

Remarks on Force-Constant Models for Lattice Dynamics*

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It is shown that the need to specify the equilibrium pressure may impose a restriction on the force constants used in calculating lattice vibration spectra. The existence of such a restriction depends upon the lattice under consideration and the generality of the force-constant model that is used. For a model including general interactions with sufficiently distant neighbors (third neighbors will usually be sufficient), specification of the equilibrium pressure imposes no restrictions. For the cubic crystals explicitly studied, one can conclude that models including third neighbor force constants are not restricted, whereas some second

neighbor models and almost all nearest neighbor models are restricted. This is true even if long-range Coulomb forces are included in addition to the short-range force constants. We also present an argument to show that the Cauchy relations of elasticity theory depend upon the vanishing of external stresses in equilibrium, contrary to the conclusions of other published work. Finally we use a simple model to study the equilibrium atomic spacing near the surface of a crystal and show that this has no influence upon the relation between the equilibrium pressure and the force constants well within the bulk of the crystal.

I. INTRODUCTION

DURING the past year two papers^{1,2} have appeared which have finally established on firm ground, with well-defined limits of validity, the so-called Huang or Born and Huang³ relations between the atomic force constants which occur in the theory of lattice dynamics. At the same time they have succeeded in deriving the one relation that had been missing in the Born and Huang formalism: a relation for the pressure in equilibrium. The point of view in both papers is to examine the consequences of rotational invariance of the potential energy for a finite crystal (or general collection of atoms), where there is no doubt as to the validity of such a procedure, and then to allow the crystal to become infinite. One result of this work has been to dispel doubts⁴ that have been raised about certain symmetry properties of the linear elastic constants as derived from atomic models.

We wish to present here an alternative derivation of the equilibrium pressure condition which ignores any problem arising in the transition to an infinite lattice, but which can be incorporated into the usual Born and Huang framework, and to discuss the consequences of this pressure condition on the choice of force-constant models. We will also discuss some remarks that have been made^{5,6} concerning the validity of the Cauchy relations of elasticity theory and treat via a simple model the question of the equilibrium spacing near the surface of a crystal.

II. EQUILIBRIUM PRESSURE CONDITION

The potential energy in lattice dynamics is usually specified as $\phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, where \mathbf{r}_i is the position of

the i th atom. This expression must be supplemented by the usual conditions of rotational and translational invariance as well as by any special symmetry properties of the system being considered. An alternative formulation which has been used^{5,6} expresses the energy in terms of a complete set of rotation- and translation-invariant coordinates such as interparticle distances and internal angles. This formulation arises naturally from the usual perturbation-theoretic treatment of the quantum mechanical problem of the electronic ground state of the system of atoms in the Born-Oppenheimer approximation, because in such a treatment we find overlap integrals and matrix elements of the electrostatic Hamiltonian between atomic orbitals centered on different nuclei which, upon evaluation, contain just the above distances and angles. This is the method we will use. We write the potential energy as $\phi(R_{12}, R_{13}, \dots, R_{ij}, \dots)$, where, for convenience, R_{ij} is the square of the distance between atoms i and j . The specification of the configuration of the system must also include coordinates to describe its center-of-mass and rigid rotational position, but these coordinates will not appear in the potential energy. Of course the coordinates R_{ij} are redundant. For a solid, where one only contemplates small displacements from equilibrium positions, it may be sufficient to use only nearest and next nearest neighbor distances (e.g., simple cubic lattice) and still have redundant coordinates. We now expand ϕ about initial equilibrium atomic positions:

$$\begin{aligned} \phi(\dots R_{ij} \dots) = & \phi(\dots R_{ij}^0 \dots) + \sum_{i>j} \frac{\partial \phi}{\partial R_{ij}} \Delta R_{ij} \\ & + \frac{1}{2} \sum_{i>j, k>l} \frac{\partial^2 \phi}{\partial R_{ij} \partial R_{kl}} \Delta R_{ij} \Delta R_{kl}, \quad (1) \end{aligned}$$

