Wave-Function Expansion in the Brillouin Zone: Silicon

A. JAMES HUGHES*
Applied Research Laboratory, Aeronutronic Division of Philco-Ford Corporation, Newport Beach, California
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Wave functions are required throughout the Brillouin zone for the treatment of many problems in solid-state physics. It therefore is of interest and considerable importance to develop analytical representations of the **k** dependence of wave functions throughout the Brillouin zone. In this paper the momentum wave functions $b_n(\mathbf{k},\mathbf{K}_s)$ in the plane-wave expansion of the Bloch function $\psi_n(\mathbf{k},\mathbf{r})$ are considered. An analytical representation for the $b_n(\mathbf{k},\mathbf{K}_s)$ based on a set of symmetrized polynomials is proposed. The specific polynomials, although they pertain to general points in the Brillouin zone, are somewhat analogous to the Kubic harmonics employed in the cellular method. A primary distinction, however, is that while formerly one was concerned with space-group operations in the group of the **k** vector, here we are concerned with operations in the group of the $\mathbf{K}_s$ vector for which $\mathbf{K}_s$ in $b_n(\mathbf{k},\mathbf{K}_s)$ is left invariant.

I. INTRODUCTION

KNOWLEDGE of wave functions throughout the Brillouin zone is required for the treatment of various problems in solid-state physics. For instance, in studying the optical spectra of solids one requires densities of states and matrix elements which depend upon the variation of the wave functions over the Brillouin zone. Historically the calculation of the density of states has received the most attention. Usually the variation of the relevant matrix elements over the Brillouin zone has been ignored and the matrix elements replaced by suitably chosen constants.

Brust[1] has investigated the matrix element which occurs in the imaginary part of the complex dielectric constant for silicon and germanium. He found that the matrix element connecting bands four and five (band four is the highest valence band and five the lowest conduction band) varied by about a factor of 2 over the Brillouin zone. The matrix element between bands four and six was found to vary by a much larger factor.

The calculation of nonlinear optical constants involves an order of complexity greater than for the linear optical constants. It is believed[2] that for the nonlinear optical absorption the relevant matrix element may vary strongly over the Brillouin zone and might even change sign. It may be that for this problem the wave functions and derived matrix elements will have to be explicitly considered.

The treatment of localized defects in semiconductors[3] by means of solid-state scattering theory using a Wannier function basis is a further example of a situation in which wave functions throughout the Brillouin zone are required. A strong point of this approach is that it incorporates detailed information concerning the energy-band structure and wave functions of the perfect crystal. Associated with this advantage, however, is the disadvantage that much numerical calculation is required.

It is apparent that in attempting to treat either optical properties or localized defects, it would be very desirable to have analytical representations of the **k** dependence of wave functions. Such representations would enable us to decrease the required numerical labor and to increase the accuracy of the solution.

In this paper, we consider the momentum wave functions $b_n(\mathbf{k},\mathbf{K})$ which occur in a plane-wave expansion of the Bloch function $\Psi_n(\mathbf{k},\mathbf{r})$. Integrals involving the Bloch function may be readily expressed in terms of the $b_n(\mathbf{k},\mathbf{K})$, and it is of interest to consider an analytic representation for them. We propose such a representation here, based on a set of symmetrized polynomials. The specific polynomials which are presented are appropriate for the diamond lattice although the general approach is applicable to other lattices. These polynomials, although they pertain only to general points in the Brillouin zone, are in a sense analogous to the Kubic harmonics employed by Von der Lage and Bethe[4] and Bell[5] in the context of the cellular method for symmetry points in the Brillouin zone. While formerly one was concerned with space-group operations which left the **k** vector invariant, we are here concerned with operations which leave **K** invariant in the momentum wave functions $b_n(\mathbf{k},\mathbf{K})$ for band n, point **k** in the Brillouin zone and for reciprocal lattice vector **K**.

The plan of this paper is as follows: Symmetry properties of Bloch functions are discussed briefly in Sec. II. The symmetry polynomials are generated in Sec. III and the results presented. The momentum wave-function expansion is developed in Sec. IV, and discussion and conclusions are contained in Sec. V.

II. SYMMETRY PROPERTIES OF BLOCH FUNCTIONS

In this section we shall discuss certain symmetry properties of Bloch functions. Symmetrized polynomials will be constructed and employed in the following sec-

* Present address: Theoretical Physics Department, Research and Engineering Division, Autonetics, Anaheim, Calif. 92803.
[1] D. Brust, Phys. Rev. **134**, A1337 (1964).
[2] N. Bloembergen, R. K. Chang, and J. Ducuing, in *Physics of Quantum Electronics*, edited by P. L. Kelly, B. Lax, and P. E. Tannewald (McGraw-Hill Book Publishing Co., Inc., New York, 1966), p. 67.
[3] J. Callaway and A. J. Hughes, Phys. Rev. **156**, 860 (1967).
[4] F. C. von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).
[5] D. G. Bell, Rev. Mod. Phys. **26**, 311 (1954).

tions. We shall here be primarily concerned with only *isolated* energy bands; that is, energy bands which do not touch or cross other bands.

For our purposes, it is necessary to specify the complete $\mathbf{k}$ dependence of a Bloch function. It is always possible to multiply a Bloch function by a phase factor $e^{i\phi(n,\mathbf{k})}$ which depends both on the band and on the wave vector. It has been found possible to formulate a convention for specifying the phase factor, apart from a constant which is the same for all states in a given band. This was done in Ref. 3, in which a prescription was given relating the 48 wave functions $\psi_n(\mathbf{k}',\mathbf{r})$ in the star of $\mathbf{k}$ so that the wave function $\psi_n(\mathbf{k},\mathbf{r})$ is as smooth as possible as the argument $\mathbf{k}$ goes over the Brillouin zone. This can be accomplished if we require that $\psi_n(\mathbf{k},\mathbf{r})$ transform under the operations of the space group according to Eq. (2.1):

$$\{\alpha|t_\alpha\}\psi_n(\mathbf{k},\mathbf{r})=\chi_n{}^{(j)}(\alpha)e^{-i\alpha\mathbf{k}\cdot\mathbf{t}_\alpha}\psi_n(\alpha\mathbf{k},\mathbf{r}). \quad (2.1)$$

In Eq. (2.1) $\{\alpha|t_\alpha\}$ is a space-group operation which for the diamond lattice may include a nonprimitive translation $\mathbf{t}_\alpha$. $\psi_n{}^{(j)}(\alpha)$ is the character for operation α in the one-dimensional representation j which is appropriate to band n. The particular representation j is chosen to ensure smoothness in the wave function $\psi_n(\mathbf{k},\mathbf{r})$ as the argument $\mathbf{k}$ goes across the interior planes which bound the various 1/48th subzones of the Brillouin zone. For an isolated band, only one-dimensional representations can arise, and only these will be considered.

Let us consider a plane-wave expansion of the Bloch function

$$\psi_n(\mathbf{k},\mathbf{r})=\frac{1}{(2\pi)^{3/2}}\sum_s b_n(\mathbf{k},\mathbf{K}_s)e^{i(\mathbf{k}+\mathbf{K}_s)\cdot\mathbf{r}}, \quad (2.2)$$

in which $\mathbf{K}_s$ is a reciprocal lattice vector. The function $b_n(\mathbf{k},\mathbf{K}_s)$ is the momentum wave function for band n. Plane-wave expansions are important not only in formal analysis but arise naturally in the pseudopotential method of band-structure calculation.

For the diamond lattice we choose the origin of coordinates for the energy-band calculation in such a way that the perfect-crystal Hamiltonian is represented by a real symmetric matrix on a plane-wave (or orthogonalized-plane-wave, OPW) basis. Then it is possible to find eigenvectors $b_n(\mathbf{k},\mathbf{K}_s)$ which are real for all $\mathbf{k}$. The indeterminancy of phase of the Bloch function therefore reduces to a question of algebraic sign which can be settled by requiring that the $b_n(\mathbf{k},\mathbf{K}_s)$ be smooth functions of $\mathbf{k}$. Throughout this work, we employ a reduced zone scheme. Therefore we write $b_n(\mathbf{k},\mathbf{K}_s)$ instead of $b_n(\mathbf{k}+\mathbf{K}_s)$.

