PHYSICAL REVIEW VOLUME 144, NUMBER 2 15 APRIL 1966

Exact Matrix Elements of a Crystal Hamiltonian between Harmonic-Oscillator Wave Functions

T. R. Koehler
IBM San Jose Research Laboratory, San Jose, California

(Received 18 October 1965)

A method is given for the exact calculation, including all anharmonic effects, of the matrix elements of the true Hamiltonian H of a crystalline solid between the eigenfunctions of any arbitrary harmonic Hamiltonian appropriate to the crystal structure. By the introduction of a variational scaling parameter a, a set of harmonic eigenfunctions can be generated from the eigenfunctions of a single such harmonic Hamiltonian. The ground-state energy W_0 of the crystal and the optimum value a_0 of a are then determined by a variational calculation which minimizes the expectation value of H between the ground-state harmonic eigenfunctions. The other diagonal matrix elements of H, calculated using the states determined by a_0, then give first-order values for the energy of one-phonon and multiphonon states. In addition, the off-diagonal matrix elements can be obtained and used in a perturbation calculation to improve the energies. It is shown that the value of W_0 will always be lower than energy obtained from a closely related variational calculation using a wave function constructed out of a product of Gaussian orbitals centered on the lattice sites. The decrease in energy is about 12% of the original kinetic energy, and is divided approximately equally between the kinetic- and potential-energy contributions. Numerical results are given for W_0 and for a few phonon energies of a model bcc crystal in which each atom interacts with its first two shells of nearest neighbors through a realistic atomic potential. Possible applications of this theory to rare-gas solids are discussed.

I. INTRODUCTION

THE details of investigations concerning the use of the ground-state eigenfunction of a linear coupled harmonic-oscillator Hamiltonian—a specialized type of correlated-Gaussian wave function[1]—as a trial wave function in a one-dimensional, many-body calculation have been presented in two previous papers.[2,3] In these papers, for computational convenience, emphasis was given to the eigenfunction of the nearest-neighbor, coupled-oscillator Hamiltonian although the formalism was applicable to a wider variety of one-dimensional trial wave functions.

The formalism will be extended to the construction of a three-dimensional, correlated-Gaussian wave function in this paper. It will be shown that the resulting trial wave function can be readily integrated over all coordinates but two, so that the expectation value of a Hamiltonian for a system of interacting atoms can be calculated without resorting to the harmonic approximation.

The wave function is particularly adaptable to the treatment of simple crystalline solids. A closely related trial wave function for such systems is a Heitler-London–type wave function in the form of a product of Gaussian orbitals centered on crystal lattice sites. This type of wave function will be called a noncorrelated-Gaussian in this paper. Such trial wave functions have been used by Mullin[4] for the calculation of the ground-state energy of solid Ne and by Nosanow[5] (who multiplied the Gaussian by a Jastrow function) for the calculation of the ground-state energy of solid He^3.

In Sec. IV of this paper it will be shown that a correlated-Gaussian wave function, constructed according to the recipe to be given in Sec. II, will always give a lower energy than the noncorrelated Gaussian. This reduction in energy can be written so as to exhibit a definite percentage decrease in kinetic energy and an indefinite, but probably smaller, decrease in potential energy so that the over-all improvement in energy is most noticeable in systems of light atoms.

The details of the construction of the correlated-Gaussian wave function and of a complete set of states based upon it (phonon states) will be given in Sec. II. In Sec. III general analytic techniques will be developed for the calculation of matrix elements of the Hamiltonian of a system of interacting atoms and specific formulas will be given for the matrix element between certain low-lying states. A variational calculation of the ground-state energy of a bcc crystal of atoms which interact with nearest and second-nearest neighbors through a Mie-Lennard-Jones 12-6 potential will be computed in Sec. IV. This result will be compared with that obtained using a noncorrelated-Gaussian wave function. These energies will be computed for a variety of particle masses. In addition, phonon energies will be computed to first order for a few **k** values.

II. CRYSTALS IN THE HARMONIC APPROXIMATION

Consider the Hamiltonian appropriate, in the harmonic approximation, to a system of particles in a

---

[1] The term correlated-Gaussian will be used exclusively to denote this restricted class of correlated-Gaussians in this paper. The restriction is explained more fully in the text in the mathematical developments of Sec. II.

[2] T. R. Koehler, Phys. Rev. **139**, A1097 (1965). This paper will be referred to as I, and any of its equations will be denoted by the prefix I.

[3] T. R. Koehler, Phys. Rev. **141**, 281 (1966). This paper will be referred to as II, and any of its equations will be denoted by the prefix II.

[4] W. J. Mullin, Phys. Rev. **134**, A1249 (1964).

[5] L. H. Nosanow, Phys. Rev. Letters **13**, 270 (1964).

crystal lattice:

$$H_1=-\tfrac{1}{2}\sum(\lambda^\iota\nabla_{\rm i}{}^{\iota,\alpha})^2+\tfrac{1}{2}\sum(r_{\rm i}{}^{\iota,\alpha}-R_{\rm i}{}^{\iota,\alpha})\times V_{\rm ij}{}^{\iota\kappa,\alpha\beta}(r_{\rm j}{}^{\kappa,\beta}-R_{\rm j}{}^{\kappa,\beta})\,, \quad (1)$$

where subscripts are used to denote a particular unit cell, the first set of superscripts to denote a particular atom in a unit cell, and the second set of superscripts to denote Cartesian coordinates. It will be assumed that there are N unit cells and ν atoms per unit cell.

In order to avoid the proliferation of superscripts and subscripts, a notation as follows will be used throughout the paper: $\mathbf{r}_{\rm i}{}^\iota$ will be used to denote the three-dimensional vector whose components are $(r_{\rm i}{}^{\iota,x},r_{\rm i}{}^{\iota,y},r_{\rm i}{}^{\iota,z})$; similarly, $\mathbf{V}_{\rm ij}{}^{\iota\kappa}$ will represent a 3×3 matrix. The symbol $r_{\rm i}$ will denote a 3ν-dimensional supervector whose components are the ν vectors $\mathbf{r}_{\rm i}{}^\iota$, and $V_{\rm ij}$ will signify a $3\nu\times3\nu$ supermatrix. Then r will be a supervector whose components are the N supervectors r_i, and V will represent a $3\nu N\times3\nu N$ matrix. Similarly, $\boldsymbol{\nabla}_{\rm i}{}^\iota$, $\nabla_{\rm i}$, and ∇ will be used to denote differentiation with respect to the indicated components of r.

In Eq. (1), $\mathbf{R}_{\rm i}{}^\iota$ is the equilibrium position of the atom whose coordinate is $\mathbf{r}_{\rm i}{}^\iota$ and whose mass is expressed nondimensionally by $(\lambda^\iota)^2$. The subscript on λ is suppressed because $\lambda_i{}^\iota=\lambda_j{}^\iota$. We shall also use $\mathbf{R}_{\rm i}$ in lattice sums to denote the points in the space lattice formed by the unit cells. This usage will always be clear from the context.

The problem of finding the eigenfunctions and eigenvalues of H_1 is an old one, and many excellent references exist in the literature.[6-9] Here, a derivation of the lowest eigenfunction of H_1 will be presented which differs somewhat from the usual derivation, but which leads more naturally into the new work which will be given later in this paper.

Because of the symmetry requirements on H_1, there are certain relationships among the $V_{\rm ij}{}^{\iota\kappa,\alpha\beta}$ as follows:

$$V_{\rm ij}=V(R_{\rm i}-R_{\rm j}) \quad (2)$$

because of the periodicity of the lattice,

$$V_{\rm ij}{}^{\iota\kappa;\alpha\beta}=V_{\rm ji}{}^{\kappa\iota;\beta\alpha} \quad (3)$$

because V is a real, Hermitian matrix,

$$\textstyle\sum_{\rm i}\mathbf{V}_{\rm ij}{}^{\iota\kappa}=0 \quad (4)$$

because V is translationally invariant, and

$$\mathbf{V}_{\rm ij}{}^{\iota\kappa}=\mathbf{V}_{\rm ji}{}^{\kappa\iota} \quad (5)$$

if the potential arises from a sum of two-body, central-force atomic interactions.

If one now substitutes $\mathbf{q}_{\rm i}{}^\iota=(\mathbf{r}_{\rm i}{}^\iota-\mathbf{R}_{\rm i}{}^\iota)/\lambda^\iota$, $\mathbf{p}_{\rm i}{}^\iota=-i\lambda^\iota\boldsymbol{\nabla}_{\rm i}{}^\iota$, and $\boldsymbol{\Phi}_{\rm ij}{}^{\iota\kappa}=\lambda^\iota\mathbf{V}_{\rm ij}{}^{\iota\kappa}\lambda^\kappa$ into Eq. (1),

$$H_1=\tfrac{1}{2}\tilde{p}p+\tfrac{1}{2}\tilde{q}\Phi q \quad (6)$$

results, where the commutation relation $(q_{\rm i}{}^{\iota,\alpha},p_{\rm j}{}^{\kappa,\beta})=i\delta_{\rm ij}{}^{\iota\kappa,\alpha\beta}$ holds. The components of Φ satisfy the relationships given by Eqs. (2)–(5) for V.

Guided by hindsight, we will try, for the ground-state eigenfunction of H_1,

$$\Psi_0=A\,\exp\{-\tfrac{1}{2}\tilde{q}Gq\}\,, \quad (7)$$

where A is a normalization constant and G a symmetric matrix. It is readily verified that

$$\tilde{p}p\Psi_0=\mathrm{Tr}(G)\Psi_0-\tilde{q}G^2q\Psi_0\,. \quad (8)$$

Thus, if one chooses

$$G^2=\Phi\,, \quad (9)$$

$$H_1\Psi_0=E_0\Psi_0 \quad (10)$$

results, with $E_0=\frac{1}{2}\,\mathrm{Tr}(G)$.

