A new real-space formulation of crystal properties in closed form

Ph. Audit

LE JOURNAL DE PHYSIQUE

Classification
Physics Abstracts
02.90 — 63.10 — 71.10 — 75.10

A new real-space formulation of crystal properties in closed form

Ph. Audit

Laboratoire P.M.T.M., Université Paris-Nord,
avenue Jean-Baptiste Clément, 93430 Villetaneuse, France

Résumé. — Afin d'élaborer une nouvelle méthode pour décrire les propriétés du cristal parfait, une étude mathématique des matrices cycliques a été récemment entreprise [*J. Physique* **42** (1981) 903] par l'auteur qui la poursuit dans le présent article. Le calcul des éléments de certaines fonctions de matrices d'interaction interatomique, de dimension infinie, constitue une méthode naturelle pour décrire les propriétés vibrationnelles, électroniques, magnétiques... du cristal. On montre que ces fonctions peuvent être calculées par une réduction considérable de l'ordre de la variable matricielle, basée sur les relations qui relient les matrices cycliques et certains polynômes orthogonaux. Des expressions exactes peuvent être ainsi obtenues sous la forme d'intégrales multiples, pour les fonctions qui décrivent des propriétés mesurables, des fonctions thermodynamiques, la fonction de Green, la densité d'états... La méthode ne requiert pas une analyse spectrale préalable du problème. On donne en particulier des expressions de la densité d'états locale et totale.

Abstract. — As a new approach to describe perfect crystal properties, the mathematical study of cyclic matrices initiated recently [*J. Physique* **42** (1981) 903] by the author is pursued in the present article. A very natural formulation of vibrational, electronic, magnetic... crystal properties is offered by calculating the elements of some functions of interatomic interaction matrices, whose dimensions are infinite. These functions can be handled by a drastic reduction of the matrix variable order, which is based on relations linking cyclic matrices and orthogonal polynomials. Exact expressions are obtained in the form of multiple integrals. They are valid for functions describing experimentally measured properties, any thermodynamic function, Green's function, density of states, etc. Their derivation does not require a prior spectral analysis of the problem. A detailed study of the density of states is undertaken, and a simple closed expression is given for this quantity.

1. **Introduction.** — There is at present a renewed interest in real-space methods for studying properties of solids, but curiously the use of cyclic matrices (circulant), although it has long been recognized [1] as offering an adequate and very natural approach, seems to be neglected. In spite of the inherent difficulties in dealing with functions of matrices of enormous dimensions, except in a purely numerical way, some success has been obtained by this method in the case of vibrational [1, 2] and electronic [3, 4] properties of crystals. But unfortunately many other developments have remained purely formal and further advances have been hindered by an insufficient elucidation of the properties of the cyclic matrices. Moreover, being generally founded on the relationship which connects the eigenvalues of a cyclic matrix and the primitive roots of unity, some previous approaches yield results often similar to those attainable with a reciprocal-space formulation; consequently one loses the most interesting expected benefit of the method, which should be a real space description of crystal properties.

To good approximation, it has been recognized that the introduction of model Hamiltonians reduce

phonon, electron, magnon... problems to a similar formulation; the choice of an appropriate local basis set : vibrational displacements, atomic orbitals, spin states... yields a formulation of dynamical equations, Schrödinger equations, spin-exchange Hamiltonians... in terms of some specific hermitian matrices of infinite dimension, which will be designated collectively as interaction matrices and labelled $\underset{\sim}{D}$ in the present article. A decomposition of $\underset{\sim}{D}$ can be obtained in terms of high-order cyclic and low-order noncyclic matrices to describe respectively the lattice and the pairwise interactions between the atoms. Our aim will be to develop a theory formally without reference to a particular system, in order to emphasize the similarities existing between many different physical properties which are simply related to the elements of some matrix function $f(\underset{\sim}{D})$. The general designation f can have many different meanings : Green's function, local or total density of states, correlation function, total energy, partition function, any thermodynamic function... The local properties, where one is interested in different behaviour of atoms for different lattice sites, are determined by the diagonal elements of $f(\underset{\sim}{D})$, whereas the solution of scattering problems is given by the off-diagonal elements of $f(\underset{\sim}{D})$. The global properties of the crystal, as the thermodynamical properties, are additive functions of the eigenstates given by the trace of $f(\underset{\sim}{D})$. The $\underset{\sim}{D}$-eigenvalues determination is not an indispensable preliminary for applying the above formalism and recently, in an article [6] subsequently to be referred to as 1, we have obtained expressions in closed form for the elements of a matrix $f(\underset{\sim}{D})$ of infinite order by taking into account the similarities of the relations fulfilled by Chebyshev orthogonal polynomials and cyclic matrices. But the validity of the above results is restricted to the case where the pairwise interactions between atoms belonging to neighbouring unit cells are simply expressed by matrices which are commutative and identical for opposite directions in space.

The consideration of functions of noncommutative matrices is beset with difficulties, but is nevertheless indispensable in order to allow the theory to treat models giving a realistic description of crystal properties. The solution of the problem is reported in the present article, and can be visualized as the generalization of the results obtained in 1. A simple example of the application of the theory is also reported.

2. The interaction matrix.

— The structure of an ideal crystal lattice is formed by the regular repetition of $L \times L \times L = N$ unit cells. In the basis defined by the primitive translation vectors e_1, e_2, e_3 of the lattice, with the origin at the zeroth cell, a unit cell is located at position vector l, which refers collectively to the three positive or negative integers l_1, l_2, l_3.

We define the matrix $\underset{\sim}{a}_l$, whose elements are regarded as parameters of different physical meaning, to des-

cribe the interaction between the s atoms of the zeroth unit cell and the s atoms of the lth unit cell. The order of $\underset{\sim}{a}_l$ is $q = sr$, where r is the dimension of the atomic basis set used to describe the physical interaction. The matrix $\underset{\sim}{a}_l$ can be easily specified in the different cases : for a *dynamical matrix* the elements are components of the force constant tensor, the invariance of the potential energy against rigid body translation leads to a relation between the diagonal and off-diagonal elements, and the atoms undergo displacements in the three directions of space, so that $r = 3$; for a *tight-binding Hamiltonian* the diagonal and off-diagonal elements represent respectively the energy of orbitals and the hopping of an electron from one orbital to another, and accordingly r will take the values of 1, 3 or 5 for s, p or d orbitals; for a *spin Heisenberg Hamiltonian* the diagonal elements equal to zero, while the off-diagonal elements are exchange integrals and $r = 1$.

