

## New Theory of Lattice Dynamics at 0°K

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It has previously been shown that the optimum choice of harmonic Hamiltonian with which to approximate a crystal Hamiltonian is one in which the force constants are equal to the ground-state expectation value of the second derivative of the crystal potential, the expectation value being computed self-consistently with the ground-state eigenfunction of the harmonic Hamiltonian. It is shown here that the appearance of ground-state averages of various derivatives of the potential is due to an explicit or implicit expansion of the potential in a Hermite polynomial series, and that such an expansion is superior to the conventional Taylor-series expansion for anharmonic systems. In addition, it is shown that one can systematically treat very anharmonic systems by expanding the Hamiltonian in a set of polynomials orthogonalized with respect to weight function chosen to cut off the potential at short range, and that explicit incorporation of an easily optimized Gaussian factor in this weight function provides a computationally convenient way of introducing certain desirable features into the general expansion.

### I. INTRODUCTION

CERTAIN steps in the development of a new approach to lattice dynamics at 0°K have been briefly described in two previous letter publications.<sup>1,2</sup> The goal of this method is the development of a unified and computationally feasible theoretical framework for the treatment of harmonic, slightly anharmonic, and very anharmonic lattices.

The essential idea of the method—which will be called the orthogonal polynomial method—is that of expanding the crystal potential in terms of a complete set of polynomials orthogonalized with respect to an appropriate weight function. The computational feasibility is, in a large part, the result of the use of certain techniques<sup>3</sup> for the exact evaluation in coordinate space of matrix elements of a crystal potential between three-dimensional harmonic oscillator wave functions.

In this paper, the theory of the orthogonal polynomial method will be described in detail. The emphasis will be on application to lattice dynamics, although other quantum-mechanical systems can be treated by this approach. In Sec. III the method will be illustrated by a comprehensive treatment of the problem of a single particle interacting with a one-dimensional potential. A reading of this section alone together with the parts of Sec. II which are necessary for an understanding of the notation will serve to give a casually interested reader a reasonable understanding of the method without subjecting him to the complication of crystal-lattice notation.

The additional details necessary for the treatment of three-dimensional crystal lattices will be given in Sec. IV, both for the case of harmonic or slightly anharmonic systems such as solid Ar or solid Ne and for the case of very anharmonic systems solid <sup>3</sup>He or solid <sup>4</sup>He.

Although a few numerical results for the latter two cases have already been given in Refs. 1 and 2, a

<sup>1</sup> T. R. Koehler, Phys. Rev. Letters **17**, 89 (1966).

<sup>2</sup> T. R. Koehler, Phys. Rev. Letters **18**, 516 (1967).

<sup>3</sup> T. R. Koehler, Phys. Rev. **144**, 789 (1966); this paper will be referred to as I.

complete presentation of these and other unpublished results will be reserved for subsequent publications. More explicit details concerning computational methods will be given then also.

### II. PRELIMINARY DISCUSSION AND NOTATION

The general problem we wish to consider is that of finding the eigenfunctions and eigenvalues of the Hamiltonian of a crystal in the Born-Oppenheimer adiabatic approximation. The Hamiltonian can be written symbolically as

$$H = K + V, \quad (1)$$

where  $K = -\frac{1}{2}\lambda^2\nabla^2$ , and it will be assumed that  $V$  is a known function of the coordinates. If the atoms in the crystal interact with a two-body central-force potential  $U(r)$ , then  $V = \frac{1}{2}\sum' U(r_{ij})$ , where  $\mathbf{r}_i$  is the coordinate of the  $i$ th particle and  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . Most of the general expressions which will be derived do not depend upon the use of a two-body central-force potential; however, explicit numerical evaluation of the expressions is most convenient for this case.

In order to save superscripts and subscripts as often as possible, a supervector and supermatrix notation will be used in which vector products will be written as  $\mathbf{r}^2 = \tilde{\mathbf{r}}\mathbf{r} = \sum_i \mathbf{r}_i \cdot \mathbf{r}_i = \sum_i \sum_\alpha r_i^\alpha r_i^\alpha$  with an obvious generalization to matrices. Superscripts will be used to denote Cartesian components of a vector. For notational convenience, simple Bravais lattices will be treated exclusively although the generalization to more complicated lattices is quite straightforward, as was shown in I.

In this notation,  $V(\mathbf{r}) = V(\mathbf{r}_1, \dots, \mathbf{r}_N)$ , where there are  $N$  atoms in the crystal. Born-von Karman boundary conditions will be assumed and the translational symmetry of the lattice requires  $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$ , where  $\mathbf{R}_i$  is the equilibrium position of the  $i$ th atom.

According to the prescription of the traditional harmonic approximation, one expands the potential in a Taylor series in terms of the displacements  $\mathbf{u} = \mathbf{r} - \mathbf{R}$  of the atoms from their equilibrium positions. The

resulting Hamiltonian

$$H = K + V_0^T + V_2^T + V_3^T + \dots, \quad (2)$$

in which the term linear in the displacements vanishes because the expansion is about an equilibrium point, is then truncated at the second term giving a harmonic Hamiltonian

$$H_h^T = -\frac{1}{2}\lambda^2 \nabla^2 + V_0^T + \frac{1}{2}\tilde{u}\Phi^T u, \quad (3)$$

which can be diagonalized by standard techniques.<sup>4</sup>

Briefly, one notes that, because of the lattice symmetry,  $\Phi^T$  can be brought into semidiagonal form by the transformation

$$[T\Phi^T T^\dagger] = \mathbf{e}_k \cdot \mathbf{D}_k \cdot \mathbf{e}_k^\dagger \delta_{kk'}, \quad (4)$$

where  $T_{ki} = \mathbf{e}_k e^{-ik \cdot \mathbf{R}_i}$ . The matrix  $\mathbf{D}_k$  is called the dynamical matrix and its roots are the squares of the phonon frequencies. The matrix  $\mathbf{e}_k$ , whose rows are polarization vectors, is then chosen to diagonalize  $\mathbf{D}_k$  so that

$$\mathbf{e}_k \cdot \mathbf{D}_k \cdot \mathbf{e}_k^\dagger = (\omega_k)^2, \quad (5)$$

where  $\omega_k$  is a diagonal matrix.