Because Eq. (2) obtains,[10] Φ can be brought into semidiagonal form by the unitary transformation

$$[T^{-1}\Phi T]_{\rm kk'}=U_{\rm k}{}^{-1}D_{\rm k}U_{\rm k'}\delta_{\rm kk'}\,, \quad (11)$$

where

$$T_{\rm ik}=\frac{1}{\sqrt{N}}e^{i\mathbf{k}\cdot\mathbf{R}_{\rm i}}U_{\rm k}\,, \quad (12)$$

and

$$D_{\rm k}=\textstyle\sum_{\rm j}\Phi(R_{\rm j})e^{-i\mathbf{k}\cdot\mathbf{R}_{\rm j}}\,, \quad (13)$$

and is called the dynamical matrix.

In the above it is assumed that the crystal is a parallelopiped with its edges parallel to the principal translation vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$, and that there are L unit cells along each direction. It is also assumed that Born–von Karman boundary conditions apply so that the $\mathbf{k}$ vectors are the N distinct wave vectors in the first Brillouin zone of the reciprocal lattice; therefore, $\sum_{\rm k}e^{i\mathbf{k}\cdot(\mathbf{R}_{\rm i}-\mathbf{R}_{\rm j})}=N\delta_{\rm ij}$ and $\sum_{\rm i}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{\rm i}}=N\delta_{\rm kk'}$. In addition, $\Phi(R_{\rm j})\equiv\Phi_{0\rm j}$ has been used which, from Eq. (2), is also equal to $\Phi_{\rm i,i+j}$. The matrix $U_{\rm k}$ is an as yet unspecified unitary matrix.

If one substitutes Eq. (4) into Eq. (13), a slightly different expression for the dynamical matrix is obtained:

$$D_{\rm k}=\textstyle\sum_{\rm j}{}'\,\Phi(R_{\rm j})(e^{-i\mathbf{k}\cdot\mathbf{R}_{\rm j}}-1)\,, \quad (14)$$

where the prime on a summation sign signifies that the $\mathbf{j}=0$ term is omitted from the sum.

If each lattice site is a center of inversion symmetry, $D_{\rm k}$ will be a real symmetric matrix; $D_{\rm k}$ will always be Hermitian. Thus $U_{\rm k}$ may be chosen so as to diagonalize $D_{\rm k}$ and

$$U_{\rm k}{}^{-1}D_{\rm k}U_{\rm k}=\omega_{\rm k}{}^2\,, \quad (15)$$

---

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

[7] G. Leibfried, *Encyclopedia of Physics* (Springer Verlag, Berlin, 1955), Vol. VII, Part 1, p. 104.

[8] J. de Launay, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. II, p. 219.

[9] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

[10] F. Bloch, Z. Physik **52**, 555 (1929).

where ω_{k} is a diagonal matrix. Then

$$G=T\omega T^{-1}, \tag{16}$$

or

$$G_{\mathbf{ij}}{}^{\iota\kappa,\alpha\beta}=\frac{1}{N}\sum_{\mathbf{k},\lambda,\delta} U_{\mathbf{k}}{}^{\iota\lambda,\alpha\delta}\omega_{\mathbf{k}}{}^{\lambda,\delta}U^{\dagger}{}_{\mathbf{k}}{}^{\lambda\kappa,\delta\beta}e^{i\mathbf{k}\cdot(\mathbf{R_i}-\mathbf{R_j})}. \tag{16a}$$

The first superscript on the ω_{k} can be thought of as labeling the branch of the phonon spectrum to which the mode belongs. It is clear that

$$E_0=\tfrac{1}{2}\sum_{\mathbf{k},\iota,\alpha}\omega_{\mathbf{k}}{}^{\iota,\alpha}. \tag{17}$$

It should be noted that the normal modes are given by

$$Q_{\mathbf{k}}{}^{\iota,\alpha}=(T^{-1}q)_{\mathbf{k}}{}^{\iota,\alpha}, \tag{18}$$

that

$$\begin{aligned}\Psi_0&=\exp(-\tfrac{1}{2}Q^{\dagger}\omega Q)\\ &\equiv|0\rangle,\end{aligned} \tag{19}$$

and that the normalized state in which $n_{\mathrm{k}}{}^{\iota,\alpha}$ phonons of frequency $\omega_{\mathrm{k}}{}^{\iota,\alpha}$, $\cdots$, and $n_{\mathrm{k}'}{}^{\kappa,\beta}$ phonons of frequency $\omega_{\mathrm{k}'}{}^{\kappa,\beta}$ are excited is given by

$$\begin{aligned}&|n_{\mathrm{k}}{}^{\iota,\alpha},\cdots,n_{\mathrm{k}'}{}^{\kappa,\beta}\rangle\\ &\quad=[(n_{\mathrm{k}}{}^{\iota,\alpha}!)^{-1/2}a^{\dagger}{}_{\mathrm{k}}{}^{\iota,\alpha}]\times\cdots\\ &\qquad\qquad\times[(n_{\mathrm{k}'}{}^{\kappa,\beta}!)^{-1/2}a^{\dagger}{}_{\mathrm{k}'}{}^{\kappa,\beta}]|0\rangle,\end{aligned} \tag{20}$$

where

$$a^{\dagger}{}_{\mathrm{k}}{}^{\iota,\alpha}=(2\omega_{\mathrm{k}}{}^{\iota,\alpha})^{-1/2}\left(\omega_{\mathrm{k}}{}^{\iota,\alpha}Q^{\dagger}{}_{\mathrm{k}}{}^{\iota,\alpha}-\frac{\partial}{\partial Q_{\mathrm{k}}{}^{\iota,\alpha}}\right).$$

The energy of the state given in Eq. (20) is

$$\begin{aligned}&E(n_{\mathrm{k}}{}^{\iota,\alpha},\cdots,n_{\mathrm{k}'}{}^{\kappa,\beta})\\ &\qquad=E_0+n_{\mathrm{k}}{}^{\iota,\alpha}\omega_{\mathrm{k}}{}^{\iota,\alpha}+\cdots+n_{\mathrm{k}'}{}^{\kappa,\beta}\omega_{\mathrm{k}'}{}^{\kappa,\beta}.\end{aligned} \tag{21}$$

In addition, $\omega_{\mathrm{k}}=\omega_{-\mathrm{k}}$ and $D_{\mathrm{k}}=D_{-\mathrm{k}}{}^{\dagger}$ will obtain. It should be noted that states given by Eq. (20) are not Hermite polynomials in the $Q^{\dagger}{}_{\mathrm{k}}{}^{\iota,\alpha}$ because $(a^{\dagger}{}_{\mathrm{k}}{}^{\iota,\alpha})^n|0\rangle=(\omega_{\mathrm{k}}{}^{\iota,\alpha}Q^{\dagger}{}_{\mathrm{k}}{}^{\iota,\alpha})^n|0\rangle$ here.

III. MATRIX ELEMENTS

A. Preliminary Discussion

We wish to use the wave function

$$\Psi_0'=A\exp\{-\tfrac{1}{2}a^2\tilde{q}Gq\} \tag{22}$$

as a trial wave function in a variational calculation of the ground-state energy of a crystal whose Hamiltonian in the adiabatic approximation is

$$H=\tfrac{1}{2}\tilde{p}p+\tfrac{1}{2}\sum_{\mathbf{i},\iota\neq\mathbf{j},\kappa}V(\mathbf{q_i}{}^{\iota}-\mathbf{q_j}{}^{\kappa}), \tag{23}$$

where V is an atomic potential and the reduced variables have the same meaning as in Eq. (6).

It is apparent that Ψ_0' is the lowest eigenfunction of the Hamiltonian

$$H_1'=\tfrac{1}{2}a^2\tilde{p}p+\tfrac{1}{2}a^4\tilde{q}\Phi q \tag{24}$$

and that the results of Sec. II can be applied to find the eigenfunctions and eigenvalues of H_1' by simply multiplying all of the $\omega_{\mathrm{k}}{}^{\iota,\alpha}$ by a^2. The lowest eigenvalue of H_1' is $E_0'=a^2E_0$.

Thus, in the calculation of, for example, the ground-state energy of the crystal described by H, one would, first, choose a particular Φ, and, therefore, a particular G; second, perform a variational calculation using Ψ_0' as a trial wave function and a as the variational parameter; and, third, perform a perturbation-theory calculation to improve upon the first-order energy if desired.

As a preliminary to the calculation of the integrals necessary to compute $\langle n|H|m\rangle$ where m and n are used to denote two states, let us consider the kinetic $\langle n|K|m\rangle$ and the potential $\langle n|V|m\rangle$ energy contributions separately. As is well known, $\tilde{p}p$ has nonzero matrix elements between states in which the phonon occupation numbers are all equal, in which case the matrix element is

$$\langle n|K|n\rangle=\tfrac{1}{2}E_0'+\tfrac{1}{2}a^2\sum(n_{\mathrm{k}}{}^{\iota,\alpha})_n\omega_{\mathrm{k}}{}^{\iota,\alpha} \tag{25}$$

and between states in which all the phonon occupation numbers but two are equal, and these two satisfy either $(n_{\mathrm{k}}{}^{\iota,\alpha})_n=(n_{\mathrm{k}}{}^{\iota,\alpha})_m+1$, $(n_{-\mathrm{k}}{}^{\iota,\alpha})_n=(n_{-\mathrm{k}}{}^{\iota,\alpha})_m+1$, or $(n_{\mathrm{k}}{}^{\iota,\alpha})_n=(n_{\mathrm{k}}{}^{\iota,\alpha})_m-1$, $(n_{-\mathrm{k}}{}^{\iota,\alpha})_n=(n_{-\mathrm{k}}{}^{\iota,\alpha})_m-1$ in which cases the matrix elements are

$$\langle n|K|m\rangle=-\tfrac{1}{2}a^2\omega_{\mathrm{k}}{}^{\iota,\alpha}[(n_{\mathrm{k}}{}^{\iota,\alpha})_n(n_{-\mathrm{k}}{}^{\iota,\alpha})_n]^{1/2} \tag{26}$$

or

$$\langle n|K|m\rangle=-\tfrac{1}{2}a^2\omega_{\mathrm{k}}{}^{\iota,\alpha}[(n_{\mathrm{k}}{}^{\iota,\alpha})_m(n_{-\mathrm{k}}{}^{\iota,\alpha})_m]^{1/2}, \tag{27}$$

respectively.

