Special Points in the Brillouin Zone

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We present sets of special points in the Brillouin zone from which the average over the Brillouin zone of a periodic function of wave vector (e.g., energy, charge density, dipole matrix elements, etc.) can be determined in a simple and accurate way once the values of the function at these points are specified. We discuss a method for generating the special-point sets and apply it to the case of crystals with cubic and hexagonal Bravais lattices.

I. INTRODUCTION

Many calculations in crystals involve the averaging over the Brillouin zone of a periodic function of wave vector. Such calculations are often long and complicated and in principle require a knowledge of the value of the function at each $\vec{k}$ point in the Brillouin zone. In practice the functional values are known or determined over a set of points in the zone and the values at other points are found by using various types of approximation and interpolation methods. To obtain sufficient accuracy in these calculations it is necessary, in general, to know the functional values over a large set of points.

In this paper we present a systematic way of choosing sets of points in the Brillouin zone which makes possible simpler and more accurate calculations of averages over the Brillouin zone of periodic functions of wave vector. With these points one may avoid the use of interpolation in the calculation of averages.

This paper is organized in the following way. In Sec. II we discuss the conditions to be satisfied by the special-point sets, and the method for obtaining these sets. A number of special-point sets for crystals with cubic or hexagonal Bravais lattices are derived in Sec. III. The accuracy of the special-point scheme is discussed briefly in Sec. IV.

II. GENERATION OF SPECIAL POINTS

Special points in the Brillouin zone from which average values (i.e., averaged over the Brillouin zone) of various quantities, such as the charge density[1-3] or energy,[1] can be calculated have recently been proposed, and the conditions to be satisfied by these points have been specified.[1-3] Up to now no systematic way of satisfying an arbitrary number of these conditions has been suggested. In this section we restate these conditions and develop a method of generating successive sets of points which will satisfy as many of these conditions as one may require for a given accuracy. This method is a generalization of the one we have previously used[2] in charge-density calculations.

We restrict ourselves to smoothly varying periodic functions of wave vector (with periodicity $\vec{G}$, where $\vec{G}$ is any reciprocal-lattice vector). Assuming $g(\vec{k})$ to be such a function we can expand it in a Fourier series:

$$g(\vec{k}) = f_0 + \sum_{m=1}^{\infty} g_m e^{i\vec{k}\cdot\vec{R}_m} . \tag{1}$$

From $g(\vec{k})$ we can construct a function $f(\vec{k})$ which has the complete symmetry of the lattice, i.e.,

$$f(\vec{k}) = \frac{1}{n_T} \sum_i g(T_i\vec{k}) , \tag{2}$$

where the T_i's range over all the operations of the lattice point group T and where n_T is the number of elements in T. We can express $f(\vec{k})$ in the form

$$f(\vec{k}) = f_0 + \sum_{m=1}^{\infty} f_m A_m(\vec{k}) , \tag{3}$$

where

$$A_m(\vec{k}) = \sum_{|\vec{R}|=C_m} e^{i\vec{k}\cdot\vec{R}}, \quad m = 1, 2, \ldots . \tag{4}$$

The sum in (4) is over equivalent lattice vectors $\vec{R}$ related to each other through the operations of T. The lattice vectors are ordered so that $0 < C_m \leq C_{m+1}$. Equation (4) associates each $A_m(\vec{k})$ with a particular "shell" of lattice vectors. The $A_m(\vec{k})$ are real functions which can be written out in terms of sums and products of cosines and they satisfy the following relations:

$$\frac{\Omega}{(2\pi)^3} \int_{BZ} A_m(\vec{k})\, d^3k = 0, \quad m = 1, 2, \ldots \tag{5}$$

$$\frac{\Omega}{(2\pi)^3} \int_{BZ} A_m(\vec{k}) A_n(\vec{k})\, d^3k = N_n \delta_{mn} , \tag{6}$$

$$A_m(\vec{k}+\vec{G}) = A_m(\vec{k}) , \tag{7}$$

$$A_m(T\vec{k}) = A_m(\vec{k}) , \tag{8}$$

$$A_m(\vec{k})\,A_n(\vec{k}) = \sum_j a_j(m,n)\,A_j(\vec{k}) , \tag{9}$$

In these expressions Ω is the volume of the primitive cell, N_n is the number of lattice vectors in shell n, $\vec{G}$ is any reciprocal-lattice vector, T is any element of the lattice point group, and the $a_j(n, m)$'s are integers which can be determined for a specific choice of n and m. We define

$$A_0(\vec{k}) = 1$$

so that $a_j(m, n)$ is defined for $j, m, n \geq 0$. By the average over the Brillouin zone, $\bar{f}$, of f we mean

$$\bar{f} = \frac{\Omega}{(2\pi)^3} \int_{BZ} f(\vec{k})\, d^3k . \tag{10}$$

Using (3) and (5) we find $\bar{f} = f_0$. The average over the Brillouin zone of $g(\vec{k})$ in (1) is obviously also equal to f_0. We now present a method for obtaining the approximate value of the integral in (10) by performing a sum over a finite number of optimally chosen $\vec{k}$ points. The approximation can be made as accurate as desired.