Clearly the matrices $\underset{\sim}{a}_l$ depend on l, i.e. are different for different neighbours, but if we assume the crystal to satisfy cyclic boundary conditions they are invariant with respect to translation so that $\underset{\sim}{a}_l$ describes the interaction between two unit cells l' and $l + l'$.

In order to construct the interaction matrix $\underset{\sim}{D}$ for a perfect infinite crystal where the range of interaction is limited to the nth neighbours, we can start by writting the block matrix which concerns the atomic rows collinear with e_1. We choose the column indice of the matrix first row elements, varying from 0 to $L - 1$, to correspond to the following sequence of l_1 values

$$0, 1, 2, ..., \frac{L-1}{2}, -\frac{L-1}{2}, ..., -2, -1 .$$

According to the above mentioned property of the $\underset{\sim}{a}_l$ matrices, we can write the $qL \times qL$ block matrix in the form of a block circulant matrix, whose first row may be written as

$$\underbrace{\underset{\sim}{a}_{000}\ \underset{\sim}{a}_{001}\ \underset{\sim}{a}_{002}\ \cdots\ \underset{\sim}{a}_{00n}}_{\substack{n \text{ nonzero elements}}}\ \underbrace{\underset{\sim}{0}\ \underset{\sim}{0}\ \cdots\ \underset{\sim}{0}\ \underset{\sim}{0}}_{\substack{L\text{-}2n\text{-}1 \text{ zero}\\ \text{elements}}}\ \underbrace{\underset{\sim}{a}_{00\bar{n}}\ \cdots\ \underset{\sim}{a}_{00\bar{2}}\ \underset{\sim}{a}_{00\bar{1}}}_{\substack{n \text{ nonzero elements}}}$$

and the elements of the next rows follow by cyclic permutation; or equivalently using the direct product notation

$$\underset{\sim}{1}_L \otimes \underset{\sim}{a}_{000} + \sum_{l_3=1}^{n} \underset{\sim}{m}_{l_3} \otimes \underset{\sim}{a}_{00l_3} + \underset{\sim}{m}_{-l_3} \otimes \underset{\sim}{a}_{00\bar{l}_3} ,$$

where $\underset{\sim}{m}_l$ (resp. $\underset{\sim}{m}_{-l}$) the topological non-symmetric cyclic matrix of order l (resp. $- l$)

$$\underset{\sim}{m}_l = (0, 0, ..., 1, ..., 0, 0)_{\text{cycl.}} , \tag{1}$$

$$\underset{\sim}{m}_{-l} = \underset{\sim}{m}_l^{-1} = (0, 0, 0, ..., 1, ..., 0, 0)_{\text{cycl.}} , \tag{2}$$

is the matrix having a single nonzero element in the first row and the lth (resp. $(L - l)$th) column [3]. The $\underset{\sim}{m}_l$ (resp. $\underset{\sim}{m}_{-l}$) matrix relates an atom with its lth neighbour situated in the direction e_3 (resp. $- e_3$).

The m_p's are commutative $L \times L$ matrices which obey the following relations

$$m_0 = m_L = 1_L,\tag{3}$$

$$m_p \, m_q = m_q \, m_p = m_{p+q}\tag{4}$$

$$(m_p)^q = m_{pq}.\tag{5}$$

An element in the kth row and lth column (labelled starting from 0) is given by

$$[m_p]_{kl} = \Delta(k + p - l), \quad (l < L/2)\tag{6}$$

where $\Delta(q)$ is the Kronecker function, or in more concise form

$$[m_p]_l = \Delta(p - l),\tag{7}$$

since a single indice is sufficient to designate the elements of the zeroth row that fully define a cyclic matrix.

The next step in the construction of the D matrix is to consider the atomic planes parallel to the plane (e_2, e_3), where the interacting units are the previously considered linear chains. An obvious generalization of the atomic row results yields the following expression for the $qL^2 \times qL^2$ block matrix describing plane interactions

$$\sum_{l_2,l_3=0}^{\pm n} m_{l_2} \otimes m_{l_3} \otimes a_{0l_2l_3},$$

where equation (3) has been used.

Further development of the same argument leads finally to the total interaction matrix D in the form

$$D = \sum_{k_1,k_2,k_3=0}^{\pm n} m_{k_1} \otimes m_{k_2} \otimes m_{k_3} \otimes a_{k_1k_2k_3}.\tag{8}$$

The D matrix is indeed a multi-level partitioned matrix, in the sense that $m_{k_1} \otimes m_{k_2} \otimes m_{k_3} \otimes a_{k_1k_2k_3}$ may be identified with the cyclic matrix m_{k_1} whose elements are identical blocks $m_{k_2} \otimes m_{k_3} \otimes a_{k_1k_2k_3}$ which may itself be partioned into blocks constituted by the matrix m_{k_2} with elements $m_{k_3} \otimes a_{k_1k_2k_3}$. This last block matrix is a cyclic matrix having the non-cyclic matrix $a_{k_1k_2k_3}$ for elements. Hence, considering the partially cyclic character of the D matrix, the element in row i and column j of the noncyclic block matrix, which is the l_1, l_2, l_3 block matrix element in the first row of the block circulant matrix, will be labelled as $[D]_{l_1l_2l_3,ij}$.

The order of the matrix D is $qN \times qN$, and for any crystal of reasonable size the dimensions of D are enormous, therefore we will find very convenient subsequently to consider a matrix d of finite order $q \times q$, derived from D. On account of equation (5) and of direct product properties we have the relation

$$m_{k_1} \otimes m_{k_2} \otimes m_{k_3} = (m_1 \otimes 1 \otimes 1)^{k_1}$$

$$\times (1 \otimes m_1 \otimes 1)^{k_2} (1 \otimes 1 \otimes m_1)^{k_3},$$

which associated with the following 1-1 correspondence between topological cyclic matrices and scalar variables

$$\frac{x}{x'} \leftrightarrow m_1 \otimes 1 \otimes 1, \qquad \frac{x'}{x} \leftrightarrow m_{-1} \otimes 1 \otimes 1,$$

$$\frac{y}{y'} \leftrightarrow 1 \otimes m_1 \otimes 1, \qquad \frac{y'}{y} \leftrightarrow 1 \otimes m_{-1} \otimes 1,$$

$$\frac{z}{z'} \leftrightarrow 1 \otimes 1 \otimes m_1, \qquad \frac{z'}{z} \leftrightarrow 1 \otimes 1 \otimes m_{-1},$$

leads from equation (8) to the matrix

$$d\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right) = \sum_{k_1,k_2,k_3=0}^{\pm n} \left(\frac{x}{x'}\right)^{k_1} \left(\frac{y}{y'}\right)^{k_2} \left(\frac{z}{z'}\right)^{k_3} a_{k_1k_2k_3},\tag{9}$$

subsequently referred to as the *characteristic interaction matrix*.