B. Computation of $\langle 0|V|0\rangle$

In the calculation of $\langle 0|V|0\rangle$, one can take advantage of the translational symmetry of H and of Ψ_0' to write

$$\begin{aligned}&\langle 0|\tfrac{1}{2}\sum_{\mathbf{i},\iota\neq\mathbf{j},\kappa}V(\mathbf{q_i}{}^{\iota}-\mathbf{q_j}{}^{\kappa})|0\rangle\\ &\qquad=\frac{N}{2}\sum_{\mathbf{j},\iota,\kappa}\int V(\mathbf{q_0}{}^{\iota}-\mathbf{q_j}{}^{\kappa})\Psi_0'^2\,dq \qquad (28)\\ &\qquad=\frac{N}{2}\sum_{\mathbf{j},\iota,\kappa}\int V(\mathbf{r_j}{}^{\iota,\kappa})\psi(\mathbf{r_j}{}^{\iota,\kappa}-\mathbf{R_j}{}^{\iota,\kappa})d\mathbf{r_j}{}^{\iota,\kappa}, \qquad (29)\end{aligned}$$

where the function

$$\psi(\mathbf{q_j}{}^{\iota,\kappa})\equiv\int\Psi_0'^2d(\mathbf{q_j}{}^{\iota,\kappa})^{+}\prod_{\mathbf{i},\lambda\neq 0,\iota;\mathbf{j},\kappa}d\mathbf{q_i}{}^{\lambda} \tag{30}$$

has been used, and where $\mathbf{q_j}{}^{\iota,\kappa}=\mathbf{q_j}{}^{\kappa}-\mathbf{q_0}{}^{\iota}$, $(\mathbf{q_j}{}^{\iota,\kappa})^{+}=\mathbf{q_j}{}^{\kappa}+\mathbf{q_0}{}^{\iota}$, $\mathbf{r_j}{}^{\iota,\kappa}=\mathbf{r_j}{}^{\kappa}-\mathbf{r_0}{}^{\iota}$, and $\mathbf{R_j}{}^{\iota,\kappa}=\mathbf{R_j}{}^{\kappa}-\mathbf{R_0}{}^{\iota}$.

Integrals involving correlated-Gaussian wave functions have been discussed in the literature[11,12]; however, the simpler expression given in (II-9) will be used here for the evaluation of Eq. (30), and a different approach will be taken in the next subsection when we discuss integrals involving the product of a general polynomial and a correlated-Gaussian.

Equation (II-9) rewritten in notation suitable to this paper is[13]

$$\int \exp(-a^2\tilde{q}Mq)\,dq_y=\left(\frac{\pi}{a^2}\right)^{3N_y/2}|M|^{-1/2}|M^{-1}{}_{xx}|^{-1/2}$$
$$\times\exp[-a^2\tilde{q}_x(M^{-1}{}_{xx})^{-1}q_x].\quad(31)$$

Here, the vector q has been broken into subvectors q_x and q_y, and the matrix M into submatrices similarly. The same notation as in II for components of inverse matrices and inverses of component matrices has been used.[14] The determinant of a matrix is written $|M|$. The number of atoms whose coordinates are integrated over is N_y.

In order to simplify the notation used later, q_y will always refer to all coordinates except $\mathbf{q}_0{}^{\iota}$ and $\mathbf{q}_{\mathrm{j}}{}^{\kappa}$, unless otherwise stated. A subscript y on matrices or other vectors will refer to the same set of coordinates; the subscript x will occasionally be used to represent ${}_0{}^{\iota}$ and ${}_{\mathrm{j}}{}^{\kappa}$.

It is clear from Eq. (16) that

$$G^{-1}=T\omega^{-1}T^{-1}.\quad(32)$$

As in II, a problem is introduced because $\omega_0{}^{0,\alpha}=0$: G^{-1} does not really exist. This results from the translational invariance of H_{I}. In II, we circumvented this problem by setting $\mathbf{q}_0{}^0=0$, and taking the limit of all expressions as $\boldsymbol{\omega}_0{}^0\rightarrow 0$. Here it is more convenient when performing integrals involving states with one or more phonons excited for one to follow the alternate procedure suggested in II, in which one integrates first over q_y, next over $(\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa})^+$, and then takes the limit of the resulting expression as $\boldsymbol{\omega}_0{}^0\rightarrow 0$.

Thus if one combines Eqs. (22), (30), and (31)

$$\psi(\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa})=A'^2(\pi/a^2)^{3(N-2)/2}\lim_{\omega_0{}^0\rightarrow 0}|G|^{-1/2}|G^{-1}{}_{xx}|^{-1/2}$$
$$\times\int\exp[-a^2q_x(G^{-1}{}_{xx})^{-1}q_x]\,d(\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa})^+\quad(33)$$

results, where

$$G^{-1}{}_{xx}=\begin{pmatrix}\mathbf{G}^{-1}{}_{00}{}^{\iota\kappa} & \mathbf{G}^{-1}{}_{0\mathrm{j}}{}^{\iota\kappa}\\ \mathbf{G}^{-1}{}_{\mathrm{j}0}{}^{\kappa\iota} & \mathbf{G}^{-1}{}_{\mathrm{jj}}{}^{\kappa\kappa}\end{pmatrix},\quad(34)$$

$\mathbf{G}^{-1}{}_{00}{}^{\iota\iota}=\mathbf{G}^{-1}{}_{\mathrm{jj}}{}^{\kappa\kappa}$ and $\mathbf{G}^{-1}{}_{0\mathrm{j}}{}^{\iota\kappa}=\mathbf{G}^{-1}{}_{\mathrm{j}0}{}^{\kappa\iota}$. The latter equality holds because we intend to treat the case of a central-force, two-body interaction, and so can use Eq. (5). The elements of Eq. (34) can be put into a form more easily evaluated in the limit $\boldsymbol{\omega}_0{}^0\rightarrow 0$ with the aid of the matrix identities given in (II-7) and (II-41):

$$(G^{-1}{}_{xx})^{-1}{}_{00}{}^{\iota\iota}$$
$$=(\mathbf{G}^{-1}{}_{00}{}^{\iota\iota}-\mathbf{G}^{-1}{}_{0\mathrm{j}}{}^{\iota\kappa}\cdot(\mathbf{G}^{-1}{}_{\mathrm{jj}}{}^{\kappa\kappa})^{-1}\cdot\mathbf{G}^{-1}{}_{\mathrm{j}0}{}^{\kappa\iota})^{-1}\quad(35)$$

and

$$(G^{-1}{}_{xx})^{-1}{}_{0\mathrm{j}}{}^{\iota\kappa}=-(\mathbf{G}^{-1}{}_{xx})^{-1}{}_{00}{}^{\iota\iota}\cdot\mathbf{G}^{-1}{}_{0\mathrm{j}}{}^{\iota\kappa}\cdot(\mathbf{G}^{-1}{}_{\mathrm{jj}}{}^{\kappa\kappa})^{-1}.\quad(36)$$

Using Eqs. (35) and (36) and noting that

$$\mathbf{G}^{-1}{}_{\mathrm{ij}}{}^{\iota\kappa}=\mathbf{T}_{\mathrm{i}0}{}^{\iota0}\cdot\boldsymbol{\omega}^{-1}{}_0{}^0\cdot\mathbf{T}^{-1}{}_{0\mathrm{j}}{}^{0\kappa}$$
$$+\sum{}'\,\mathbf{T}_{\mathrm{ik}}{}^{\iota\lambda}\cdot\boldsymbol{\omega}^{-1}{}_{\mathrm{k}}{}^{\lambda}\cdot\mathbf{T}^{-1}{}_{\mathrm{kj}}{}^{\lambda\kappa},\quad(37)$$

where $\sum'$ represents the sum over all frequencies except $\omega_0{}^{0,\alpha}$, $\alpha=1, 2, 3$, one can obtain

$$\lim_{\omega_0{}^0\rightarrow 0}(G^{-1}{}_{xx})^{-1}{}_{00}{}^{\iota\iota}=(\mathbf{F}^{-1}{}_{\mathrm{jj}}{}^{\kappa-\iota,\kappa-\iota})^{-1},\quad(38)$$

$$\lim_{\omega_0{}^0\rightarrow 0}(G^{-1}{}_{xx})^{-1}{}_{0\mathrm{j}}{}^{\iota\kappa}=-[1+O(\omega_0)](G^{-1}{}_{xx})^{-1}{}_{00}{}^{\iota\iota},\quad(39)$$

and

$$\lim_{\omega_0{}^0\rightarrow 0}|G^{-1}{}_{xx}|=\tfrac{1}{2}N^{-3}|\mathbf{F}^{-1}{}_{\mathrm{jj}}{}^{\kappa-\iota,\kappa-\iota}|\prod_{\alpha}(\omega_0{}^{0,\alpha})^{-1/2},\quad(40)$$

where

$$\mathbf{F}^{-1}{}_{\mathrm{jj}}{}^{\kappa-\iota,\kappa-\iota}=\lim_{\omega_0{}^0\rightarrow 0}[\mathbf{G}^{-1}{}_{\mathrm{jj}}{}^{\kappa\kappa}$$
$$-\mathbf{G}^{-1}{}_{\mathrm{j}0}{}^{\kappa\iota}\cdot(\mathbf{G}^{-1}{}_{00}{}^{\iota\iota})^{-1}\cdot\mathbf{G}^{-1}{}_{0\mathrm{j}}{}^{\iota\kappa}]\quad(41)$$

and is the appropriately labeled element of the inverse of the matrix F formed by striking out the $({}_0{}^{\iota})$ row and column of G.