The exact value of the integral in (10) would be obtained immediately if there were a point $\vec{k}_0$ which satisfied

$$A_m(\vec{k}_0) = 0, \quad m = 1, 2, \ldots, N \tag{11}$$

for $N = \infty$. Then using (3) we would immediately have $\bar{f} = f_0 = f(\vec{k}_0)$. Such a point does not in fact exist. The expansion coefficients f_m normally drop rapidly in magnitude as m becomes large so that we actually require (11) to be satisfied for a finite value of N. Baldereschi[1] has obtained for the cubic crystals the point k_0, which satisfies (11) for $N = 2$ or $N = 3$ depending on the lattice symmetry. This point, called the "mean-value point" by Baldereschi, gives surprisingly good results when used to calculate the average electron charge density[1,2] and energy[1] in a number of diamond and zinc-blende crystals. We have previously[2] used three points (called "representative k points" in Ref. 2) which satisfy (11) for the first seven nearest neighbors of an fcc-lattice-structure crystal in charge-density calculations. We show in Sec. III a better scheme which involves the use of only two points.

To satisfy (11) for large values of N, a many-point scheme becomes necessary. We impose the following conditions on the points $\vec{k}_i$ and their weighting factors α_i:

$$\sum_{i=1}^{n} \alpha_i A_m(\vec{k}_i) = 0, \quad m = 1, \ldots, N \tag{12}$$

$$\sum_{i=1}^{n} \alpha_i = 1 . \tag{13}$$

With these conditions on $\vec{k}_i$ and α_i one can easily show by using (3), (12), and (13) that the average over the Brillouin zone, f_0, of $f(\vec{k})$ is

$$f_0 = \sum_{i=1}^{n} \alpha_i f(\vec{k}_i) - \sum_m{}' \sum_i \alpha_i f_m A_m(\vec{k}_i) , \tag{14a}$$

where the prime on the sum over m indicates that those m for which $A_m(k)$ satisfies (12) are excluded from the sum. The first f_m to appear in (14a) is f_{N+1}. Since the expansion coefficients f_m normally drop rapidly in magnitude when m becomes large, by making N in (12) large enough we should have to a good approximation

$$f_0 = \sum_{i=1}^{n} \alpha_i f(\vec{k}_i) \quad . \tag{14b}$$

Equation (14b) presents a simple way of calculating the average over the Brillouin zone of a periodic function $f(\vec{k})$. All we need are the values of $f(\vec{k})$ for certain $\vec{k}$ points. We define the special points to be those which satisfy (12) by using a minimum number of points for a given value of N. The special points and their corresponding weighting factors are derived for the cubic and hexagonal Bravais-lattice crystals in Sec. III. In the following we discuss how one can generate sets of points that satisfy (12) for N as large as one may require.

Suppose that the points $\vec{k}_1$ and $\vec{k}_2$ satisfy $A_m(\vec{k}) = 0$ for certain values of m denoted by $\{N_1\}$ (for $\vec{k}_1$) and $\{N_2\}$ (for $\vec{k}_2$). From these two points we can generate a new set of points that will satisfy (12) for m in either $\{N_1\}$ or $\{N_2\}$. One can easily show (see the Appendix) that the new points $\vec{k}_i$ are related to $\vec{k}_1$ and $\vec{k}_2$ by

$$\vec{k}_i = \vec{k}_1 + T_i\,\vec{k}_2 , \tag{15}$$

with

$$\alpha_i = \text{const.}$$

and with T_i ranging over all the operations of the lattice point group. The new points $\vec{k}_i$ obtained in this way can be used in a similar process to generate larger sets of points which will satisfy (12) for larger values of N. In each such process each one of the original points gives rise to a number of new points. These points can always be transformed to equivalent points lying in the irreducible part of the Brillouin because the $A_m(\vec{k})$'s satisfy (7) and (8). When this is done the resulting points do not all necessarily have identical weighting factors. This arises from the fact that several of the original points may have been transformed into a single point of the irreducible zone.

When $\vec{k}_2$ in (15) is a symmetry point the set of

points $T\vec{k}_2$ does not contain too many elements. However, when this is not the case the number of points generated from an application of (15) can increase rapidly (e.g., by a factor of 48 in the cubic crystals). By a proper choice of $\vec{k}_1$ and $\vec{k}_2$ this can be avoided. We will now apply (15) to generate the special-point sets for the cubic and hexagonal Bravais-lattice structures.