This matrix has been defined with reference to the reciprocal space representation of D : a Fourier series which can be written, for a given wave vector $\mathbf{q} = (q_x, q_y, q_z)$, as

$$d(\mathbf{q}) = \sum_{k_1,k_2,k_3=0}^{\pm n} (e^{-iq_x})^{k_1} (e^{-iq_y})^{k_2} (e^{-iq_z})^{k_3} a_{k_1k_2k_3}.\tag{10}$$

The two series (9) and (10) differ by their weight factors only, which are orthogonal functions in both cases (see Eq. (16) below) and this property will be of great utility in the present work.

3. **Functions of the interaction matrix.** — Considering the interaction matrix of a perfect infinite crystal, where interactions of an atom with its neighbours situated outside a domain K centred on this atom are neglected, we have

$$D = \sum_{k^i \in K} m_{k_1^i} \otimes m_{k_2^i} \otimes m_{k_3^i} \otimes a_{k_1^i k_2^i k_3^i}.\tag{11}$$

In order to calculate functions of the matrix D which can be defined, for example, by power series it is clearly necessary to obtain first an expression for D^p, where p is some positive integer. But in equation (11), whereas the cyclic matrix factors are commutative and satisfy the simple relations (1)-(7), on the contrary the a_i's do not commute with each other and hence they do not obey some principles of elementary calculus as for instance the multinomial development rules of ordinary algebra with numbers. To write expressions comprising noncommutative factors, we shall adopt the convention of representing by one overlined factor the entire set of factors which can be derived from it by permutation of its terms. Thus for example $\overline{AB}$ is equal to $AB + BA$. Hence our conven-

tion allows us to express in condensed form, using equations (4), (5), the matrix

$$\underset{\sim}{D}{}^P = \sum_{p_0 + p_1 + \ldots = p} \underset{\sim}{m}_{p_0 k_1^0 + p_1 k_1^1 + \cdots} \otimes \underset{\sim}{m}_{p_0 k_2^0 + p_1 k_2^1 + \cdots}$$

$$\otimes \underset{\sim}{m}_{p_0 k_3^0 + p_1 k_3^1 + \cdots} \otimes \overline{\underset{\sim}{a}_{k_1^0 k_2^0 k_3^0}^{p_0} \underset{\sim}{a}_{k_1^1 k_2^1 k_3^1 \ldots}^{p_1}}, \quad (12)$$

whose elements, according to equation (7), are given by

$$[\underset{\sim}{D}{}^P]_{l_1 l_2 l_3} = \sum_{p_0 + p_1 + \ldots = p} \Delta(p_0 \, k_1^0 + p_1 \, k_1^1 + \cdots - l_1)$$

$$\times \; \Delta(p_0 \, k_2^0 + p_1 \, k_2^1 + \cdots - l_2)$$

$$\times \; \Delta(p_0 \, k_3^0 + p_1 \, k_3^1 + \cdots - l_3) \, \overline{\underset{\sim}{a}_{k_1^0 k_2^0 k_3^0}^{p_0} \underset{\sim}{a}_{k_1^1 k_2^1 k_3^1 \ldots}^{p_1}}. \quad (13)$$

In order to proceed further we must introduce some considerations on orthogonal polynomials of degree n and specifically on Chebyshev polynomials of the second kind $C_p(x)$, whose properties are strongly related to those of cyclic matrices as shown in 1.

An important property of these polynomials is that they satisfy the rule [13]

$$C_p(2 \cos \theta) = 2 \cos p\theta$$

or according to de Moivre's theorem

$$C_p(e^{i\theta} + e^{-i\theta}) = e^{ip\theta} + e^{-ip\theta}.$$

A similar relation applies to any scalar variable x in the form

$$C_p(x + x^{-1}) = x^p + x^{-p}, \quad (14)$$

and it holds also, from equation (5), for the $\underset{\sim}{m}_p$ matrices, so that

$$\cdot \, C_p(\underset{\sim}{m}_1 + \underset{\sim}{m}_{-1}) = \underset{\sim}{m}_p + \underset{\sim}{m}_{-p},$$

which has proved to be a useful property [3, 6].

As usual $\langle \ldots, \ldots \rangle$ denotes the scalar product; by a change of variables and a generalization of the one-dimensional definition [13], we have in n dimensions

$$\langle f(x_1, \ldots, x_n), C_{p_1}(x_1) \ldots C_{p_n}(x_n) \rangle = \frac{1}{[1 + \Delta(p_1)] \ldots [1 + \Delta(p_n)] (2\pi)^n}$$

$$\times \int_{-1}^{1} \ldots \int dx_1 \ldots dx_n \, C_{p_1}(2 \, x_1) \ldots C_{p_n}(2 \, x_n)(1 - x_1^2)^{-1/2} \ldots (1 - x_n^2)^{-1/2} f(2 \, x_1, \ldots, 2 \, x_n), \quad (15a)$$

$$= \frac{1}{[1 + \Delta(p_1)] \ldots [1 + \Delta(p_n)] \pi^n} \int_0^\pi \ldots \int d\theta_1 \ldots d\theta_n$$

$$\times \cos p_1 \, \theta_1 \ldots \cos p_n \, \theta_n f(2 \cos \theta_1, \ldots, 2 \cos \theta_n). \quad (15b)$$

The C_p polynomials being of degree n, we have obviously

$$\langle x^q, C_p(x) \rangle = 0, \quad q < p$$

and consequently :

$$4 \left\langle \left(\frac{x'}{x}\right)^l \left(\frac{x}{x'}\right)^q, C_0(x) \, C_0(x') \right\rangle = \Delta(q - l), \quad (16)$$

taking into account the relation $C_0(x) = 2$.

