makes the computed value of $|V^{\text{exchange}}(\mathbf{r})|$ too large in the regions of overlap. With these considerations in mind, we replace $z(r)/r$ in Eq. (4.18) by

$$6\left\{\left(\frac{3}{32\pi^2r^2}\right)\sum_{n,l}^{\text{core}}2(2l+1)P_{nl}{}^2+\frac{3X}{8\pi\Omega_s}\right\}^{\frac{1}{3}} \text{ for } r\leq r_s,$$

and by zero 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 $\sum_{n,l}{}^{\text{core}}$ 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 assumption that the density distributions of core electrons on neighboring atoms do not overlap and that

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

(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 $z(r)/r$ in Eq. (4.18) with the above estimates of $6[3\rho(r)/8\pi]^{\frac{1}{3}}$ and carrying out the integration numerically, we obtain for the silicon crystal

$$V_{000}{}^{(0)\text{ exchange}}=-0.99551 \text{ ry}. \quad (4.20)$$

Thus

$$V_{000}{}^{(0)}=V_{000}{}^{(0)\text{ Coulomb}}+V_{000}{}^{(0)\text{ exchange}}=-1.99904 \text{ ry}. \quad (4.21)$$

In all calculations for the silicon crystal we used a rounded-off value of $V_{000}{}^{(0)}$: $V_{000}{}^{(0)}=-1.99900$ ry.

V. NUMERICAL RESULTS FOR THE SILICON CRYSTAL

We obtain approximations to the energy eigenvalues associated with the electronic states of different symmetry types having $\mathbf{k}=0$ in the silicon crystal by inserting the numbers E_{nl}, $A_{nl}(K)$, and $v(\mathbf{g})$ from Tables I–III in the determinant of Eq. (2.9), equating the factor determinants to zero, and solving each one for E. Each factor determinant belongs to a particular symmetry classification. In this work we have been interested only in their lowest roots. The addition of more symmetrized plane-wave combinations to the trial function[3] increases the order of the determinant of Eq. (2.9), and hence increases the order of some of its component factor determinants. The successive

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[19] H. Bethe and A. Sommerfeld, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 422.

[20] R. H. Parmenter, Phys. Rev. **86**, 552 (1952).

approximations to the various eigenvalues obtained by this procedure, beginning with only one symmetry combination of plane waves in the trial function and successively adding others, are summarized in Table IV. As noted there, the *n*th approximation to the energy of a state of given symmetry type is the lowest root of an *n*th order determinantal equation for that symmetry type.

From our best approximations for the energy eigenvalues of the valence and conduction states, as given in Table IV, we obtain an estimate of the difference between the highest valence state energy, $E_{\Gamma_{25'}}$, and the lowest conduction state energy, $E_{\Gamma_{15}}$:

$$(E_{\Gamma_{15}})_6-(E_{\Gamma_{25'}})_6=0.2616 \text{ ry}\simeq 3.6 \text{ ev}.$$

Bell and his co-workers[21] obtained for this difference in silicon crystal the value of 1.3 ev from their calculations based on an adaptation of Kohn's variational formulation of the cellular method.[22] Both their calculations and ours agree in fixing the Γ_{15} state at a lower energy than the $\Gamma_{2'}$ state, in contrast with the results of Yamaka and Sugita,[23] which make the lowest conduction state nondegenerate.

It is interesting to note that all of the numerical results given in this paper were computed from five numbers: Z, a, and the three coefficients appearing in the exponents of (3.2)–(3.6). The numbers given in Tables I–IV are the end products of a great deal of numerical work. In the later stages of this work we were fortunate in having the assistance of the Illiac computer at the University of Illinois: the final determinantal equations were solved with the help of Illiac, and the machine was also used to check the evaluations of the complicated expressions for $A_{nl}(K)$ and $v(\mathbf{g})$.

VI. DISCUSSION

The numerical results of the last section for the successive approximations to the eigenvalues of the valence and lowest conduction band states in silicon at $\mathbf{k}=0$ should be compared with: (*A*) Fig. 2 of Herman's first publication on diamond,[4] (*B*) Fig. 1 of the preliminary work by Herman and Callaway on germanium,[7] and (*C*) Figs. 2 and 4 of Herman's more refined work on germanium.[6] The order of the states at $\mathbf{k}=0$ which we find is the same as in (*A*) and (*B*). The rate of convergence of the successive approximations to the eigenvalues of all four symmetry types, adjusted for the differences in energy scales, appears to be about the same as in (*A*). For the Γ_{15} and $\Gamma_{25'}$ solutions the convergence rate again is comparable to (*C*), but our sequence of approximations to the $\Gamma_{2'}$ energy is very different from that given in (*C*) in that our $\Gamma_{2'}$ energy remains well above the Γ_{15} energy in all approximations, but does not level off quite as abruptly after the second approximation as in (*C*). From these comparisons it appears that our more consistent treatment of the effects of exchange in these calculations has not significantly improved the rate of convergence of the OPW procedure. Also, the convergence in the case of the Γ_{15} and $\Gamma_{25'}$ solutions for silicon, where the trial function contains terms coming from orthogonalization to core state wave functions made from the $2p$ atomic orbitals, does not appear much more rapid than in the corresponding solutions for diamond, where the trial function contains no such terms. It is possible that we would have obtained better convergence if we had used more accurate numerical solutions of Eq. (3.1) for the atomic core wave functions than the analytical functions (3.7)–(3.9) and the corresponding energy eigenvalues of Table I. But from our experience with these calculations we have tentatively concluded that for solutions of symmetry types Γ_{15} and $\Gamma_{25'}$ at $\mathbf{k}=0$, a trial function must contain roughly six symmetry combinations of orthogonalized plane waves in order to provide estimates of energies to two significant figures. It should be possible to reduce the number of independent terms in the linear trial function necessary to obtain a given accuracy in these cases by including terms other than symmetry combinations of orthogonalized plane waves. Some of the possible ways in which this might be done have been mentioned by Herring [3] and Herman.[5]

Table IV. Sequences of estimates of the energies (in Rydbergs) of valence and conduction states in silicon crystal with $\mathbf{k}=0$.