III. SPECIAL POINTS

A. Face-Centered-Cubic Bravais Lattice

This Bravais lattice includes the diamond, zinc-blende, and rocksalt crystal structures. A good choice for a starting point $\vec{k} = (k_x k_y k_z)$ is $\vec{k}_1 = (\frac{1}{2}, \frac{1}{2}, 0)$ (units of $2\pi/a$, where a is the lattice constant). Another possible starting point is the point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. These points are better than other possible starting points because they appear to lead to the smallest possible point sets. With the choice of $\vec{k}_1 = (\frac{1}{2}, \frac{1}{2}, 0)$ or $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ Eq. (11) is satisfied for the infinite set of nearest-neighbor shells represented by the lattice vectors $\vec{R} = (R_1, R_2, R_3)$ (units of a) whenever at least one R_i is a half-integer. Equation (11) is therefore satisfied for $m = 1$, 3, 5, 7, etc. We will choose our second point so that (11) is satisfied for the even m's. The point $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ satisfies (11) for $m = 2$, 4, 6, etc. The set of points $T\vec{k}_2$ consists of eight different elements. Combining $\vec{k}_1 = (\frac{1}{2}, \frac{1}{2}, 0)$ or $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with $\vec{k}_2$ as in (15) we should get eight points. We find, however, that for either choice of $\vec{k}_1$ these eight points are related by the symmetry operations of T to only two distinct points of the irreducible zone. Six of these points correspond to $\vec{k}_1 = (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ and the other two to $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The normalized weighting factors for $\vec{k}_1$ and $\vec{k}_2$ are therefore $\alpha_1 = \frac{3}{4}$ and $\alpha_2 = \frac{1}{4}$, respectively. This leads to the simplest possible two-point scheme for the approximate determination of f_0 in the fcc Bravais-lattice crystals; i.e., we have from (14b)

$$f_0 = \tfrac{1}{4}[3f(\vec{k}_1) + f(\vec{k}_2)] .$$

The accuracy of these two points in determining f_0 is at least as good as the three-point scheme we have previously[2] used. These two points satisfy (12) for an infinite number of m, but not for all m. The first failure occurs for $m = 8$, corresponding to the eighth-largest nearest-neighbor shell represented by the lattice vector $\vec{R} = (2, 0, 0)$ (units of a). Other failures occur for $\vec{R} = (2, 2, 0)$, $(2, 2, 2)$, $(4, 0, 0)$, etc. The point $\vec{k} = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ satisfies (11) for the lattice vectors $(2, 0, 0)$, $(2, 2, 0)$, and $(2, 2, 2)$. The points $\vec{k}_1$ and $\vec{k}_2$ can be used with this point as in (15) to generate a set of ten points from which the average over the zone of $f(\vec{k})$ can be found with a higher degree of accuracy. The coordinates and relative weights of these points are

$$\vec{k}_1 = (\tfrac{7}{8}, \tfrac{3}{8}, \tfrac{1}{8}), \quad \alpha_1 = \tfrac{3}{16}; \quad \vec{k}_2 = (\tfrac{7}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_2 = \tfrac{3}{32};$$

$$\vec{k}_3 = (\tfrac{5}{8}, \tfrac{5}{8}, \tfrac{1}{8}), \quad \alpha_3 = \tfrac{3}{32}; \quad \vec{k}_4 = (\tfrac{5}{8}, \tfrac{3}{8}, \tfrac{3}{8}), \quad \alpha_4 = \tfrac{3}{32};$$

$$\vec{k}_5 = (\tfrac{5}{8}, \tfrac{3}{8}, \tfrac{1}{8}), \quad \alpha_5 = \tfrac{3}{16}; \quad \vec{k}_6 = (\tfrac{5}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_6 = \tfrac{3}{32};$$

$$\vec{k}_7 = (\tfrac{3}{8}, \tfrac{3}{8}, \tfrac{3}{8}), \quad \alpha_7 = \tfrac{1}{32}; \quad \vec{k}_8 = (\tfrac{3}{8}, \tfrac{3}{8}, \tfrac{1}{8}), \quad \alpha_8 = \tfrac{3}{32};$$

$$\vec{k}_9 = (\tfrac{3}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_9 = \tfrac{3}{32}; \quad \vec{k}_{10} = (\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_{10} = \tfrac{1}{32} .$$