Substituting equation (16) in equation (13) we have

$$[\underset{\sim}{D}{}^P]_{l_1 l_2 l_3} = 2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} \sum_{p_i} \left(\frac{x}{x'}\right)^{p_0 k_1^0 + p_1 k_1^1 + \cdots} \left(\frac{y}{y'}\right)^{p_0 k_2^0 + p_1 k_2^1 + \cdots} \right.$$

$$\left. \times \left(\frac{z}{z'}\right)^{p_0 k_3^0 + p_1 k_3^1 + \cdots} \overline{\underset{\sim}{a}_{k_1^0 k_2^0 k_3^0}^{p_0} \underset{\sim}{a}_{k_1^1 k_2^1 k_3^1}^{p_1} \ldots}, C_0(x) \, C_0(x') \, C_0(y) \, C_0(y') \, C_0(z) \, C_0(z') \right\rangle, \quad (17)$$

so that the process of introducing variables $x, x', \ldots$ results in annihilation of all the terms forbidden by the cyclic matrix properties in the multinomial development of the noncommutative matrices $\underset{\sim}{a}_i$. Rearranging terms we have

$$[\underset{\sim}{D}{}^P]_{l_1 l_2 l_3} = 2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} \left(\sum_{k^i \in K} \left(\frac{x}{x'}\right)^{k_1^i} \left(\frac{y}{y'}\right)^{k_2^i} \left(\frac{z}{z'}\right)^{k_3^i} \underset{\sim}{a}_{k_1^i k_2^i k_3^i}\right)^p, C_0(x) \right.$$

$$\left. \times \; C_0(x') \, C_0(y) \, C_0(y') \, C_0(z) \, C_0(z') \right\rangle \quad (18)$$

$$= 2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} \left(\underset{\sim}{d}\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)\right)^p, C_0(x) \, C_0(x') \, C_0(y) \, C_0(y') \, C_0(z) \, C_0(z') \right\rangle,$$

and more generally for any function $f(x)$ expressible as a power series in x we get

$$[f(\underset{\sim}{D})]_{l_1 l_2 l_3} = 2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} f\left(\underset{\sim}{d}\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)\right), C_0(x) C_0(x') C_0(y) C_0(y') C_0(z) C_0(z') \right\rangle. \tag{19}$$

As a special interesting case, let us consider the element

$$[f(\underset{\sim}{D})]_{000} = 2^6 \left\langle f\left(\underset{\sim}{d}\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)\right), C_0(x) C_0(y) C_0(z) C_0(x') C_0(y') C_0(z') \right\rangle. \tag{20}$$

Repeated $L^3 = N$ times, this element forms the diagonal of the matrix $f(\underset{\sim}{D})$. Then an expression for the trace follows readily

$$\mathrm{Tr}\, f(\underset{\sim}{D}) = N\, 2^6 \left\langle \mathrm{Tr}\, f\left(\underset{\sim}{d}\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)\right), C_0(x) C_0(y) C_0(z) C_0(x') C_0(y') C_0(z') \right\rangle. \tag{21}$$

On account of equation (15), the results obtained in equations (19)-(21) appear to be expressed as multiple integrals of some $f(\underset{\sim}{d})$ matrix elements that will be denoted $g\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)$; the integrals' orders are respectively

2, 4, 6 for 1, 2, 3-dimensional lattice spaces. But sometimes the function $g\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)$ can be written in the form

$g_1\left(\frac{x}{x'} + \frac{x'}{x}, \frac{y}{y'} + \frac{y'}{y}, \frac{z}{z'} + \frac{z'}{z}\right)$ and we prove now that the integrals' orders are simply equal to the lattice-space dimensionality in that special case. By taking advantage of the Chebyscheff's polynomials property

$$\langle x^k, C_l(x) \rangle = [1 + \Delta(l)]^{-1} \frac{k!}{\frac{k+l}{2}! \frac{k-l}{2}!},$$

it follows from equation (16) that the scalar product

$$4 \left\langle \left(\frac{x'}{x}\right)^l \left(\frac{x}{x'} + \frac{x'}{x}\right)^k, C_0(x) C_0(x') \right\rangle = 4 \sum_{k_1 + k_2 = k} \frac{k!}{k_1! k_2!} \left\langle \left(\frac{x}{x'}\right)^{k_1 - k_2 - l}, C_0(x) C_0(x') \right\rangle =$$

$$= [1 + \Delta(l)] \langle x^k, C_l(x) \rangle.$$

This result can be extended easily to other variables and functions so that

$$2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} g_1\left(\frac{x}{x'} + \frac{x'}{x}, \frac{y}{y'} + \frac{y'}{y}, \frac{z}{z'} + \frac{z'}{z}\right), C_0(x) C_0(x') C_0(y) C_0(y') C_0(z) C_0(z') \right\rangle =$$

$$= [1 + \Delta(l_1)] [1 + \Delta(l_2)] [1 + \Delta(l_3)] \langle g_1(x, y, z), C_{l_1}(x) C_{l_2}(y) C_{l_3}(z) \rangle. \tag{22}$$

When applicable this result should be useful for handling certain types of scalar product.

Generally, the solution of a physical problem is given by just a few elements of the $\underset{\sim}{D}$ matrix function, or perhaps even a single one. According to equation (15), the results here reduce the calculation to the integration of $\underset{\sim}{d}$-matrix function elements. Moreover, we may remark that we are not concerned with writing the matrix $\underset{\sim}{D}$; instead the characteristic interaction matrix $\underset{\sim}{d}$ can be used from the start. Considering the difference in size between $\underset{\sim}{d}$ and $\underset{\sim}{D}$ matrices, the economy of work is very important, but above all the results are given by expressions whose analytic properties may be guessed with some facility, even in the case where the integrals are to be found numerically.

This theory takes the periodicity of the lattice into account by means of cyclic-matrices properties and contact must be made with the familiar Bloch's theorem approach. We have stressed already that the $\underset{\sim}{d}$ matrix is constructed in close analogy with the q-space dynamical matrix or Hamiltonian, and comparison of equations (9) and (10) gives the rule for deducing, from $\underset{\sim}{d}(\mathbf{q})$, the matrix $\underset{\sim}{d}\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)$ subsequently used to apply theorem (19). Hence it appears that the method is usuable and easily understood without reference to cyclic matrices. Regarding applications, an obvious advantage of the present method is to give exact closed-form expressions of the desired functions accessible to experiment without the prior requirement of obtaining the dispersion relation, then to

integrate over the Brillouin zone and finally obtain the density of states by approximate methods.