The  $n$ th term in the expansion of the Hamiltonian given in Eq. (3) is

$$V_n^T = \frac{1}{n!} \Phi_n^T(i_1, \alpha_1; \dots; i_n, \alpha_n) u_{i_1}^{\alpha_1} \dots u_{i_n}^{\alpha_n}, \quad (6)$$

where

$$\Phi_n^T(i_1, \alpha_1; \dots; i_n, \alpha_n) = \left[ \frac{\partial^n}{\partial r_{i_1}^{\alpha_1} \dots \partial r_{i_n}^{\alpha_n}} \right] V \Big|_{r=R}. \quad (7)$$

Vector and matrix products will be written either as in Eq. (6), or in the more conventional and less cumbersome notation described earlier and used in Eq. (3). Open products will be written, for example, as  $\mathbf{u}u$  or  $\mathbf{u}_i \mathbf{u}_i$ . In particular  $\nabla \nabla V$  defines a matrix whose components are  $\nabla_i^\alpha \nabla_j^\beta V$ .

Since a variety of harmonic Hamiltonians and eigenfunctions of harmonic Hamiltonians play an important role in this theory, it is useful to establish a notation which is consistent enough for one to derive general expressions but sufficiently flexible for one to differentiate between different harmonic systems. An arbitrary harmonic Hamiltonian will be denoted by  $H_h$ , the quadratic term in  $H_h$  will be  $\frac{1}{2}\tilde{u}\Phi u$ , and the kinetic-energy term in all Hamiltonians will be  $-\frac{1}{2}\lambda^2 \nabla^2$ . A specific harmonic Hamiltonian and its quadratic term will be denoted by, for example,  $H_h^T$  and  $\tilde{u}\Phi^T u$  as was done in Eq. (3). The normalized ground-state eigenfunction of  $H_h$  will be written  $|0\rangle$  and of  $H_h^T$  will be written  $|T, 0\rangle$ , or simply as  $|0\rangle$  when the reference is clear. In general, anything written within the ket symbol will denote a normalized wave function.

<sup>4</sup> See, e.g., A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3, or any of the several references given in I.

As was discussed in I,

$$|0\rangle = A \exp(-\frac{1}{2}\tilde{u}\Gamma u), \quad (8)$$

where  $A$  is a normalization constant,  $\Gamma = G/\lambda^2$ , and  $G^2 = \Phi$ . It is notationally convenient to use both  $G$  and  $\Gamma$ , and  $\gamma_k = \omega_k/\lambda^2$  will also be used. In constructing  $|T, 0\rangle$ , for example, one simply substitutes  $\Gamma^T$  for  $\Gamma$  in Eq. (8). In this paper  $|0\rangle$  or some subscripted form of  $|0\rangle$  will always designate the normalized exponential of some quadratic form—that is, a correlated-Gaussian wave function.

Numerical results are obtainable from this theory primarily because of the techniques described in I for the exact analytic integration of a correlated-Gaussian wave function over all coordinates but a few. Thus, one can, for example, evaluate the expression

$$\langle 0|V|0\rangle = \frac{1}{2}N \sum_i \langle 0|U(r_{0i})|0\rangle \quad (9)$$

exactly by performing only three-dimensional numerical integration in coordinate space. For the purposes of this paper we wish only to note that the expressions to be derived can be evaluated numerically.

A few formulas which will be used extensively throughout this paper are as follows:

$$\begin{aligned} \langle 0|fHg|0\rangle &= \frac{1}{4}\lambda^2 \text{Tr}G \langle 0|fg|0\rangle + \langle 0|fVg|0\rangle \\ &\quad - \frac{1}{8}\lambda^2 \langle 0|fg \left[ \frac{1}{-\nabla^2} f + \frac{1}{-\nabla^2} g \right. \\ &\quad \left. - \frac{2}{fg} (\nabla f) \cdot (\nabla g) \right] |0\rangle, \quad (10) \end{aligned}$$

$$\langle 0|u_i^\alpha V|0\rangle = \frac{1}{2}G^{-1}_{ij} \alpha^\beta \langle 0|\nabla_j^\beta V|0\rangle, \quad (11)$$

and

$$\begin{aligned} \langle 0|u_i^\alpha u_j^\beta V|0\rangle &= \frac{1}{2}\delta_{ij} \alpha^\beta \langle 0|V|0\rangle \\ &\quad + \frac{1}{4}G^{-1}_{ii'} \alpha^\alpha G^{-1}_{jj'} \beta^\beta \langle 0|\nabla_{i'}^{\alpha'} \nabla_{j'}^{\beta'} V|0\rangle. \quad (12) \end{aligned}$$

Equation (10) results immediately from the identity

$$\begin{aligned} \langle 0|f(\nabla_i^\alpha)^2 g|0\rangle &= \frac{1}{4}[\langle 0|f[(\nabla_i^\alpha)^2 g]|0\rangle - 2\langle 0|(\nabla_i^\alpha f)(\nabla_i^\alpha g)|0\rangle \\ &\quad + \langle 0|[(\nabla_i^\alpha)^2 f]g|0\rangle]. \quad (13) \end{aligned}$$

Equation (11) is a result of integration by parts and Eq. (12) is derived by applying Eq. (10) twice.

### III. ONE-DIMENSIONAL MODEL

#### A. Conventional Harmonic Approximation

Although the theory is directed towards three-dimensional crystals, we have found that its essential features can be illustrated with a minimum of notational complications in terms of a simple model of a single particle interacting with a one-dimensional potential. In this case, the Hamiltonian is

$$H = -\frac{1}{2}\lambda^2 \frac{d^2}{dx^2} + V(x). \quad (14)$$

If one were to treat this model in the conventional harmonic approximation, one would first expand the potential in a Taylor series about some point  $x_0$  to obtain

$$H = -\frac{1}{2}\lambda^2 \frac{d^2}{du^2} + V_0 + \sum \frac{1}{n!} \Phi_n^T u^n, \quad (15)$$

where, in analogy with the previous notation,

$$\Phi_n^T = \left. \frac{d^n V}{dx^n} \right|_{x=x_0},$$

and  $u = x - x_0$ . This Hamiltonian is then truncated to give

$$H_h^T = -\frac{1}{2}\lambda^2 \frac{d^2}{du^2} + V_0^T + \frac{1}{2}\Phi^T u^2. \quad (16)$$

The normalized eigenfunctions of  $H_h^T$  are well known to be

$$|T, n\rangle = (2^n n!)^{-1/2} H_n[(\gamma^T)^{1/2} u] |T, 0\rangle, \quad (17)$$

where

$$|T, 0\rangle = (\pi/\gamma^T)^{1/2} \exp(-\frac{1}{2}\gamma^T u^2), \quad (18)$$

$\gamma^T = g^T/\lambda^2$ , and  $(g^T)^2 = \Phi^T$ . The unperturbed eigenvalues of  $H_h$  will be denoted by  $E_n^T$ , while the diagonal matrix elements of  $H$  in the representation  $|n\rangle$  will be denoted by  $E_n$ .