These ten points satisfy (12) for all m except those which correspond to nearest-neighbor shells represented by lattice vectors of the form $\vec{R} = (4n_1, 4n_2, 4n_3)$, where the n_i's are integers. The first failure occurs for $m = 37$, corresponding to the lattice vector $(4, 0, 0)$. Other failures occur for $\vec{R} = (4, 4, 0)$, $(4, 4, 4)$, etc. Thus, for the first 150 different nearest neighbors, these ten points satisfy (12) except for the three lattice vectors $(4, 0, 0)$, $(4, 4, 0)$ and $(4, 4, 4)$. If desired, the accuracy of these special points can be further increased by using the point $\vec{k} = (\frac{1}{16}, \frac{1}{16}, \frac{1}{16})$, which satisfies (11) for the three lattice vectors $(4, 0, 0)$, $(4, 4, 0)$ and $(4, 4, 4)$. The ten points combined with $\vec{k}$ as in (15) give rise to a grid of 60 points in the Brillouin zone. For these 60 points (12) is satisfied except for lattice vectors of the form $\vec{R} = (8n_1, 8n_2, 8n_3)$ (n_i's being integers). The first error for these points occurs for $\vec{R} = (8, 0, 0)$, corresponding to $m \simeq 150$. For over the first 500 nearest neighbors these 60 points satisfy (12) except for $\vec{R} = (8, 0, 0)$, $(8, 8, 0)$ and $(8, 8, 8)$. The extension to higher point sets can be carried out by using the $\vec{k}$ points $\frac{1}{16}(1/2^n, 1/2^n, 1/2^n)$, $n = 1, 2, \ldots$. In each such extension the magnitude of the smallest lattice vector for which (12) is not satisfied is doubled.

The weighing factor α_i of each special point $\vec{k}_i$ is easily determined by the following general rule. Let n_i be the number of different (i.e., not related by a reciprocal-lattice vector) wave vectors obtained when $\vec{k}_i$ is acted upon by every element of T. Then α_i is proportional to n_i and the normalized weighing factors are given by

$$\alpha_i = n_i / \sum_j n_j . \tag{16}$$

As an example of the use of (16) consider the two special points $\vec{k}_1 = (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ and $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ discussed above. We see that there are 24 different wave vectors related to $\vec{k}_1$ through the operations of T and eight different wave vectors related to $\vec{k}_2$. We have therefore $n_1 = 24$ and $n_2 = 8$ and using (16) we get

$$\alpha_1 = \tfrac{24}{24+8} = \tfrac{3}{4}$$

and

$$\alpha_2 = \frac{8}{24+8} = \frac{1}{4} .$$

The weighting factor α_i is also proportional to the volume of $\vec{k}$ space occupied by $\vec{k}_i$.

The special point $\vec{k} = (0.6223, 0.2953, 0)\ (2\pi/a)$ proposed by Baldereschi[1] satisfies (12) for $m = 1$, 2 and gives a minimum for $m = 3$. This is the best single point for the calculation of averages in crystals with the fcc Bravais lattice when the expansion coefficients are significant only for the first few nearest-neighbor shells.

B. Body-Centered-Cubic Bravais Lattice

The points $(\frac{1}{2}, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (units of $2\pi/a$, where a is the lattice constant) are equally suitable as starting points. All three points lead to identical special-point sets. Choosing $\vec{k}_1$ to be any one of these points (11) is satisfied for all lattice vectors $\vec{R} = \frac{1}{2}(R_1, R_2, R_3)$ (units of a) whenever R_1, R_2, and R_3 are all odd (for the bcc lattice structures R_1, R_2, R_3 are simultaneously odd or even). The point $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ can be used with $\vec{k}_1$ to generate, as in (15), a new set of points. These points correspond to only two distinct points of the irreducible zone. They are

$$\vec{k}_1 = (\tfrac{3}{4}, \tfrac{1}{4}, \tfrac{1}{4}), \quad \alpha_1 = \tfrac{1}{2}; \quad \vec{k}_2 = (\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}), \quad \alpha_2 = \tfrac{1}{2} ,$$

where the α_i's are the weighting factors. These two points satisfy (12) except for the shells represented by lattice vectors of the form $\vec{R} = (2n_1, 2n_2, 2n_3)$, where the n_i's are integers. The first error occurs for $\vec{R} = (2, 0, 0)$, which is the sixth-largest lattice vector. Other errors occur for $\vec{R} = (2, 2, 0)$ and $(2, 2, 2)$. The two points $\vec{k}_1$ and $\vec{k}_2$ above have the same coordinates as the two points found for the fcc Bravais lattice. The weighting factors are different because of differences in symmetry. To go beyond the two-point scheme we can use $\vec{k} = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$, which satisfies (11) for the lattice vectors $(2, 0, 0)$, $(2, 2, 0)$, and $(2, 2, 2)$. This point can therefore be used with $\vec{k}_1$ and $\vec{k}_2$ to obtain the higher set of special points. When this is done we find the following eight points:

$$\vec{k}_1 = (\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_1 = \tfrac{1}{16}; \quad \vec{k}_2 = (\tfrac{3}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_2 = \tfrac{3}{16};$$

$$\vec{k}_3 = (\tfrac{3}{8}, \tfrac{3}{8}, \tfrac{1}{8}), \quad \alpha_3 = \tfrac{3}{16}; \quad \vec{k}_4 = (\tfrac{3}{8}, \tfrac{3}{8}, \tfrac{3}{8}), \quad \alpha_4 = \tfrac{1}{16};$$