Thus substituting Eq. (38) into Eq. (34) and Eqs. (38)–(40) into Eq. (33) we find that

$$\lim_{\omega_0{}^0\rightarrow 0}q_x(G^{-1}{}_{xx})^{-1}q_x=\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa}\cdot(\mathbf{F}^{-1}{}_{\mathrm{jj}}{}^{\kappa-\iota,\kappa-\iota})^{-1}\cdot\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa},\quad(42)$$

that

$$\psi(\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa})=\pi^{-3/2}a^3|\mathbf{F}^{-1}{}_{\mathrm{jj}}{}^{\kappa-\iota,\kappa-\iota}|^{-1/2}$$
$$\times\exp[-a^2\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa}\cdot(\mathbf{F}^{-1}{}_{\mathrm{jj}}{}^{\kappa-\iota,\kappa-\iota})^{-1}\cdot\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa}],\quad(43)$$

and that

$$A'^2=2^{3/2}a^3\prod{}'(a^2\omega_k{}^{\alpha})^{1/2}/(\pi^{(N-3)/2}N^{3/2}\Omega).\quad(44)$$

In Eq. (44) $\prod'$ signifies that the three $\omega_0{}^{0,\alpha}$ are omitted from the product, and Ω, the volume of the system, arises from the integral over $d(\mathbf{q}_{\mathrm{j}}{}^{\iota,\kappa})^+$.

C. Computation of General Matrix Element

It follows from Eqs. (18)–(20) that the computation of the general matrix $\langle n|V|m\rangle$ will require performing

---

[11] S. F. Boys, Proc. Roy. Soc. (London) **A253**, 402 (1960).

[12] K. Singer, Proc. Roy. Soc. (London) **A253**, 412 (1960).

[13] Strictly speaking, Eq. (31) is valid only when the integrals are over all space. Here, however, the matrix M will be such that the particles are localized in a region of space that is much smaller then the lattice, and the correction to Eq. (31) due to finite limits on the integration will be completely negligible. The single exception to this statement is discussed immediately following Eq. (44).

[14] The essential aspect of the notation is that, in order to save writing unnecessary parentheses, $M^{-1}{}_{ij}$ or $M^{\dagger}{}_{ij}$ are used to denote the ijth component of M^{-1} or $M^{\dagger}$, respectively.

an integral of the form

$$\sum_{\substack{\iota\kappa\cdots\lambda\\ \mathbf{i}\,\mathbf{j}\cdots\mathbf{l}}}\int M^{\iota\,\kappa\cdots\lambda}_{\mathbf{i}\,\mathbf{j}\cdots\mathbf{l}}\mathbf{q}_{\mathbf{i}}{}^{\iota}\mathbf{q}_{\mathbf{j}}{}^{\kappa}\sum_{\substack{\mathbf{m},\,\mathbf{n}\\ \mu,\,\nu}}V(q_{\mathbf{m}}{}^{\mu}-q_{\mathbf{n}}{}^{\nu})\Phi_0{}'^2\,dq$$

$$=\sum_{\substack{\iota\kappa\cdots\lambda\\ \mathbf{j}\cdots\mathbf{l}}}\int M'^{\iota\,\kappa\cdots\lambda}_{\quad\mathbf{j}\cdots\mathbf{l}}\sum_{\mathbf{n},\mu,\nu}V(\mathbf{q}_0{}^{\mu}-\mathbf{q}_{\mathbf{n}}{}^{\nu})\Phi_0{}'^2\,dq\,, \quad (45)$$

where the equality follows from the symmetry properties of V and Φ_0' and

$$M'^{\iota\,\kappa\cdots\lambda}_{\quad\mathbf{j}\cdots\mathbf{l}}=\sum_{\mathbf{i}}M^{\iota\quad\kappa\quad\cdots\quad\lambda}_{\mathbf{i},\,\mathbf{j}-\mathbf{i},\,\cdots,\,\mathbf{l}-\mathbf{i}}\,. \quad (46)$$

The tensor M will have the form

$$M^{\iota\cdots\iota'\kappa\cdots\kappa'}_{\mathbf{i}\cdots\mathbf{i}'\mathbf{j}\cdots\mathbf{j}'}=\sum_{\substack{\alpha\cdots\alpha'\\ \delta\cdots\delta'}}T_{\mathbf{i}\mathbf{k}}{}^{\iota\lambda,\alpha\beta}\cdots T_{\mathbf{i}'\mathbf{k}'}{}^{\iota'\lambda',\alpha'\beta'}$$

$$\times T^{\dagger}{}_{\mathbf{p}\mathbf{j}}{}^{\mu\kappa,\nu\delta}\cdots T^{\dagger}{}_{\mathbf{p}'\mathbf{j}'}{}^{\mu'\kappa',\nu'\delta'}\,, \quad (47)$$

where there will be one factor of the form $T_{\mathbf{i}\mathbf{k}}{}^{\iota\lambda,\alpha\beta}$ for each phonon of energy $\omega_{\mathbf{k}}{}^{\lambda\beta}$ excited in $\langle n|$, and one factor of the form $T^{\dagger}{}_{\mathbf{p}\mathbf{j}}{}^{\mu\kappa,\nu\delta}$ for each phonon of energy $\omega_{\mathbf{p}}{}^{\mu,\nu}$ excited in $|m\rangle$. The properties of the $T_{\mathbf{i}\mathbf{k}}{}^{\iota\lambda}$ are such that

$$M'^{\iota\kappa\cdots\lambda}_{\quad\mathbf{j}\cdots\mathbf{l}}=M'^{\iota\kappa\cdots\lambda}_{\quad\mathbf{j}\cdots\mathbf{l}}\Delta(\mathbf{k}+\cdots+\mathbf{k}'-\mathbf{p}-\cdots-\mathbf{p}')\,, \quad (48)$$

where $\Delta(\mathbf{k})=1$ if $\mathbf{k}$ equals zero or a reciprocal lattice vector, and $\Delta(\mathbf{k})=0$ otherwise. Thus V only has matrix elements between states of equal reduced wave vector as would be expected. It is clear that this result follows from the periodicity of the lattice.

Next, consider the integral

$$\int\tilde{q}vV(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\Phi_0{}'^2\,dq=A'^2\int\tilde{q}vV(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})$$

$$\times\exp(-\tilde{q}Gq)\,dq\,, \quad (49)$$

where v is a vector whose elements can be functions of the $\mathbf{q}_{\mathbf{i}}{}^{\iota,\alpha}$. If one now integrates by parts in each term that results from the inner product, one finds that the integrated term vanishes[15] and

$$\int\tilde{q}vV(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\Phi_0{}'^2\,dq=\frac{1}{2a^2}\int\Phi_0{}'^2\tilde{\nabla}G^{-1}vV(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\,dq \quad (50)$$

results. For the integrals of interest in calculating $\langle n|H|m\rangle$, $G^{-1}v$ will always involve either the product $(\boldsymbol{\nabla}G^{-1}T)_{\mathbf{i}\mathbf{k}}{}^{\iota\kappa,\alpha\beta}$ or $(T^{\dagger}G^{-1}\nabla)_{\mathbf{k}\mathbf{i}}{}^{\kappa\iota,\beta\alpha}$ which, from Eq. (16), are equal to $(\omega_{\mathbf{k}}{}^{\kappa,\beta})^{-1}\nabla_{\mathbf{i}}{}^{\iota,\alpha}T_{\mathbf{i}\mathbf{k}}{}^{\iota\kappa,\alpha\beta}$ or $(\omega_{\mathbf{k}}{}^{\kappa,\beta})^{-1}T^{\dagger}{}_{\mathbf{k}\mathbf{i}}{}^{\kappa\iota,\beta\alpha}\nabla_{\mathbf{i}}{}^{\iota,\alpha}$, respectively.

Thus, if each term in $\tilde{q}v$ is of nth degree in the $q_{\mathbf{i}}{}^{\iota,\alpha}$, it is clear that repeated application of Eq. (50) n times will reduce the original integral to one involving only products of $\Phi_0{}'^2$ and of the nth order derivatives of $V(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})$. Furthermore, each of the resulting matrix products can be expressed explicitly in terms of the $\omega_{\mathbf{k}}{}^{\kappa,\beta}$ and the $T_{\mathbf{i}\mathbf{k}}{}^{\iota\kappa,\alpha\beta}$.

Applying Eq. (50) twice we obtain

$$\int\tilde{q}M^{(2)}qV(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\Phi_0{}'^2\,dq$$

$$=\tfrac{1}{2}a^{-2}\,\mathrm{Tr}(G^{-1}M^{(2)})\int V(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\Phi_0{}'^2\,dq$$

$$+\frac{1}{4a^4}\int\Phi_0{}'^2\nabla G^{-1}M^{(2)}G^{-1}\nabla V(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\,dq \quad (51)$$

$$=\tfrac{1}{2}a^{-2}\,\mathrm{Tr}(G^{-1}M^{(2)})\int V(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\psi(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\,d\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa}$$

$$+\frac{1}{4a^4}\int\psi(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\nabla G^{-1}M^{(2)}G^{-1}\nabla V(\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa})\,d\mathbf{q}_{\mathbf{j}}{}^{\iota,\kappa}\,, \quad (52)$$

where $M^{(2)}$ is a second-rank tensor.

