

## Renormalization and Statistical Mechanics in Many-Particle Systems. I. Hamiltonian Perturbation Method\*

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A general system composed of many weakly interacting bosons and/or fermions is considered. The object is to develop a procedure for renormalizing the single-particle creation operators, so as to remove the interactions to successively higher orders of perturbation. The basic idea is that creation operators  $\theta_i^\dagger$  must satisfy the Hamiltonian commutator equations  $[\mathcal{H}, \theta_i^\dagger] = \omega_i \theta_i^\dagger$ , where  $\mathcal{H}$  is the Hamiltonian and  $\omega_i$  are the particle energies. For the many-weakly-interacting-particle system, the zeroth-order boson and fermion creation operators satisfy these equations to zeroth order. It is shown that if the creation operators are renormalized so as to satisfy the Hamiltonian commutator equations to order  $m$ , and also to satisfy the appropriate boson commutators and fermion anticommutators to order  $m$ , then the problem is solved to order  $m$ . In particular, the vectors formed by operating on the ground state with the renormalized creation operators, according to the usual boson and fermion occupation-number representation, are eigenvectors of  $\mathcal{H}$  and are orthonormal, all to order  $m$ . A procedure is obtained for finding the  $(m+1)$ -order contributions to the particle creation energies, in terms of the  $m$ -order operators. Explicit first-order calculations of these general results are provided for a system of bosons and a system of fermions, and these first-order results are shown to include similar results of Rayleigh-Schrödinger perturbation theory, the random-phase approximation, and the method of thermodynamic Green's functions. The problem of anharmonic lattice dynamics is studied in detail, and a method of undetermined coefficients is used to renormalize the phonon creation operators to first order. The phonon energies are calculated to second order, and this calculation shows that the interactions between renormalized phonons cannot be removed in second order. Statistical averages of the phonon energies give the energy shifts and lifetimes which have been calculated previously by various propagator techniques. In addition, the renormalized energies are used to calculate the temperature-dependent part of the Helmholtz free energy correct to second order. As a final example, electron-phonon interactions in a normal metal are studied. The electron and phonon creation operators are renormalized to first order, the particle energies are calculated to second order, and statistical averages of the particle energies recover the usual thermodynamic Green's-function results for energy shifts and lifetimes. These examples show the simplicity by which the renormalization procedure obtains a great amount of detailed information about the single-particle nature of a many-particle system.

### I. INTRODUCTION

WE consider a perturbation problem with Hamiltonian given by  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ , where  $\mathcal{H}_0$  is solved exactly in terms of noninteracting bosons and fermions, and  $\mathcal{H}_1 \ll \mathcal{H}_0$ . The object is to develop a procedure for renormalizing the single-particle creation operators and energies, keeping the single-particle quantum numbers fixed. Within the spirit of perturbation theory, this procedure turns out to be straightforward and gives directly the renormalized particle energies and lifetimes. The theory also shows to what order of perturbation a given Hamiltonian can be diagonalized in terms of particles which are labeled by the zeroth-order quantum numbers. Finally, the renormalization procedure greatly simplifies the derivation of statistical averages, and clears up a difficulty which has been encountered in the use of temperature-dependent energy levels.

The starting point of the present work is the observation that if  $[\mathcal{H}, \theta^\dagger] = \omega \theta^\dagger$  for some operator  $\theta^\dagger$  and number  $\omega$ , then  $\theta^\dagger \psi$  is an eigenfunction of  $\mathcal{H}$  if  $\psi$  is an eigenfunction of  $\mathcal{H}$ . Previous workers have applied this idea to nonperturbation problems, thinking of  $\theta^\dagger$  as a creation operator for  $\mathcal{H}$ . Suhl and Werthamer<sup>1</sup> studied the electron-gas problem, referring to the method as a

higher random-phase approximation. Koringa<sup>2</sup> studied spin waves in the  $S = \frac{1}{2}$  antiferromagnet, calling the procedure an operator method. Anderson<sup>3</sup> studied the problem of superconductivity, again referring to the procedure as a random-phase approximation. Pines<sup>4</sup> calls it the equation-of-motion method in discussing the application to the electron gas.