where $R_{ij}^0 = \sum_{\alpha} (X_{ij}^{\alpha})^2$ is the equilibrium value of R_{ij} , $\Delta R_{ij} = \sum_{\alpha} [2X_{ij}^{\alpha} u_{ij}^{\alpha} + (u_{ij}^{\alpha})^2]$, $u_{ij}^{\alpha} = u_i^{\alpha} - u_j^{\alpha}$, $X_{ij}^{\alpha} = X_i^{\alpha} - X_j^{\alpha}$, and X_i^{α} , u_i^{α} are Cartesian components of the equilibrium position and displacement from equilibrium respectively of atom i .

Because the coordinates R_{ij} are redundant, $\partial \phi / \partial R_{ij}$

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¹ L. T. Hedén, *Arkiv Fysik* **18**, 369 (1960).

² G. Leibfried and W. Ludwig, *Z. Physik* **160**, 80 (1960).

³ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

⁴ J. Laval, *Compt. rend.* **232**, 1947 (1951). For other references see reference 5 of reference 2.

⁵ I. Stakgold, *Quart. Appl. Math.* **8**, 169 (1950).

⁶ P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., 1956), Vol. V, p. 1.

$\neq 0$ even though we are expanding about the equilibrium position. However it must still be true that $(\partial\phi/\partial u_i^\alpha)_0 = 0$ for all i , α , or

$$\sum_{j, j \neq i} \frac{\partial\phi}{\partial R_{ij}} X_{ij}^\alpha = 0. \quad (2a)$$

Until now we could have been discussing an arbitrary collection of atoms. If we now specialize to an infinite lattice, the number of relations (2a) is equal to three times the number of atoms in the unit cell. Using Born and Huang's notation, these relations are

$$\sum_{l', k'} \frac{\partial\phi}{\partial R(l-l'; k, k')} X^\alpha(l-l'; k, k') = 0, \quad (2b)$$

where \sum' means omit $l=l', k=k'$; l is the cell index and k specifies the atom within the cell. The result is the same for all l . We are ignoring here any questions of surface effects which have been adequately treated in references 1 and 2, but will discuss the size of the surface region in Sec. 5. We do assume that either the interatomic forces are short-range or that all sums occurring in the calculation of vibration spectra and the various macroscopic parameters such as equilibrium stresses converge. If long-range Coulomb effects occur (in ionic crystals or because of polarization), we assume that they can be treated in the manner discussed by Born and Huang in paragraphs 30–31 of reference 3; i.e., a macroscopic electric field can be introduced to remove the convergence difficulties. With this understanding we may now use either the method of homogeneous deformation, reference 3 paragraph 11, or the method of long waves, reference 3 paragraph 26, together with a subsidiary calculation of the equilibrium pressure, reference 3 paragraph 29, to derive the following expression for the equilibrium stresses:

$$C_{\alpha\beta} = \frac{1}{v_a} \sum_{l', k, k'} \frac{\partial\phi}{\partial R(l-l'; k, k')} \times X^\alpha(l-l'; k, k') X^\beta(l-l'; k, k'), \quad (3)$$

where v_a is the volume of the unit cell. The values on the left-hand side are determined by experiment; the most usual values are $C_{\alpha\beta} = 0$. As mentioned in reference 2, one must be careful to only include values of the $C_{\alpha\beta}$ consistent with the symmetry of the crystal being considered; e.g., a cubic crystal will not remain cubic under any stress other than an isotropic pressure.