$$\vec{k}_5 = (\tfrac{5}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_5 = \tfrac{3}{16}; \quad \vec{k}_6 = (\tfrac{5}{8}, \tfrac{3}{8}, \tfrac{1}{8}), \quad \alpha_5 = \tfrac{3}{16};$$

$$\vec{k}_7 = (\tfrac{5}{8}, \tfrac{3}{8}, \tfrac{3}{8}), \quad \alpha_7 = \tfrac{1}{16}; \quad \vec{k}_8 = (\tfrac{7}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_6 = \tfrac{1}{16} ,$$

where the α_i's are the relative weighting factors. These points satisfy (12) except for lattice vectors of the form $\vec{R} = (4n_1, 4n_2, 4n_3)$. The first error occurs for $\vec{R} = (4, 0, 0)$, which corresponds to $m = 28$ in (12). Larger point sets can be constructed in a similar way by using the points $\vec{k} = \frac{1}{8}\ (1/2^n, 1/2^n, 1/2^n)$, $n = 1, 2, \ldots$. The weighting factor of each special point can be determined from (16).

The special point $\vec{k} = (\frac{1}{6}, \frac{1}{6}, \frac{1}{2})\ (2\pi/a)$ suggested by Baldereschi[1] satisfies (12) for $m = 1, 2$ and minimizes (12) for $m = 3$. This is the best single point for the calculation of averages in crystals with the bcc Bravais lattice.

C. Simple-Cubic Bravais Lattice

The best starting point is $\vec{k}_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ (units of $2\pi/a$, where a is the lattice constant), which is identical with the special point obtained by Baldereschi.[1] This point satisfies (11) for all lattice vectors $\vec{R} = (R_1, R_2, R_3)$ whenever at least one of the components R_i is odd. To satisfy (11) for lattice vectors with even R_i we use the point $\vec{k}_2 = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ to generate a new set of points as in (15). We find the following four points:

$$\vec{k}_1 = (\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_1 = \tfrac{1}{8}; \quad \vec{k}_2 = (\tfrac{3}{8}, \tfrac{1}{8}, \tfrac{1}{8}), \quad \alpha_2 = \tfrac{3}{8};$$

$$\vec{k}_3 = (\tfrac{3}{8}, \tfrac{3}{8}, \tfrac{1}{8}), \quad \alpha_2 = \tfrac{3}{8}; \quad \vec{k}_4 = (\tfrac{3}{8}, \tfrac{3}{8}, \tfrac{3}{8}), \quad \alpha_4 = \tfrac{1}{8} .$$

These four points satisfy (12) except for the shells represented by lattice vectors of the form $\vec{R} = (4n_1, 4n_2, 4n_3)$, where the n_i's are integers. The first error occurs for $\vec{R} = (4, 0, 0)$, which corresponds to the fourteenth-largest shell.

Higher point sets can be obtained in a similar way by using the points $\vec{k}_i = \frac{1}{8}\ (1/2^n, 1/2^n, 1/2^n)$ for $n = 1, 2, \ldots$. The weighting factors for points in the larger special-point sets can be obtained from (16).

D. Hexagonal Bravais Lattice

The system of crystals with a hexagonal Bravais lattice includes the wurtzite and the hexagonal-close-packed crystal structures.

To describe the special-point sets we pick the origin of coordinates such that the primitive translation vectors in real and reciprocal space are given by

$$\vec{R}_1 = \tfrac{1}{2} a\hat{x} + \tfrac{1}{2}\sqrt{3}\, a\hat{y}, \quad \vec{R}_2 = \tfrac{1}{2} a\hat{x} - \tfrac{1}{2}\sqrt{3}\, a\hat{y}, \quad \vec{R}_3 = c\hat{z},$$

$$\vec{G}_1 = (2\pi/a)(\hat{x} + \tfrac{1}{3}\sqrt{3}\,\hat{y}), \quad \vec{G}_2 = (2\pi/a)(\hat{x} - \tfrac{1}{3}\sqrt{3}\,\hat{y}),$$

$$\vec{G}_3 = (2\pi/c)\,\hat{z} .$$

We will represent a special point $\vec{k} = (2\pi/a)(k_x, k_y, (a/c)k_z)$ of the Brillouin zone by $\vec{K} = (k_x, \sqrt{3}\,k_y, k_z)$ to avoid the repetition of the various factors.

A good starting point is $\vec{K} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{4})$, which satisfies (11) for the first nearest neighbors in the z direction and in the $z = 0$ plane. The best choice for a second point is $\vec{K}' = (\frac{2}{9}, 0, 0)$. When $\vec{K}$ and $\vec{K}'$ are combined according to (15) and the resulting points are taken to the irreducible part of the Brillouin zone we find the following three points:

$\vec{K}_1=(\frac{2}{9},0,\frac{1}{4})$, $\vec{K}_2=(\frac{4}{9},0,\frac{1}{4})$, $\vec{K}_3=(\frac{5}{9},\frac{1}{3},\frac{1}{4})$.