Since the $b_n(\mathbf{k},\mathbf{K}_s)$ contain the nontrivial variation in wave function over the Brillouin zone we wish to determine the equations which they obey. Proceeding as in Ref. 3, we consider the effect of $\{\alpha|t_\alpha\}$ on $\psi_n(\mathbf{k},\mathbf{r})$ when the wave function is given by Eq. (2.2):

$$\begin{aligned}\{\alpha|t_\alpha\}\psi_n(\mathbf{k},\mathbf{r})&=(2\pi)^{-3/2}\sum_s b_n(\mathbf{k},\mathbf{K}_s)\{\alpha|t_\alpha\}e^{i(\mathbf{k}+\mathbf{K}_s)\cdot\mathbf{r}}\\&=(2\pi)^{-3/2}e^{-i\alpha\mathbf{k}\cdot\mathbf{t}_\alpha}\sum_s b_n(\mathbf{k},\mathbf{K}_s)\\&\quad\times e^{-i\alpha\mathbf{K}_s\cdot\mathbf{t}_\alpha}e^{i\alpha(\mathbf{k}+\mathbf{K}_s)\cdot\mathbf{r}}. \quad (2.3)\end{aligned}$$

We next substitute the phase-wave expansion, Eq. (2.2), directly into the right-hand side of Eq. (2.1) and obtain

$$\begin{aligned}\{\alpha|t_\alpha\}\psi_n(\mathbf{k},\mathbf{r})&=\frac{\chi_n{}^{(j)}(\alpha)}{(2\pi)^{3/2}}\\&\quad\times e^{-i\alpha\mathbf{k}\cdot\mathbf{t}_\alpha}\sum_t b_n(\alpha\mathbf{k},\mathbf{K}_t)e^{-i(\alpha\mathbf{k}+\mathbf{K}_t)\cdot\mathbf{r}}. \quad (2.4)\end{aligned}$$

Comparison of Eqs. (2.3) and (2.4) yields the desired relationship:

$$b_n(\alpha\mathbf{k},\mathbf{K}_s)=\chi_n{}^{(j)}(\alpha)b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)e^{-i\mathbf{K}_s\cdot\mathbf{t}_\alpha}. \quad (2.5)$$

For the diamond lattice with our choice of origin, the factor $\exp[-\mathbf{K}_s\cdot\mathbf{t}_\alpha]$ is always real. Equation (2.5) is fundamental to this paper and forms the basis for the polynomial development to be presented.

Consider $b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)$ in Eq. (2.5) and let α range over the 48 operations in the space group of the diamond lattice. Certain of the operations $\{\alpha|t_\alpha\}$ are such as to leave $\mathbf{K}_s$ invariant if $\mathbf{K}_s$ is not a general reciprocal lattice vector. That is, $\alpha^{-1}\mathbf{K}_s=\mathbf{K}_s$ for all operations α^{-1} considered. These operations form a group which we will call the group of $\mathbf{K}_s$. Thus we may make use of a standard projection technique[6] to obtain functions $b_n(\mathbf{k},\mathbf{K}_s)$ which form a basis for an irreducible one-dimensional representation associated with the group of the $\mathbf{K}_s$ vector. Viewed in this manner, the analogy between the group of the $\mathbf{k}$ vector as applied to energy-band calculations at symmetry points in the Brillouin zone and the present application to the group of the $\mathbf{K}_s$ vector is manifest.

For the operations α in the group of $\mathbf{K}_s$, it is evident that Eq. (2.5) may be rearranged to yield

$$b_n(\mathbf{k},\mathbf{K}_s)=\frac{1}{g}\sum_\alpha{}' b_n(\alpha\mathbf{k},\mathbf{K}_s)\chi_n{}^{(j)}(\alpha)e^{i\mathbf{K}_s\cdot\mathbf{t}_\alpha}. \quad (2.6)$$

In (2.6) g is the number of operations in the group of $\mathbf{K}_s$. In order to obtain explicit functions $b_n(\mathbf{k},\mathbf{K}_s)$, it is necessary to insert appropriate trial functions into $b_n(\alpha\mathbf{k},\mathbf{K}_s)$ on the right-hand side of Eq. (2.6). The form of trial function we have employed consists of various powers of k_x, k_y, k_z. That is, we consider a trial function $(k_x)^l(k_y)^m(k_z)^n$ where l, m, and n are integers. Although this is certainly not the only kind of trial function which might be used, it has considerable advantage for the use

[6] R. S. Knox and A. Gold, *Symmetry in the Solid State* (W. A. Benjamin, Inc., New York, 1964), p. 41.

we intend to make of it. The actual generation of polynomials by employing Eq. (2.6) is described in the next section.

For any α, Eq. (2.5) may be rewritten as

$$b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)=b_n(\alpha\mathbf{k},\mathbf{K}_s)\chi_n{}^{(j)}(\alpha)e^{i\mathbf{K}_s\cdot\mathbf{t}_\alpha}. \quad (2.7)$$

Let us consider the reciprocal lattice vectors of a given type, that is, those reciprocal lattice vectors which can be obtained from any one of them by operation of any of the α in the point group of the crystal. Only one $b_n(\mathbf{k},\mathbf{K}_s)$ of a given type need be obtained by the methods of Eq. (2.6). Having obtained an explicit form for $b_n(\mathbf{k},\mathbf{K}_s)$, we obtain $b_n(\mathbf{k},\mathbf{K}_s')$, where $\mathbf{K}_s'$ is any other vector of that type, by substituting into the right-hand side of (2.7). This procedure is then carried out type by type for as many types of lattice vectors as is necessary or practical to include in Eq. (2.2).

III. GENERATION OF SYMMETRY POLYNOMIALS

All reciprocal lattice vectors for the cubic lattice belong to one of seven types. These are listed in Table I. We note for the diamond lattice, e.g., diamond, silicon, and germanium, all coordinates of a given lattice vector are of the same parity, that is, all odd or all even. For example, a in the set $\{a,0,0\}$ must be even.

The utility of the polynomial expansion procedure which is developed here is increased by the fact that it is frequently possible to obtain satisfactory wave functions using plane waves of relatively small $|\mathbf{K}_s|$. The $\mathbf{K}_s$ which appear belong to the more symmetric types in the table. For example, in Ref. 3, only types 1, 2, and 3 occur.

A comment on notation is in order. We will employ the usual O_h labeling[7] for the four one-dimensional irreducible representations of interest in the wave-function expansion. We also employ the same O_h labeling for all groups of the $\mathbf{K}_s$ vector. Since all groups we shall need to consider are subgroups of O_h, this notation is convenient and consistent. From Table I we note that the group of the $\mathbf{K}_s$ vector for some of the types does not contain four one-dimensional representations. In these cases we will not obtain four distinct sets of polynomials. Our O_h labeling of the one-dimensional representations is therefore homomorphic to the one-dimensional representations of the group of the $\mathbf{K}_s$ vector.

To obtain symmetry polynomials we begin by applying Eq. (2.6) for $\mathbf{K}_s=0$. For this vector the group contains all 48 operations and the translational phase factor $\exp(i\mathbf{K}_s\cdot\mathbf{t}_\alpha)$ drops out. We thus obtain the same polynomials as given by Von der Lage and Bethe[4] and Bell.[5] We have extended the polynomials to higher order than was done by these authors. The results are given in Table II. We have followed the usual procedure of normalizing the polynomials to 4π over the unit sphere. In the table, x, y, z stand for the direction cosines $k_x/|k|$, $k_y/|k|$, $k_z/|k|$ and functions within the square brackets are to be taken without normalization factors.

The next wave-vector type is the set of eight vectors of the form $\{a,a,a\}$. In applying Eq. (2.6), we have for definiteness chosen to work with the vector (a,a,a) where all coordinates are positive. The six operations in the group C_{3v} of the vector (a,a,a) do not contain any nonprimitive translations. Hence there are no selection requirements due to the parity of the parameter a. We obtain Eq. (3.1) as the generating function for this set

TABLE I. A list of the various types or groups of lattice vectors. The first column lists one member of each group. The second column lists the number of vectors in the group and the third column lists the number of operations in the group of the **K** vector for the various vector groups. The number of one-dimensional irreducible representations in the group of the **K** vector is given in the fourth column.