The relationship between the force constants

$$\partial\phi/\partial R(l-l'; k, k'), \quad \partial^2\phi/\partial R(l-l''; k, k'') \partial R(l-l'''; k', k''')$$

and the usual force constants $[\partial^2\phi/\partial u_\alpha(l; k) \partial u_\beta(l'; k')]_0$ is

$$\left[\frac{\partial^2\phi}{\partial u_\alpha(l; k) \partial u_\beta(l'; k')} \right]_0 = -2 \frac{\partial\phi}{\partial R(l-l'; k, k')} \delta_{\alpha\beta} - 4 \sum_{\substack{l'', k'', k''', \\ k'', l'' \neq k, l; \\ k''', l''' \neq k', l'}} \frac{\partial^2\phi}{\partial R(l-l''; k, k'') \partial R(l-l'''; k', k''')} \times X^\alpha(l-l''; k, k'') X^\beta(l-l'''; k', k'''). \quad (4)$$

We will now use relations (2b), (3), and (4) to discuss possible restrictions on force-constant models for different crystals with cubic symmetry.

III. RESTRICTIONS ON FORCE-CONSTANT MODELS

When making a force-constant model for the calculation of a lattice vibration spectrum, one must pick a number of force constants less than or equal to the number of experimental values available for their determination (e.g., elastic constants, piezoelectric constants, infrared absorption frequencies, inelastic neutron scattering data, etc.). Because of the basic short-range character of interatomic forces in most cases (long-range Coulomb effects are explicitly introduced where necessary), a cutoff is usually introduced by assuming that beyond neighbors of a certain separation all force constants are zero. If only some of the force constants joining a particular pair of neighbors can be included, an intuitive method is used to eliminate some constants (e.g., central springs are most important). Most calculations of vibration spectra have been for crystals of the cubic system. For simple crystals of this system the force constants, as restricted by symmetry, satisfy all of the Born and Huang relations identically, but we must examine explicitly the restriction imposed by the specification of the equilibrium pressure. We will study by example the restrictions this condition imposes on the other free choice of force constants.

It may be readily seen that the number of force constants $\partial\phi/\partial R_{ij}$ and $\partial^2\phi/\partial R_{ij} \partial R_{kl}$ will far exceed the number of conventional force constants when one takes into account interactions with somewhat distant neighbors. There is almost no doubt but that if third neighbor interactions are included, the specification of the equilibrium pressure will not impose any additional restriction on the choice of symmetry-limited force constants for a general lattice. This fact has been verified for all of the cubic lattices studied in this section. We will thus confine our attention to the cases of nearest neighbor (nn) and next nearest neighbor (nnn) interactions.

(1) Simple Cubic Lattice

(A) Nearest neighbors only

The usual force-constant matrix for the neighbor at (100) is

$$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}.$$

Using the notation $(000) \equiv 0$, $(100) \equiv 1$, we find only two of our new constants: $\partial\phi/\partial R_{10} = -E$, $\partial^2\phi/\partial R_{10}^2 \equiv -A$. The relations between the two types of constants, using Eq. (4), are $\alpha = 2E + 4A$, $\beta = 2E$. The specification of zero equilibrium pressure (the usual experimental condition) requires $E = 0$. Thus β is not a free parameter but has a value specified by the equilibrium pressure, in this case zero. It is interesting that the inclusion of β as a free parameter in an *nn* model leads to an apparent lack of rotational invariance of the potential energy.⁷ The explanation of this behavior has been given by Epstein.⁸

(B) Next nearest neighbor model

The usual force-constant matrix for the neighbor at (110) is

$$\begin{pmatrix} \mu & \nu & 0 \\ \nu & \mu & 0 \\ 0 & 0 & \lambda \end{pmatrix}.$$

If we call $(110) \equiv 2$ and $(010) \equiv 3$, then we find the following new force constants in addition to those of (A): $\partial\phi/\partial R_{20} = -F$, $\partial^2\phi/\partial R_{20}^2 \equiv -B$, $\partial^2\phi/\partial R_{10}\partial R_{20} \equiv -C$, $\partial^2\phi/\partial R_{10}\partial R_{30} \equiv -D$. With the aid of simple diagrams one can show that these are the only new independent constants. The vanishing-pressure condition is $E + 2F = 0$. We find the following equations relating the two types of force constants:

$$\begin{aligned} A &= \alpha + \beta + 4\lambda, \\ B &= \mu + \frac{1}{2}\beta, \\ C &= -\frac{1}{2}\beta - \lambda, \\ D &= 2(\nu - \mu + \lambda), \\ F &= \lambda. \end{aligned}$$