The weighting factor for each point is $\frac{1}{3}$. These three points satisfy (12) for the first-eight nearest-neighbor "shells." (In ordering the nearest-neighbor shells we are assuming a c/a ratio close to $\frac{2}{3}\sqrt{6}$; the exact value of this ratio is, however, immaterial in the scheme for generating the special points.) The first failure occurs for the six-fold ring of nearest neighbors represented by $\vec{R}=3\vec{R}_1$. To satisfy (12) for this ring we use the point $K=(\frac{1}{9},\frac{1}{9},0)$ with the three points above to generate the following six points:

$$\vec{K}_1=(\tfrac{1}{9},\tfrac{1}{9},\tfrac{1}{4}),\quad \alpha_1=\tfrac{1}{9};\quad \vec{K}_2=(\tfrac{2}{9},\tfrac{2}{9},\tfrac{1}{4}),\quad \alpha_2=\tfrac{1}{9};$$
$$\vec{K}_3=(\tfrac{4}{9},\tfrac{4}{9},\tfrac{1}{4}),\quad \alpha_3=\tfrac{1}{9};\quad \vec{K}_4=(\tfrac{1}{3},\tfrac{1}{9},\tfrac{1}{4}),\quad \alpha_4=\tfrac{2}{9};$$
$$\vec{K}_5=(\tfrac{5}{9},\tfrac{1}{9},\tfrac{1}{4}),\quad \alpha_5=\tfrac{2}{9};\quad \vec{K}_6=(\tfrac{4}{9},\tfrac{2}{9},\tfrac{1}{4}),\quad \alpha_6=\tfrac{2}{9}.$$

For the first 30 nearest neighbors these six points satisfy (12) except when $|\vec{R}|=2c$. The point $\vec{K}=(0,0,\frac{1}{8})$ satisfies (12) for this lattice vector and when combined with the above six points results in the following set of 12 points:

$$\vec{K}_1=(\tfrac{1}{9},\tfrac{1}{9},\tfrac{1}{8}),\quad \alpha_1=\tfrac{1}{18};\quad \vec{K}_2=(\tfrac{1}{9},\tfrac{1}{9},\tfrac{3}{8}),\quad \alpha_2=\tfrac{1}{18};$$
$$\vec{K}_3=(\tfrac{2}{9},\tfrac{2}{9},\tfrac{1}{8}),\quad \alpha_3=\tfrac{1}{18};\quad \vec{K}_4=(\tfrac{2}{9},\tfrac{2}{9},\tfrac{3}{8}),\quad \alpha_4=\tfrac{1}{18};$$
$$\vec{K}_5=(\tfrac{4}{9},\tfrac{4}{9},\tfrac{1}{8}),\quad \alpha_5=\tfrac{1}{18};\quad \vec{K}_6=(\tfrac{4}{9},\tfrac{4}{9},\tfrac{3}{8}),\quad \alpha_6=\tfrac{1}{18};$$
$$\vec{K}_7=(\tfrac{1}{3},\tfrac{1}{9},\tfrac{1}{8}),\quad \alpha_7=\tfrac{1}{9};\quad \vec{K}_8=(\tfrac{1}{3},\tfrac{1}{9},\tfrac{3}{8}),\quad \alpha_8=\tfrac{1}{9};$$
$$\vec{K}_9=(\tfrac{5}{9},\tfrac{1}{9},\tfrac{1}{8}),\quad \alpha_9=\tfrac{1}{9};\quad \vec{K}_{10}=(\tfrac{5}{9},\tfrac{1}{9},\tfrac{3}{8}),\quad \alpha_{10}=\tfrac{1}{9};$$
$$\vec{K}_{11}=(\tfrac{4}{9},\tfrac{2}{9},\tfrac{1}{8}),\quad \alpha_{11}=\tfrac{1}{9};\quad \vec{K}_{12}=(\tfrac{4}{9},\tfrac{2}{9},\tfrac{3}{8}),\quad \alpha_{12}=\tfrac{1}{9}.$$

For these 12 points the first failure to satisfy (12) occurs for m corresponding to $|\vec{R}_m|=4c$. Succeeding failures occur for $|\vec{R}|^2=27a^2$, $|\vec{R}|^2=27a^2+16c^2$, $|\vec{R}|^2=81a^2$, etc. Larger sets of points can be constructed to remove these failures by using the points $\vec{K}=(0,0,1/2^{n+3})$, $(2/3^{n+2},0,0)$, and $(1/3^{n+2},1/3^{n+2},0)$, $n\geq 1$. The weighting factors for the larger point sets can be obtained from (16).