Here we take advantage of the simplification offered by perturbation problems, and try to develop this idea into a rigorous theory. Let us re-examine the basic idea. Suppose we have found a number of operators  $\theta_i^\dagger$  such that

$$[\mathcal{H}, \theta_i^\dagger] = \omega_i \theta_i^\dagger, \quad (1.1)$$

where  $\omega_i$  are real, positive numbers. Then if  $\mathcal{H}\psi = E\psi$ , (1.1) leads to

$$\mathcal{H}\theta_i^\dagger\psi = (E + \omega_i)\theta_i^\dagger\psi. \quad (1.2)$$

Now (1.1) alone does not serve as a prescription for finding the solutions of  $\mathcal{H}$  because of the following circumstances:

- (i) We need at least one eigenfunction to start with;
- (ii) There is no obvious way of finding all the  $\theta_i^\dagger$  and hence getting the complete set of eigenfunctions, or for

<sup>2</sup> J. Koringa, *Phys. Rev.* **125**, 1972 (1962).

<sup>3</sup> P. W. Anderson, *Phys. Rev.* **112**, 1900 (1958).

<sup>4</sup> D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1964).

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<sup>1</sup> H. H. Suhl and N. R. Werthamer, *Phys. Rev.* **122**, 359 (1961).

that matter, any subset which may be required for a particular calculation;

(iii)  $\theta_i^\dagger \psi$  does not have to be an eigenfunction of  $\mathcal{H}$ ; it can be zero.

For perturbation problems, however, these difficulties can be avoided by assuming that the complete set of solutions of  $\mathcal{H}_0$  is available. We then try to improve each creation operator of  $\mathcal{H}_0$  by satisfying the Hamiltonian commutator equations (1.1) to a higher order. We also find it necessary to satisfy the appropriate creation and annihilation operator commutators and anticommutators to the same order. In this way the theory naturally gives single-particle-creation energies and system-excitation energies, but not the corrected ground-state energy (at least not directly). Thus the procedure is particularly valuable for calculating the temperature-dependent parts of statistical averages.

In Sec. II we show that the problem is solved to a given order if the Hamiltonian commutator equations, as well as the particle commutators and anticommutators, are satisfied to that order. This is followed by a derivation of the particle-creation energies and the system Helmholtz free energy to the next higher order. First-order calculations for specific examples are discussed in more detail in Sec. III, and the general first-order results are compared with other standard perturbation methods. The method is applied to the problem of anharmonic lattice dynamics in Sec. IV, and the phonon energies and lifetimes, as well as the system free energy, are calculated to second order. In Sec. V we study electron-phonon interactions in normal metals, and calculate the renormalized phonon and electron energy levels to second order. Some concluding remarks are given in Sec. VI.

## II. GENERAL THEORY

### A. Zeroth-Order Occupation-Number Representation

The zeroth-order Hamiltonian  $\mathcal{H}_0$  describes a system of noninteracting particles occupying single-particle states. Each single-particle state is labeled by a set of quantum numbers; the set is denoted by  $\kappa$  for boson states,  $\lambda$  for fermion states. For definiteness we might think of particles in a box, with periodic boundary conditions, so that the single-particle states are momentum-like eigenstates.