	Γ_1	$\Gamma_{25'}$	Γ_{15}	$\Gamma_{2'}$
E_1 [a]	−1.3498	−0.3996	−0.3996	0.0338
E_2	−1.4624	−0.7312	−0.5443	−0.0310
E_3	−1.4629	−0.7663	−0.5472	−0.0655
E_4	−1.4733	−0.7670	−0.5789	−0.0766
E_5	−1.4747	−0.8217	−0.5929	
E_6	−1.4793	−0.8597	−0.5981	

[a] The subscript attached to E refers to the order of the secular determinant used in solving for E.

There are several inadequacies of the present work to which we should like to draw attention. One which we believe may be of comparatively small importance for the present work, but which is related to a question of considerable general interest, is the estimation of $v(000)$, or the average potential in the crystal. We believe that the method used in Sec. IV to estimate this quantity cannot be expected to approximate it to better than 5%, even assuming that the atomic core wave functions used are correct. We have experimented with other choices for the value of $v(000)$ and find that a 10% change in it changes only slightly the convergence of the successive approximations to the energies for $\mathbf{k}=0$ and their relative separations.

Some of the degeneracies in the energy levels for $\mathbf{k}=0$ which we have obtained are removed when a

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[21] Bell, Hensman, Jenkins, and Pincherle, Proc. Phys. Soc. (London) **A67**, 562 (1954).

[22] W. Kohn, Phys. Rev. **87**, 472 (1952).

[23] E. Yamaka and T. Sugita, Phys. Rev. **90**, 992 (1953).

more correct crystal Hamiltonian including relativistic effects is used in place of the crystal Hamiltonian given in Eq. (2.6). A complete treatment of the energy band structure of silicon would include a determination of the magnitudes of the splittings and displacements of the various levels arising from spin and relativistic effects, particularly, the spin-orbit interaction.[24]

No effort has been made to determine the crystal eigensolutions for $\mathbf{k}$ vectors other than $\mathbf{k}=0$. Once the factored secular determinants have been obtained for other wave vectors, the quantities E_{nl}, $A_{nl}(K)$, and $v(\mathbf{K})$ which enter into them can be taken from Tables I–III or computed from Eqs. (4.4) and (4.12) to (4.14); the solution of the resulting determinantal equations is a routine procedure which has been programmed for several of the automatic computers in use at present.

In connection with calculations of the sort described here, it is important to ask how sensitive the results are to changes in the quantities which are put in at the beginning of the calculations, such as the crystal potential and the atomic core wave functions. In analyzing the effects of such changes, one must be sure that all quantities which depend on the changed inputs are modified appropriately in the new determination of the final results. We are not aware of any work on the sensitivity of the results or the rate of convergence of OPW energy band calculations to changes in the inputs which satisfies the last requirement. We would like to encourage other workers with access to modern computing facilities to investigate this question, and have tried to organize the calculations for silicon which we have described to facilitate such a study. It might appear from a comparison of the preliminary results of Herman and Callaway for germanium crystal,[7] based on calculations excluding exchange effects, and the very different results of Herman's more refined calculations[6] for the same crystal, in which consideration was given to exchange effects, that a change in the crystal potential comparable in magnitude to the exchange contribution to that potential would produce such a violent change in the results as the reversal of the order of the $\Gamma_{2'}$ and Γ_{15} solutions. We believe that such a conclusion cannot at present be drawn from this comparison, because in the transition from the first calculation to the second, it would appear from the papers[6,7] that the inputs of type E_{nl} and $v(\mathbf{K})$ were changed, but appropriate changes were not made in the $A_{nl}(K)$ type inputs. But the coefficients $A_{nl}(K)$ with exchange included should be different from those without exchange, because they should be computed from core wave functions which differ in these two cases. The energies calculated by the OPW method depend on a delicate balance of all of these numbers, and small changes in the $A_{nl}(K)$ can modify them profoundly, as we found in our preliminary calculations for diamond. It would be interesting to see how our results for silicon would be affected if the Slater exchange term were modified or omitted from the crystal potential, the atomic core eigenfunctions $\varphi_{nlm}(\mathbf{r})$ and energies E_{nl} redetermined, either by methods we have outlined, or better, by strictly numerical procedures, and the calculations for the valence and conduction states repeated. A calculation along these lines would settle the question as to how sensitive the results of energy band calculations are to the assumed crystal potential.

If it turns out that the order of the bands and the energy intervals between them are not highly sensitive to small variations in the crystal potential, then the use of the HFS equations, as in this work, would be justified for many types of investigation. On the other hand, if the calculated energy band structure is highly sensitive to small variations in the crystal potential, then it is doubtful that crystals can be adequately treated by the HFS equations, and efforts should be made to apply a more accurate form of the HF equations to the solution of energy band problems. It may well be that these efforts would also fail, and that the HF equations cannot be made to give information about the behavior of the aggregate of electrons in a crystal which is sufficiently precise for many purposes, because they do not adequately describe the correlations of the electronic motions beyond those introduced by exchange. In that case, the methods for treating the many-electron problem introduced by Bohm and Pines[25] might make it possible to salvage at least part of the existing structure of energy band concepts.

VII. ACKNOWLEDGMENTS

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[24] R. J. Elliott, Phys. Rev. **96**, 266 (1954); **96**, 280 (1954).

[25] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953), and other references given there.