It should be noted again that the coordinates of the special points $\vec{k}=(2\pi/a)(k_x,k_y,(a/c)k_z)$ of the Brillouin zone are related to the coordinates of $\vec{K}=(K_x,K_y,K_z)$ by $k_x=K_x$, $k_y=\frac{1}{3}\sqrt{3}\,K_y$, $k_z=K_z$.

IV. ACCURACY OF AVERAGES OBTAINED FROM THE SPECIAL-POINT SCHEME

How accurate is the special-point scheme in determining the average over the Brillouin zone, f_0, of a periodic function $f(\vec{k})$? How does the accuracy change with successive approximations when the number of points are increased? In this section we examine the accuracy of the special-point scheme using two complementary approaches which will prove useful.

The error ϵ in the value of f_0 using the point schemes described in Sec. III can be obtained from (14a) and (14b) and is equal to

$$\epsilon=\sum_i{}'\sum_m \alpha_i A_m(\vec{k}_i) f_m . \tag{17}$$

When (12) is not satisfied, the special points have the property that

$$\sum_i \alpha_i A_m(\vec{k}_i)=S_m N_m ,\quad S_m=\pm 1 \tag{18}$$

with N_m defined as in (6). Using this in (17) we find

$$\epsilon=\sum_m{}' S_m N_m f_m . \tag{19}$$

To obtain an estimate of this error we need the behavior of f_m. Using (3) and (6) we find

$$f_m=\frac{1}{N_m}\frac{\Omega}{(2\pi)^3}\int f(\vec{k})A_m(\vec{k})\,d^3k .$$

Assuming $f(k)$ to be a smoothly varying function we can expand it in a Taylor series and perform the integral over the Brillouin zone to obtain the asymptotic behavior of f_m. We will consider here only the case of the cubic crystals. The smallest vectors R_m associated with those f_m which appear in (19) are then of the form $(R,0,0)$, $(R,R,0)$, (R,R,R). For these lattice vectors we find, on carrying out the integration for the case of the fcc lattice structure, that f_m drops at least as fast as $(1/N_m)(1/|\vec{R}_m|^3)$ for large $|\vec{R}_m|$. This implies that

$$\epsilon\simeq\sum_m{}'\frac{S_m}{|\vec{R}_m|^3} . \tag{20}$$

The error therefore decreases rapidly as (12) is satisfied for larger N (and hence larger $|\vec{R}_m|$). In going from one set of special points to the next higher set of points the magnitude of the smallest $\vec{R}_m$'s occurring in (20) is increased by a factor of 2. We therefore expect the error ϵ to get reduced by a factor of nearly 8 for each successive approximation. This result can also be obtained in a different way.

Let D be the difference in the value of the average f_0 obtained from two consecutive approximations. Let $F_i^{(0)}$ be the value of $f(\vec{k})$ at one of the original points $\vec{k}_i$ and let $F_i^{(j)}$ for $j=1,\cdots,8$ be the values of $f(\vec{k})$ at the eight points obtained from $\vec{k}_i$ in going to the higher-order approximation. These eight points actually lie on the corners of a cube centered at the original point $\vec{k}_i$ for the case of the cubic crystals. The value of D is

$$D=\sum_i \alpha_i\left(F_i^{(0)}-\frac{1}{8}\sum_{j=1}F_i^{(j)}\right),$$

where the α_i's are the weighting factors for the original points $\vec{k}_i$. Assuming $f(\vec{k})$ to be a smoothly varying function that can be expanded in a Taylor series about each point $\vec{k}_i$, we find in going to third order in the expansion

$$D=\tfrac{1}{2}(\Delta k/2)^2\sum_i \alpha_i\nabla_k^2 f(\vec{k}_i), \tag{21}$$

where Δk is the length of the cube about each point $\vec{k}_i$. We found previously that the magnitude of the error ϵ is reduced by a factor of about 8 in each successive approximation. Since D is the difference in the errors of two successive approximations, if we ignore the smaller error, which is about 10% of the larger one, then we can take $D = \epsilon$. Therefore to minimize ϵ we will try to minimize D.

A reduction in the value of D can occur if we are interested in sums of averages. For example, the sum of the average energies of several bands can usually be more accurately determined than the average energy of each band individually. This is because the different bands do not have the same curvature everywhere; in particular, the lowest band normally has a different sense of curvature than the next few higher bands. This causes cancellations in (21) when taking sums of averages for these bands. The same effect appears in charge-density calculations based on a small number of points.[2]

The difference in the value of f_0 obtained from two nonconsecutive approximations can also be expressed in the form of (21) with $(\Delta k)^2$ replaced by some mean value $(\Delta k)^2$. This implies that if the Taylor expansion of $f(\vec{k})$ to third order were sufficient then the "best" single point k_0 would satisfy

$$\nabla_k^2 f(\vec{k}_0) = 0 \ .$$

Since the functional dependence of $f(k)$ on $\vec{k}$ is not known, in general, this equation cannot be used to determine $\vec{k}_0$. The best thing to do to minimize D is therefore to restrict $\vec{k}_0$ to satisfy the condition (11) for N as large as possible. This has been done by Baldereschi[1] for the cubic crystals.

