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The One-Dimensional Crystal. I. General*

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The electron-density function is considered at a set of n^3 equidistant points covering the period of a row with high indices $[n^2n1]$, with $n=1000$. This one-dimensional representation of the crystal yields as much information as the conventional evaluation at the n by n by n points of a grid defined by three sets of lines parallel to the co-ordinate axes. The summation of the Fourier series is thereby considerably simplified. The function can be evaluated rapidly at isolated points. The method is also applicable to the calculation of structure factors.

Introduction

The electron-density function $\rho(x, y, z)$ of a crystal is periodic in the distances a, b, c parallel to x, y, z, respectively. It is customary to evaluate this function (or one of its projections or sections) within one cell (or one mesh), at the points of a grid defined by the intersections of lines parallel to the co-ordinate axes. We propose to show that, in certain cases, the electron density may be more easily calculated at any one of a set of equidistant points covering the period of a row with high indices. The method can also be applied to the computation of structure factors.

Principle of the method

First consider the two-dimensional case. Let a function $g(x, y)$ be periodic in a and b parallel to x and y (Fig. 1). Consider a multiple mesh OAP_nC, consisting of n meshes in a row along the y axis. Its diagonal OP_n is

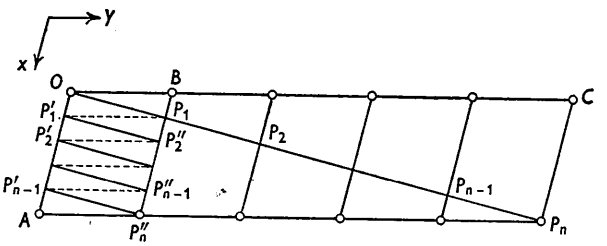

Fig. 1. Mesh $OABP''_n$ and diagonal OP_n of a row of meshes.

divided into n equal line segments by the boundaries of successive meshes. Let OP_n be divided into n^2 equal parts by a set of non-equivalent points. The latter have translation-equivalent points in mesh $OABP''_n$, which fall on a grid of n by n points (Fig. 2(*a*)) different from the usual one (Fig. 2(*b*)) in that one set of lines is oblique, instead of parallel, to the y axis. Provided n is chosen large enough, any point (x, y) of the mesh may be approximated by a point (X) of the set on the row $OP_n[n^2 1]$. The function $g(x, y)$ can thus be replaced by a one-dimensional function $g(X)$.

Now take the three-dimensional case. Consider (Fig. 3(*a*)) a multiple cell $OADECFGH$ consisting of n cells in a row along the y axis. Its diagonal plane is a net with mesh $OAGH$ (Figs. 3(*a*), (*b*)); the latter is divided into n equal areal segments by successive (010) net planes. Then consider a multiple mesh $OJKH$ consisting of n^2 meshes along the x axis. Its diagonal OK

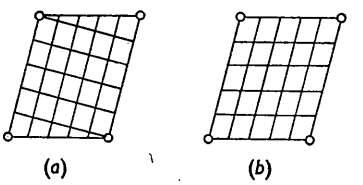

Fig. 2. (*a*) Proposed grid of points. (*b*) Usual grid of points.

is the period of the row $[n^2n1]$; it is divided into n^2 equal line segments by successive (100) net planes. Let OK be divided into n^3 equal parts by a set of non-equivalent points. Translation-equivalent points in the original cell fall on a grid of n by n by n points (hereafter referred to as 'the grid'), situated (Fig. 3(*a*)) at the intersections of three sets of lines; one set, parallel to OC [001], is parallel to the z axis, while the other two sets, parallel to OK $[n^2n1]$ and OH $[0n1]$, are slightly oblique to the x and y axes, respectively. Again, provided n is chosen sufficiently large, the three-dimensional function, say $\rho(x, y, z)$, can be replaced by $\rho(X)$, where X is the fractional co-ordinate of a point of the set on the row OK $[n^2n1]$, given in terms of the period OK $(0 < X \leqslant 1)$.

One may wonder why the special row $[n^2n1]$ has been selected for the purpose. Other special cases and the

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general case of row [*uvw*], with *u*, *v*, *w* coprime integers, are not interesting because they do not lead to a convenient grid of translation-equivalent points in the cell (Donnay & Hamburger, 1948*a*).