We introduce the occupation-number representation in the usual way.<sup>5</sup> The complete, orthonormal set of eigenfunctions of  $\mathcal{H}_0$  is composed of appropriately symmetrized products of single-particle functions. Each system eigenfunction is placed in one-to-one correspondence with a state vector  $|\cdots n_\kappa \cdots n_\lambda \cdots(0)\rangle$  which specifies the number of particles in each single-particle state. Here  $n_\kappa = 0, 1, 2, \dots$ ,  $n_\lambda = 0, 1$ , and the  $(0)$  in the

state vector indicates a zeroth-order vector, i.e., an eigenvector of  $\mathcal{H}_0$ . The order of the set of  $n_\kappa$  is arbitrary, while the order of the set of  $n_\lambda$  is fixed according to some prescribed arrangement of the quantum numbers  $\lambda, \lambda', \dots$ . The state vectors form a complete orthonormal set:

$$\langle \cdots n_\kappa' \cdots n_\lambda' \cdots(0) | \cdots n_\kappa \cdots n_\lambda \cdots(0) \rangle = \prod_\kappa \delta(n_\kappa', n_\kappa) \prod_\lambda \delta(n_\lambda', n_\lambda), \quad (2.1)$$

$$\sum \cdots n_\kappa \cdots n_\lambda \cdots | \cdots n_\kappa \cdots n_\lambda \cdots(0) \rangle \times \langle \cdots n_\kappa \cdots n_\lambda \cdots(0) | = 1. \quad (2.2)$$

It is now possible to define a set of zeroth-order boson creation operators  $A_{0\kappa}^\dagger$  and a set of zeroth-order fermion creation operators  $C_{0\lambda}^\dagger$  such that the following properties [(2.3)–(2.7)] are satisfied.

*Transformations.*

$$\begin{aligned} A_{0\kappa}^\dagger | \cdots n_\kappa \cdots n_\lambda \cdots(0) \rangle &= (n_\kappa + 1)^{1/2} | \cdots n_\kappa + 1 \cdots n_\lambda \cdots(0) \rangle, \\ A_{0\kappa} | \cdots n_\kappa \cdots n_\lambda \cdots(0) \rangle &= (n_\kappa)^{1/2} | \cdots n_\kappa - 1 \cdots n_\lambda \cdots(0) \rangle, \\ C_{0\lambda}^\dagger | \cdots n_\kappa \cdots n_\lambda \cdots(0) \rangle &= (1 - n_\lambda) (-1)^{p_\lambda} | \cdots n_\kappa \cdots 1_\lambda \cdots(0) \rangle, \\ C_{0\lambda} | \cdots n_\kappa \cdots n_\lambda \cdots(0) \rangle &= n_\lambda (-1)^{p_\lambda} | \cdots n_\kappa \cdots 0_\lambda \cdots(0) \rangle, \end{aligned} \quad (2.3)$$

where  $p_\lambda$  is the sum of  $n_{\lambda'}$  which stand to the left of the  $n_\lambda$  position.

*Commutators and anticommutators.*

$$\begin{aligned} [A_{0\kappa}, A_{0\kappa'}] &= 0, \quad [A_{0\kappa}, A_{0\kappa'}^\dagger] = \delta_{\kappa\kappa'}; \\ [C_{0\lambda}, C_{0\lambda'}]_+ &= 0, \quad [C_{0\lambda}, C_{0\lambda'}^\dagger]_+ = \delta_{\lambda\lambda'}; \\ [A_{0\kappa}, C_{0\lambda}] &= [A_{0\kappa}, C_{0\lambda}^\dagger] = 0. \end{aligned} \quad (2.4)$$

Here and throughout the paper we use the notation  $[A, B]$  for a commutator, and  $[A, B]_+$  for an anticommutator.

*Ground state.* We can always arrange things so that the lowest energy state of  $\mathcal{H}_0$  is the vacuum

$$|\cdots 0_\kappa \cdots 0_\lambda \cdots(0)\rangle = |0(0)\rangle.$$

Then we find

$$A_{0\kappa} |0(0)\rangle = C_{0\lambda} |0(0)\rangle = 0. \quad (2.5)$$

*Hamiltonian.* The Hamiltonian can be written in the form

$$\mathcal{H}_0 = G_0 + \sum_\kappa \omega_{0\kappa} A_{0\kappa}^\dagger A_{0\kappa} + \sum_\lambda \omega_{0\lambda} C_{0\lambda}^\dagger C_{0\lambda}, \quad (2.6)$$

where  $G_0$  is the zeroth-order ground-state energy and  $\omega_{0\kappa}, \omega_{0\lambda}$  are the single-particle energies.