3.1 THE SYMMETRIC CASE.

— In primitive crystals the atom at the origin has sometimes identical interactions with all its neighbours located at positions given by indices of the same absolute value, so that

$$g_{k_1 k_2 k_3} = g_{|k_1| |k_2| |k_3|}, \qquad (23)$$

and consequently the $\underset{\sim}{D}$ matrix being symmetric can be expressed in terms of the symmetric topological cyclic matrices

$$\underset{\sim}{M}_p = \underset{\sim}{m}_p + \underset{\sim}{m}_{-p}. \qquad (24)$$

The results obtained in 1 refer to this simple special case and we discuss now consistency with the present results. On account of equations (9), (23) the characteristic interaction matrix is written

$$
\underset{\sim}{d}\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right) = \sum_{\mathbf{k}} \left(\left(\frac{x}{x'}\right)^{k_1} + \left(\frac{x'}{x}\right)^{k_1}\right)\left(\left(\frac{y}{y'}\right)^{k_2} + \left(\frac{y'}{y}\right)^{k_2}\right)\left(\left(\frac{z}{z'}\right)^{k_3} + \left(\frac{z'}{z}\right)^{k_3}\right) g_{k_1 k_2 k_3}
$$

$$
= \sum_{\mathbf{k}} C_{k_1}\left(\frac{x}{x'} + \frac{x'}{x}\right) C_{k_2}\left(\frac{y}{y'} + \frac{y'}{y}\right) C_{k_3}\left(\frac{z}{z'} + \frac{z'}{z}\right) g_{k_1 k_2 k_3},
$$

$$(25)$$

by employing equation (14).

Thus, in this case, performing the scalar product in equation (18) gives terms like

$$
\left\langle \left(\frac{x'}{x}\right)^{l_1}\left(C_{k_1}\left(\frac{x}{x'} + \frac{x'}{x}\right)\right)^q, C_0(x) C_0(x') \right\rangle = \frac{1}{2}\left\langle \left(\left(\frac{x}{x'}\right)^{l_1} + \left(\frac{x'}{x}\right)^{l_1}\right)\left(C_{k_1}\left(\frac{x}{x'} + \frac{x'}{x}\right)\right)^q, C_0(x) C_0(x') \right\rangle
$$

$$
= \frac{1}{2}\left\langle C_{l_1}\left(\frac{x}{x'} + \frac{x'}{x}\right)\left(C_{k_1}\left(\frac{x}{x'} + \frac{x'}{x}\right)\right)^q, C_0(x) C_0(x') \right\rangle, \qquad (26)
$$

and since (22) is valid the last equation can be written

$$
\left\langle \left(\frac{x'}{x}\right)^{l_1}\left(C_{k_1}\left(\frac{x}{x'} + \frac{x'}{x}\right)\right)^q, C_0(x) C_0(x') \right\rangle = \frac{1}{4} \left\langle C_{l_1}(x) (C_{k_1}(x))^q, C_0(x) \right\rangle
$$

$$
= \frac{1}{2} \left\langle (C_{k_1}(x))^q, C_{l_1}(x) \right\rangle. \qquad (27)
$$

Hence it turns out that equations (18), (19), (20), (21) can be simplified in this special case by giving to the characteristic interaction matrix the new form

$$
\underset{\sim}{d}(x, y, z) = \sum_{\mathbf{k}} C_{k_1}(x) C_{k_2}(y) C_{k_3}(z) g_{k_1 k_2 k_3} \qquad (28)
$$

and performing the scalar product with the polynomial product $C_{l_1}(x) C_{l_2}(y) C_{l_3}(z)$; this method is fully developed in 1.

4. The density of states.

— An obvious advantage of the present theory is to give directly (without the aid of the spectrum) expressions in closed form for functions which are attainable experimentally. Nevertheless the local density of states [7], though it is inaccessible to most experiments, is sometimes important if one is interested in different behaviour of atoms for different lattice sites, and it can be easily derived through the Green's function.

In matrix notation the Green's function reads

$$
\underset{\sim}{G}(E) = ((E + i\varepsilon)\underset{\sim}{1} - \underset{\sim}{D})^{-1} \qquad (29)
$$

where ε is a positive small quantity; the unit matrix $\underset{\sim}{1}$ will be omitted as understood. In order to use theorem (19), we define the characteristic Green's function and develop to first order in ε

$$
g(E) = (E + i\varepsilon - \underset{\sim}{d})^{-1} = \frac{\text{adj}\,(E - \underset{\sim}{d}) + i\varepsilon \dfrac{\partial}{\partial E}\text{adj}\,(E - \underset{\sim}{d})}{\det\,(E - \underset{\sim}{d}) + i\varepsilon \dfrac{\partial}{\partial E}\det\,(E - \underset{\sim}{d})}
$$

$$
= \frac{\text{adj}\,(E - \underset{\sim}{d})}{\det\,(E - \underset{\sim}{d})} + i\varepsilon \frac{\det\,(E - \underset{\sim}{d})\dfrac{\partial}{\partial E}\text{adj}\,(E - \underset{\sim}{d}) - \text{adj}\,(E - \underset{\sim}{d})\dfrac{\partial}{\partial E}\det\,(E - \underset{\sim}{d})}{[\det\,(E - \underset{\sim}{d})]^2 + \varepsilon^2\left[\dfrac{\partial}{\partial E}\det\,(E - \underset{\sim}{d})\right]^2}, \qquad (30)
$$

where the adjoint of $\underset{\sim}{A}$ is written adj $\underset{\sim}{A}$, and hence it turns out that the elements of the real part of the Green's function can be written from theorem (19) as

$$[\text{Re } \underset{\sim}{G}(E)]_{l_1 l_2 l_3} = 2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} \left(E - \underset{\sim}{d}\left(\frac{x}{x'}, \frac{y}{y'}, \frac{z}{z'}\right)\right)^{-1}, C_0(x) \, C_0(x') \, C_0(y) \, C_0(y') \, C_0(z) \, C_0(z') \right\rangle. \tag{31}$$