Transformation of co-ordinates

Consider (Fig. 3(*a*)) the two systems of co-ordinates:

$$a = OA,\ b = OB,\ c = OC$$

and

$$\mathfrak{a} = OK/n^2,\ \mathfrak{b} = OH/n,\ \mathfrak{c} = OC.$$

The matrix

$$\begin{pmatrix} 1 & 1/n & 1/n^2 \\ 0 & 1 & 1/n \\ 0 & 0 & 1 \end{pmatrix} \qquad (1)$$

expresses the transformation from system **abc** to system $\mathfrak{abc}$ and from indices *hkl* to indices $\mathfrak{hkl}$. It follows (*International Tables*, vol. 1, pp. 73–4) that the transformation of fractional co-ordinates $\mathfrak{x}$, $\mathfrak{y}$, $\mathfrak{z}$, measured in terms of $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$, to *x*, *y*, *z*, measured in terms of *a*, *b*, *c*, is given by the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 1/n & 1 & 0 \\ 1/n^2 & 1/n & 1 \end{pmatrix}, \qquad (2)$$

that the inverse transformations, $\mathfrak{abc}$ to **abc** and $\mathfrak{hkl}$ to *hkl*, are given by

$$\begin{pmatrix} 1 & -1/n & 0 \\ 0 & 1 & -1/n \\ 0 & 0 & 1 \end{pmatrix}, \qquad (3)$$

and that the transformation *x*, *y*, *z* to $\mathfrak{x}$, $\mathfrak{y}$, $\mathfrak{z}$ is given by

$$\begin{pmatrix} 1 & 0 & 0 \\ -1/n & 1 & 0 \\ 0 & -1/n & 1 \end{pmatrix}. \qquad (4)$$

The numerical value of *n* is determined by the accuracy with which a given point *x*, *y*, *z* is located in the cell. If its co-ordinates are given to *m* decimal places, the cell can be subdivided into $(10^m)^3$ 'uncertainty parallelepipeds'. Although the rounding off of the co-ordinates arbitrarily places the point at the origin of such a parallelepiped, all we really know is that the point lies somewhere in its interior. If no accuracy is to be lost in the transformations, every parallelepiped must contain one of the n^3 points of the grid. Hence n^3 must be equal to $(10^m)^3$, or $n = 10^m$. For practical purposes we assume the co-ordinates *x*, *y*, *z* to be given to three significant places ($m = 3$), and we therefore take $n = 1000$.