In the conventional harmonic approximation, the leading correction to the ground-state energy in perturbation theory would be

$$\frac{1}{4!} \Phi_4^T \langle T, 0 | u^4 | T, 0 \rangle - \frac{1}{3g^T} \frac{1}{(3!)^2} (\Phi_3^T)^2 \langle T, 0 | H_3 u^3 H_0 | T, 0 \rangle^2, \quad (19)$$

and it is clear that the structure of perturbation theory is complicated by the fact that the final order of a perturbation correction depends both upon the order of the term in the Taylor series and the order in which it is being treated in perturbation theory.

### B. Hermite Polynomial Expansion and Self-Consistent Harmonic Approximation

An alternative approach is obviously sensible. One could treat  $V - \frac{1}{2}g^T u^2$  as a perturbation to  $H_h$ . Then the ground-state energy to first order is simply  $E_0^T = \langle T, 0 | H | T, 0 \rangle$ . It is readily shown that

$$E_0^T = \frac{1}{4}g^T + \langle T, 0 | V | T, 0 \rangle. \quad (20)$$

In this form an entire series of what were higher-order terms of the form  $(1/n!) \Phi_n^T \langle T, 0 | u^n | T, 0 \rangle$  appear in first-order perturbation theory. The expression for the ground-state energy given in Eq. (20) resembles that obtained from a variational calculation so it now seems

obvious to use an arbitrary Gaussian as a variational wave function and to minimize  $E_0$  with respect to  $g$ . The minimization is readily carried out and one finds that  $dE_0/dg = 0$  if  $g = g^c$ , where  $g^c$  is determined by the self-consistent condition

$$(g^c)^2 = \lambda^2 \langle c, 0 | \frac{d^2 V}{dx^2} | c, 0 \rangle, \quad (21)$$

where Eq. (12) has been used to cast Eq. (21) into the form given. The superscript  $c$  will be used to designate wave functions, etc., which are determined from some self-consistent condition.

One could now consider  $H_h^c$  to be the optimum harmonic Hamiltonian with which to approximate  $H$  and then could use the eigenfunctions of this Hamiltonian as a basis for perturbation theory using  $V - \frac{1}{2}\Phi^c u^2$  as the perturbation. If this is done, terms involving the ground-state expectation value of various derivatives of the potential appear. An understanding of the significance of these terms furnishes an insight into the self-consistent harmonic approximation and also suggests a possible way in which the theory can be extended.

Suppose instead of expanding the potential in a Taylor series, one were to expand it in terms of an arbitrary set of Hermite polynomials—we will call this Hermite polynomial method. This expansion of the potential will be written

$$V(x) = \sum V_n^H \quad (22a)$$

$$= \sum (2^n n!)^{-1} \Phi_n^H H_n[(\sqrt{\gamma})u]. \quad (22b)$$

The  $n$ th coefficient in the expansion

$$\Phi_n^H = \langle 0 | V H_n | 0 \rangle \quad (23)$$

can be written in a different form if one uses the identity

$$\langle 0 | V H_n[(\sqrt{\gamma})u] | 0 \rangle = -\frac{1}{\gamma} \langle 0 | \frac{dV}{du} H_{n-1} | 0 \rangle, \quad (24)$$

which can be obtained by using the recursion relations among the Hermite polynomials and integrating once by parts. Applying Eq. (24)  $n$  times to the numerator of Eq. (23) one obtains

$$\Phi_n^H = \gamma^{-n/2} \langle 0 | \frac{d^n V}{du^n} | 0 \rangle. \quad (25)$$

The Hermite polynomial expansion actually includes the Taylor-series expansion as a limiting case since

$$\lim_{\gamma \rightarrow \infty} \langle 0 | \frac{d^n V}{du^n} | 0 \rangle = \left. \frac{d^n V}{du^n} \right|_{u=0} \quad (26)$$

and

$$\lim_{\gamma \rightarrow \infty} \gamma^{-n/2} H_n[(\sqrt{\gamma})u] = u^n. \quad (27)$$

The Hamiltonian to second order is now

$$H_h^H = -\frac{1}{2}\lambda^2 \frac{d^2}{du^2} + \langle 0|V|0\rangle + \langle 0|\frac{dV}{du}|0\rangle u + \frac{1}{2}\langle 0|\frac{d^2V}{du^2}|0\rangle \left(u^2 - \frac{1}{2\gamma}\right). \quad (28)$$

The origin of coordinates should be chosen to eliminate the term linear in  $u$ . If this is done, it is clear that, in the special case when the self-consistent condition is met,  $|c,0\rangle$  is the ground-state eigenfunction of the harmonic Hamiltonian  $H_h^e$ . In other cases, the ground-state eigenfunction of  $H_h^H$  is not equal to  $|0\rangle$ .

Since an expansion of the potential still occurs in the Hermite polynomial method there may be more than one term of the expansion contributing to a particular matrix element  $\langle m|V|n\rangle$ . However, the number of terms is considerably less than for the Taylor-series expansion. The most obvious example is  $\langle 0|V|n\rangle$  to which only the term  $V_n^H$  contributes while in the Taylor series all of the terms included in

$$i = \sum_{s=0}^{\infty} V_{n+2s}$$

contribute. In the general matrix element of a Hermite polynomial expansion, nonzero contributions are given by terms of order  $|m-n|, |m-n|+2, \dots, m+n$ .

A few additional features of the method become apparent if one approaches the problem from the point of view of the matrix formulation of quantum mechanics and computes the lowest-order matrix elements of the Hamiltonian using the eigenfunctions of an arbitrary harmonic Hamiltonian. While this approach is exactly equivalent to the previously described method, it has the conceptual advantage that the formal expansion of the potential *per se* is never introduced.

The matrix elements can be written down in an almost mechanical way. The matrix elements of the kinetic energy are well known to be

$$\langle m|-\frac{1}{2}\lambda^2 \frac{d^2}{dx^2}|n\rangle = \frac{1}{4}g(1+2n)\delta_{mn} - \frac{1}{4}g[m(m-1)]^{1/2}\delta_{m,n+2} - \frac{1}{4}g[n(n-1)]^{1/2}\delta_{m+2,n}. \quad (29)$$

A simple recursion relationship,

$$\langle m|V|n\rangle = \frac{1}{(2\gamma m)^{1/2}} \langle m-1|\frac{dV}{dx}|n\rangle + \binom{n}{m}^{1/2} \langle m-1|V|n-1\rangle, \quad (30)$$

can be used to express the matrix elements  $\langle m|V|n\rangle$  in terms of the first row elements

$$\langle 0|V|n\rangle = (2^n n!)^{-1/2} \Phi_n^H.$$

TABLE I. Matrix elements of a one-dimensional Hamiltonian between an arbitrary set of harmonic wave functions, and those between a self-consistently determined (sc) set.