Using Eqs. (25), (33), and (52) one can obtain explicit expressions for certain matrix elements as follows:

$$\langle{}_{\mathbf{k}}{}^{\iota,\alpha}|H|{}_{\mathbf{k}}{}^{\iota,\alpha}\rangle=\langle0|H|0\rangle+\tfrac{1}{2}a^2\omega_{\mathbf{k}}{}^{\iota,\alpha}+H_{\mathbf{k}}{}^{\iota\iota,\alpha\alpha}\,, \quad (53)$$

$$\langle{}_{\mathbf{k}}{}^{\iota,\alpha}|H|{}_{\mathbf{k}}{}^{\kappa,\beta}\rangle=H_{\mathbf{k}}{}^{\iota\kappa,\alpha\beta}\,,\quad \iota,\alpha\neq\kappa,\beta\,, \quad (54a)$$

$$\langle{}_{\mathbf{k}}{}^{\iota\alpha},{}_{-\mathbf{k}}{}^{\kappa\beta}|H|0\rangle=H_{\mathbf{k}}{}^{\iota\kappa,\alpha\beta}\,,\quad \iota,\alpha\neq\kappa,\beta\,, \quad (54b)$$

and

$$\langle{}_{\mathbf{k}}{}^{\iota\alpha},{}_{-\mathbf{k}}{}^{\iota\alpha}|H|0\rangle=-\tfrac{1}{2}a^2\omega_{\mathbf{k}}{}^{\iota,\alpha}+H_{\mathbf{k}}{}^{\iota\iota,\alpha\alpha}\,, \quad (55)$$

where

$$H_{\mathbf{k}}{}^{\iota\kappa,\alpha\beta}=\frac{N}{4a^2(\omega_{\mathbf{k}}{}^{\iota,\alpha}\omega_{\mathbf{k}}{}^{\kappa,\beta})^{1/2}}\sum_{\mathbf{j}}\int\psi(\mathbf{r}_{\mathbf{j}}{}^{\lambda,\mu}-\mathbf{R}_{\mathbf{j}}{}^{\lambda,\mu})$$

$$\times(T^{\dagger}\nabla)_{\mathbf{k}}{}^{\iota,\alpha}(\nabla T)_{\mathbf{k}}{}^{\kappa,\beta}V(r_{\mathbf{j}}{}^{\lambda,\mu})\,d\mathbf{r}_{\mathbf{j}}{}^{\lambda,\mu} \quad (56)$$

and the superscripts and subscripts in the bra and ket state vectors have their most obvious meaning. In Eq. (56), since $V(r_{\mathbf{j}}{}^{\lambda,\mu})$ is a function only of $\mathbf{r}_0{}^{\lambda}$ and $\mathbf{r}_{\mathbf{j}}{}^{\mu}$, the vector ∇T has only six components; the notation $(T^{\dagger}\nabla)_{\mathbf{k}}{}^{\iota,\alpha}(\nabla T)_{\mathbf{k}}{}^{\kappa,\beta}$ is used to indicate that the open product is taken.

Note that the last two terms in Eq. (53) give the phonon energies to first order, and that Eqs. (55) and (56) are the matrix elements which are required for the computation of second-order correction to the ground-state energy due to two phonon processes. It would be expected that $H_{\mathbf{k}}{}^{\iota\iota,\alpha\alpha}\sim\tfrac{1}{2}a^2\omega_{\mathbf{k}}{}^{\iota,\alpha}$ and that $H_{\mathbf{k}}{}^{\iota\kappa,\alpha\beta}\sim0$, $\iota\alpha\neq\kappa\beta$.

IV. NUMERICAL WORK

A. The Dynamical Matrix

The theoretical developments presented in Secs. II and III have been applied to obtain numerical results

---

[15] The integrated term vanishes by reason of the periodicity of the lattice. Strictly speaking the lattice and the wave function should be continued out of the $L\times L\times L$ region being considered. See, e.g., E. H. Lieb, Phys. Rev. **130**, 2518 (1963), Ref. 17.

for a simplified, but instructive, model of a solid—a bcc crystal in which each atom interacts with its nearest and second-nearest neighbor through a Mie-Lennard-Jones 12-6 potential. The details of the calculation will illustrate certain features of the application of the theory, and will bring out the implication of Eqs. (29) and (53) from a computational point of view.

In constructing the matrix G to obtain a suitable trial wave function, one can proceed along two different routes: A model harmonic Hamiltonian H_1 can be chosen, and its eigenfunctions and eigenvalues then are used for the calculation of the matrix elements of the crystal Hamiltonian H, or, alternately, an arbitrary set of $\omega_{\mathbf{k}}$ and $U_{\mathbf{k}}$ can be chosen either *ad hoc*, or as a result of some variational procedure. We have followed the former procedure exclusively. This guarantees that Ψ_0 at least be a reasonable choice for a trial wave function, and, in addition, restricts the number of free parameters to a controllable amount.

Two different model harmonic Hamiltonians were investigated. In one, each atom interacted with its nearest and second-nearest neighbors with a Hooke's-law central force; a set of eigenfunctions could be generated by varying the second-nearest-neighbor force constant, while the nearest-neighbor force constant was held at unity. In the other model Hamiltonian, a nearest-neighbor only interaction was used in which

$$\mathbf{V}_{\mathbf{ij}}{}^{\alpha\alpha}=-\tfrac{1}{8}\,, \tag{57}$$

$$\mathbf{V}_{\mathbf{ij}}{}^{\alpha\beta}=-(3\rho/8)(R_{\mathbf{ij}}{}^{\alpha}R_{\mathbf{ij}}{}^{\beta}/R_{\mathbf{ij}}{}^{2})\,,\quad \alpha\neq\beta\,, \tag{58}$$

where $\mathbf{i}$ and $\mathbf{j}$ denote nearest neighbors. Then $\mathbf{V}_{\mathbf{ii}}$ is determined by Eq. (4), and the remaining matrix elements equal zero. Equations (57) and (58) with $\rho=1$ would arise from a Hooke's law central-force interaction. Since there is only one atom per unit cell in the model chosen, we have dropped the first set of superscripts in Eqs. (57) and (58), and will continue to do so in the remainder of this section.[16]

It was found that of all the wave functions tried, the one resulting from the potential given by Eqs. (57) and (58) with $\rho\approx 0.9$ gave the lowest value of $\langle 0|H|0\rangle$, and so this case will be considered exclusively in the remainder of this paper. However, the value of $\langle 0|H|0\rangle$ was not too sensitive to the value of ρ, and also was not much lower than that obtained from the first model described when the second-nearest-neighbor force constant was ≈ 0.1.

It should be kept in mind that the model harmonic Hamiltonian is only a tool and that one is free to choose it without regard for the elastic constants, etc. of the substance whose properties are governed by the true Hamiltonian H. Of course, one should select a model Hamiltonian whose ground-state eigenfunction gives a good value for $\langle 0|H|0\rangle$.

Details of the construction of the dynamical matrix are discussed in Refs. 6–9. In the example considered here one can readily find

$$\mathbf{D}_{\mathbf{k}}{}^{\alpha\alpha}=1-\cos(k_x)\cos(k_y)\cos(k_z) \tag{59}$$

and

$$\mathbf{D}_{\mathbf{k}}{}^{\alpha\beta}=\rho\sin(k_\alpha)\sin(k_\beta)\cos(k_\gamma)\,,\quad \alpha\neq\beta\neq\gamma\neq\alpha\,, \tag{60}$$

where the nearest neighbor of (0,0,0) is located at (1,1,1).

As is well known, the symmetry of a cubic lattice is such that the roots and eigenvectors of $\mathbf{D}_{\mathbf{k}}$ need only be found in the 1/48—which can be called the irreducible part—of the first Brillouin zone determined by the conditions $k_x\geq 0$, $k_y\leq k_x$, and $k_z\leq k_y$. In the remainder of the zone, the roots are repeated and the eigenvectors may be obtained from simple symmetry operations on the vectors of the irreducible part of the zone. The $\boldsymbol{\omega}_{\mathbf{k}}$ and $\mathbf{U}_{\mathbf{k}}$ were determined numerically by means of an IBM 7094 FORTRAN IV computer program at all points in $\mathbf{k}$ space—which in this case form an fcc lattice—within the irreducible part of the first Brillouin zone of a crystal containing $N=L^3$ atoms. Effects due to variations in N will be discussed later.

B. Calculation of Ground-State Energy

The Mie-Lennard-Jones 12-6 potential is given by

$$V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]\,. \tag{61}$$

Thus the Hamiltonian appropriate to the crystal described in the preceding subsection is

$$H=-\tfrac{1}{2}\lambda^2\sum\nabla_i{}^2+2\sum_{i\neq j}(r_{ij}{}^{-12}-r_{ij}{}^{-6})\,, \tag{62}$$

where $\mathbf{R}_{\mathbf{i}}$ and $\mathbf{R}_{\mathbf{j}}$ are nearest or second-nearest neighbors, $\lambda^2=\hbar^2/(m\sigma^2\epsilon)$ and σ and ϵ are used as units of distance and energy, respectively. Here it is not necessary to incorporate λ into the transformations given immediately preceding Eq. (6); however, the right-hand side of Eqs. (25)–(27) must then by multiplied by λ^2.

In order to evaluate $W_0\equiv\langle 0|H|0\rangle$ it is necessary to determine $\mathbf{F}^{-1}{}_{\mathbf{jj}}$ for the eight nearest neighbors and six second-nearest neighbors of (0,0,0). By substituting Eqs. (12) and (37) into Eq. (41), one can obtain

$$\mathbf{F}^{-1}{}_{\mathbf{jj}}=(2/N)\sum_{\mathbf{k}\neq 0}(1-e^{i\mathbf{k}\cdot\mathbf{R}_{\mathbf{j}}})\mathbf{U}_{\mathbf{k}}\cdot\boldsymbol{\omega}_{\mathbf{k}}{}^{-1}\cdot\mathbf{U}_{\mathbf{k}}{}^{\dagger}\,. \tag{63}$$

Since the lattice defined by the $\mathbf{R}_{\mathbf{j}}$ has the same symmetry as that defined by the $\mathbf{k}$ vectors, and the sum in Eq. (63) is over all $\mathbf{k}$ vectors (except $\mathbf{k}=0$), $\mathbf{F}^{-1}{}_{\mathbf{jj}}$ is the same for all equivalent neighbors of the origin. One can, therefore, speak of the irreducible zone of coordinate space. It is convenient to use the conventions $\sum^{(I)}$ to designate a sum over all vectors in the irreducible zone of either coordinate or $\mathbf{k}$ space and $\sum^{(E)}$ to designate a sum over all vectors equivalent to a particular vector in the irreducible zone. In addition, a bar over a symbol

---

[16] This means the same symbol is used for $\mathbf{R}_{\mathbf{j}}$ as for $\mathbf{R}_{\mathbf{j}}-\mathbf{R}_0$. However, no confusion arises from this because $\mathbf{R}_0\equiv 0$.

will designate that its subscripts refer to vectors in the irreducible zone and that the quantity represented by this symbol is identical for all equivalent vectors.