*State vectors.* The properly normalized state vectors are given by

$$\begin{aligned} | \cdots n_\kappa \cdots n_\lambda \cdots(0) \rangle &= \prod_\kappa (n_\kappa!)^{-1/2} (A_{0\kappa}^\dagger)^{n_\kappa} \prod_\lambda (C_{0\lambda}^\dagger)^{n_\lambda} |0(0)\rangle, \end{aligned} \quad (2.7)$$

<sup>5</sup> See, e.g., F. Mandl, *Introduction to Quantum Field Theory* (Interscience Publishers, Inc., New York, 1959).

where the order of the  $C_{0\lambda}^\dagger$  operators is the same as the prescribed ordering of the set  $\lambda, \lambda', \dots$ .

From (2.3) it follows that the Hilbert space is separable into boson and fermion subspaces; indeed it is further separable to single-particle subspaces. Also from (2.3), the state vectors are eigenvectors of the number operators  $A_{0\kappa}^\dagger A_{0\kappa}$ ,  $C_{0\lambda}^\dagger C_{0\lambda}$ , with eigenvalues  $n_\kappa, n_\lambda$ , respectively. In addition these operators, together with  $\mathcal{H}_0$ , form a complete set of commuting operators, since the simultaneous eigenvectors are completely determined (aside from phase factors).<sup>6</sup>

In subsequent development we wish to make use of a lemma which amounts to the equivalence of two definitions of a number, namely, any operator  $\theta$  which commutes with all  $A_{0\kappa}^\dagger, A_{0\kappa}, C_{0\lambda}^\dagger, C_{0\lambda}$  is a number in the space of  $\mathcal{H}_0$ . That is, if  $[\theta, A_{0\kappa}^\dagger] = [\theta, A_{0\kappa}] = [\theta, C_{0\lambda}^\dagger] = [\theta, C_{0\lambda}] = 0$ , then  $\theta$  is a number when operating on any  $|\dots n_\kappa \dots n_\lambda \dots (0)\rangle$ . To show this, first operate on  $|0(0)\rangle$  with the commutators  $[\theta, A_{0\kappa}^\dagger], [\theta, C_{0\lambda}^\dagger]$ , and use (2.5) to get the relations  $A_{0\kappa}^\dagger |0(0)\rangle = C_{0\lambda}^\dagger |0(0)\rangle = 0$ . This shows that  $\theta |0(0)\rangle$  is a multiple (including zero) of  $|0(0)\rangle$ , since  $|0(0)\rangle$  is the only vector which satisfies (2.5) for all  $\kappa, \lambda$ . Then operating on any  $|\dots n_\kappa \dots n_\lambda \dots (0)\rangle$ ,  $\theta$  can be commuted through the  $A_{0\kappa}^\dagger, C_{0\lambda}^\dagger$  to operate on  $|0(0)\rangle$ , according to the form of the state vectors given by (2.7). Thus  $\theta$  is a number in the space of  $\mathcal{H}_0$ .

From (2.4) and (2.6), it follows that all the  $A_{0\kappa}^\dagger, C_{0\lambda}^\dagger$  satisfy the Hamiltonian commutator equation (1.1).