1	{0,0,0}	1	48	4
2	{a,a,a}	8	6	2
3	{a,0,0}	6	8	4
4	{a,a,0}	12	4	4
5	{a,b,b}	24	2	2
6	{a,b,0}	24	2	2
7	{a,b,c}	48	1	1

[7] J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964), p. 23.

TABLE II. Symmetry polynomials for the (0,0,0) reciprocal lattice vector and the four one-dimensional representations. For this vector, the polynomials are identical to those derived by Von der Lage and Bethe (Ref. 4) for use in an application of the cellular method.

Γ_1 type

$\alpha_0=1$

$\alpha_4=\frac{1}{4}5(3\times7)^{1/2}(x^4+y^4+z^4-\frac{3}{5})$

$\alpha_6=\frac{1}{8}3\times7\times11(2\times13)^{1/2}(x^2y^2z^2+(1/22)[\alpha_4]-(1/105))$

$\alpha_8=\frac{1}{16}5\times13(3\times11\times17)^{1/2}(x^8\times y^8+z^8-(28/5)[\alpha_6]-(210/143)[\alpha_4]-\frac{1}{6})$

Γ_2 type

$\beta_6=\frac{1}{8}(2\times3\times5\times7\times11\times13)^{1/2}(x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-{}^2y^2))$

$\beta_{10}=\frac{17}{32}(2\times3\times5\times7\times11\times13\times19)^{1/2}(x^8(y^2-z^2)+y^8(z^2-x^2)+z^8(x^2-y^2)-(14/17)[\beta_6])$

$\beta_{12}=\frac{1}{64}5\times19\times23(2\times7\times11\times13\times17)^{1/2}(x^{10}(y^2-z^2)+y^{10}(z^2-x^2)+z^{10}(x^2-y^2)-(3\times15/23)[\beta_{10}]-(14\times15/17\times19)[\beta_6])$

Γ_1' type

$\alpha_9'=\frac{1}{8}(6\times5\times7\times11\times13\times17\times19)^{1/2}xyz(x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2))$

$\alpha_{13}'=\frac{1}{16}(3\times5\times23)[\frac{1}{2}(7\times11\times13\times17\times19)]^{1/2}(xyz\{x^8(y^2-z^2)+y^8(z^2-x^2)+z^8(x^2-y^2)\}-(18/23)[\alpha_9'])$

$\alpha_{15}'=\frac{1}{32}(3\times5\times29)[\frac{1}{2}(5\times7\times13\times17\times19\times23\times31)]^{1/2}\times(xyz\{x^{10}(y^2-z^2)+y^{10}(z^2-x^2)+z^{10}(x^2-y^2)\}-(11\times5/29)[\alpha_{13}']-(6\times11/5\times23)[\alpha_9'])$

Γ_2' type

$\beta_3'=(3\times5\times7)^{1/2}xyz$

$\beta_7'=(11/4)(3\times5\times7\times13)^{1/2}(xyz(x^4+y^4+z^4)-(5/11)[\beta_3'])$

$\beta_9'=1/24[13\times17(2\times11\times15\times19)^{1/2}](xyz(x^6+y^6+z^6)-(3\times7/17)[\beta_7']-(5\times7/11\times13)[\beta_3'])$

of polynomials:

$$\{x^l(y^m z^n \pm y^n z^m)+y^l(x^n z^m \pm x^m z^n) +z^l(x^m y^n \pm x^n y^m)\}. \quad (3.1)$$

We thus obtain only two sets of polynomials. A choice of the + sign yields polynomials appropriate to both Γ_1 and Γ_2' wave functions and the − sign yields polynomials appropriate to Γ_2 and Γ_1' wave functions.

Actually to obtain the symmetry polynomials we proceed as follows: For a given order $p=l+m+n$, all possible combinations l, m, n are substituted into Eq. (3.1). From the resulting collection of functions, various terms or combinations of terms are selected in such a manner as to yield the maximum number of linearly independent functions possible for a given order p. These are then orthonormalized function by function. The resulting two sets of polynomials for the (a,a,a) reciprocal lattice vector are contained in Table III. We see that more than one polynomial of a given type may be obtained for some of the orders.

The momentum wave functions $b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)$ and the associated wave functions are, however, distinct and different for each of the four one-dimensional representations even though they were derived employing only two different sets of polynomials. This may be seen as follows: We substitute the polynomials which represent $b_n(\mathbf{k},\mathbf{K}_s)$ into the right-hand side of Eq. (2.7) and let α run over *all* 48 operations of the O_h group. Collecting like terms we obtain (except for a numerical factor of 6) the eight different $b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)$ associated with the eight vectors in the set $\{a,a,a\}$.

The full group containing 48 operations and four one-dimensional irreducible representations has thus been employed to derive the $b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)$. The general principles of group theory assure us that if nonzero functions can be obtained for the Γ_1, Γ_2, Γ_1', Γ_2' representations, then these four functions must be distinct.

Before proceeding to the next type of vector, one further comment is in order. The reader will note that, once having obtained functions representing $b_n(\mathbf{k},\mathbf{K}_s)$, only eight suitably chosen operations from O_h would be required to obtain the eight different $b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)$. This suggests that a group of order six is needed to obtain the initial $b_n(\mathbf{k},\mathbf{K}_s)$ followed by a product application of the elements of a group of order eight. Thus symbolically, we might write $O_h=G\times V$ where V is the group of the $\mathbf{K}_s$ vector and G contains the operations α needed to obtain the different $b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)$. Thus one might expect that a direct product, semidirect product, or factor group decomposition would be useful. We have not explored this in any detail other than to note that none of the groups of the $\mathbf{K}_s$ vectors in Table I are proper invariant subgroups of the group O_h. Thus product or factor group decompositions, if possible at all, could not be obtained straightforwardly in the usual manner.

The next wave-vector group to be treated in detail is the set $\{a,0,0\}$ containing six vectors. We again choose

TABLE III. Symmetry polynomials for the set $\{a,a,a\}$ of eight vectors of the form (a,a,a). For this set of vectors we have only two distinct sets of polynomials for the four representations Γ_1, Γ_2, Γ_1', and Γ_2'.

Γ_1 and Γ_2' types

$\alpha_0^+=1$

$\alpha_1^+=(x+y+z)$

$\alpha_2^+=(5)^{1/2}(xy+yz+xz)$

$\alpha_{3,1}^+=\frac{5}{2}(7/3)^{1/2}(x^3+y^3+z^3-\frac{3}{5}[\alpha_1^+])$

$\alpha_{3,2}^+=(1\times3\times5\times7)^{1/2}xyz$

$\alpha_{4,1}^+=5/4(3\times7)^{1/2}(x^4+y^4+z^4-\frac{3}{5})$

$\alpha_{4,2}^+=(3\times5\times7)^{1/2}xyz(x+y+z)$

$\alpha_{5,1}^+=\frac{1}{8}(3\times7)(3\times11)^{1/2}((x^5+y^5+z^5)-(10/9)[\alpha_{3,1}^+]-3/7[\alpha_1^+])$

$\alpha_{5,2}^+=\frac{1}{8}(3\times5\times7\times11)^{1/2}(x^4(y+z)+y^4(x+z)+z^4(x+y) -6xyz(xy+yz+xz))$

Γ_2 and Γ_1' types

$\alpha_3^-=\frac{1}{2}(5\times7)^{1/2}(x^2(y-z)+y^2(z-x)+z^2(x-z))$

$\alpha_4^-=\frac{1}{2}(3\times5\times7)^{1/2}(x^3[y-z)+y^3(z-x)+z^3(x-y))$

$\alpha_5^-=\frac{3}{4}(5\times7\times11)^{1/2}\{x^4(y-z)+y^4(z-x)+z^4(x-y)-\frac{2}{3}[\alpha_3^-]\}$

$\alpha_{6,1}^-=11/4(3\times7\times13)^{1/2}\{x^5(y-z)+y^5(z-x) +z^5(x-y)-(10/11)[\alpha_4^-]\}$