Element	Value
$\langle 0 H 0\rangle$	$E_0$
$\langle 0 H 1\rangle$	$\langle 0 V 1\rangle$
(sc)	0
$\langle 0 H 2\rangle$	$-2^{-3/2}g + \langle 0 V 2\rangle$
(sc)	0
$\langle 0 H 3\rangle$	$\langle 0 V 3\rangle$
$\langle 1 H 1\rangle$	$E_0 + \frac{1}{2}g + \sqrt{2}\langle 0 V 2\rangle$
(sc)	$E_0 + g$
$\langle 1 H 2\rangle$	$\sqrt{2}\langle 0 V 1\rangle + \sqrt{3}\langle 0 V 3\rangle$
(sc)	$\sqrt{3}\langle 0 V 3\rangle$
$\langle 1 H 3\rangle$	$-\frac{1}{2}(\frac{3}{2})^{1/2}g + \sqrt{3}\langle 0 V 2\rangle + 2\langle 0 V 4\rangle$
(sc)	0
$\langle 2 H 2\rangle$	$E_0 + g + 2\sqrt{2}\langle 0 V 2\rangle + \sqrt{6}\langle 0 V 4\rangle$
(sc)	$E_0 + 2g$
$\langle 2 H 3\rangle$	$\sqrt{3}\langle 0 V 1\rangle + 3\sqrt{2}\langle 0 V 3\rangle + \sqrt{10}\langle 0 V 5\rangle$
(sc)	$3\sqrt{2}\langle 0 V 3\rangle$
$\langle 3 H 3\rangle$	$E_0 + \frac{3}{2}g + 3\sqrt{2}\langle 0 V 2\rangle + 3\sqrt{6}\langle 0 V 4\rangle$
(sc)	$E_0 + 3g$

The matrix elements  $\langle m|H|n\rangle$ ,  $m \leq n \leq 3$  are listed in Table I.

The results obtain if one assumes that the self-consistent condition  $\langle 0|V|2\rangle = 2^{-3/2}g$  is fulfilled, that the origin of coordinates has been chosen to make  $\langle 0|V|1\rangle = 0$ , and that terms of higher order than  $\langle 0|V|3\rangle$ , shown in the rows of Table I, labeled (sc) are small. It is clear that the introduction of the self-consistent condition simplifies the structure of perturbation theory. Since the Hamiltonian has zero matrix elements between the first and second excited states, the leading perturbation theory corrections to the ground state and first excited state are particularly simple.

It can be readily shown that the self-consistent condition is sufficient to cause all off-diagonal contributions involving  $g$  and  $\langle 0|V|2\rangle$  to vanish and all diagonal contributions to be of the forms  $E_0 + ng$ .

### C. General Polynomial Method

Although the lowest order of the self-consistent harmonic approximation probably yields a good value for the energies of the ground state and the lowest excited state in a fairly harmonic system and the next order of perturbation theory should be adequate for a mildly anharmonic system, it is clear that the calculation would have to be carried quite a bit further for an adequate treatment of a very anharmonic system. Since the one-dimensional problem is being studied in order to furnish some insight into useful techniques for problems in three dimension, an alternative technique for very anharmonic systems is desirable.

A well-defined procedure, which is a logical extension of the Hermite polynomial method, is for one to either expand the potential or compute the matrix elements of the Hamiltonian in a representation of polynomials orthogonalized with respect to an arbitrary function which will be written as  $f|0\rangle$ . The Gaussian part is retained because it is anticipated that it represents the gross behavior of the ground-state wave function in some region of space and that this part of the wave function can be readily optimized. Of course,  $f$  is chosen to make  $f|0\rangle$  a computationally convenient, reasonable guess for the ground-state wave function of the true Hamiltonian. We will use  $|f\rangle$  to signify  $f|0\rangle/\langle 0|f^2|0\rangle^{1/2}$ .

The polynomials will be designated by  $B_m(x)$  and will satisfy

$$\langle f|B_m B_n|f\rangle \propto \delta_{mn}. \quad (31)$$

These are various methods for the construction of a set of polynomials orthogonalized with respect to a given weight function. In the work that has been done to date we have found that the most convenient technique is to use the recursion relationship

$$B_m(x) = x^m - \sum_{n=0}^{m-1} \beta_{mn} B_n(x), \quad (32)$$

where

$$\beta_{mn} = \langle f|x^m B_n|f\rangle / \langle f|B_n^2|f\rangle. \quad (33)$$

In this paper, explicit expressions for only

$$\beta_{10} = \langle f|x|f\rangle \quad (34)$$

and

$$\beta_{20} = \langle f|x^2|f\rangle \quad (35)$$

are needed. Equation (11) can be used to express  $\beta_{10}$  and  $\beta_{20}$  in terms of Gaussian averages of derivatives of  $f^2$ . This latter form is useful if one wishes to think of expanding both  $f^2$  and  $V$  in terms of an arbitrary set of Hermite polynomials and then retaining terms to a certain order in each expansion.

By using Eq. (10) one can readily derive an expression for the ground-state energy  $E_0 = \langle f|H|f\rangle$  as

$$E_0 = \frac{1}{4}g + \langle f|V_{\text{eff}}'|f\rangle, \quad (36)$$

where

$$V_{\text{eff}}' = V - \frac{1}{4}\lambda^2 V^2 \ln f^2. \quad (37)$$

The second term on the right-hand side of Eq. (37) is the price paid in kinetic energy for the gain in potential energy resulting from the modification in the wave function introduced by  $f$ , which will generally be used to cut off the potential at short range in hard-core problems. We will occasionally want to work with expressions in which integrals over Gaussian weight factors are explicitly written and will then use  $V_{\text{eff}} = f^2 V_{\text{eff}}'$ .

One can readily derive an implicit optimization condition for  $g$  by differentiating Eq. (36) with respect to  $g$  to obtain

$$\frac{1}{4}\lambda^2 = \langle f|x^2 V_{\text{eff}}'|f\rangle - \langle f|V_{\text{eff}}'|f\rangle \langle f|x^2|f\rangle. \quad (38)$$

Subsequent application of Eq. (12) provides a more explicit expression for the self-consistent  $g$ ,

$$(g^e)^2 = \lambda^2 \frac{\langle 0|d^2 V_{\text{eff}}/dx^2|0\rangle - \langle 0|d^2 f^2/dx^2|0\rangle \langle f|V_{\text{eff}}'|f\rangle}{\langle 0|f^2|0\rangle}. \quad (39)$$

In this form it is clear that the optimization condition is not simply a substitution of  $V_{\text{eff}}$  for  $V$  in Eq. (20).