$$[\mathcal{H}_0, A_{0\kappa}^\dagger] = \omega_{0\kappa} A_{0\kappa}^\dagger, \quad (2.8a)$$

$$[\mathcal{H}_0, C_{0\lambda}^\dagger] = \omega_{0\lambda} C_{0\lambda}^\dagger, \quad (2.8b)$$

where  $\omega_{0\kappa}, \omega_{0\lambda}$  are all real and positive. We know that  $A_{0\kappa}^\dagger, C_{0\lambda}^\dagger$  are all of the creation operators, and operating on the vacuum they give all the eigenvectors. As was pointed out in Sec. I, however, we do not know this from (2.8) alone. For example, for any operator  $\Omega^\dagger$  such that  $[\mathcal{H}_0, \Omega^\dagger] = \omega \Omega^\dagger$  with  $\omega$  any number (including zero), then also

$$[\mathcal{H}_0, A_{0\kappa}^\dagger \Omega^\dagger] = (\omega_{0\kappa} + \omega) A_{0\kappa}^\dagger \Omega^\dagger, \quad (2.9a)$$

$$[\mathcal{H}_0, C_{0\lambda}^\dagger \Omega^\dagger] = (\omega_{0\lambda} + \omega) C_{0\lambda}^\dagger \Omega^\dagger. \quad (2.9b)$$

Obviously  $A_{0\kappa}^\dagger \Omega^\dagger, C_{0\lambda}^\dagger \Omega^\dagger$  are not the correct creation operators. Interesting examples which illustrate the difficulties listed in Sec. I are obtained by taking  $\Omega^\dagger$  as  $A_{0\kappa}^\dagger$  or  $C_{0\lambda}^\dagger$ . When operating on the vacuum,  $A_{0\kappa}^\dagger A_{0\kappa}^\dagger$  leads only to states with even  $n_\kappa$ , while  $C_{0\lambda}^\dagger C_{0\lambda}^\dagger$  gives zero when operating on any eigenstate. Taking  $\Omega^\dagger$  as a number operator, we note that  $A_{0\kappa}^\dagger A_{0\kappa}^\dagger A_{0\kappa}, C_{0\lambda}^\dagger C_{0\lambda}^\dagger C_{0\lambda}$  are operators which satisfy (1.1); however, these operators give zero when operating on the vacuum and on many other eigenvectors, while in other cases they give another (unnormalized) eigenvector.

The operators  $A_{0\kappa}^\dagger \Omega^\dagger, C_{0\lambda}^\dagger \Omega^\dagger$  in these examples all fail to satisfy the boson commutator or fermion anti-commutator relations. Also note that the  $A_{0\kappa}^\dagger, C_{0\lambda}^\dagger$  are arbitrary to a multiplicative constant of modulus 1; this is merely an eigenvector phase factor.

## B. Higher Order Creation Operators and Particle Energies

Let the Hamiltonian be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 + \dots, \quad (2.10)$$

where

$$\mathcal{H}_0^\dagger = \mathcal{H}_0, \mathcal{H}_1^\dagger = \mathcal{H}_1, \dots,$$

and

$$\mathcal{H}_1 \sim \epsilon \mathcal{H}_0, \mathcal{H}_2 \sim \epsilon^2 \mathcal{H}_0, \dots$$

Here  $\epsilon$  is the expansion parameter, a real positive number  $\ll 1$ , and  $\sim$  means "is of order." We assume the validity of perturbation theory, so that all eigenfunctions are analytic functions of  $\epsilon$  for small  $\epsilon$ . Suppose for each operator  $A_{0\kappa}^\dagger, C_{0\lambda}^\dagger$ , we find an "mth-order-correct" operator  $A_\kappa^\dagger, C_\lambda^\dagger$  of the form

$$A_\kappa^\dagger = A_{0\kappa}^\dagger + A_{1\kappa}^\dagger + \dots + A_{m\kappa}^\dagger, \quad (2.11a)$$

$$C_\lambda^\dagger = C_{0\lambda}^\dagger + C_{1\lambda}^\dagger + \dots + C_{m\lambda}^\dagger, \quad (2.11b)$$

where  $A_{0\kappa}^\dagger, C_{0\lambda}^\dagger \sim 1, A_{1\kappa}^\dagger, C_{1\lambda}^\dagger \sim \epsilon, \dots$ , such that the Hamiltonian commutator equations are satisfied to order  $\epsilon^m$ ; that is