$\alpha_{6,2}^-=\frac{1}{2}(3\times5\times7\times13)^{1/2}\{x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\}$

$\alpha_7^-=\frac{1}{4}(11\times13)(7\times15/46)^{1/2}\{x^6(y-z)+y^6(z-x)+z^6(x-y) -(15/13)[\alpha_{5,1}^-]-(5/11)[\alpha_3^-]\}$

$\alpha_{5,1}^-=\frac{1}{4}(5\times13)[\frac{1}{6}(11\times17)]^{1/2}\{x^7(y-z)+y^7(z-x)+z^7(x-y) -7/5[\alpha_{6,1}^-]-3\times5\times7/11\times13[\alpha_4^-]\}$

$(a,0,0)$ with a positive as the initial momentum wave function. Carrying out the operations in Eq. (2.6) for the eight operations in the group of $(a,0,0)$ we obtain the following two generating functions:

$$\begin{aligned} &m,\ n \text{ odd } [1-\chi(J)e^{i\pi a/2}]x^l\{y^m z^n+\chi(JC_2)y^n z^m\}; \\ &m,\ n \text{ even } [1+\chi(J)e^{i\pi a/2}]x^l\{y^m z^n+\chi(JC_2)y^n z^m\}. \end{aligned} \quad (3.2)$$

We have selection requirements in Eq. (3.2) due to the presence of nonprimitive translations in the group of $(a,0,0)$. We recall that a must always be even for the diamond lattice. Table IV contains the polynomials for m and n odd and Table V contains the polynomials for m and n even. The identifications of the various representations are made in the table captions.

Next consider the $(a,a,0)$-type of vector. The group of the $\mathbf{K}_s$ vector contains four operations and four one-dimensional representations. Using a trial function $x^l y^m z^n$ we obtain a generating function

$$[1+(-)^n\chi(J)][x^l y^m+\chi(JC_2)x^m y^l]. \quad (3.3)$$

Thus Γ_1 and Γ_2 polynomials will be even in z, and Γ_1' and Γ_2' polynomials will be odd in z. The polynomials derived for this wave vector are given in Tables VI and VII.

The (a,b,c) vector has only two operations in the group of $\mathbf{K}_s$ vector. The polynomial generating function for the two one-dimensional representations is

$$x^l[y^m z^n+\chi(JC_2)y^n z^m]. \quad (3.4)$$

TABLE IV. A list of polynomials for the wave vector $(a,0,0)$ in which only odd powers of both y and z occur. For $a=2$, 6, 10, etc., the + sign functions are Γ_1 and the − sign functions are Γ_2. For $a=4$, 8, 12, etc., the + sign functions are Γ_2' and the − sign functions are Γ_1'.

M, N odd; $\chi(JC_2)=+1$

$\alpha_2^+=(3\times5)^{1/2}yz$

$\alpha_3^+=(3\times5\times7)^{1/2}xyz$

$\alpha_4^+=\frac{1}{2}(3\times7)(5)^{1/2}\{x^2yz-(1/7)[\alpha_2^+]\}$

$\alpha_5^+=\frac{3}{2}(3\times5\times7\times11)^{1/2}\{x^3yz-\frac{1}{3}[\alpha_3^+]\}$

$\alpha_6^+=\frac{1}{8}(3\times11)[\frac{1}{2}(3\times5\times7\times13)]^{1/2}\times\{x^4yz-(6/11)[\alpha_4^+]-(1/3\times7)[\alpha_2^+]\}$

$\alpha_7^+=\frac{1}{8}(3\times11\times13)[\frac{1}{2}(5\times7)]^{1/2}\{x^5yz-(10/13)[\alpha_5^+]-(5/3\times11)[\alpha_3^+]\}$

M, N odd; $\chi(JC_2)=-1$

$\alpha_4^-=\frac{3}{2}(5\times7)^{1/2}(y^3z-yz^3)$

$\alpha_5^-=\frac{3}{2}(5\times7\times11)^{1/2}x(y^3z-yz^3)$

$\alpha_6^-=\frac{1}{4}(3\times11)(7\times13)^{1/2}\{x^2(y^3z-yz^3)-(1/11)[\alpha_4^-]\}$

$\alpha_7^-=\frac{1}{4}(3\times13)(5\times7\times11)^{1/2}\{x^3(y^3z-yz^3)-(3/13)[\alpha_5^-]\}$

$\alpha_8^-=\frac{1}{16}(3\times5\times13)(7\times11\times17)^{1/2}\{x^4(y^3z-yz^3)-\frac{2}{5}[\alpha_6^-]-(3/11\times13)[\alpha_4^-]\}$

$\alpha_9^-=\frac{1}{16}(3\times17)(5\times7\times11\times13\times19)^{1/2}\{x^5(y^3z-yz^3)-(10/17)[\alpha_7^-]-(1/13)[\alpha_5^-]\}$

The two sets of polynomials for this lattice vector are given in Table VIII.

The next type, the $(a,b,0)$ vector also has only two operations in the group of the K_s vector. The polynomial generating function is

$$[1+(-)^n\chi(J)e^{i\pi/2(a+b)}]x^ly^mz^n. \tag{3.5}$$

This merely groups the terms as even or odd in z according to

$$1+(-)^n\chi(J)e^{i\pi/2(a+b)}. \tag{3.6}$$

The resulting polynomials are given in Table IX.

The final type of vector in Table I is the vector (a,b,c) which is a general vector. The group of the K_s vector is trivial, containing only the identity operation. Thus no simplifications, by the use of Eq. (2.6), are possible. An lth-order term would be expected to contain all $(2l+1)$ spherical harmonics. The applicability of Eq. (2.7) is, however, unaffected and of course does not depend on the order of the group of the $\mathbf{K}_s$ vector.

TABLE V. A list of polynomials for the wave vector $(a,0,0)$ in which only even powers of both y and z occur. For $a=2$, 6, 10, etc., the + sign functions are Γ_2' and the − sign functions are Γ_1'. For $a=4$, 8, 12, etc., the + sign functions are Γ_1 and the − sign functions are Γ_2.

M, N even; $\chi(JC_2)=+1$

$\beta_0^+=1$

$\beta_1^+=(3)^{1/2}x$

$\beta_2^+=\frac{3}{2}(5)^{1/2}(x^2-\frac{1}{3})$

$\beta_3^+=\frac{5}{2}(7)^{1/2}\{x^3-\frac{3}{5}[\beta_1^+]\}$

$\beta_4^+=\frac{1}{8}(3\times5\times7)\{x^4-(6/7)[\beta_2^+]-\frac{1}{5}\}$

$\beta_5^+=\frac{1}{8}(7\times9)(11)^{1/2}\{x^5-(10/9)[\beta_3^+]-(3/7)[\beta_1^+]\}$

$\beta_6^+=\frac{1}{16}(3\times7\times11)(13)^{1/2}\{x^6-(15/11)[\beta_4^+]-(5/7)[\beta_2^+]-(1/7)\}$

$\beta_7^+=\frac{1}{16}(3\times11\times13)(15)^{1/2}\{x^7-(3\times7/13)[\beta_5^+]-(5\times7/3\times11)[\beta_3^+]-\frac{1}{3}[\beta_1^+]\}$

M, N even; $\chi(JC_2)=-1$

$\beta_3^-=\frac{1}{2}(3\times5\times7)^{1/2}x(y^2-z^2)$

$\beta_4^-=\frac{3}{2}(5\times7)^{1/2}x^2(y^2-z^2)$

$\beta_5^-=\frac{3}{4}(3\times5\times7\times11)^{1/2}\{x^3(y^2-z^2)-\frac{1}{3}[\beta_3^-]\}$

$\beta_6^-=11/4(3\times7\times13)^{1/2}\{x^4(y^2-z^2)-(5/11)[\beta_4^-]\}$

$\beta_7^-=\frac{1}{16}(3\times11\times13)[\frac{1}{2}(5\times7)]^{1/2}\{x^5(y^2-z^2)-(10/13)[\beta_5^-]-(5/3\times11)[\beta_3^-]\}$

$\beta_8^-=\frac{1}{16}(13\times15)[\frac{1}{2}(3\times11\times17)]^{1/2}\{x^6(y^2-z^2)-(14/15)[\beta_6^-]-(5\times7/11\times13)[\beta_4^-]\}$

TABLE VI. The Γ_1 and Γ_2 types of polynomials for the $(a,a,0)$ reciprocal lattice vector.