We can also derive a different expression for D. By using (3) and (4) we find that

$$\nabla_k^2 f(k) = -\sum_m (a/2\pi)^2 |\vec{R}_m|^2 f_m A_m(\vec{k}) \ , \tag{22}$$

where the lattice vectors are of the form $a\vec{R}_m$ and $\vec{k}$ is measured in units of $2\pi/a$.

Using (12) and (18) we get

$$D = -\tfrac{1}{2}(\Delta k/2)^2 \sum_m{}' |\vec{R}_m|^2 S_m N_m f_m \ , \tag{23}$$

where the summation is only over those m for which (12) is not satisfied. In each set of successive approximations, (12) is satisfied for a larger set of m values and the number of terms in D decreases. Furthermore the length of the cubes (Δk) about each point is reduced by a factor of 2 in each successive approximation. The asymptotic behavior of f_m was found to be of the form $(1/N_m)(1/|\vec{R}_m|^3)$. Substitution in (23) therefore gives

$$D \approx (\Delta k)^2 / |R_m| \ , \tag{24}$$

where $|R_m|$ is the smallest lattice vector for which (12) is not satisfied. Since the magnitude of this lattice vector increases by a factor of 2 in each successive approximation and (Δk) decreases by a factor of 2, D decreases by a factor of about 8 in each successive approximation. It is interesting to note that the number of special points increases by a factor of nearly 8 for each consecutive approximation as the number of special points becomes large.

In conventional calculations of averages a reduction in the value of D takes place mainly through a reduction in the size of Δk as more points are used. The "effective" $|\vec{R}_m|$ occurring in (24) is much smaller in these calculations than is the case when a set of special points containing a comparable number of points are employed. For a given accuracy one therefore needs a smaller number of points if one chooses the grid of points in the Brillouin zone to coincide with the special points.

The use of the special points can be extended to the construction of interpolation formulas.

APPENDIX

We want to show that if

$$A_m(\vec{k}) = \sum_{|\vec{R}|=C_m} e^{i\vec{k}\cdot\vec{R}} = 0 \tag{A1}$$

is satisfied by $\vec{k}_1$ for $m = m_1$ and by $\vec{k}_2$ for $m = m_2$ then the set consisting of the n_T points obtained from

$$\vec{k}_i = \vec{k}_1 + T_i\vec{k}_2 \tag{A2}$$

for $i = 1, \ldots, n_T$ satisfy

$$\sum_i \alpha_i A_m(\vec{k}_i) = 0 \tag{A3}$$

with $\alpha_i = 1/n_T = \text{const.}$ for $m = m_1$ *and* for $m = m_2$. The sum in (A1) is over equivalent lattice vectors related to each other by the operations T_i of the lattice point group T, which has n_T elements.

From our choice of $\vec{k}_1$ and $\vec{k}_2$ we know that

$$A_m(\vec{k}_1)A_m(\vec{k}_2) = 0 \tag{A4}$$

is satisfied for $m = m_1$ and for $m = m_2$. Using (A1) this can be expressed as

$$\left(\sum_{|\vec{R}|=C_m} e^{i\vec{k}_1\cdot\vec{R}}\right)\left(\sum_{|\vec{R}|=C_m} e^{i\vec{k}_2\cdot\vec{R}}\right) = 0 \ . \tag{A5}$$

This equation is equivalent to

$$\left(\sum_{|\vec{R}|=C_m} e^{i\vec{k}_1\cdot\vec{R}}\right)\left(\sum_j e^{i\vec{k}_2\cdot T_j\vec{R}}\right) = 0 \ . \tag{A6}$$

The dot product $\vec{k}_2\cdot(T_j\vec{R})$ is equal to $(T_i\vec{k}_2)\cdot\vec{R}$, where $T_i = T_j^{-1}$. We can therefore rewrite (6) in the form

$$\sum_t \sum_{|\vec{R}|=C_m} e^{i(\vec{k}_1+T_t\vec{k}_2)\cdot\vec{R}} = 0 \ . \tag{A7}$$

Using the definition (A1) of $A_m(\vec{k})$ in Eq. (A7) is seen to be identical to

$$\sum_t A_m(\vec{k}_1 + T_t\vec{k}_2) = 0 \ . \tag{A8}$$

Using (A2) this can be expressed as

$$\sum_t A_m(\vec{k}_t) = 0 \ . \tag{A9}$$

Equation (A9), except for a constant multiplicative factor, is equivalent to (A3), which we wanted to show.

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