From equation (30) the imaginary part of the characteristic Green's function may be written

$$\text{Im } g(E) = \pi \, \frac{\det(E - \underset{\sim}{d}) \frac{\partial}{\partial E} \text{adj} (E - \underset{\sim}{d}) - \text{adj} (E - \underset{\sim}{d}) \frac{\partial}{\partial E} \det(E - \underset{\sim}{d})}{\left[\frac{\partial}{\partial E} \det(E - \underset{\sim}{d})\right]^2} \, \delta\left[\frac{\det(E - \underset{\sim}{d})}{\frac{\partial}{\partial E} \det(E - \underset{\sim}{d})}\right], \tag{32}$$

and on account of

$$f(x) \, \delta(f(x)) = 0$$

we have

$$\text{Im } g(E) = -\pi \, \frac{\text{adj} (E - \underset{\sim}{d})}{\frac{\partial}{\partial E} \det(E - \underset{\sim}{d})} \, \delta\left[\frac{\det(E - \underset{\sim}{d})}{\frac{\partial}{\partial E} \det(E - \underset{\sim}{d})}\right], \tag{33}$$

which, according to the relation [8]

$$\frac{\partial}{\partial E} \det \underset{\sim}{A}(E) = \text{Tr} \left\{ \text{adj} \, \underset{\sim}{A}(E) \frac{\partial}{\partial E} \underset{\sim}{A}(E) \right\} \tag{34}$$

can be written as

$$\text{Im } g(E) = -\pi \, \frac{\text{adj} (E - \underset{\sim}{d})}{\text{Tr adj} (E - \underset{\sim}{d})} \, \delta\left[\frac{\det(E - \underset{\sim}{d})}{\text{Tr adj} (E - \underset{\sim}{d})}\right].$$

The derivative of the argument of the δ function is given by

$$\frac{\partial}{\partial E} \frac{\det(E - \underset{\sim}{d})}{\text{Tr adj} (E - \underset{\sim}{d})} = \frac{\text{Tr adj} (E - \underset{\sim}{d}) \frac{\partial}{\partial E} \det(E - \underset{\sim}{d}) - \det(E - \underset{\sim}{d}) \frac{\partial}{\partial E} \text{Tr adj} (E - \underset{\sim}{d})}{[\text{Tr adj} (E - \underset{\sim}{d})]^2}$$

$$= 1 + \det(E - \underset{\sim}{d}) \frac{\partial}{\partial E} [\text{Tr adj} (E - \underset{\sim}{d})]^{-1},$$

and for a given eigenvalue E_n of the $\underset{\sim}{d}$ matrix, it takes the value

$$\left| \frac{\partial}{\partial E} \frac{\det(E - \underset{\sim}{d})}{\text{Tr adj} (E - \underset{\sim}{d})} \right|_{E = E_n} = 1,$$

so that equation (33) can be rewritten in the form

$$\text{Im } g(E) = -\pi \, \frac{\text{adj} (E - \underset{\sim}{d})}{\text{Tr adj} (E - \underset{\sim}{d})} \sum_n \delta(E - E_n), \tag{35}$$

by turning the Dirac δ function property [10, 11]

$$\delta(f(E)) = \sum_n \frac{\delta(E - E_n)}{|f'(E_n)|} \tag{36}$$

to advantage.

From equations (34) and (35) we finally have

$$[\text{Im } \underset{\sim}{G}(E)]_{l_1 l_2 l_3} = -\pi \, 2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} \frac{\text{adj} (E - \underset{\sim}{d})}{\text{Tr adj} (E - \underset{\sim}{d})} \, \delta\left[\frac{\det(E - \underset{\sim}{d})}{\text{Tr adj} (E - \underset{\sim}{d})}\right], \right.$$

$$\left. C_0(x) \, C_0(x') \, C_0(y) \, C_0(y') \, C_0(z) \, C_0(z') \right\rangle, \tag{37a}$$

$$= -\pi 2^6 \left\langle \left(\frac{x'}{x}\right)^{l_1} \left(\frac{y'}{y}\right)^{l_2} \left(\frac{z'}{z}\right)^{l_3} \frac{\mathrm{adj}\,(E - \underline{d})}{\mathrm{Tr}\,\mathrm{adj}\,(E - \underline{d})} \sum_n \delta(E - E_n),\, C_0(x) \right.$$

$$\left. \times\, C_0(x')\, C_0(y)\, C_0(y')\, C_0(z)\, C_0(z') \right\rangle. \qquad (37b)$$

The local density of states consists of only one diagonal element of this matrix [9]

$$n_i(E) = -\pi^{-1}[\mathrm{Im}\,\underline{G}(E)]_{000,ii} \qquad (38)$$

where the indice i stands for a coordinate of the local basis set. Equation (38) can be rewritten on account of equations (37a, b)

$$n_i(E) = 2^6 \left\langle \frac{[\mathrm{adj}\,(E - \underline{d})]_{ii}}{\mathrm{Tr}\,\mathrm{adj}\,(E - \underline{d})} \delta\left[\frac{\det(E - \underline{d})}{\mathrm{Tr}\,\mathrm{adj}\,(E - \underline{d})}\right],\, C_0(x)\, C_0(y)\, C_0(z)\, C_0(x')\, C_0(y')\, C_0(z') \right\rangle \qquad (39a)$$

$$= 2^6 \left\langle \frac{[\mathrm{adj}\,(E - \underline{d})]_{ii}}{\mathrm{Tr}\,\mathrm{adj}\,(E - \underline{d})} \sum_n \delta(E - E_n),\, C_0(x)\, C_0(y)\, C_0(z)\, C_0(x')\, C_0(y')\, C_0(z') \right\rangle \qquad (39b)$$

and finally summing the diagonal elements given by (39) we obtain for the total density of states the expression

$$n(E) = q^{-1} \sum_i n_i(E) = 2^6\, q^{-1} \left\langle \delta\left[\frac{\det(E - \underline{d})}{\mathrm{Tr}\,\mathrm{adj}\,(E - \underline{d})}\right],\, C_0(x)\, C_0(y)\, C_0(z)\, C_0(x')\, C_0(y')\, C_0(z') \right\rangle \qquad (40a)$$

$$= 2^6\, q^{-1} \left\langle \sum_n \delta(E - E_n),\, C_0(x)\, C_0(y)\, C_0(z)\, C_0(x')\, C_0(y')\, C_0(z') \right\rangle \qquad (40b)$$

$$= 2^6\, q^{-1} \left\langle \mathrm{Tr}\,\delta(E - \underline{d}),\, C_0(x)\, C_0(y)\, C_0(z)\, C_0(x')\, C_0(y')\, C_0(z') \right\rangle.$$

The equation

$$\frac{\det(E - \underline{d})}{\mathrm{Tr}\,\mathrm{adj}\,(E - \underline{d})} = 0$$

defines an hypersurface S in $\mathbf{R}^6$ and it is clear that the scalar product in equation (40a) can be written, according to equation (15a), as a surface integral over S; so that the *bands limits* and the *forbidden energy gaps* are thereby easy to determine from the structure of the integrand, full results being obtained by calculation of the integral.