Γ_1 type

$\alpha_0^+=1$

$\alpha_1^+=(\frac{3}{2})^{1/2}(x+y)$

$\alpha_{2,1}^+=(3\times5)^{1/2}xy$

$\alpha_{2,2}^+=\frac{3}{2}(5)^{1/2}(z^2-\frac{1}{3})$

$\alpha_{3,1}^+=5/4(3\times7)^{1/2}((x+y)z^2-\frac{1}{5}[\alpha_1^+])$

$\alpha_{3,2}^+=\frac{1}{4}(5\times7)^{1/2}(x^2(x-3y)+y^2(y-3x))$

$\alpha_{4,1}^+=\frac{1}{8}(3\times5\times7)(z^4-(6/7)[\alpha_{2,2}^+]-\frac{1}{5}[\alpha_0^+])$

$\alpha_{4,2}^+=\frac{1}{2}(3\times7)(5)^{1/2}(xyz^2-(1/7)[\alpha_{2,1}^+])$

$\alpha_{4,3}^+=\frac{3}{8}(5\times7)^{1/2}(x^4+y^4-6x^2y^2)$

Γ_2 type

$\alpha_1^-=(\frac{3}{2})^{1/2}(x-y)$

$\alpha_2^-=\frac{1}{2}(3\times5)^{1/2}(x^2-y^2)$

$\alpha_{3,1}^-=5/4(3\times7)^{1/2}((x-y)z^2-\frac{1}{5}[\alpha_1^-])$

$\alpha_{3,2}^-=\frac{1}{2}(5\times7)^{1/2}(x^2(x+3y)-y^2(y+3x))$

$\alpha_{4,1}^-=\frac{1}{4}(3\times7)(5)^{1/2}((x^2-y^2)z^2-1/7[\alpha_2^-])$

$\alpha_{4,2}^-=\frac{3}{2}(5\times7)^{1/2}xy(x^2-y^2)$

TABLE VII. The Γ_1' and Γ_2' types of polynomials for the $(a,a,0)$ reciprocal lattice vector.

Γ_1' type

$\beta_2^-=[\frac{1}{2}(3\times5)]^{1/2}(x-y)z$

$\beta_3^-=\frac{1}{2}(3\times5\times7)^{1/2}(x^2-y^2)z$

$\beta_{4,1}^-=\frac{1}{4}(3\times7)(5)^{1/2}((x-y)z^3-3/7[\beta_2^-])$

$\beta_{4,2}^-=\frac{3}{4}(5\times7)^{1/2}(x^3-y^3+3xy(x-y))z$

$\beta_{5,1}^-=\frac{3}{4}(3\times5\times7\times11)^{1/2}((x^2-y^2)z^3-\frac{1}{3}[\beta_3^-])$

$\beta_{5,2}^-=\frac{3}{2}(5\times7\times11)^{1/2}(x^2-y^2)xyz$

$\beta_{6,1}^-=\frac{1}{6}(3\times11)(2\times3\times7\times13)^{1/2}((x-y)z^5-(10/11)[\beta_{4,1}^-]-(5/3\times7)[\beta_3^-])$

Γ_2' type

$\beta_1^+=(3)^{1/2}z$

$\beta_2^+=[\frac{1}{2}(3\times5)]^{1/2}(x+y)z$

$\beta_{3,1}^+=\frac{5}{2}(7)^{1/2}(z^3-\frac{3}{5}[\beta_1^+])$

$\beta_{3,2}^+=(3\times5\times7)^{1/2}xyz$

$\beta_{4,1}^+=\frac{1}{4}(3\times7)(2)^{1/2}((x+y)z^3-(5/3\times7)[\beta_2^+])$

$\beta_{4,2}^+=\frac{3}{4}(5\times7)^{1/2}(x^3+y^3-3xy(x+y))z$

$\beta_{5,1}^+=\frac{1}{8}(7\times9)(11)^{1/2}(z^5-(10/9)[\beta_{3,1}^+]-(3/7)[\beta_1^+])$

$\beta_{5,2}^+=\frac{3}{2}(3\times5\times7\times11)^{1/2}(xyz^3-\frac{1}{3}[\beta_{3,2}^+])$

$\beta_{5,3}^+=\frac{3}{8}(5\times7\times11)^{1/2}(x^4+y^4-6x^2y^2)z$

To illustrate the polynomials and procedures developed in this section, the first few terms in the polynomial expansion of the momentum wave functions $b_n(\mathbf{k},\alpha^{-1}\mathbf{K}_s)$ for the fifteen lowest plane waves and for a Γ_2' band symmetry are presented in Table X. In this table, x, y, and z stand for the usual direction cosines. Normalization constants of the polynomials are disregarded. The characteristic behavior of the wave functions should be noted. First we see that $b_n(\mathbf{k},0,0,0)$ vanishes on the planes $x=0$, $y=0$, or $z=0$ as required for a Γ_2' function. Those $b_n(\mathbf{k},\mathbf{K}_s)$'s whose $\mathbf{K}$ vectors differ by operations such as y, x, z, etc. are seen to be simply related across bounding planes $x=y$, etc. Thus rows three and four of Table X are seen to be equal for a $\mathbf{k}$ in the plane $\mathbf{k}_x=\mathbf{k}_y$. Similarily, $b_n(\mathbf{k},\mathbf{K}_s)$'s whose $\mathbf{K}$ vectors differ by operations of the form $\bar{x}$, y, z, etc., are simply related across bounding planes $x=0$, etc. Rows ten and eleven of the table are thus negatives of each other for $k_x=0$, etc.

IV. MOMENTUM WAVE-FUNCTION EXPANSION

The intent of this section is to present an expansion for the momentum wave functions $b_n(\mathbf{k},\mathbf{K}_s)$ of Eq. (2.2) employing the polynomials which have been developed.

TABLE VIII. The two sets of polynomials for the (a,b,b) reciprocal lattice vector.

Γ_1 and Γ_2' type

$\alpha_0{}^+=1$

$\alpha_{1,1}{}^+=(3)^{1/2}x$

$\alpha_{1,2}{}^+=(\frac{3}{2})^{1/2}(y+z)$

$\alpha_{2,1}{}^+=3/2\,(5)^{1/2}(x^2-\frac{1}{3})$

$\alpha_{2,2}{}^+=[\frac{1}{2}(3\times5)]^{1/2}x(y+z)$

$\alpha_{2,3}{}^+=(3\times5)^{1/2}yz$

$\alpha_{3,1}{}^+=5/4\,(7)^{1/2}(x^3-\frac{3}{5}[\alpha_{1,1}{}^+])$

$\alpha_{3,2}{}^+=5/4\,(3\times7)^{1/2}(x^2(y+z)-\frac{1}{5}[\alpha_{1,2}{}^+])$

$\alpha_{3,3}{}^+=(3\times5\times7)^{1/2}xyz$

$\alpha_{4,1}{}^+=\frac{1}{8}(3\times5\times7)(x^4-(6/7)[\alpha_{2,1}{}^+]-\frac{1}{5})$

$\alpha_{4,2}{}^+=\frac{1}{4}(3\times7)\,(5)^{1/2}(x^3(y+z)-(3/7)[\alpha_{2,2}{}^+])$

$\alpha_{4,3}{}^+=\frac{1}{2}(3\times7)\,(5)^{1/2}(x^2yz-(1/7)[\alpha_{2,3}{}^+])$

$\alpha_{4,4}{}^+=3\,(5\times7)^{1/2}(y^2z^2-\frac{1}{8}[\alpha_{4,1}{}^+]+(1/7)[\alpha_{2,1}{}^+]-(1/3\times5))$