In addition to this, two other independent optimizations are possible. These are the choice of  $x_0$  in  $u = x - x_0$  and a transformation  $f(x) \rightarrow f(x - x_0')$ . The conditions  $dE_0/dx_0 = 0$  and  $dE_0/dx_0' = 0$  give

$$\langle 0|\frac{dV_{\text{eff}}}{dx}|0\rangle - \langle f|V_{\text{eff}}'|f\rangle \langle 0|\frac{df^2}{dx}|0\rangle = 0 \quad (40)$$

and

$$\langle 0|\frac{dV_{\text{eff}}}{dx}|0\rangle - \langle 0|f^2\frac{dV}{dx}|0\rangle - \langle f|V_{\text{eff}}'|f\rangle \langle 0|\frac{df^2}{dx^2}|0\rangle = 0, \quad (41)$$

respectively. Equations (40) and (41) can be combined to give  $\langle f|dV/dx|f\rangle = 0$ . Of these expressions, only Eq. (40) will be used.

The first excited state of  $H$  is approximated by  $B_1|f\rangle$  and the second excited state by  $B_2|f\rangle$ . Equations (10) and (32)–(35) may be used to obtain the matrix elements shown in Table II which is constructed in a manner similar to Table I. Equation (40) is used for the (sc) results.

Thus, the explicit retention of the Gaussian weight factor enables one to derive a simple optimization condition, the fulfillment of which is sufficient to provide two of the intuitively appealing features of the

TABLE II. Matrix elements of a one-dimensional Hamiltonian in the general polynomial method. In the self-consistent (sc) values the optimum choice of origin of coordinates is also assumed.

Element	Value
$\langle f H f\rangle$	$E_0$
$\langle f H 1\rangle$	$\langle f B_1^2 f\rangle^{-1/2} [\langle f u V_{\text{eff}}' f\rangle - \langle f u f\rangle \langle f V_{\text{eff}}' f\rangle]$
(sc)	0
$\langle f H 2\rangle$	$\langle f B_2^2 f\rangle^{-1/2} [\langle f u^2 V_{\text{eff}}' f\rangle - \langle f u^2 f\rangle \langle f V_{\text{eff}}' f\rangle - \lambda^2/4] - \beta_{21} \langle f H 1\rangle]$
(sc)	0
$\langle 1 H 1\rangle$	$E_0 - 2 \frac{\langle f u f\rangle \langle f H 1\rangle}{\langle f B_1^2 f\rangle^{1/2}} + \frac{\langle f u^2 V_{\text{eff}}' f\rangle - \langle f V_{\text{eff}}' f\rangle \langle f u^2 f\rangle + \lambda^2/4}{\langle f u^2 f\rangle - \langle f u f\rangle^2}$
(sc)	$E_0 + \frac{\frac{1}{2}\lambda^2}{\langle f u^2 f\rangle - \langle f u f\rangle^2}$

self-consistent harmonic approximation; i.e., the Hamiltonian has zero matrix elements between the ground state and the first and second excited states.

Equations (11) and (12) can be used to rewrite the expression for the energy of the first excited state as

$$E_1 = E_0 + \left[ \frac{1}{g} + \frac{\lambda^2}{2g^2} \left( \frac{\langle 0 | d^2 f^2 / dx^2 | 0 \rangle}{\langle 0 | f^2 | 0 \rangle} - \frac{\langle 0 | df^2 / dx | 0 \rangle^2}{\langle 0 | f^2 | 0 \rangle^2} \right) \right]^{-1}. \quad (42)$$

In this form it is clear that Eq. (42) reduces to the Hermite polynomial value given in Table I in the limit  $f \rightarrow 1$ .

#### IV. THREE-DIMENSIONAL MODEL

##### A. Hermite Polynomial Method and Self-Consistent Harmonic Approximation

The generalization of the results of Sec. III to three dimensions is quite straightforward. However, since the approach differs from the conventional harmonic approximation, it is worth presenting the calculations in some detail. In most equations, the change from one to three dimensions can be effected by replacing  $g$  with  $\text{Tr}G$  in kinetic-energy terms and replacing  $g^{-1}$  by  $G^{-1}$  in other terms.

The form of the model harmonic Hamiltonian and of its ground-state eigenfunctions have been given previously in Eqs. (3) and (8), respectively. One can readily evaluate the expectation value of the true crystal Hamiltonian, to obtain

$$E_0 = \frac{1}{4} \text{Tr}G + \langle 0 | V | 0 \rangle, \quad (43)$$

and can then differentiate this expression to show that  $\partial E_0 / \partial G_{ij} = 0$  if the self-consistent condition

$$\langle G^c \rangle^2 = \lambda^2 \langle c, 0 | \nabla \nabla V | c, 0 \rangle \quad (44)$$

is met, where Eq. (12) has been used. One can also obtain this result by transforming to normal coordinates and considering the frequencies and the polarization vectors as variational parameters, but the result is most directly obtained in coordinate space by the method outlined above.

As in the one-dimensional case, the appearance here of ground-state expectation values of various derivatives of the potential can be linked to an expansion either of the potential or of the crystal Hamiltonian in a set of polynomials. Here they are three-dimensional polynomials orthogonalized with respect to the weight function  $\exp(-\tilde{u}\Gamma u)$ .

The polynomials can be obtained from the generating function

$$H_n(k_1^{n_1}, k_2^{n_2}, \dots, k_m^{n_m}) = \exp(\tilde{u}\Gamma u) (-\nabla_{k_1} / \gamma_{k_1})^{n_1} \dots \times (-\nabla_{k_m} / \gamma_{k_m})^{n_m} \exp(-\tilde{u}\Gamma u), \quad (45)$$

where the number of phonons with wave vector  $k_i$  is specified by the constant

$$n_i, m \leq n, n = \sum_{i=1}^m n_i$$

and

$$\nabla_k^\alpha = T_{k_i}^{\alpha\beta} \nabla_i^\beta. \quad (46)$$

In Eq. (45) and in several of the remaining equations in this section, the superscripts which indicate Cartesian components or phonon branches are omitted for notational convenience.