Thus the specification of the equilibrium pressure does not restrict the choice of the usual force constants if all five are not zero. A few special cases are worthy of mention:

(a) Let $\mu = \nu = \lambda = 0$, reducing us again to an *nn* model. We have $A = \alpha + \beta$, $B = \frac{1}{2}\beta$, $C = -\frac{1}{2}\beta$, and thus can apparently justify an *nn* model by including three-body terms in the potential energy (see below). It is however highly unlikely that such a special case will arise. In particular, of our new constants only F is a first derivative of ϕ and since there is reason to expect the first

derivatives to contribute appreciably to the usual force constants, any model setting $\lambda = 0$ is very unrealistic. Recently the *nn* α - β model, also known as the Rosenstock-Newell model,⁹ has been used by Wallis¹⁰ to study surface waves in diatomic crystals. Wallis mentions the apparent lack of rotational invariance of the model as one of its unrealistic features. We see now that the model is legitimate if either an appropriate external pressure is applied at the surface, or the surface atom equations of motion are modified to include the effect of the constant C .

(b) The popular model $\mu = \nu$, $\lambda = 0$ (*nn central and noncentral springs and nnn central springs*) can also be criticized because $F = 0$. The inclusion of force constants such as $\partial^2\phi/\partial R_{10}\partial R_{30}$ implies the existence of three- or more-body forces. These can arise from the three- and four-center integrals that appear in calculations of the electronic ground states of many atom systems using LCAO trial functions.⁶

(2) Body-Centered Cubic Lattice

The usual force constants are

$$\text{nn at } (\frac{1}{2}\frac{1}{2}\frac{1}{2}): \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}; \quad \text{nnn at } (100): \begin{pmatrix} \mu & 0 & 0 \\ 0 & \nu & 0 \\ 0 & 0 & \nu \end{pmatrix}.$$

If we let $(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \equiv 1$, $(100) \equiv 2$, $(\frac{1}{2} - \frac{1}{2} - \frac{1}{2}) \equiv 3$, then the new-type constants are $\partial\phi/\partial R_{10}$, $\partial\phi/\partial R_{20}$, $\partial^2\phi/\partial R_{10}^2$, $\partial^2\phi/\partial R_{20}^2$, $\partial^2\phi/\partial R_{10}\partial R_{20}$, $\partial^2\phi/\partial R_{10}\partial R_{30}$. The vanishing-pressure condition connects the two first derivatives. We see that an *nn* model has one independent constant while an *nnn* model has no restrictions.

(3) Face-Centered Cubic Lattice

The usual force constants are

$$\text{nn at } (110): \begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & \gamma \end{pmatrix}; \quad \text{nnn at } (200): \begin{pmatrix} \mu & 0 & 0 \\ 0 & \nu & 0 \\ 0 & 0 & \nu \end{pmatrix}.$$

If we let $(110) \equiv 1$, $(200) \equiv 2$, $(-110) \equiv 3$, $(101) \equiv 4$, then the new-type constants are $\partial\phi/\partial R_{10}$, $\partial\phi/\partial R_{20}$, $\partial^2\phi/\partial R_{10}^2$, $\partial^2\phi/\partial R_{20}^2$, $\partial^2\phi/\partial R_{10}\partial R_{20}$, $\partial^2\phi/\partial R_{10}\partial R_{30}$, $\partial^2\phi/\partial R_{10}\partial R_{40}$. The vanishing-pressure condition connects the two first derivatives. In this case an *nn* model is not a central-force model because $\partial^2\phi/\partial R_{10}\partial R_{40}$ connects only nearest neighbors. This constant may be expected to be smaller than $\partial^2\phi/\partial R_{10}^2$. However, the vanishing pressure condition still restricts one of the three usual force constants. An *nnn* model has no restrictions.