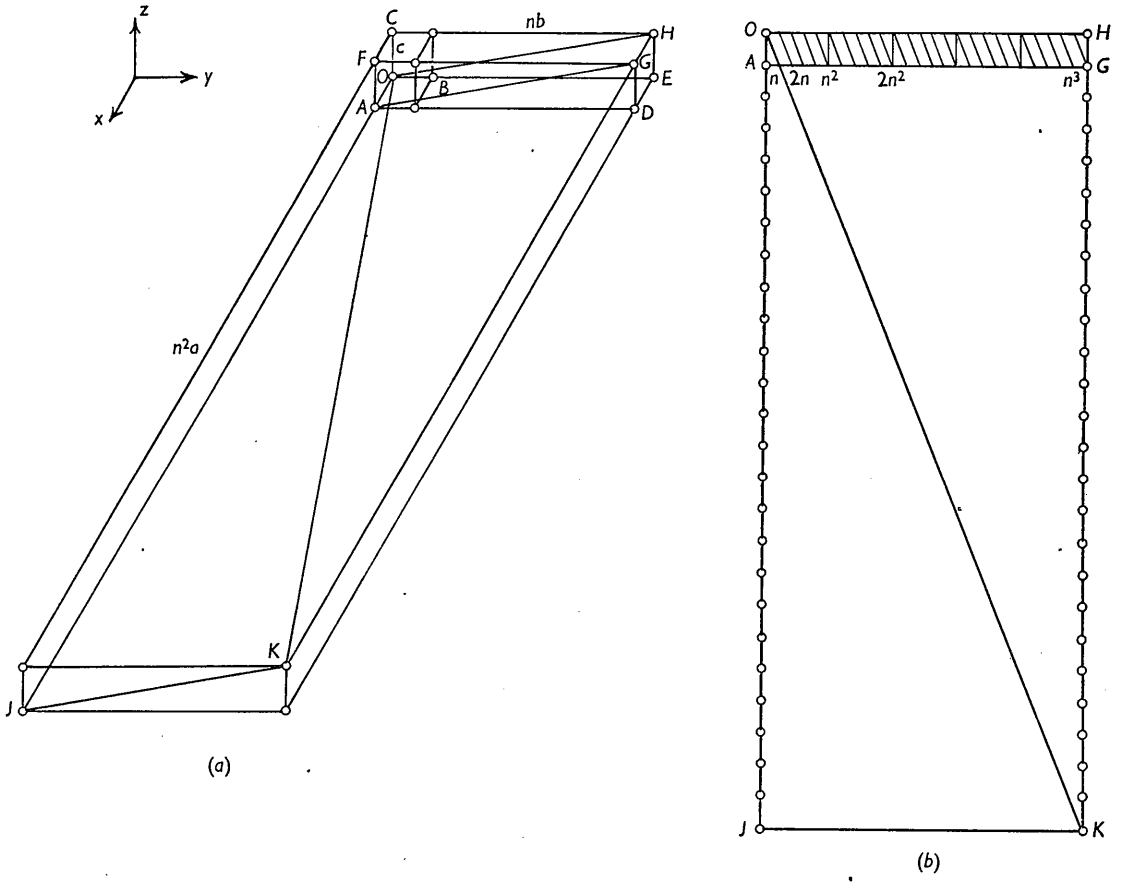

Fig. 3. (*a*) Body-diagonal *OK* of a twice-multiple cell (n^2a, *nb*, *c*). (*b*) Mesh *OAGH* and multiple mesh *OJKH* with diagonal *OK*.

Any point in the cell being given by its co-ordinates x, y, z, the co-ordinates $\mathfrak{x}, \mathfrak{y}, \mathfrak{z}$ of the same point can be obtained rigorously by using matrix (4):

$$\mathfrak{x}=x; \quad \mathfrak{y}=y-x/n; \quad \mathfrak{z}=z-y/n.$$

They are rounded to three decimals, however, so that the rounded-off co-ordinates $\mathfrak{x}', \mathfrak{y}', \mathfrak{z}'$ designate *a point of the grid*, namely, the one that lies closest to the given point in the cell:

$$\left.\begin{aligned} &\mathfrak{x}'=x; \\ &\mathfrak{y}'=y \text{ if } x<0{\cdot}500, \quad \mathfrak{y}'=y-0{\cdot}001 \text{ if } x\geqslant 0{\cdot}500; \\ &\mathfrak{z}'=z \text{ if } y<0{\cdot}500, \quad \mathfrak{z}'=z-0{\cdot}001 \text{ if } y\geqslant 0{\cdot}500. \end{aligned}\right\} \quad (5)$$

The transformation of the co-ordinates $\mathfrak{x}', \mathfrak{y}', \mathfrak{z}'$ to the co-ordinate X consists in finding the point of the row OK that is translation equivalent to the given point $\mathfrak{x}', \mathfrak{y}', \mathfrak{z}'$. The mesh $OAGH$ (Fig. 4) contains n^3 points, translation equivalent to the set of n^3 points on the row OK. Notice that the given point lies in the areal segment numbered $n\mathfrak{z}'$, falls within that segment on the

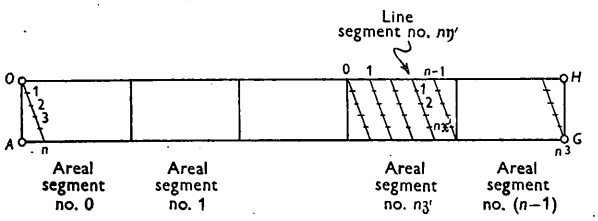

Fig. 4. Mesh $OAGH$ divided into n areal segments numbered from 0 to $(n-1)$. Each areal segment contains n line segments numbered from 0 to $(n-1)$ along OH. Each line segment contains n points. The total number of points reached at the end of each line segment is indicated along AG.

line segment numbered $n\mathfrak{y}'$, and is the $(n\mathfrak{x}')$th point on this line. (Notice that the first areal segment and the first line segment are numbered *zero*.) Since each areal segment contains n^2 points and each line segment n points, the point considered ranks $(\mathfrak{z}'n^3+\mathfrak{y}'n^2+\mathfrak{x}'n)$th among the n^3 points on the row. Dividing its rank by n^3 gives the desired fractional co-ordinate

$$X=\mathfrak{z}'+\mathfrak{y}'/n+\mathfrak{x}'/n^2. \quad (6)$$

Since we have chosen $n=1000$, X is a number consisting of nine decimals only. The first class of three digits (thousandths) represents $\mathfrak{z}'$, the second class (millionths) represents $\mathfrak{y}'$, and the third class (billionths) $\mathfrak{x}'$.