$\alpha_{4,5}{}^+=\frac{3}{4}(5\times7)^{1/2}x(y^2(y-3z)+z^2(z-3y))$

Γ_2 and Γ_1' type

$\alpha_1{}^-=(\frac{3}{2})^{1/2}(y-z)$

$\alpha_{2,1}{}^-=[\frac{1}{2}(3\times5)]^{1/2}x(y-z)$

$\alpha_{2,2}{}^-=\frac{1}{2}(3\times5)^{1/2}(y^2-z^2)$

$\alpha_{3,1}{}^-=5/4\,(3\times7)^{1/2}(x^2(y-z)-\frac{1}{5}[\alpha_1{}^-])$

$\alpha_{3,2}{}^-=\frac{1}{2}(3\times5\times7)^{1/2}x(y^2-z^2)$

$\alpha_{3,3}{}^-=\frac{1}{4}(5\times7)^{1/2}(y^3-z^3+3yz(y-z))$

$\alpha_{4,1}{}^-=\frac{1}{4}(3\times7)\,(5)^{1/2}(x^3(y-z)-(3/7)[\alpha_{2,1}{}^-])$

$\alpha_{4,2}{}^-=\frac{1}{4}(3\times7)\,(5)^{1/2}(x^2(y^2-z^2)-(1/7)[\alpha_{2,2}{}^-])$

$\alpha_{4,3}{}^-=\frac{3}{2}(5\times7)^{1/2}yz(y^2-z^2)$

$\alpha_{4,4}{}^-=\frac{3}{4}(5\times7)^{1/2}x(y^2(y+3z)-z^2(z+3y))$

TABLE IX. The two sets of polynomials for the lattice vector $(a,b,0)$. For the case in which $\frac{1}{2}(a+b)$ is even, Γ_1 and Γ_2 are even in z and Γ_1' and Γ_2' are odd in z. For the case in which $\frac{1}{2}(a+b)$ is odd, the labeling would be reversed.

z even

$\alpha_0=1$

$\alpha_{1,1}=(3)^{1/2}x$

$\alpha_{1,2}=(3)^{1/2}y$

$\alpha_{2,1}=\frac{3}{2}(5)^{1/2}(z^2-\frac{1}{3})$

$\alpha_{2,2}=\frac{1}{2}(3\times5)^{1/2}(x^2-y^2)$

$\alpha_{2,3}=(3\times5)^{1/2}xy$

$\alpha_{3,1}=\frac{3}{4}(2\times5\times7)^{1/2}(x^3-\frac{3}{5}[\alpha_{1,1}])$

$\alpha_{3,2}=\frac{3}{4}(2\times5\times7)^{1/2}(y^3-\frac{3}{5}[\alpha_{1,2}])$

$\alpha_{3,3}=\frac{1}{2}(3\times5\times7)^{1/2}x(y^2-z^2)$

$\alpha_{3,4}=\frac{1}{2}(3\times5\times7)^{1/2}y(x^2-z^2)$

$\alpha_{4,1}=\frac{1}{8}(3\times5\times7)(z^4-(6/7)[\alpha_{2,1}]-\frac{1}{5})$

$\alpha_{4,2}=\frac{1}{4}(3\times7)\,(5)^{1/2}((x^4-y^4)-(6/7)[\alpha_{2,2}])$

$\alpha_{4,3}=3\,(5\times7)^{1/2}(x^2y^2-\frac{1}{8}[\alpha_{4,1}]+(1/7)[\alpha_{2,1}]-(1/15))$

$\alpha_{4,4}=\frac{1}{2}(3\times7)\,(5)^{1/2}(xyz^2-(1/7)[\alpha_{2,3}])$

$\alpha_{4,5}=\frac{3}{2}(5\times7)^{1/2}xy(x^2-y^2)$

z odd

$\beta_1=(3)^{1/2}z$

$\beta_{2,1}=(3\times5)^{1/2}xz$

$\beta_{2,2}=(3\times5)^{1/2}yz$

$\beta_{3,1}=\frac{5}{2}(7)^{1/2}(z^3-\frac{3}{5}[\beta_1])$

$\beta_{3,2}=(3\times5\times7)^{1/2}xyz$

$\beta_{3,3}=\frac{1}{2}(3\times5\times7)^{1/2}z(x^2-y^2)$

$\beta_{4,1}=\frac{1}{4}(3\times7)\,(2\times5)^{1/2}(xz^3-(3/7)[\beta_{2,1}])$

$\beta_{4,2}=\frac{1}{4}(3\times7)\,(2\times5)^{1/2}(yz^3-(3/7)[\beta_{2,2}])$

$\beta_{4,3}=\frac{3}{4}(2\times5\times7)^{1/2}xz(x^2-3y^2)$

$\beta_{4,4}=\frac{3}{4}(2\times5\times7)^{1/2}yz(y^2-3x^2)$

$\beta_{5,1}=\frac{1}{8}(7\times9)(z^5-(10/9)[\beta_{3,1}]-(3/7)[\beta_1])$

$\beta_{5,2}=\frac{3}{4}(3\times5\times7\times11)^{1/2}(xyz^3-\frac{1}{3}[\beta_{3,2}])$

$\beta_{5,3}=\frac{3}{4}(3\times5\times7\times11)^{1/2}(z^3(x^2-y^2)-\frac{1}{3}[\beta_{3,3}])$

$\beta_{5,4}=\frac{3}{2}(3\times5\times7\times11)^{1/2}xyz(x^2-y^2)$

$\beta_{5,5}=\frac{3}{8}(5\times7)^{1/2}z(x^4+y^4-6x^2y^2)$

TABLE X. The form of the polynomial expansion for a Γ_2' band symmetry and the 15 lowest plane waves. The characteristic behavior is illustrated by this table.

	$\mathbf{K}_s$	$b_5(\mathbf{k},\mathbf{K}_s)$
1	000	$A_1(xyz)+A_2\{xyz(x^4+y^4+z^4)-(5/11)xyz\}$
2	111	$B_1+B_2(x+y+z)+B_3(xy+yz+xz)$
3	$\bar{1}11$	$B_1+B_2(-x+y+z)+B_3(-xy+yz-xz)$
4	$1\bar{1}1$	$B_1+B_2(x-y+z)+B_3(-xy-yz+xz)$
5	$11\bar{1}$	$B_1+B_2(x+y-z)+B_3(xy-yz-xz)$
6	$\bar{1}\bar{1}1$	$-B_1+B_2(x+y-z)+B_3(-xy+yz+xz)$
7	$1\bar{1}\bar{1}$	$-B_1+B_2(-x+y+z)+B_3(xy-yz+xz)$
8	$\bar{1}1\bar{1}$	$-B_1+B_2(x-y+z)+B_3(xy+yz-xz)$
9	$\bar{1}\bar{1}\bar{1}$	$-B_1+B_2(x+y+z)-B_3(xy+yz+xz)$
10	200	$C_1+C_2x+C_3(x^2-\frac{1}{3})+C_4\{x^3-\frac{3}{5}x\}$
11	$\bar{2}00$	$-C_1+C_2x-C_3(x^2-\frac{1}{3})+C_4\{x^3-\frac{3}{5}x\}$
12	020	$C_1+C_2y+C_3(y^2-\frac{1}{3})+C_4\{y^3-\frac{3}{5}y\}$
13	$0\bar{2}0$	$-C_1+C_2y-C_3(y^2-\frac{1}{3})+C_4\{y^3-\frac{3}{5}y\}$
14	002	$C_1+C_2z+C_3(z^2-\frac{1}{3})+C_4\{z^3-\frac{3}{5}z\}$
15	$00\bar{2}$	$-C_1+C_2z-C_3(z^2-\frac{1}{3})+C_4\{z^3-\frac{3}{5}z\}$

We expand any particular $b_n(\mathbf{k},\mathbf{K}_s)$ as a sum of appropriate polynomials. Since each polynomial may, without affecting the transformation properties of the polynomial, be multiplied by any function of $\mathbf{k}$ which is invariant under all operations of the symmetry group, the following expression would be an acceptable expansion for $b_n(\mathbf{k},\mathbf{K}_s)$:

$$b_n(\mathbf{k},\mathbf{K}_s)=\sum_j [\sum_i A_{ji}|\mathbf{k}|^i]B_j(\Gamma_m,\mathbf{K}_s)P_j(\Gamma_m,\mathbf{K}_s). \quad (4.1)$$

In Eq. (4.1) Γ_m is the one-dimensional representation appropriate to band n, A_{ji} is the expansion coefficient for $|\mathbf{k}|^i$ and the jth polynomial, $P_j(\Gamma_m,\mathbf{K}_s)$, is the jth polynomial appropriate to Γ_m and lattice vector $\mathbf{K}_s$, and $B_j(\Gamma_m,\mathbf{K}_s)$ is the associated expansion coefficient. In order to apply Eq. (4.1) to silicon, we must establish the ranges of the indices i and j. Before attempting to do this, let us consider earlier applications involving symmetrized polynomials, although the present application is apparently original in this paper, so the connection with earlier work is by analogy only.