⁷ See Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), second edition, Eq. (4.33).

⁸ P. S. Epstein, *Phys. Rev.* **70**, 915 (1946).

⁹ H. B. Rosenstock and G. F. Newell, *J. Chem. Phys.* **21**, 1607 (1953).

¹⁰ R. F. Wallis, *Phys. Rev.* **116**, 302 (1959).

(4) *Diamond Lattice*

The usual force constants are¹¹

$$nn \text{ at } (\frac{1}{2}\frac{1}{2}\frac{1}{2}): \begin{bmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{bmatrix}; \quad nnn \text{ at } (110): \begin{bmatrix} \mu & \nu & \delta \\ \nu & \mu & \delta \\ -\delta & -\delta & \lambda \end{bmatrix}.$$

If we let $(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \equiv 1$, $(110) \equiv 2$, $(011) \equiv 4$, $(\frac{1}{2} - \frac{1}{2} - \frac{1}{2}) \equiv 3$, then the new type constants are $\partial\phi/\partial R_{10}$, $\partial\phi/\partial R_{20}$, $\partial^2\phi/\partial R_{10}^2$, $\partial^2\phi/\partial R_{20}^2$, $\partial^2\phi/\partial R_{10}\partial R_{20}$, $\partial^2\phi/\partial R_{10}\partial R_{30}$, $\partial^2\phi/\partial R_{20}\partial R_{40}$. As always, the vanishing-pressure condition connects the first derivatives. The second neighbor sublattice is face-centered cubic, and thus the constant $\partial^2\phi/\partial R_{20}\partial R_{40}$ may again be considered smaller than the other second neighbor constants because it involves two second neighbor distances. It is only included because the triangle (000), (110), (011) is equilateral. If we were to set this constant equal to zero on the strength of the above magnitude argument, the force constants in a general nnn model would be restricted.

The considerations for zincblende are very similar to those for diamond.

It is possible to include point-ion Coulomb forces and polarization forces in the above treatment by merely splitting the usual force constants into long- and short-range parts. To conclude this section, we note that as more experimental information is included in force-constant models and thus more force constants are used, the vanishing-pressure condition loses all importance.

IV. CAUCHY RELATIONS

Stakgold⁵ and Löwdin⁶ have proposed definitions of the elastic constants based on a finite-strain analysis. They express the potential energy for a homogeneous deformation in a power series in the finite strains and define the elastic constants as the coefficients of the quadratic terms in this series. The linear terms in this series have as coefficients the equilibrium or initial stresses. This definition makes the elastic constants independent of the initial state of stress of a sample. If instead one defines the elastic constants as the coefficients of the terms quadratic in the infinitesimal strains, one finds additional terms which make the elastic constants depend upon the initial stresses because the finite strains contain parts linear and quadratic in the infinitesimal strains.¹² In the linear theory of elasticity the potential energy per unit volume of a homogeneously deformed medium is used as the potential energy density for calculating the elastic equations of motion. The linear equations of motion should arise from all terms in the energy density which are quadratic in the infinitesimal strains. Thus the Cauchy relations between the observed elastic constants

should depend upon the initial stresses. Explicit expressions for cubic crystals are given in Eq. (5.13) of reference 2.

V. SURFACE SPACING PROBLEM

We wish to study, now, the influence of the details of the surface of a crystal on the equilibrium pressure condition. Consider a finite chain of $2N$ identical atoms with free ends in equilibrium. The position of the n th atom is denoted as X_n , $0 \leq n \leq 2N-1$. We assume that the energy of the chain can be expressed in terms of a sum of two-body potentials which only act between nearest neighbors and next nearest neighbors:

$$\Phi = \sum_{n=1}^{2N-1} \phi(X_n - X_{n-1}) + \sum_{n=2}^{2N-1} \phi(X_n - X_{n-2}). \quad (5)$$