Thus we may write, in general,

$$W_0/N=\tfrac{1}{4}a^2\lambda^2\sum_{\mathbf{k},\alpha}\omega_{\mathbf{k}}{}^{\alpha}/N$$
$$+\tfrac{1}{2}\textstyle\sum_{\mathrm{i}}{}^{(I)}\,\bar{N}_{\mathrm{i}}{}^{(E)}\bar{\psi}_{\mathrm{i}}(\mathbf{r}-\overline{\mathbf{R}}_{\mathrm{i}})\,d\mathbf{r}\,, \quad (64)$$

where $\bar{\psi}_{\mathrm{i}}(\mathbf{r}-\mathbf{R}_{\mathrm{i}})\equiv\bar{\psi}(\mathbf{r}_{\mathrm{i}}-\mathbf{R}_{\mathrm{i}})$ has been used, and where $\bar{N}_{\mathrm{i}}{}^{(E)}$ is the number of atoms located at lattice sites equivalent to $\overline{\mathbf{R}}_{\mathrm{i}}$, $\bar{N}_{\mathbf{k}}{}^{(E)}$ will be used later in a similar vein. In the case of nearest and second-nearest-neighbor interactions only considered here, Eq. (64) becomes

$$\frac{W_0}{N}=\frac{a^2\lambda^2}{4N}\sum_{\mathbf{k},\alpha}\omega_{\mathbf{k}}{}^{\alpha}+4\int V(r)\bar{\psi}_{111}(\mathbf{r}-\overline{\mathbf{R}}_{111})\,d\mathbf{r}$$
$$+3\int V(r)\bar{\psi}_{200}(\mathbf{r}-\overline{\mathbf{R}}_{200})\,d\mathbf{r}$$
$$\equiv K+V(1,1,1)+V(2,0,0)\,. \quad (65)$$

As a first step toward finding $\mathbf{F}^{-1}{}_{\mathrm{jj}}$ we may rewrite Eq. (63) as

$$\mathbf{F}^{-1}{}_{\mathrm{jj}}=\textstyle\sum_{\mathbf{k}}{}^{(I)}\,\overline{\mathbf{F}}_{\mathrm{j}}{}^{(\mathbf{k})}\,, \quad (66)$$

where

$$\overline{\mathbf{F}}_{\mathrm{j}}{}^{(\mathbf{k})}=(\bar{N}_{\mathbf{k}}{}^{(E)}/24N)\textstyle\sum_{\mathbf{k}}{}^{(E)}(1-e^{i\mathbf{k}\cdot\mathbf{R}_{\mathrm{j}}})\mathbf{U}_{\mathbf{k}}\cdot\omega_{\mathbf{k}}{}^{-1}\cdot\mathbf{U}_{\mathbf{k}}{}^{\dagger} \quad (67)$$

and the sum prescribed by $\sum_{\mathbf{k}}{}^{(E)}$ involves a summation over all 48 combinations of reflection and permutation operations on the components of **k**. The general expression for such a sum is rather messy; however, in the special cases considered here it is readily found that

$$(\overline{\mathbf{F}}_{(1,1,1)}{}^{(\mathbf{k})})^{\alpha\alpha}=(16/3N)[1-\cos(k_x)\cos(k_y)\cos(k_z)]$$
$$\times\mathrm{Tr}(\mathbf{U}_{\mathbf{k}}\cdot\boldsymbol{\omega}_{\mathbf{k}}{}^{-1}\cdot\mathbf{U}_{\mathbf{k}}{}^{\dagger})\,, \quad (68)$$

$$(\overline{\mathbf{F}}_{(1,1,1)}{}^{(\mathbf{k})})^{\alpha\beta}=(16/3N)$$
$$\times\textstyle\sum_{\alpha,\beta,\gamma}{}^{(\mathrm{CP})}\,[\sin(k_\alpha)\sin(k_\beta)\cos(k_\gamma)]$$
$$\times(\mathbf{U}_{\mathbf{k}}\cdot\boldsymbol{\omega}_{\mathbf{k}}{}^{-1}\cdot\mathbf{U}_{\mathbf{k}}{}^{\dagger})^{\alpha\beta}\,, \quad (69)$$

$$(\overline{\mathbf{F}}_{(2,0,0)}{}^{(\mathbf{k})})^{xx}=(4/N)\textstyle\sum_{\beta}\,[1-\cos(2k_\beta)]$$
$$\times(\mathbf{U}_{\mathbf{k}}\cdot\boldsymbol{\omega}_{\mathbf{k}}{}^{-1}\cdot\mathbf{U}_{\mathbf{k}}{}^{\dagger})^{\beta\beta}\,, \quad (70)$$

$$(\overline{\mathbf{F}}_{(2,0,0)}{}^{(\mathbf{k})})^{yy}=(\overline{\mathbf{F}}_{(2,0,0)}{}^{(\mathbf{k})})^{zz}$$
$$=(2/N)\textstyle\sum_{\alpha,\beta,\gamma}{}^{(\mathrm{CP})}[2-\cos(2k_\beta)-\cos(2k_\gamma)]$$
$$\times(\mathbf{U}_{\mathbf{k}}\cdot\boldsymbol{\omega}_{\mathbf{k}}{}^{-1}\cdot\mathbf{U}_{\mathbf{k}}{}^{\dagger})^{\alpha\alpha}\,, \quad (71)$$

and

$$(\overline{\mathbf{F}}_{(2,0,0)})^{\alpha\beta}=0\,. \quad (72)$$

In these expressions it is understood that α, β, and γ all refer to a different Cartesian coordinate and that $\sum_{\alpha,\beta,\gamma}{}^{(\mathrm{CP})}$ indicates that the sum of the three cyclic permutations of $\alpha=x$, $\beta=y$, and $\gamma=z$ is taken. Note that Eqs. (68) and (69) describe a matrix whose diagonal elements are all equal, and whose off-diagonal elements are all equal.

If one transforms each integral in Eq. (65) to a primed coordinate system in which θ is measured from the axis defined by $\mathbf{R}_{\mathrm{i}}$, the integrals on the right-hand side of Eq. (65) become

$$V(1,1,1)=8a^3\gamma_\perp{}^{(1)}(\gamma_\parallel{}^{(1)}/\pi)^{1/2}\int V(r')$$
$$\times\exp\{-a^2[\gamma_\perp{}^{(1)}r'^2\sin^2\theta+\gamma_\parallel{}^{(1)}(r'\cos\theta-b)^2]\} \quad (73)$$

and

$$V(2,0,0)=6a^3\gamma_\perp{}^{(2)}(\gamma_\parallel{}^{(2)}/\pi)^{1/2}\int V(r')$$
$$\times\exp\{-a^2[\gamma_\perp{}^{(2)}r'^2\sin^2\theta+\gamma_\parallel{}^{(2)}(r\cos\theta-2b/\sqrt{3})^2]\}\,, \quad (74)$$

where the nearest-neighbor distance is b,

$$\gamma_\perp{}^{(1)}=[(\overline{\mathbf{F}}_{(1,1,1)}{}^{(\mathbf{k})})^{\alpha\alpha}-(\overline{\mathbf{F}}_{(1,1,1)}{}^{(\mathbf{k})})^{\alpha\beta}]^{-1}\,, \quad (75\mathrm{a})$$

$$\gamma_\parallel{}^{(1)}=[(\overline{\mathbf{F}}_{(1,1,1)}{}^{(\mathbf{k})})^{\alpha\alpha}+2(\overline{\mathbf{F}}_{(1,1,1)}{}^{(\mathbf{k})})^{\alpha\beta}]^{-1}\,, \quad (75\mathrm{b})$$

and

$$\gamma_\perp{}^{(2)}=[(\mathbf{F}_{(2,0,0)}{}^{(\mathbf{k})})^{yy}]^{-1}\,, \quad (76\mathrm{a})$$

$$\gamma_\parallel{}^{(2)}=[(\overline{\mathbf{F}}_{(2,0,0)}{}^{(\mathbf{k})})^{xx}]^{-1}\,. \quad (76\mathrm{b})$$

The sum over frequencies necessary to obtain the kinetic-energy contribution to W_0 and the appropriate sums specified by Eq. (67) necessary to evaluate $\sum\omega_{\mathbf{k}}{}^{\alpha}/N$, $\gamma_\perp{}^{(1)}$, $\gamma_\parallel{}^{(2)}$, $\gamma_\perp{}^{(2)}$, and $\gamma_\parallel{}^{(2)}$ were performed simultaneously with the computer diagonalization of $\mathbf{D}_{\mathbf{k}}$. The results for a few values of $L(N=L^3)$ are given in Table I. Apparently these quantities approach their value in the limit $N\rightarrow\infty$ for rather small values of N.[17] Of course, it is necessary to take into account many shells of nearest neighbors in the calculation of the ground-state energy of a true crystal, and a larger value of N would undoubtedly be required for the accurate calculation of the $\overline{\mathbf{F}}_{\mathrm{m}}$ for more distant neighbors.