5. Example of application : the diatomic chain dynamics.

In order to illustrate the feasibility of the method we consider now briefly a simple case : the vibrations of a diatomic linear chain with nearest neighbour interactions only.

The interaction matrix is [1, 2]

$$\underline{D} = (\underline{a}_0,\, \underline{a}_1,\, \underline{0},\, ...,\, \underline{0},\, \underline{a}_{-1})_{\mathrm{cycl.}}, \qquad (41)$$

with

$$\underline{a}_0 = \begin{bmatrix} 2\,\gamma/\mu_1 & -\gamma/(\mu_1\,\mu_2)^{1/2} \\ -\gamma/(\mu_1\,\mu_2)^{1/2} & 2\,\gamma/\mu_2 \end{bmatrix},$$

$$\underline{a}_1 = \begin{bmatrix} 0 & 0 \\ -\gamma/(\mu_1\,\mu_2)^{1/2} & 0 \end{bmatrix},$$

$\underline{a}_{-1}$ being the transpose of $\underline{a}_1$, where μ_1 *and* μ_2 are the two atomic species masses and γ the nearest neighbour force constant. In this example the $\underline{a}$

matrices are clearly noncommutative. The characteristic interaction matrix reads

$$\underline{d} = \underline{a}_0 + \frac{x}{x'}\underline{a}_1 + \frac{x'}{x}\underline{a}_{-1}; \qquad (42)$$

and for this one dimensional case theorem (19) applies in the form

$$[f(\underline{D})]_l = 4 \left\langle \left(\frac{x'}{x}\right)^l f\left(\underline{d}\left(\frac{x}{x'}\right)\right),\, C_0(x)\, C_0(x') \right\rangle, \qquad (43)$$

or

$$\mathrm{Tr}\,f(\underline{D}) = 4\,N \left\langle \mathrm{Tr}\,f\left(\underline{d}\left(\frac{x}{x'}\right)\right),\, C_0(x)\, C_0(x') \right\rangle. \qquad (44)$$

For example the density of states $n(\omega^2)$ can be readily evaluated according to equation (40)

$$n(\omega^2) = 2 \left\langle \delta(\omega^2 - \omega_1^2) + \delta(\omega^2 - \omega_2^2),\, C_0(x) \right.$$

$$\left. \times\, C_0(x') \right\rangle, \qquad (45)$$

where ω_1^2, ω_2^2, the eigenvalues of the characteristic dynamical matrix (42)

$$\underline{d}\left(\frac{x}{x'}\right) = \frac{\gamma}{(\mu_1\,\mu_2)^{1/2}}\begin{bmatrix} 2\left(\dfrac{\mu_2}{\mu_1}\right)^{1/2} & -1 - \dfrac{x'}{x} \\[2mm] -1 - \dfrac{x}{x'} & 2\left(\dfrac{\mu_1}{\mu_2}\right)^{1/2} \end{bmatrix}, \qquad (46)$$

are given by

$$\omega_{1,2}^2 = \frac{\gamma}{(\mu_1\,\mu_2)^{1/2}}\left[\left(\frac{\mu_1}{\mu_2}\right)^{1/2} + \left(\frac{\mu_2}{\mu_1}\right)^{1/2}\right.$$
$$\left. \pm \left(\frac{\mu_1}{\mu_2} + \frac{\mu_2}{\mu_1} + \frac{x}{x'} + \frac{x'}{x}\right)^{1/2}\right]. \qquad (47)$$

Using the reduced squared frequency

$$\bar{\omega}^2 = \omega^2(\mu_1\,\mu_2)^{1/2}/\gamma, \qquad (48)$$

the density of states (45) reads, from equation (36),

$$n(\bar{\omega}^2) = 4\left|\bar{\omega}^2 - \left(\frac{\mu_2}{\mu_1}\right)^{1/2} - \left(\frac{\mu_1}{\mu_2}\right)^{1/2}\right|$$
$$\times \left\langle \delta\left(J - \frac{x}{x'} - \frac{x'}{x}\right), C_0(x)\,C_0(x')\right\rangle \qquad (49)$$

where

$$J = \left(\bar{\omega}^2 - 2\left(\frac{\mu_2}{\mu_1}\right)^{1/2}\right)\left(\bar{\omega}^2 - 2\left(\frac{\mu_1}{\mu_2}\right)^{1/2}\right) - 2. \qquad (50)$$

The scalar product in (49) can be evaluated using equation (22), so that

$$n(\bar{\omega}^2) = 2\left|\bar{\omega}^2 - \left(\frac{\mu_2}{\mu_1}\right)^{1/2} - \left(\frac{\mu_1}{\mu_2}\right)^{1/2}\right|\langle \delta(J - x), C_0(x)\rangle, \qquad (51)$$

or, from equation (15),

$$n(\bar{\omega}^2) = \frac{1}{\pi}\left|\bar{\omega}^2 - \left(\frac{\mu_2}{\mu_1}\right)^{1/2} - \left(\frac{\mu_1}{\mu_2}\right)^{1/2}\right|\int_{-1}^{1}\frac{\delta(J - 2x)}{(1 - x^2)^{1/2}}\,\mathrm{d}x$$
$$= \frac{1}{2\pi}\left|\bar{\omega}^2 - \left(\frac{\mu_2}{\mu_1}\right)^{1/2} - \left(\frac{\mu_1}{\mu_2}\right)^{1/2}\right|\left(1 - \frac{J^2}{4}\right)^{-1/2}. \qquad (52)$$

Hence from equation (50) the spectrum of squared frequencies has the analytic form

$$n(\bar{\omega}^2) = \frac{1}{\pi}\left(\bar{\omega}^2 - \left(\frac{\mu_2}{\mu_1}\right)^{1/2} - \left(\frac{\mu_1}{\mu_2}\right)^{1/2}\right)\left[\bar{\omega}^2\left(2\left(\frac{\mu_2}{\mu_1}\right)^{1/2} + 2\left(\frac{\mu_1}{\mu_2}\right)^{1/2} - \bar{\omega}^2\right)\right.$$
$$\left. \times \left(\bar{\omega}^2 - 2\left(\frac{\mu_2}{\mu_1}\right)^{1/2}\right)\left(\bar{\omega}^2 - 2\left(\frac{\mu_1}{\mu_2}\right)^{1/2}\right)\right]^{-1/2}, \qquad (53)$$

which is a well established result [2].