We think of the function ϕ as a typical diatomic molecule potential, e.g., the Morse potential, or "6-12" potential (see Fig. 1). We assume, at first, that the function ϕ is independent of the position of a pair of atoms in the chain. Because the short-range repulsion is very strong, we expect all nn spacings to be close to the spacing, a , in an infinite chain. We thus write $X_n = na + x_n$. The value of a is determined by the condition (3) applied to a one-dimensional chain with zero external force:

$$\phi'(a) + 2\phi'(2a) = 0, \quad [\phi'(a) \equiv (d\phi/dr)_{r=a}].$$

We can also derive this result directly from the equilibrium conditions below by demanding that the nn spacing far from the surface be uniform. We determine the equilibrium separations in the chain by writing the equations of equilibrium for all of the atoms. We linearize the equations by again making use of the

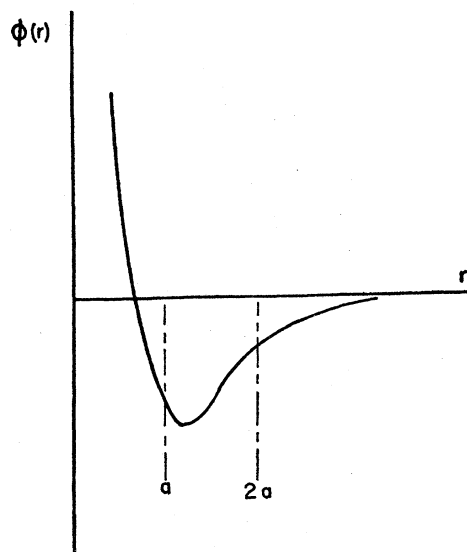


FIG. 1. The form of the two-body potential. Here a is the equilibrium spacing well within the solid.

¹¹ E.g., F. Herman, J. Phys. Chem. Solids 8, 405 (1959).

¹² See, e.g., reference 2 Eq. (5.3) or reference 5 Eq. (2.1).

strong short-range force to expand the two-body potentials as follows:

$$\begin{aligned}\phi(X_n - X_{n-1}) &\equiv \phi(a + x_n - x_{n-1}) = \phi(a) + K(x_n - x_{n-1}) \\ &\quad + \frac{1}{2}\lambda(x_n - x_{n-1})^2 + \cdots, \quad (6) \\ \phi(X_n - X_{n-2}) &\equiv \phi(2a + x_n - x_{n-2}) = \phi(2a) + K'(x_n - x_{n-2}) \\ &\quad + \frac{1}{2}\lambda'(x_n - x_{n-2})^2 + \cdots,\end{aligned}$$

where $K \equiv \phi'(a)$, $K' \equiv \phi'(2a)$, $\lambda \equiv \phi''(a)$, $\lambda' \equiv \phi''(2a)$. For any reasonable potential, $K < 0$, $\lambda > 0$, $K' > 0$, $\lambda' < 0$; i.e., $r = 2a$ is beyond the inflection point in Fig. 1. The equations of equilibrium are then

$$\begin{aligned}0 &= K - \lambda(x_0 - x_1) - \lambda'(x_0 - x_2), \\ 0 &= -\lambda(x_1 - x_2) - \lambda(x_1 - x_0) + K' - \lambda'(x_1 - x_3), \quad (7) \\ 0 &= -\lambda(2x_2 - x_1 - x_3) - \lambda'(2x_2 - x_4 - x_0).\end{aligned}$$

Introducing the notation $x_n - x_{n-1} = a_n$, $(K + K')/\lambda = \mathcal{K}$, $K'/\lambda = \mathcal{K}'$, $\lambda'/\lambda = \delta$, Eqs. (7) become

$$\begin{aligned}-\mathcal{K} &= a_1 + \delta(a_1 + a_2), \\ -\mathcal{K}' &= (a_2 - a_1) + \delta(a_3 + a_2), \\ 0 &= (a_3 - a_2) + \delta(a_4 + a_3 - a_2 - a_1), \\ &\quad \vdots \\ 0 &= (a_n - a_{n-1}) + \delta(a_{n+1} + a_n - a_{n-1} - a_{n-2}).\end{aligned} \quad (8)$$