The correlated-Gaussian wave function considered in this paper can best be compared with a Heitler-London-type wave function Ψ' constructed out of a product of Gaussian orbitals centered about the equilibrium sites

TABLE I. Calculations of $\sum\omega_k{}^{\alpha}/N$, $\gamma_\parallel{}^{(1)}$, $\gamma_\perp{}^{(1)}$, $\gamma_\parallel{}^{(2)}$, and $\gamma_\perp{}^{(2)}$ for various values of L.

L	$\sum\omega_k{}^{\alpha}/N$	$\gamma_\parallel{}^{(1)}$	$\gamma_\perp{}^{(1)}$	$\gamma_\parallel{}^{(2)}$	$\gamma_\perp{}^{(2)}$
10	2.83911	1.53971	0.40797	0.39093	0.42129
20	2.83963	1.53948	0.40893	0.39212	0.42188
30	2.83966	1.53947	0.40898	0.39218	0.42191
40	2.83966	1.53947	0.40899	0.39219	0.42192
50	2.83966	1.53947	0.40899	0.39219	0.42192

---

[17] In the example considered in I and II, where exact expressions are available for $S(N)\equiv\sum\omega_{\mathbf{k}}/N$, for example [see e.g., Eqs. (II-10) and (II-13)] it is readily found that $[S(\infty)-S(N)]/-S(\infty)\approx N^{-2}$ so that the convergence to the limiting value is quite rapid.

of each particle. Such a wave function results if G is set equal to a'^2I in Eq. (7), where I is the identity. In this case, Eq. (65) would become

$$W_0'/N=3a'^2\lambda^2/4+4\int V(r)\psi'(\mathbf{r}-\overline{\mathbf{R}}_{111})\,dr$$

$$+3\int V(r)\psi'(\mathbf{r}-\overline{\mathbf{R}}_{200})\,dr, \quad (77)$$

$$=K'+V'(1,1,1)+V'(2,0,0), \quad (77a)$$

where

$$\psi'(\mathbf{r}-\overline{\mathbf{R}}_i)=a'^3(2/\pi)^{3/2}\exp[-\tfrac{1}{2}a'^2(\mathbf{r}-\overline{\mathbf{R}}_i)]. \quad (78)$$

Thus the integrals in Eq. (77) are given by Eqs. (72) and (73) with $\gamma_\perp^{(1)}=\gamma_{\shortparallel}^{(1)}=\gamma_\perp^{(2)}=\gamma_{\shortparallel}^{(2)}=\frac{1}{2}$.

Suppose that a variational calculation has been performed and that the value of a', which minimizes Eq. (77), has been determined. If one then chooses $a^2\gamma_{\shortparallel}^{(1)}=\frac{1}{2}a'^2$, the parts of the integrals necessary to evaluate $V(1,1,1)$ and $V'(1,1,1)$ which have to overcome the hard-core overlap between nearest neighbors are equal, but, since $\gamma_\perp^{(1)}<\gamma_{\shortparallel}^{(1)}$, the exponential in Eq. (72) is large over a greater region of space in which $V(r)$ is attractive than is the exponential in the integral expression for $V'(1,1,1)$. Thus it is found that $V(1,1,1)<V'(1,1,1)$. Since $\gamma_{\shortparallel}^{(2)}<\gamma_{\shortparallel}^{(1)}$, Ψ allows the second-nearest neighbors to approach closer than Ψ' does, but not so close that the hard cores begin to overlap. Since the potential dies off rapidly, this results in $V(2,0,0)$ being less than $V'(2,0,0)$. Thus V will be less than V' by an undefined amount.

Next consider

$$K/K'=\sum \omega_{\mathbf{k}}^{\gamma}/(6N\gamma_{\shortparallel}^{(1)}). \quad (79)$$

One can evaluate this quantity readily using the values for $\sum \omega_{\mathbf{k}}^{\gamma}/N$ and $\gamma_{\shortparallel}^{(1)}$ given in Table I for $L=50$ and $K/K'=0.88$ results.[18] Of course, in a variational calculation of W_0, one would minimize with respect to a, and should find that $(W_0'-W_0)/K'>0.12$. Thus it follows that one can improve any computation of the ground-state energy of a bcc crystal in which a wave function of the type Ψ' is used by using Ψ instead of Ψ', and that this improvement will be at least equal to 12% of the original kinetic energy. Since there is nothing special about a bcc crystal, the preceding statement probably applies to any crystal.

A variational calculation in which both W_0 and W_0' were computed at various values of λ has been performed. The results are shown in Fig. 1 together with the decrease in total energy. This decrease when expressed as a percentage of the kinetic energy obtained by using the correlated Gaussian wave function was approximately 14%, which is seen to be slightly greater than the expected 12% minimum and was divided roughly equally between the kinetic and potential energies; the division would be equal if the crystal potential were only composed of a constant and a Harmonic term. As would be expected, the improvement in energy becomes greater as λ increases, because the effects of correlation are more important in crystals composed of light atoms. Further discussion of the significance of the numerical results will be deferred until Sec. V.

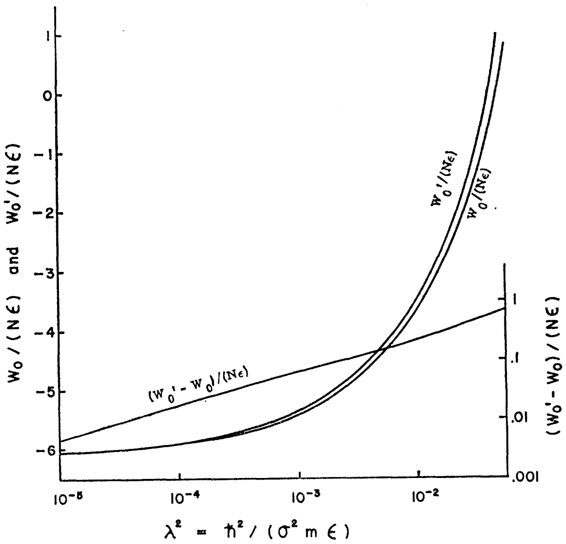

FIG. 1. Ground-state energy per particle measured in units of ϵ as calculated using a noncorrelated $[W_0'/(N\epsilon)]$ and correlated $[W_0/(N\epsilon)]$ Gaussian wave function. The difference of these two quantities is also shown on an expanded scale.

The value $b=1.095\sigma$ was used for the nearest-neighbor distance in all calculations. This value is the classical equilibrium distance for the model chosen.

In order to avoid the artificial singularity produced by the r^{-12} term in the potential, we modified the Mie-Lennard-Jones potential by multiplying it by a factor $[1-\exp(-cr^{12})]$ with $c=10\,000$. This did not noticeably alter the value of the potential for $r\gtrsim 0.3$, but did produce a function which approached a large positive constant as $r\to 0$, and also possessed continuous nonsingular derivatives. The energy calculations were insensitive to rather wide variations in c.

C. Calculation of Phonon Energies

The phonon energies to first order for a system with one atom per unit cell are given by the second and third terms on the right-hand side of Eq. (53) with the appropriate modification of superscripts; thus we may write

$$E_{\mathbf{k}}^{\alpha}=\tfrac{1}{2}a^2\lambda^2\omega_{\mathbf{k}}^{\alpha}+H_{\mathbf{k}}^{\alpha\alpha} \quad (80)$$

---

[18] In I the value for the quantity equivalent to what is called K/K' here was found to be $8/\pi^2=0.81$.

and

$$H_{\mathbf{k}}{}^{\alpha\alpha}=N(4a^2\omega_{\mathbf{k}}{}^{\alpha})^{-1}\sum\nolimits_{\mathbf{j}}{}^{(I)}\sum{}^{(E)}\psi(\mathbf{r}_{\mathbf{j}}-\mathbf{R}_{\mathbf{j}})$$
$$\times\sum\nolimits_{\beta\beta'}(T^{\dagger}{}_{\mathbf{kj}}{}^{\alpha\beta}-T^{\dagger}{}_{\mathbf{k}0}{}^{\alpha\beta})\nabla_{\mathbf{j}}{}^{\beta}$$
$$\times\nabla_{\mathbf{j}}{}^{\beta'}(T_{\mathbf{jk}}{}^{\beta'\alpha}-T_{\mathbf{j}0}{}^{\beta'\alpha})V(r_{\mathbf{j}})d\mathbf{r}_{\mathbf{j}}\quad(81)$$
$$=(2a^2\omega_{\mathbf{k}}{}^{\alpha})^{-1}\sum\nolimits_{\mathbf{j}}{}^{(I)}\sum{}^{(E)}\psi(\mathbf{r}_{\mathbf{j}}-\mathbf{R}_{\mathbf{j}})(1-e^{i\mathbf{k}\cdot\mathbf{R}_{\mathbf{j}}})$$
$$\times\sum\nolimits_{\beta\beta'}\tilde{U}_{\mathbf{k}}{}^{\alpha\beta}\nabla_{\mathbf{j}}{}^{\beta}\nabla_{\mathbf{j}}{}^{\beta'}U_{\mathbf{k}}{}^{\beta'\alpha}V(r_{\mathbf{j}})d\mathbf{r}_{\mathbf{j}},\quad(82)$$

where Eq. (56) has been written more explicitly by using $\boldsymbol{\nabla}_{\mathbf{j}}V(r_{\mathbf{j}})=-\boldsymbol{\nabla}_0V(r_{\mathbf{j}})$ to obtain (81) and (82) then follows from Eq. (12). If one takes the indicated derivatives

$$H_{\mathbf{k}}{}^{\alpha\alpha}=(2a^2\omega_{\mathbf{k}}{}^{\alpha})^{-1}\sum\nolimits_{j}{}^{(I)}\sum{}^{(E)}\psi(\mathbf{r}_{\mathbf{j}}-\mathbf{R}_{\mathbf{j}})(1-e^{i\mathbf{k}\cdot\mathbf{R}_{\mathbf{j}}})$$
$$\times\int\left\{\frac{V'(r_{\mathbf{j}})}{r_{\mathbf{j}}}+\left[V''(r_{\mathbf{j}})-\frac{V'(r_{\mathbf{j}})}{r_{\mathbf{j}}}\right]\frac{[(\mathbf{r}_{\mathbf{j}}\cdot\mathbf{U}_{\mathbf{k}})_{\mathbf{k}}{}^{\alpha}]^2}{r_{\mathbf{j}}{}^2}\right\}d\mathbf{r}_{\mathbf{j}}\quad(83)$$

results.