The construction of the polynomials is simplified if one notes the commutation rule

$$[\nabla_k^\alpha, Q_{k'}^{\alpha'}] = \delta_{k, -k'}^{\alpha, \alpha'} \quad (47)$$

and a differential expression

$$\nabla_k \exp(-\tilde{u}\Gamma u) = -(2\gamma_k Q_k) \exp(-\tilde{u}\Gamma u), \quad (48)$$

where  $Q_k^\alpha = T_{k_i}^{\alpha\beta} u_i^\beta$  is a normal mode of the model harmonic Hamiltonian. An equivalent of Eq. (11) is now

$$\langle 0 | Q_k f | 0 \rangle = (1/2\gamma_k) \langle 0 | \nabla_k f | 0 \rangle. \quad (49)$$

These polynomials are almost, but not quite, constructed from products of Hermite polynomials in the normal modes. The difference obtains from the use of running wave modes and is reflected in the commutator Eq. (47). However, the complete polynomial is made up of products of  $H_n(k^m, -k^{n-m})$ . Two useful recursion relations for these simpler polynomials are

$$H_n(k^m, -k^{n-m}) = 2(\gamma_k)^{1/2} Q_k H_{n-1}(k^{m-1}, -k^{n-m}) - 2(n-m) H_{n-2}(k^{m-1}, -k^{n-m-1}) \quad (50)$$

and

$$\nabla_k^\alpha H_n(k^m, -k^{n-m}) = 2(\gamma_k)^{1/2} (n-m) H_{n-1}(k^m, -k^{n-m}). \quad (51)$$

Some of the lowest-order polynomials are as follows:

$$H_0 = 1, \quad (52a)$$

$$H_1(k) = 2(\gamma_k)^{1/2} Q_k, \quad (52b)$$

$$H_2(k_1, k_2) = 4(\gamma_{k_1} \gamma_{k_2})^{1/2} Q_{k_1} Q_{k_2} - 2\delta_{k_1, -k_2}, \quad (52c)$$

$$H_3(k_1, k_2, k_3) = 8(\gamma_{k_1} \gamma_{k_2} \gamma_{k_3})^{1/2} Q_{k_1} Q_{k_2} Q_{k_3} - 2[(\gamma_{k_1})^{1/2} Q_{k_1} \delta_{k_2, -k_3} + (\gamma_{k_2})^{1/2} Q_{k_2} \delta_{k_3, -k_1} + (\gamma_{k_3})^{1/2} Q_{k_3} \delta_{k_1, -k_2}]. \quad (52d)$$

A few of the matrix elements of the crystal Hamiltonian are given in Table III. Terms of higher order than the third derivative are omitted and it is assumed that the equilibrium condition  $\langle 0 | uV | 0 \rangle = 0$  holds. Conservation of crystal momentum holds for all elements. This is indicated either by the choice of  $\mathbf{k}$  values used or by the symbol  $\Delta(\mathbf{k})$  which has the value of unity for  $\mathbf{k} = 0$  or a reciprocal lattice vector and is zero otherwise. The numerical factors in the matrix elements

TABLE III. Matrix elements of a three-dimensional crystal Hamiltonian between an arbitrary and a self-consistent (sc) set of harmonic oscillator wave functions.

Element	Value
$\langle 0 H 0\rangle$	$E_0$
$\langle 0 H k\rangle$	0
$\langle 0 H k^\alpha, -k^\beta\rangle$	$-\frac{1}{2}\omega_k^\alpha\delta^{\alpha\beta} + [\lambda^2/2(\omega_k^\alpha\omega_k^\beta)^{1/2}]\langle 0 \nabla_k\nabla_{-k}V 0\rangle$
	(sc) 0
$\langle 0 H k_1, k_2, k_3\rangle$	$\lambda^3(8\omega_{k_1}\omega_{k_2}\omega_{k_3})^{-1/2}\langle 0 \nabla_{k_1}\nabla_{k_2}\nabla_{k_3} 0\rangle\Delta(k_1+k_2+k_3)$
$\langle k H k\rangle$	$(E_0 + \frac{1}{2}\omega_k)\delta^{\alpha\beta} + \frac{\lambda^2}{2(\omega_k^\alpha\omega_k^\beta)^{1/2}}\langle 0 \nabla_k\nabla_{-k}V 0\rangle$
	(sc) $(E_0 + \omega_k)\delta^{\alpha\beta}$
$\langle k_1 H k_2, k_3\rangle$	$\lambda^3(8\omega_{k_1}\omega_{k_2}\omega_{k_3})^{-1/2}\langle 0 \nabla_{-k_1}\nabla_{k_2}\nabla_{k_3}V 0\rangle\Delta(-k_1+k_2+k_3)$
$\langle k_1 H k_1, k_2, k_3\rangle$	$[-\frac{1}{2}\omega_{k_2} + \lambda^2(4\omega_{k_2}\omega_{k_3})^{-1/2}\langle 0 \nabla_{k_2}\nabla_{-k_2}V 0\rangle]\delta_{k_2, -k_3}$
	(sc) 0
$\langle k_1 k_2 H k_1 k_2\rangle$	$E_0 + \frac{1}{2}\omega_{k_1} + \frac{1}{2}\omega_{k_2} + \frac{1}{2}\frac{\lambda^2}{\omega_{k_1}}\langle 0 \nabla_{k_1}\nabla_{-k_1}V 0\rangle + \frac{1}{2}\frac{\lambda^2}{\omega_{k_2}}\langle 0 \nabla_{k_2}\nabla_{-k_2}V 0\rangle$
	(sc) $E_0 + \omega_{k_1} + \omega_{k_2}$
$\langle k_1, k_2' H k_1, k_2, k_3\rangle$	$\lambda^3(8\omega_{k_1}\omega_{k_2}\omega_{k_3})^{-1/2}\langle 0 \nabla_{-k_1}\nabla_{k_2}\nabla_{k_3}V 0\rangle\Delta(k_2+k_3-k_2)$
$\langle k_1, k_2, k_3 H k_1, k_2, k_3\rangle$	$E_0 + \frac{1}{2}\omega_{k_1} + \frac{1}{2}\omega_{k_2} + \frac{1}{2}\omega_{k_3} + \frac{1}{2}\lambda^2\left\{\frac{1}{\omega_{k_1}}\langle 0 \nabla_{-k_1}\nabla_{k_1}V 0\rangle + \frac{1}{\omega_{k_2}}\langle 0 \nabla_{-k_2}\nabla_{k_2}V 0\rangle + \frac{1}{\omega_{k_3}}\langle 0 \nabla_{-k_3}\nabla_{k_3}V 0\rangle\right\}$
	(sc) $E_0 + \omega_{k_1} + \omega_{k_2} + \omega_{k_3}$

are different from those given when one or more  $\mathbf{k}$  values are identical in either of the two states. These factors are such that one can divide by the factorial of the number of phonons and sum over all  $\mathbf{k}$  values in an intermediate state sum using the values given in the table without worrying about counting states twice. The label (sc) indicates that the self-consistent condition is fulfilled for that value.