These equations may be rewritten in a much more convenient form by using as the new n th equation the sum of the first n old equations. Making use of the relation $\mathcal{K} + \mathcal{K}' = 0$ and assuming a symmetric solution, so that $a_{N+1} = a_{N-1}$, we find the equilibrium positions given by the solution of the following set of linear equations:

$$\begin{pmatrix} -\mathcal{K} \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \begin{pmatrix} 1+\delta & \delta & 0 & \cdots \\ \delta & 1+2\delta & \delta & 0 \\ 0 & \delta & 1+2\delta & \delta \\ \vdots & 0 & \vdots & \vdots \\ \cdots & 0 & \delta & 1+2\delta \\ \cdots & 0 & 2\delta & 1+2\delta \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ 0 \\ a_N \end{pmatrix}. \quad (9)$$

By Cramer's rule the solution for a_n can be written as the quotient of two determinants. The denominator is the determinant D_N of the square matrix in Eq. 9 and the numerator is the same determinant with the n th column replaced by the vector on the left-hand side of Eq. 9. Expanding by minors of the first row we find that D_N is determined by

$$D_N = (1+\delta)\Delta_{N-1} - \delta^2\Delta_{N-2}, \quad (10)$$

where Δ_{N-i} is D_N with its first i rows and columns deleted. Further, Δ_n satisfies the homogeneous linear second order difference equation:

$$\Delta_n = (1+2\delta)\Delta_{n-1} - \delta^2\Delta_{n-2}. \quad (11)$$

The solution we want is

$$\Delta_n = \rho_1^n + \rho_2^n, \quad (12)$$

where

$$\rho_{1,2} = \frac{1}{2}[1 + 2\delta \pm (1 + 4\delta)^{1/2}],$$

and we have picked $\Delta_0 = 2$. We may then express a_n as

$$a_n = \frac{(-1)^n \mathcal{K} \delta^{n-1} \Delta_{N-n}}{(1+\delta)\Delta_{N-1} - \delta^2\Delta_{N-2}}. \quad (13)$$

In all realistic cases, $|\delta| \ll 1$ and we then find $\rho_1 \approx 1 + 2\delta - \delta^2$ and $\rho_2 \approx \delta^2$. It is then sufficient to use $\rho_1 = 1$ and $\rho_2 = 0$. We also note that $\mathcal{K} < 0$ and $\delta < 0$ and find the approximate result

$$a_n \approx |\mathcal{K} \delta^{n-1}|. \quad (14)$$

If $\delta = 0.01$, we are effectively within the chain in two atom spacings, or in a distance comparable to the range of the interatomic force. It would be interesting if a potential could be found such that δ were positive. In this case a_n would change sign from one atom to the next. However, only extremely unlikely potentials give a positive δ .

If there is an external pressure on the chain none of the above results are changed in form; we merely change the value of \mathcal{K} . We represent the pressure by a force P to the right on atom 0, and P to the left on atom $2N-1$. The condition determining a is now $0 = P + K + 2K'$ and $\mathcal{K} = (K + K' + P)/\lambda$. It is possible to extend this calculation easily in a number of ways:

(1) We may assume that the potential energy of a pair or of a number of pairs near the surface is different than in the interior. This changes the spacings in the region of altered pair potentials but beyond that region the deviation from the equilibrium spacing within the chain approaches zero as $a_n \propto \delta^n$. The pressure will still be related to the interior force constants by the reasonable demand that equilibrium spacing within the crystal be a constant. Our conclusion here seems to disagree with the remark in reference 1 that the equilibrium stresses depend on a basic way on the surface force constants.

(2) We may treat the surface layer spacing for two- and three-dimensional crystals in the above manner if we assume a semi-infinite crystal, i.e., we ignore the

attempt of the edges and corners to shrink the surface layer.