In the example considered here each of the $\psi(\mathbf{r}_{\mathbf{j}}-\mathbf{R}_{\mathbf{j}})$ is cylindrically symmetric about $\mathbf{R}_{\mathbf{j}}$ and Eq. (83) assumes a simpler form when expressed in terms of the coordinate system used in Eq. (64). Thus one can obtain

$$H_{\mathbf{k}}{}^{\alpha\alpha}=(4a^2\omega_{\mathbf{k}}{}^{\alpha})^{-1}\sum_{\substack{\mathbf{R}_{\mathbf{j}}=(0,1,1)\\(2,0,0)}}N_{\mathbf{j}}{}^{(E)}$$
$$\times\int\left\{\mathrm{Tr}(\bar{\mathbf{D}}_{\mathbf{k}}{}^{\mathbf{j}})\left[\left(\frac{V'}{r}-V''\right)\cos^2\theta+V''+\frac{V'}{r}\right]\right.$$
$$\left.+(\tilde{\mathbf{U}}_{\mathbf{k}}\cdot\bar{\mathbf{D}}_{\mathbf{k}}{}^{j}\cdot\mathbf{U}_{\mathbf{k}})^{\alpha\alpha}\left(V''-\frac{V'}{r}\right)(3\cos^2\theta-1)\right\}$$
$$\times\bar{\psi}_{\mathbf{m}}{}'(\mathbf{r}-\bar{\mathbf{R}}_{\mathbf{m}})\,d\mathbf{r},\quad(84)$$

where

$$\bar{D}_{\mathbf{k}}{}^{j,\alpha\beta}=(N_{\mathbf{j}}{}^{(E)})^{-1}\sum\nolimits_{\mathbf{k}}{}^{(E)}(1-e^{-i\mathbf{k}\cdot\mathbf{R}_{\mathbf{j}}})R_{\mathbf{j}}{}^{\alpha}R_{\mathbf{j}}{}^{\beta}/R_{\mathbf{j}}{}^2.\quad(85)$$

Results from a numerical calculation of $a^2\lambda^2\omega_{\mathbf{k}}{}^{\alpha}$ and of $E_{\mathbf{k}}{}^{\alpha}$ for $\mathbf{k}=(0.4\pi,\ 0.3\pi,\ 0.1\pi)$ are shown in Table II. The value of a^2 was chosen to be that which minimized W_0 for each different choice of λ^2, and the particular $\mathbf{k}$ vector was simply considered to be a typical random choice. It is interesting to note that, even though the only connection between the model Hamiltonian and the true crystal comes from the variational selection of a^2, the first-order phonon energies were within about 10% of the zero-order energies. This result obtained throughout most of the phonon spectrum although the energy values are not tabulated here.

The value $L=10$ was used in the phonon calculation.

V. DISCUSSION

The techniques described in this paper should provide a useful new approach to the calculation of the ground-state energy and phonon spectrum of crystalline solids—especially those of simple structure. In particular we intend to apply this theory to solid Ne and to solid He^3 and He^4 at 0°K.

TABLE II. Zeroth- and first-order phonon energies at various values of λ^2 for $k=(0.4\pi,0.3\pi,0.1\pi)$.

λ^2	$a^2\lambda^2\omega_k{}^{\alpha}$	$E_k{}^{\alpha}$
0.00001	0.0451	0.0475
	0.0624	0.0637
	0.0204	0.0128
0.0001	0.143	0.153
	0.197	0.207
	0.0645	0.0432
0.001	0.494	0.509
	0.683	0.705
	0.223	0.170
0.01	1.75	1.85
	2.41	2.71
	0.790	0.851

It is anticipated that the calculation of the ground-state energy of solid neon will require little more than the extension of our present computer programs so that elements of F^{-1} can be obtained for many nearest neighbors, and the rather trivial modifications required to treat the fcc structure. Mullin[4] has calculated the ground-state energy of solid Ne using what was essentially[19] a noncorrelated-Gaussian wave function, and has obtained a total energy of −431 cal/mole with a kinetic-energy contribution of approximately 90 cal/mole. We would expect to improve upon this result by at least 10 cal/mole.

The results of Mullin's are equal to those obtained by Nosanow and Shaw[20] who calculated the ground-state energy of neon and other rare-gas solids using a wave function constructed out of a product of the optimum (as determined by a Hartree calculation) single-particle wave functions which are spherically symmetric about a lattice site. We, therefore, conclude that the correlated-Gaussian wave function is superior to this Hartree wave function, and, as will be discussed later, is considerably easier to work with.

A straightforward calculation of the ground-state energy of solid He^3 or He^4 would be for one to use a correlated-Gaussian wave function multiplied by a Jastrow function. This should result in an improvement over the result of Nosanow[5] by at least 10% of his kinetic energy—an amount of the order of 4 cal/mole. Since, however, there are certain unsettled questions[21,22] concerning the validity of retaining only the first term in the cluster expansion in the Nosanow calculation, a perturbation-theory approach using the correlated-Gaussian wave function is more attractive. Here the

---

[19] In reality he used a noncorrelated-Gaussian multiplied by a Jastrow function. However, he found that the Jastrow function had little effect other than eliminating the singularity in the Mie-Lennard-Jones potential at $r\ll\sigma$ so that the calculation was equivalent to simply using a less singular potential as was done here.

[20] L. H. Nosanow and G. L. Shaw, Phys. Rev. **128**, 546 (1962).

[21] K. A. Brueckner, Seminar, Stanford University, 1965 (unpublished).

[22] D. J. Rosenwald (private communication).

results are unpredictable, and one cannot say *a priori* whether a reasonable value could be obtained for the energy by retaining only a few higher order terms although, in principle, convergence could be obtained by brute force.

It is obvious that a first-order calculation of W_0 for He^3 or He^4 will give a poor value. In fact, since objections may arise concerning the use of a wave function derived from the harmonic approximation to treat solid He^3 or He^4 where the atoms on the average reside on a local potential maximum, we should like to point out again that the Hamiltonian from which the trial wave function is derived need not bear any relationship other than that of identical crystal structure to the true crystal Hamiltonian which uses atomic potentials. The harmonic Hamiltonian serves merely to enable one to find a correlated ground-state wave function and complete set of excited states which can be readily integrated over all but a few coordinates. In addition, the Gaussian shape is not as bad at the particles' equilibrium position as it is when two particles overlap. In calculations of the ground-state energy of loosely bound systems using Gaussian wave functions, the inadequacy of the wave function at the equilibrium position contributes less to the poor results obtained from such calculations than does the fact that the wave function does not fall off rapidly enough when two particles approach, and thus is forced, in the variational calculation, to have too much curvature and, consequently, too much kinetic energy.

The numerical work involved in using the correlated-Gaussian wave function is not too difficult, and is of the type that can be performed quite readily on a high-speed digital computer. The $\boldsymbol{\omega}_{\mathbf{k}}$ and $\mathbf{U}_{\mathbf{k}}$ can be computed once and stored on magnetic tape, and then the calculation of W_0 or $E_{\mathbf{k}}{}^{\alpha}$ involves one or two integrals for each shell of equivalent nearest neighbors used. One can readily test many different model Hamiltonians by computing the various parameters that enter into the energy calculations for small values of L, and then can perform only one large scale calculation of the phonon spectrum of the most promising harmonic Hamiltonian.

Except for obtaining values for a few $E_{\mathbf{k}}{}^{\alpha}$, we have not calculated any matrix elements of H other than $\langle 0|H|0\rangle$. It may prove in practice that the use of Eq. (49) for obtaining a general matrix element will cause difficulty because the integrals involve derivatives of the potential which, in the case of the Mie-Lennard-Jones potential, are more singular than the potential. This problem arises primarily from the choice of the analytic form for the potential, and in a perturbation-theory calculation it may be better to use the Slater-Kirkwood form.

While the numerical results shown in Fig. 1 do not apply to any real substance, and, therefore, are not physically meaningful, we feel that they have this significance: If one performs a variational calculation using a noncorrelated-Gaussian and obtains an energy W_0', and if the value of λ, to which this corresponds in Fig. 1, is λ_1, the result of a calculation using a correlated-Gaussian will probably be approximately $W_0(\lambda_1)$.

It should be pointed out that, while Eq. (29) is a rather simple looking expression for $\langle 0|V|0\rangle$, the calculation would be very difficult by ordinary methods for loosely bound systems. In effect, Eq. (29) is an exact expression for what would be written as the expectation value of a sum over the harmonic term and all of the anharmonic terms in the conventional expansion of a Hamiltonian in terms of the $q_{\mathbf{k}}{}^{l,\alpha}$. Thus all of the anharmonic effects are taken into account in this theory.

Although the orientation of this section has been primarily directed towards discussing the calculation of the ground-state energy for various systems, we feel that this work will ultimately be as useful for the calculation of the phonon spectra—or more precisely the excitation spectra—of solids. One can, in principle, now compute the phonon energies exactly using perturbation theory and a knowledge of the atomic interaction. Of course, electronic effects must be taken into account in systems for which they are important.

We have not discussed the problem of constructing a properly symmetrized function out of a sum over permutations of Ψ_0'. This issue was taken up in II, and the results obtained there are applicable to the three-dimensional wave function considered here.

ACKNOWLEDGMENTS

The author has appreciated discussing various phases of this work with H. Morawitz. In addition he wishes to thank A. D. McLean and M. Yoshimine for the use of a computer subroutine.[23]

---

[23] A. D. McLean and M. Yoshimine, IBM J. Res. Develop. 9, 203 (1965).