For example, given

$$x=0{\cdot}789, \quad y=0{\cdot}456, \qquad z=0{\cdot}123;$$

we have

$$\mathfrak{x}=0{\cdot}789, \quad \mathfrak{y}=0{\cdot}456-0{\cdot}000,789, \quad \mathfrak{z}=0{\cdot}123-0{\cdot}000,456;$$

whence

$$\mathfrak{x}'=0{\cdot}789, \quad \mathfrak{y}'=0{\cdot}455, \qquad \mathfrak{z}'=0{\cdot}123,$$

and

$$X=0{\cdot}123,455,789.$$

Conversely, given any point X of the set on the row, from equation (6) we find the corresponding $\mathfrak{x}', \mathfrak{y}', \mathfrak{z}'$ of the grid:

$$\left.\begin{aligned} \mathfrak{x}'&=n^2X-n^2\mathfrak{z}'-n\mathfrak{y}'=n^2X(\text{mod. } 1), \\ \mathfrak{y}'&=nX-n\mathfrak{z}'-\mathfrak{x}'/n=nX(\text{mod. } 1)-nX(\text{mod. } 0{\cdot}001), \\ \mathfrak{z}'&=X-\mathfrak{y}'/n-\mathfrak{x}'/n^2=X-X(\text{mod. } 0{\cdot}001). \end{aligned}\right\} \quad (7)$$

Here $\mathfrak{x}', \mathfrak{y}', \mathfrak{z}'$ and $\mathfrak{x}, \mathfrak{y}, \mathfrak{z}$ coincide. Let x', y', z' be the co-ordinates of the point in the cell that is rigorously translation equivalent to the point X on the row. Matrix (2), combined with equations (7), then yields

$$\begin{aligned} x'&=\mathfrak{x}=n^2X(\text{mod. } 1), \\ y'&=\mathfrak{y}+\mathfrak{x}/n=nX(\text{mod. } 1)-nX(\text{mod. } 0{\cdot}001) \\ &\qquad +n^2X(\text{mod. } 1)/n, \\ z'&=\mathfrak{z}+\mathfrak{y}/n+\mathfrak{x}/n^2=X-X(\text{mod. } 0{\cdot}001) \\ &\qquad +[nX(\text{mod. } 1)-nX(\text{mod. } 0{\cdot}001)]/n \\ &\qquad +n^2X(\text{mod. } 1)/n^2. \end{aligned}$$

Since $n=1000$, $X(\text{mod. } 0{\cdot}001)=nX(\text{mod. } 1)/n$, etc., these equations can be written

$$x'=n^2X(\text{mod. } 1), \quad y'=nX(\text{mod. } 1), \quad z'=X. \quad (8)$$

For example, given

$$X=0{\cdot}123,455,789,$$

we have

$$\mathfrak{x}'=0{\cdot}789=\mathfrak{x}, \quad \mathfrak{y}'=0{\cdot}455=\mathfrak{y}, \quad \mathfrak{z}'=0{\cdot}123=\mathfrak{z};$$

and

$$x'=0{\cdot}789, \qquad y'=0{\cdot}455,789, \quad z'=0{\cdot}123,455,789.$$

The transformation of indices, according to matrix (1), is

$$\mathfrak{h}=h+k/n+l/n^2. \quad (9)$$

The index $\mathfrak{h}$ refers to a unit length $\mathfrak{a}$. We want an index H referring to the unit length OK, which is n^2 times larger, so that

$$H=n^2h+nk+l. \quad (10)$$

With $n=1000$, the value of H reads 'h millions, k thousands, and l'. Since h, k and l do not exceed ± 499, there exists a unique H for every hkl.

Application to electron density

The electron density is usually written

$$\rho(xyz)=\frac{1}{V}\sum_h\sum_k\sum_l F_{hkl}\exp[-2\pi i(hx+ky+lz)]. \quad (11)$$

In this equation x, y, z refer to a point in the cell. We make an approximation if we replace it by the neighboring point x', y', z' whose co-ordinates are given by equation (8). With this approximation, the effect of which will be discussed later, we find, from (8) and (10), that

$$hx'+ky'+lz'=h[n^2X(\text{mod. } 1)]+k[nX(\text{mod. } 1)]+lX.$$

If we write n^2X instead of n^2X(mod. 1), and likewise nX instead of nX(mod. 1), we only add an integer to the expression, which does not affect the function (because of its periodicity). It follows that

$$hx'+ky'+lz'=(n^2h+nk+l)\,X=HX.$$

Letting $F_{hkl}=F_H$ and replacing $\sum_h\sum_k\sum_l$ by $\sum_H$, expression (11) becomes