The two main applications of symmetrized polynomials have been for wave-function expansion (Von der Lage and Bethe[4]) and for energy-band-structure expansions (Callaway[8]). Let us consider the wave-function expansion first. Von der Lage and Bethe[4] were concerned with finding solutions to a radial Schrödinger equation which was separable in polar coordinates by virtue of the fact that the one-electron periodic potential was assumed to be spherical within the unit cell. The wave function ψ_s for the point Γ in the Brillouin zone may thus be written in the form

$$\psi_s=\sum_{l,t} A_{lt}K_{slt}(x,y,z)R_l(E,\mathbf{r}). \quad (4.2)$$

In this r space expansion, s denotes the type (transforms according to a given row of an irreducible representation at the point Γ) of wave function and l is the order of the radial wave function. K_{slt} is a symmetrized polynomial (Kubic harmonic) of type s and order l and R_l is the lth-order radial portion of the wave function ψ_s. In (4.2) l is summed over those orders containing type s, and t is summed over the multiple polynomials of type s which may occur for the higher orders of l.

To put Eq. (4.2) in a form more nearly equivalent to (4.1), we expand $R_l(E,r)$ in a power series in r for small r. We would find that the series contains odd and even powers of r with the leading term on R_l being r^l. Thus the lowest power of r which would occur in Eq. (4.2) is directly related to the order of the lowest-order polynomial K_{slt} containing type s.

The second common application of symmetrized polynomials is in an expansion of $E(\mathbf{k})$ in the Brillouin zone. This energy-band-structure expansion may be written as [using notation similar to that of Eq. (4.2)]

$$E(\mathbf{k})=\sum_{l,t,m} A_{l,t,m}|\mathbf{k}|^m K_{s,l,t}(k_x,k_y,k_z). \quad (4.3)$$

As is well known, the type s appropriate to $E(\mathbf{k})$ is the totally symmetric Γ_1 representation and due to time-reversal symmetry, only even powers of $\mathbf{k}$ appear in Eq. (4.3). As noted in Sec. III, the polynomials $K_{s,l,t}$ in Eq. (4.3) are identical to those obtained in expanding $b_n(\mathbf{k},\mathbf{K}_s=0,0,0)$ for a Γ_1 band.

We now return to Eq. (4.1) to determine the powers of $\mathbf{k}$ that should be expected to occur in expansions of the $b_n(\mathbf{k},\mathbf{K}_s)$ for silicon. In Ref. 3 the pseudopotential plane-wave method was employed to obtain energy bands and wave functions for silicon. Therein, in order to keep the numerical labor within reasonable bounds, the secular equation was truncated after 15 plane waves. The 15 plane waves employed were the (000) plane wave, the eight plane waves of the type (111), and the six plane waves of the type (200) (units $2\pi/a$). In this section we shall employ a $\mathbf{k}\cdot\mathbf{p}$ perturbation technique using basis states at $\mathbf{k}=0$ constructed from the 15 plane waves to determine which powers of $\mathbf{k}$ are appropriate in Eq. (4.1). Finally we will check the form of the $\mathbf{k}\cdot\mathbf{p}$ results with the numerical wave functions obtained as in Ref. 3 along a line between the points Γ and Q [coordinates $2\pi/a$ (0,0,0) and $2\pi/a$ (3,2,1)] and quite close to the Γ point.

In applying the $\mathbf{k}\cdot\mathbf{p}$ technique we are interested only in the form of the wave function and not in numerical values. Thus several simplifications and short cuts may be employed. The article by Kane[9] was followed in general and an equation for wave functions to second order in the perturbation was taken from Schiff.[10]

Table XI contains symmetrized combinations of plane waves for the Γ_1, Γ_2', Γ_{25}', and Γ_{15} irreducible representations of the "little" group at $\mathbf{k}=0$ as obtained following Mariot.[11] For the perturbation Hamiltonian both the $|\mathbf{k}|^2$ and $\mathbf{k}\cdot\mathbf{p}$ terms[9] are considered. The diagonal term $|\mathbf{k}|^2$ is trivial. The basis states which are coupled by the nondiagonal $\mathbf{k}\cdot\mathbf{p}$ term can be easily ascertained by group-theory considerations. In order for two states, say Γ_α and Γ_β, to be coupled by the $\mathbf{k}\cdot\mathbf{p}$ term, the the cross product $\Gamma_\alpha\times\Gamma_\beta$ must contain the vector representation Γ_{15}. These results are contained in Table XII. An X in Table XII indicates that a (nonzero) coupling is group-theory-allowed. Table XII relates to "whole" representations. It does not follow and indeed is not the case that, for example, any row of Γ_{25}' will couple with every row of Γ_{15} in the manner indicated in this table. The correct degenerate wave functions at $\mathbf{k}=0$ are, however, linear combinations of the "pure" states given

[8] J. Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 99.

[9] E. O. Kane, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1966), Vol. 1, p. 75.

[10] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Publishing Co., Inc., New York, 1955), p. 154.

[11] L. Mariot, *Group Theory and Solid State Physics* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962), p. 86.

in Table XI and thus are coupled according to Table XII. Since we are interested only in the form of the wave functions and not in numerical values, second-order nondegenerate perturbation theory is adequate. The results which show the terms which occur in Eq. (4.1) when applied to silicon are given in Table XIII. Next numerical wave functions for the eight bands in question were graphed and found to agree with Table XIII.

The momentum wave function $b_5(\mathbf{k},\mathbf{K}_s=0,0,0)$ is shown in the table with $|k|^3$ as the leading term. This particular $b_n(\mathbf{k},\mathbf{K}_s)$ remains zero in both first- and second-order perturbation theory and was therefore obtained instead by graphing the numerical wave functions. The extension of the present section to wave functions containing more plane waves follows easily using the results of Sec. III.

TABLE XI. Symmetrized combinations of plane waves for the diamond lattice and for the Γ_1, Γ_{25}', and Γ_{15} irreducible representations of the group of the $\mathbf{k}$ vector at $\mathbf{k}=0$. (See Ref. 11.)

Band	1	2	3	4	5	6	7	8
Rep.	Γ_1	Γ_{25}'	Γ_{25}'	Γ_{25}'	Γ_2'	Γ_{15}	Γ_{15}	Γ_{15}
Row 1		XY	XZ	YZ	XYZ	Z	Y	X
$\downarrow\mathbf{K}_s$								
000	+	0	0	0	0	0	0	0
111	+	+	+	+	+	+	+	+
$\bar{1}11$	−	+	+	−	+	−	−	+
$1\bar{1}1$	−	+	−	+	+	−	+	−
$11\bar{1}$	−	−	+	+	+	+	−	−
$\bar{1}\bar{1}1$	−	−	+	+	−	−	+	+
$1\bar{1}\bar{1}$	−	+	+	−	−	+	+	−
$\bar{1}1\bar{1}$	−	+	−	+	−	+	−	+
$\bar{1}\bar{1}\bar{1}$	+	+	+	−	−	−	−	−
200	0	0	0	+	+	0	0	0
$\bar{2}00$	0	0	0	+	−	0	0	0
020	0	0	+	0	+	0	0	0
$0\bar{2}0$	0	0	+	0	−	0	0	0
002	0	+	0	0	+	0	0	0
$00\bar{2}$	0	+	0	0	−	0	0	0

It should be noted, however, that we have not established whether a given polynomial in Eq. (4.1) should be multiplied by a power series in $|\mathbf{k}|$ containing both even and odd terms, but merely that near $\mathbf{k}=0$ a realistic expansion of $b_n(\mathbf{k},\mathbf{K}_s)$ will generally have a leading term of fairly low order and may contain both even and odd terms. Specifics of expansions such as (4.1) will have to be determined from a more detailed numerical application than is reported here.