We have just obtained the expression of the density of states as a first example of application of the present theory, but an obvious advantage of the method is just its ability to give expressions for measurable quantities without spectrum calculations. As a second illustration, we show the method to be capable of giving a closed form expression for the specific heat C_v of the diatomic linear chair. Starting from the formal expression in terms of an infinite sum over the normal modes frequencies [12], we find that

$$C_v/k_B = \mathrm{Tr}\left\{\left(\frac{\hbar}{2\,k_B\,T}\right)^2 \underline{D}\,\sinh^{-2}\left(\frac{\hbar}{2\,k_B\,T}\,\underline{D}^{1/2}\right)\right\} \qquad (54)$$

and using the result of equation (44) we obtain the trace of this infinite order matrix in the form

$$C_v/k_B = 4\,N\left\langle \mathrm{Tr}\left\{\underline{d}'\,\sinh^{-2}(\underline{d}'^{1/2})\right\}, C_0(x)\right.$$
$$\times C_0(x')\left.\right\rangle, \qquad (55)$$

where the matrix $\underline{d}' = \left(\dfrac{\hbar}{2\,k_B\,T}\right)^2 \underline{d}$ has for eigenvalues

$\omega_{1,2}'^2 = \left(\dfrac{\hbar}{2\,k_B\,T}\right)^2 \omega_{1,2}^2$ so that equation (55) takes the form

$$C_v/k_B = 4\,N\left\langle \omega_1'^2\,\sinh^{-2}\omega_1' + \omega_2'^2\,\sinh^{-2}\omega_2',\right.$$
$$C_0(x)\,C_0(x')\left.\right\rangle, \qquad (56)$$

which from equations (15), (22) can be rewritten as

$$C_v/k_B = 2\,NK^2\int_0^{\pi}\Omega(\theta)\,\mathrm{d}\theta \qquad (57)$$

where

$$K^2 = \left(\frac{\hbar}{2\,k_B\,T}\right)^2\frac{\gamma}{(\mu_1\,\mu_2)^{1/2}}$$

and

$$\Omega(\theta) = \left[\left(\frac{\mu_1}{\mu_2}\right)^{1/2} + \left(\frac{\mu_2}{\mu_1}\right)^{1/2} + \left(\frac{\mu_1}{\mu_2} + \frac{\mu_2}{\mu_1} + \cos\theta\right)^{1/2}\right]\sinh^{-2}\left\{K\left[\left(\frac{\mu_1}{\mu_2}\right)^{1/2} + \left(\frac{\mu_2}{\mu_1}\right)^{1/2}\right.\right.$$

$$\left.\left. + \left(\frac{\mu_1}{\mu_2} + \frac{\mu_2}{\mu_1} + \cos\theta\right)^{1/2}\right]^{1/2}\right\} + \left[\left(\frac{\mu_1}{\mu_2}\right)^{1/2} + \left(\frac{\mu_2}{\mu_1}\right)^{1/2} - \left(\frac{\mu_1}{\mu_2} + \frac{\mu_2}{\mu_1} + \cos\theta\right)^{1/2}\right]$$

$$\times \sinh^{-2}\left\{K\left[\left(\frac{\mu_1}{\mu_2}\right)^{1/2} + \left(\frac{\mu_2}{\mu_1}\right)^{1/2} - \left(\frac{\mu_2}{\mu_1} + \frac{\mu_1}{\mu_2} + \cos\theta\right)^{1/2}\right]^{1/2}\right\}.$$

Therefore an expression in closed form has been obtained for the specific heat without a prior calculation of the frequency spectrum. Other functions of the dynamical matrix $\underset{\sim}{D}$ could be easily calculated; some more examples of application of the present theory to lattice dynamics problems will be presented in a forthcoming paper.

6. Conclusion. — The simplicity of the example treated above should not obscure the general character of the present theory. Its range of applicability includes every model describing any crystal properties in terms of pair interactions where the range of interaction, though finite, is not limited. Nevertheless the algebra becomes more complicated as the dimensionality of the crystal increases; the order of the multiple integral in the solution is proportional to this dimensionality. Lack of symmetry in the interaction also doubles the order of the integral which is, in any event, never superior to six. The complexity of the integrands

increases with the number of interacting neighbour atoms to be considered, whereas the order of the characteristic interaction matrix is proportional to the number of atoms in the unit cell and to the dimension of the local basis set. Hence, as everywhere else, any refinement of the model is a source of increasing complexity in the algebra, which nevertheless remains extremely simple as compared to other methods.

Finally, this method allows direct calculation (without sampling $E(\mathbf{q})$) of exact closed-form expressions for measurable crystal properties. Being not essentially limited to the calculation of Green's function diagonal elements (as the recursion method), and involving no approximation (in contrast with the moment method for instance), it deals with crystal periodicity in a most natural way (dual with Bloch's theorem) which could prove to be less adequate to treat problems involving large deviations from periodicity.

References

[1] BORN, M., *Rep. Prog. Phys.* **9** (1942) 294.
[2] DEAN, P., *J. Inst. Maths. Applics* **3** (1967) 98.
[3] LÖWDIN, P. O., PAUNEZ, R. and DE HEER, J., *J. Math. Phys.* **1** (1960) 461.
[4] CALAIS, J. L. and APPEL, K., *J. Math. Phys.*, **5** (1964) 1001.
[5] ELLIOTT, R. J., KRUMHANSL, J. A. and LEATH, P. L., *Rev. Mod. Phys.* **46** (1974) 465.
[6] AUDIT, Ph., *J. Physique* **42** (1981) 903.
[7] FRIEDEL, J., *Adv. Phys.* **3** (1954) 446.
[8] LANCASTER, P., *Theory of Matrices*, (Acad. Press N.Y.) 1969, p. 195.

[9] HEINE, V., *Solid State Phys.* **35** (1980) 1.
[10] MESSIAH, A., *Mécanique Quantique*, (Dunod,, Paris) 1969, tome 1.
[11] The author is grateful to Prof. J. Labbé who helped him to clarify this point.
[12] MARADUDIN, A. A., MONTROLL, E. W., WEISS, G. H., IPATOVA, I. P., *Solid State Phys. Suppl.* **3** (1971) 130.
[13] ABRAMOWITZ, M. and STEGUN, J., *Handbook of Mathematical functions* (Dover), 1970.