$$\rho(X)=\frac{1}{V}\sum_H F_H\exp[-2\pi iHX]. \qquad (12)$$

Expressing the phase angle in cycles ($1^{c.}=1$ cycle$=2\pi$ radians) and decimal parts thereof (Villarceau, 1870 *a*, *b*), in order to take advantage of the periodic character of the function, we finally write

$$\rho(X)=\frac{1}{V}\sum_H F_H\exp[-iHX^{c.}(\text{mod. }1)]. \qquad (13)$$

This expression is particularly suited to the computation of the electron density at selected points, for instance, at a tentative atomic site X_0. In order to ascertain whether the atom is correctly placed, the immediate neighborhood of the trial position X_0 is explored by evaluating the electron density at the six points

$$\left.\begin{aligned}X_{1,2}&=\mathfrak{z}'+\mathfrak{y}'/n+(\mathfrak{x}'\pm 0{\cdot}001)/n^2,\\ X_{3,4}&=\mathfrak{z}'+(\mathfrak{y}'\pm 0{\cdot}001)/n+\mathfrak{x}'/n^2,\\ X_{5,6}&=\mathfrak{z}'\pm 0{\cdot}001+\mathfrak{y}'/n+\mathfrak{x}'/n^2,\end{aligned}\right\} \qquad (14)$$

which form a pseudo-octahedron around X_0. The value of the electron-density function should be smaller at these points than at X_0.

Equation (13) can also be used to make a preliminary survey of crystal space or of Patterson space. The function is evaluated at 10 by 10 by 10 points, where (n being again taken as 1000) X can be expressed as 'p thousandths, q millionths, and r billionths', with p, q, r equal to zero or multiples of 100. This means taking every hundredth point on every hundredth line in every hundredth areal segment. Regions of minima can thus be blocked out.

In practice we put X into a standard calculating machine and multiply by H, which, inside of intervals separated by large gaps, increases by one at a time. We read the first three decimal places of the product, rounded off if necessary, and transfer them to a table in which the F_H's are arranged in order of decreasing absolute values. The *Tables for Harmonic Synthesis* (Donnay & Hamburger, 1948*b*) list the values of $F\cos x$ (and therefore $F\sin x$) to one decimal place, for F ranging from 1 to 100, with x given in millicycles. Using these tables we find $F_H\cos HX$ and $F_H\sin HX$ for all values of H and add them in an adding machine. The final sum is $\rho(X)$.

Application to structure factors

With the one-dimensional representation of the crystal, the structure factor takes the form

$$F_H=\sum_n f_n\exp[-iHX_n^{c.}].$$

It is useful when the trigonometric expansion is cumbersome and is particularly appropriate when digital computers, such as I.B.M. machines, are available. In this case summing over all the atoms in the cell, or over half their number if a center of symmetry is present, is not a serious objection. The advantage lies in the fact that the angle is obtained by one multiplication (HX_n) rather than as the sum of three products ($hx+ky+lz$).

Discussion of the approximation

Let us evaluate Δ(mod. 1), where

$$\Delta=(hx+ky+lz)-HX.$$

In view of equations (10) and (6), and since $\mathfrak{x}'=x$ from equations (5), we have

$$\Delta(\text{mod. }1)=[k(y-\mathfrak{y}'-\mathfrak{x}'/n)+l(z-\mathfrak{z}'-\mathfrak{y}'/n-\mathfrak{x}'/n^2)](\text{mod. }1).$$

Using equations (5) again, it can be shown that the maximum value of Δ(mod. 1) is

$$0{\cdot}000{,}5\,|\,k\,|+0{\cdot}000{,}500{,}5\,|\,l\,|.$$

Taking $K=L=20$, the maximum Δ(mod. 1) is

$$0{\cdot}01+0{\cdot}010,\,01=0{\cdot}020,\,02,$$

corresponding to an angular difference of $20^{mc.}$.

This difference is of the same order of magnitude as that of the uncertainty attached to $hx+ky+lz$, when x, y, z are given to three decimal places only:

$$0{\cdot}0005\,(h+k+l)=0{\cdot}0005\times 60=0{\cdot}030,$$

or a maximum possible angular error of $30^{mc.}$.

Finally, it might be remarked that using x', y', z' instead of x, y, z means substituting a point inside the uncertainty parallelepiped for the point at its origin. Since the latter, however, is placed at the origin only because of the lack of accuracy with which its location is known, and really stands for any point inside the parallelepiped, the substituted point x', y', z' is as good as any other, and using it does not increase the error in the final result.

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