(3) We may include third and further neighbor interactions. The algebra then becomes tedious: The order of the difference equation for Δ_{N-n} rises with each further interaction. Only the limiting case of Coulomb interactions is of importance. This case has been treated by Lennard-Jones and Dent¹³ and

¹³ J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. (London) **A121**, 247 (1928).

others.^{14,15} They have included polarization effects, and interesting surface clustering tendencies have been found.¹⁴ Our one-dimensional calculation should also be corrected for polarization effects.

ACKNOWLEDGMENT

We wish to thank Dr. M. Lax for a helpful discussion.

¹⁴ K. Molière, W. Rathje, and I. N. Stranski, Discussions Faraday Soc. **5**, 21 (1949).

¹⁵ M. M. Nicolson, Proc. Roy. Soc. (London) **A228**, 490 (1955).

Decoupling of Bloch Bands in the Presence of Homogeneous Fields*

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Following up an earlier communication, wave functions are constructed in Sec. 2 of this paper which are valid if a charge moves in a superposition of a periodic electric potential and a uniform magnetic field. The wave functions are not themselves solutions of the Schroedinger equation, but yield the traditional effective Hamiltonian for this problem. Contrary to the electric field case the manifold of states linked by the "band index" does not form a Bloch band; the reason is that the cellular transforms of the Bloch-like functions are modified by the Peierls phase. At present, the derivation of these results is in closed form, but justifiable only "to all powers of the magnetic field." This was also the case for the previous electric derivation. The limitation may not be genuine. The third section of the paper does in fact prove directly the existence of closed Bloch bands in the presence of a homogeneous electric field; the case of free electrons is given as an example. One expects from this that the new results for the magnetic field are at least in part also independent of the power series method used for their justification. The fourth section extends the procedure to crossed electric and magnetic fields.

1. INTRODUCTION

IN a previous communication having a similar title,¹ one of us has put forward the notion that homogeneous fields must have a very special relationship to the energy bands of a Bloch particle. The basis for this idea is that energy bands arise from the translational symmetry of the crystalline field and that this symmetry is not removed physically by the presence of the applied field. Commonly employed formalisms do not seem to support this viewpoint. The notion is, however, followed up in I for the case of a homogeneous electric field. It is shown that one can modify the Bloch functions in powers of the field in such a way that there is no inter-band coupling and the particle is confined to one band only. Within this band the particle moves according to the law

$$\mathbf{k} = \mathbf{k}_0 + e\mathbf{E}t/\hbar. \quad (1)$$

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¹ Gregory H. Wannier, Phys. Rev. **117**, 432, (1960). In the following referred to as I. There is an error in the Eqs. (36)-(40) of that paper where x should be replaced by ξ throughout. This error was pointed out to us by E. Blount.

The procedure yields, simultaneously with the wave functions, an effective one-band Hamiltonian \mathcal{H}_q for the particle. This Hamiltonian reads

$$\mathcal{H}_q = W_q(\mathbf{k}) - e\mathbf{E} \cdot \mathbf{r}. \quad (2)$$

Here $W_q(\mathbf{k})$ is the (modified) energy band function for the band of index q , and \mathbf{r} is the lattice vector operator, an operator conjugate to \mathbf{k} within the band q .

In the present paper the notions of reference 1 will be pushed further in two directions. First of all the analogous procedure is carried out in Sec. 2 for the case of a homogeneous magnetic field. It is seen that because of the presence of the Peierls phase² the ensemble of states linked together by the band index q ceases to be a band. Instead of this, it becomes a manifold of just a structure that its effective Hamiltonian takes the form

$$\mathcal{H} = W_q(\mathbf{P}/\hbar), \quad (3a)$$

where \mathbf{P} is given by

$$\mathbf{P} = \mathbf{p} - (e/c)\mathbf{A}. \quad (3b)$$

² R. Peierls, Z. Physik **80**, 763 (1933).