The momentum wave-function expansion [Eq. (4.1)], which explicitly displays the transformation properties [Eq. (2.5)] of the $b_n(\mathbf{k},\mathbf{K}_s)$, pertains to general points in the Brillouin zone. Although the behavior of the $b_n(\mathbf{k},\mathbf{K}_s)$ at general points on the Brillouin zone is of much more importance in volume integrals over the Brillouin zone than is the behavior of the $b_n(\mathbf{k},\mathbf{K}_s)$ at symmetry points, it is nonetheless of interest to examine Eqs. (2.5) and (4.1) near a symmetry point. This has been done for the Γ symmetry point [the origin for the expansion in Eq. (4.1)].

TABLE XII. Bands (irreducible representations) which are coupled by the nondiagonal $\mathbf{k}\cdot\mathbf{p}$ term in the perturbing Hamiltonian. An X in Table XII indicates that a nonzero coupling is allowed. This table is incomplete in that couplings to higher bands have been ignored. For example, the representation Γ_{12}' is contained in the 15×15 matrix (bands 9 and 10) and would couple to Γ_{25}', for instance. For our purposes, the incomplete table is adequate.

		Band 1	2,3,4	5	6,7,8
		Rep.			
Band	Rep.	Γ_1	Γ_{25}'	Γ_2'	Γ_{15}
1	Γ_1	0	0	0	X
2,3,4	Γ_{25}'	0	0	X	X
5	Γ_2'	0	X	0	0
6,7,8	Γ_{15}	X	X	0	0

Momentum wave functions $b_n(\mathbf{k},\mathbf{K}_s)$ were obtained numerically for small values of $\mathbf{k}$ along the Γ-Q line in the Brillouin zone. Using Eq. (2.5) we obtained $b_n(-\mathbf{k},\mathbf{K}_s)$ from the $b_n(\mathbf{k},\mathbf{K}_s)$. In performing this transformation the identification of the band symmetries was taken from Ref. 3. Thus the $b_n(\mathbf{k},\mathbf{K}_s)$ are known as we approach the Γ point from both the positive and negative directions along the Q-Γ-$\bar{Q}$ line in the Brillouin zone. A comparison of momentum wave functions $b_n(\mathbf{k},\mathbf{K}_s)$ with $b_n(-\mathbf{k},\mathbf{K}_s)$ in the limit as $\mathbf{k}\rightarrow 0$ along the $\Gamma-Q$ line reveals discontinuities in function in the $b_n(\mathbf{k},\mathbf{K}_s)$ for bands 2, 4, 5, and 8 at the point Γ. In Ref. 3 these bands were identified as Γ_2', Γ_1', Γ_1, and Γ_2, respectively. This identification was made in order to obtain continuity and smoothness in the wave functions across the boundary planes of the 48 subzones in the Brillouin zone.

A new character assignment in Eq. (2.5) could be made which would obtain continuity in the $b_n(\mathbf{k},\mathbf{K}_s)$ at the point Γ. Thus Eq. (2.5) yields $\chi_n^{(j)}(J)=+1$ for bands 1 to 4 and $\chi_n^{(j)}(J)=-1$ for bands 5 to 8. This character assignment which obtains continuity at Γ apparently produces discontinuities across entire plans in the interior of the Brillouin zone for bands 2, 4, 5, and 8. Apparently behavior of the wave functions at Γ is such that we may consider them to be "bonding" and "antibonding" in the Brillouin zone with respect to the

TABLE XIII. Leading powers of $|\mathbf{k}|$ which occur in the expansion of silicon momentum wave functions $b_n(\mathbf{k},\mathbf{K}_s)$ for the eight lowest valence bands and for the 15 lowest plane waves. Second-order "$\mathbf{k}\cdot\mathbf{p}$" perturbation theory was employed and both the diagonal and nondiagonal perturbing terms included. The momentum wave function $b_5(\mathbf{k},\mathbf{K}=0,0,0)$ for band 5 and the (0,0,0) reciprocal lattice vector was obtained by graphing numerical wave functions.

	Band 1	2,3,4	5	6,7,8
$\{\mathbf{K}_s\}$				
{0,0,0}	0,2	2	[3]	1,3
{1,1,1}	0,1,2,3	0,1,2,3	0,1,2,3	0,1,2,3
{2,0,0}	2	0,1,2,3	0,1,2,3	1,2,3

inversion operation J at the point Γ. This "bonding" and "antibonding" classification in k space is closely associated with and "dual" to the "bonding" and "antibonding" classification which emerges from the usual r-space "tight-binding-approximation" treatment for the Γ point.

The main point here is that apparently, at least in the numerical example being considered, the continuity symmetry classification appropriate for general points in the Brillouin zone is not the same as that required at the symmetry point Γ. Thus, with respect to general points, the point Γ may be regarded as an isolated point of singularity for the momentum wave functions. It would be of interest, but in the present context somewhat more difficult, to examine the $b_n(\mathbf{k},\mathbf{K}_s)$ at other symmetry points. It may be that other symmetry points also represent points of singularity.

V. DISCUSSION AND CONCLUSIONS

The motivation for the development of wave-function expansions of the sort treated in this paper is clear. There is a wide variety of semiconductor problems in which it would be very useful to have analytical representations of the $\mathbf{k}$ dependence of wave functions. Hopefully, such representations will make feasible theoretical treatment of problems which in the past has not been practical.

An important point for discussion concerns the usefulness and convergence of the proposed expansions. Because of the complexity of the wave functions and the fact that theory for the determination and symmetry properties of Bloch functions for interacting bands—bands exhibiting quasidegeneracy—is not fully developed, many questions remain unanswered.

The expansion which has been developed is based on a plane-wave expansion of the wave function, or, in a pseudopotential approach, the pseudowave function. Hence the area of general usefulness of the expansion should include those semiconductors and metals whose energy-band structures are represented fairly well by pseuodpotential plane-wave expansions.

The symmetry polynomials have been normalized to 4π over the unit sphere. They are therefore not orthonormal over the actual Brillouin zone. In view of the general form of Eq. (4.1) we expect that the expansion will be useful over the actual Brillouin zone. At any rate, the principal difficulties which such expansions may encounter appear to lie in the occurrence of quasidegeneracies rather than in the distinction between a spherical "Brillouin" zone and the actual Brillouin zone.

The main questions concerning wave-function expansions which are not completely resolved relate to the occurrence of quasidegeneracies in the energy-band structure. The difficulty[3] is that if one constructs energy bands according to the usual "energy-ordering" scheme, the resulting wave functions are not always smooth functions of $\mathbf{k}$ throughout the Brillouin zone. Problems arise at points of quasidegeneracy where two bands approach closely. These are accidental in that they are not required by symmetry. Near a point of quasidegeneracy the behavior of the energy bands (as defined above) and the associated wave functions is the following: Although the energy bands do not cross, the wave functions vary rapidly with $\mathbf{k}$ in a small region in which the bands interact strongly. Away from the region of close approach the wave functions are such that the bands appear to have crossed and thus switched symmetries.

The bands could either be treated as a set of isolated bands and defined according to their symmetry type or could be defined conventionally. Each procedure has advantages and disadvantages depending on whether one's principal interest is in wave functions or the density of states. Employment of an expansion such as (4.1) would be simplest if the "single-symmetry" definition were employed, although the behavior of such an expansion at the point of quasidegeneracy is not clear. Evidently the expansions would not be diagonal in the band index at the point of quasidegeneracy. The off-diagonal terms are small and it appears they can be neglected,[12] provided that the energy band is continued through the degeneracy according to symmetry.

Since quasidegeneracies are numerous in the conduction bands of silicon—and would probably be found in other materials as well if *both* energy bands and wave functions were to be carefully considered—these problems are of interest in a practical development of expansions. The valence bands in silicon are much simpler with quasidegeneracies occurring seldom if at all. While we believe the proposed expansion will be useful for both valence and conduction bands, certainly its application will be more straightforward for the valence bands than for the conduction bands.

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[12] J. Callaway and A. James Hughes (unpublished).