The table shows that the same simplifying features are present in the three-dimensional self-consistent case as in the one-dimensional case. The structure of the matrix elements in the Hermite polynomial method is simpler than is found for a Taylor-series expansion. For example, in the cubic  $\langle 0|H|k_1, k_2, k_3\rangle$  term there is no contribution from a term obtained by contraction on two indices. This, of course, is a result of expanding the potential in the same set of wave functions that is used to compute matrix elements. In this approach, the cubic term only gives rise to processes involving three phonons.

### B. General Polynomial Method in Three Dimensions

In the three-dimensional version of the general polynomial method, one obviously expands the potential or the Hamiltonian in terms of a set of polynomials which obey the orthogonality condition

$$\langle f|B_n^\dagger(k_1, \dots, k_n)B_m(k_1', \dots, k_m')|f\rangle \propto \delta_{mn}\delta(k_1, \dots, k_n; k_1', \dots, k_n'), \quad (53)$$

where

$$|f\rangle = f(x_1, \dots, x_N)|0\rangle / \langle 0|f^2|0\rangle^{1/2}, \quad (54)$$

and  $\delta(k_1, \dots, k_n; k_1', \dots, k_n')$  is used to denote a quantity which is unity if the indices to the left of the semi-colon are identical with some permutation of the indices to the right and is zero otherwise.

The numerical methods necessary to work with this approach will be discussed in a subsequent paper. Here it will only be pointed out that calculations will become very difficult if one wishes to include terms of higher order than  $\langle 0|\nabla\nabla f^2|0\rangle$  and  $\langle 0|\nabla\nabla V|0\rangle$ . Hence, one should hope that a judicious choice of  $f$  will make  $|f\rangle$  close enough to the true ground-state wave function so that results obtained from the few formulas to be given in this section will give good values for  $E_0$  and for the excitation spectrum of the crystal.

We have found that it is convenient to break up the construction of an  $n$ th-order polynomial into two steps. First, a set of  $n$ th-order polynomials

$$P_n(i_1, \dots, i_n) = u_{i_1} \dots u_{i_n} - \sum_{j=1}^n \binom{n}{j} P_j(i_1, \dots, i_{n-j}) B_{n-j}(k_1, \dots, k_{n-j}), \quad (55)$$

which satisfy

$$\langle f|P_n(i_1, \dots, i_n)B_m(k_1, \dots, k_m)|f\rangle = 0 \quad m < n \quad (56)$$

are constructed. Fulfillment of this equation requires

$$\beta_{m, m-n} = \frac{\langle f|u_{i_1} \dots u_{i_n} B_{m-n}(k_1, \dots, k_{m-n})|f\rangle}{\langle f|B_{m-n}^2|f\rangle}. \quad (57)$$

Then, the

$$B_n(k_1, \dots, k_n) = \sum_{(i_1, \dots, i_n)} S_n(k_1, \dots, k_n; i_1, \dots, i_n) \times P_n(i_1, \dots, i_n) \quad (58)$$

are made. The orthogonality condition is satisfied if

$$S_n(k_1, \dots, k_n; i_1, \dots, i_n) \langle f | P_n(i_1, \dots, i_n) P_n(j_1, \dots, j_n) | f \rangle \times S_n^\dagger(j_1, \dots, j_n; k_1', \dots, k_n') = \mu_n(k_1, \dots, k_n) \delta(k_1, \dots, k_n; k_1', \dots, k_n'). \quad (59)$$

It is convenient to uniquely specify the  $S$  matrices by requiring

$$S_n(k_1, \dots, k_n; i_1, \dots, i_n) S_n^\dagger(i_1, \dots, i_n; k_1, \dots, k_n) = \delta(k_1, \dots, k_n; k_1, \dots, k_n). \quad (60)$$

The ground-state energy is given by

$$E_0 = \frac{1}{4} T_r G + \langle f | V_{\text{eff}}' | f \rangle, \quad (61)$$

where

$$V_{\text{eff}}' = V - \frac{1}{4} \lambda^2 \nabla^2 \ln f^2. \quad (62)$$

As in Sec. III C we will also use  $V_{\text{eff}}' = f^2 V_{\text{eff}}'$ . The optimum  $G$  is given here implicitly by

$$\frac{1}{4} \lambda^2 \delta_{ij} = \langle f | u_i u_j V_{\text{eff}}' | f \rangle - \langle f | V_{\text{eff}}' | f \rangle \langle f | u_i u_j | f \rangle \quad (63)$$

and more explicitly by

$$(G^\epsilon)_{ij}^2 = \lambda^2 \frac{\langle 0 | \nabla_i \nabla_j V_{\text{eff}}' | 0 \rangle - \langle 0 | \nabla_i \nabla_j f^2 | 0 \rangle \langle f | V_{\text{eff}}' | f \rangle}{\langle 0 | f^2 | 0 \rangle}. \quad (64)$$

Optimization of the lattice parameter leads to the condition

$$\langle 0 | \nabla_i V_{\text{eff}}' | 0 \rangle - \langle f | \nabla_i V_{\text{eff}}' | f \rangle \langle 0 | \nabla_i f^2 | 0 \rangle = 0. \quad (65)$$

A few of the lowest-order polynomials and related equations are given below:

$$B_0 = 1, \quad (66a)$$

$$B_1(k) = S_1(k, i) u_i, \quad (66b)$$

and

$$P_2(i, j) = u_i u_j - \sum \beta_{21}(i, j; k) B_1(k) - \langle f | u_i u_j | f \rangle, \quad (66c)$$

where

$$S_1(k, i) S_1(k', j) \langle f | u_i u_j | f \rangle = \gamma_1(k) \delta_{kk'}. \quad (66d)$$

Since the matrix elements in the three-dimensional orthogonal polynomial method are quite similar to those given in Table II, only the elements for the case in which Eqs. (63) and (65) hold are given in Table IV.

If the excitation energy  $\langle k | H | k \rangle - E_0$  of a one-phonon state is called  $\nu_k$ , one can write in analogy with Eq. (42)

$$\nu_k = \left\{ \left[ S_1 \left( G^{-1} + \frac{1}{2} \lambda^2 G^{-1} \frac{\langle 0 | \nabla \nabla f^2 | 0 \rangle}{\langle 0 | f^2 | 0 \rangle} G^{-1} \right) S_1^\dagger \right]_{kk} \right\}^{-1}. \quad (67)$$

It is interesting that the phonon energies are not given

TABLE IV. Matrix elements of a three-dimensional crystal Hamiltonian in the orthogonal polynomial method with the assumption that the self-consistent equation is satisfied and that the lattice parameter has been optimized.

Element	Value
$\langle f   H   f \rangle$	$E_0$
$\langle f   H   k \rangle$	0
$\langle f   H   k^\alpha, -k^\beta \rangle$	0
$\langle k^\alpha   H   k'^\beta \rangle$	$(E_0 + \lambda^2 / 2\mu_1(k)) \delta_{kk'} \delta^{\alpha\beta}$

by the roots of the  $G$  matrix as they would be if one made the most obvious combination of the work of Nosanow and Werthamer<sup>5</sup> with the self-consistent harmonic approximation; that is, if one simply substituted  $V_{\text{eff}}$  for  $V$  in Sec. IV A. However, it is readily shown that

$$\lim_{k \rightarrow 0} [S_1 G^{-1} S_1^\dagger]_{kk} = O\left(\frac{1}{k}\right)$$

and

$$\lim_{k \rightarrow 0} [S_1 G^{-1} \langle 0 | \nabla \nabla f^2 | 0 \rangle G^{-1} S_1^\dagger]_{kk} = O(1),$$

so that

$$\lim_{k \rightarrow 0} \nu_k = \omega_k.$$

One can show that Eqs. (63) and (65) are sufficient to provide  $\langle f | H P_2(i, j) | 0 \rangle = 0$  so that  $\langle f | H | k, -k \rangle = 0$  and, one does not have to construct the state  $|k, -k\rangle$  explicitly and thus can avoid a complicated matrix diagonalization. This is one of the reasons for constructing the polynomials in two steps.

Another reason is that the  $P_i$  form a complete nonorthogonal set of wave functions, and their use in perturbation theory<sup>6</sup> may provide a simpler alternative to conventional<sup>7</sup> techniques for the computation of the  $|V_3|^2$  correction to  $E_0$ . This is because the  $P_i$  enable one to avoid a double sum over  $\mathbf{k}$  vectors and to work in coordinate space where the matrix elements of higher derivatives will quite rapidly become small for all but nearest neighbors. Thus, the  $P_i$  polynomials may prove to be useful in the Hermite polynomial method.

A few of the  $P_i$  for the  $f=1$  are listed below:

$$P_0 = 1, \quad (67')$$

$$P_1(i) = u_i, \quad (67'')$$

$$P_2(i_1, i_2) = u_{i_1} u_{i_2} - \frac{1}{2} \Gamma^{-1}_{i_1 i_2}, \quad (67''')$$

$$P_3(i_1, i_2, i_3) = u_{i_1} u_{i_2} u_{i_3} - \frac{1}{2} (\Gamma^{-1}_{i_1 i_2} u_{i_3} + \Gamma^{-1}_{i_2 i_3} u_{i_1} + \Gamma^{-1}_{i_3 i_1} u_{i_2}). \quad (67''''')$$

<sup>5</sup> L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965).

<sup>6</sup> An approach could be used based on the ideas discussed by P. O. Löwdin, J. Math. Phys. **3**, 969 (1962).

<sup>7</sup> Computer implementation of a conventional calculation involving a conversion to normal modes and an intermediate state sum has been described by A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N. Y.) **15**, 337 (1961).



## V. DISCUSSION

An approach to vibrational problems in quantum systems has been presented which can be used as an alternative to a host of other methods in simple problems, but which should provide a good computational method for dealing with anharmonicity in more complicated systems. Although the emphasis here has been on lattice problems, there should be possible applications in molecular vibrational analysis.

A notable feature of the method is the appearance of derivatives of the potential averaged over the ground-state wave function of a harmonic system. A formulation involving terms of this type has also been obtained by Horner<sup>8</sup> who used a Green's-function formalism and summed an infinite class of diagrams of the conventional Taylor-series expansion. The self-consistent expression (49) is not new; it first appeared in literature in the work of Hooten<sup>9</sup> and Born<sup>10</sup> some time ago and has subsequently been rederived in other papers.<sup>11</sup>

However, to the author's knowledge, the connection between the above mentioned results and an implicit or explicit Hermite polynomial expansion of the potential was first made in Ref. 2. The diagram summation in Horner's work is thus an alternative way of obtaining the unitary transformation which regroups terms in a Taylor-series expansion to form a Hermite polynomial expansion.

Recognition of this expansion serves two useful purposes. First of all, it is satisfying for one to know which results of a complicated derivation can be obtained by more elementary means. Second, this approach leads naturally into the general polynomial method which provides a well-defined prescription for combining some of the features of the self-consistent harmonic approximation with the approach to the calculation of the ground-state energy of very anharmonic crystals used by Nosanow. In addition, a well-defined procedure is provided for extending the latter calculation to the computation of phonon spectra and possibly to a perturbation theory correction to the lower-order results. The use of a Jastrow function as a

<sup>8</sup> H. Horner, *Z. Physik* **205**, 72 (1967).

<sup>9</sup> D. J. Hooten, *Phil. Mag.* **46**, 422, 433 (1955); *Z. Physik* **142**, 42 (1955).

<sup>10</sup> M. Born, in *Festschrift zur Feier des Zweihundertjährigen Bestehens der Akademie der Wissenschaften in Göttingen. I. Mathematisch-Physikalische Klasse* (Springer-Verlag, Berlin, 1951), p. 1.

<sup>11</sup> See the references given in Ref. 12, this paper.

weight factor in defining a set of polynomials is at least a rigorous way of treating such a function in higher order even though the function may have been originally introduced only in order to cut off the potential at short range in a ground-state energy calculation.

Extension of the self-consistent harmonic approximation to finite temperature is reported in an accompanying paper.<sup>12</sup> This extension cannot be performed as elegantly in the Hermite polynomial framework as in a Green's-function approach. However, one can derive a finite temperature perturbation formalism by a method similar to that used in Ref. 7. We believe that an avenue for future development is the rigorous formulation of the finite temperature version of and an elegant formulation of the zero-degree version of the general polynomial method.

The structure of terms entering into perturbation theory has been shown to be simpler in the self-consistent harmonic approximation than in conventional lattice dynamics. However, as was pointed out in this paper, the elimination of terms involving contraction of the indices from multiphonon matrix elements is not due to the self-consistent harmonic approximation, but rather follows if one works in the same set of wave function in which one made the expansion of the potential. Using an arbitrary Hermite polynomial expansion one could follow the general procedure of the conventional harmonic approximation by expanding the potential, retaining terms to second order and diagonalizing the resulting harmonic Hamiltonian. If one were to use the harmonic wave functions so obtained as a basis for perturbation calculations, the structure of the theory would be the same as that exhibited in the conventional harmonic approximation except in the particular case when the self-consistent equation is satisfied. This procedure gives rise to a variety of harmonic approximations which include the Taylor-series expansion on one hand and the self-consistent harmonic approximation on the other.

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<sup>12</sup> N. S. Gillis, N. R. Werthamer, and T. R. Koehler, following paper, *Phys. Rev.* **165**, 951 (1968).