$$[\mathcal{H}, A_\kappa^\dagger] = \omega_\kappa A_\kappa^\dagger + 0(\epsilon^{m+1}), \quad (2.12a)$$

$$[\mathcal{H}, C_\lambda^\dagger] = \omega_\lambda C_\lambda^\dagger + 0(\epsilon^{m+1}), \quad (2.12b)$$

with  $\omega_\kappa, \omega_\lambda$  real positive numbers. The notation  $0(\epsilon^m)$  stands for a quantity of order  $\epsilon^m$ . From (2.12) we know that if  $\psi$  is an mth-order-correct eigenfunction of  $\mathcal{H}$ , with energy  $E$ , then  $A_\kappa^\dagger \psi, C_\lambda^\dagger \psi$  are also mth-order eigenfunctions of  $\mathcal{H}$ , with energies  $E + \omega_\kappa, E + \omega_\lambda$ , respectively. The possibility  $A_\kappa^\dagger \psi = 0$  or  $C_\lambda^\dagger \psi = 0$  is ruled out because these analytic functions are not zero when  $\epsilon = 0$ . Thus the mth-order eigenvectors of  $\mathcal{H}$  are

$$\begin{aligned} & |\dots n_\kappa \dots n_\lambda \dots (m)\rangle \\ & = \prod_\kappa (n_\kappa!)^{-1/2} (A_\kappa^\dagger)^{n_\kappa} \prod_\lambda (C_\lambda^\dagger)^{n_\lambda} |0(m)\rangle, \end{aligned} \quad (2.13)$$

where  $|0(m)\rangle$  is the mth-order-correct ground state. In addition, these are all of the mth-order eigenvectors, since the set is in a one-to-one correspondence with the complete zeroth-order set.

Regarding orthonormality, we expect that different vectors of the set (2.13) are orthogonal to order  $\epsilon^m$ , even if they represent degenerate states, since they are obtained as perturbation corrections to completely specified orthogonal zeroth-order states. The vectors may not be properly normalized, however, the error being possibly of order  $\epsilon$ . Thus, it should always be possible to satisfy the appropriate particle commutators and anticommutators; we take these as a further con-

<sup>6</sup> P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, England, 1947), 3rd ed.

dition to be satisfied by the  $m$ th-order operators:

$$\begin{aligned} [A_\kappa, A_{\kappa'}] &= 0(\epsilon^{m+1}), & [A_\kappa, A_{\kappa'}^\dagger] &= \delta_{\kappa\kappa'} + 0(\epsilon^{m+1}); \\ [C_\lambda, C_{\lambda'}] &= 0(\epsilon^{m+1}), & [C_\lambda, C_{\lambda'}^\dagger] &= \delta_{\lambda\lambda'} + 0(\epsilon^{m+1}); \end{aligned} \quad (2.14)$$

$[A_\kappa, C_\lambda]$  and  $[A_\kappa, C_\lambda^\dagger]$  are of order  $\epsilon^{m+1}$ .

If (2.12) and (2.14) are satisfied, it follows directly that the eigenvectors (2.13) are orthonormal to order  $m$  and the Hamiltonian is diagonal to order  $m$ :

$$\begin{aligned} \langle \cdots n_\kappa' \cdots n_\lambda' \cdots (m) | \cdots n_\kappa \cdots n_\lambda \cdots (m) \rangle \\ = \prod_\kappa \delta(n_\kappa', n_\kappa) \prod_\lambda \delta(n_\lambda', n_\lambda) + 0(\epsilon^{m+1}), \end{aligned} \quad (2.15)$$

$$\mathcal{H} = G(m) + \sum_\kappa \omega_\kappa A_\kappa^\dagger A_\kappa + \sum_\lambda \omega_\lambda C_\lambda^\dagger C_\lambda + 0(\epsilon^{m+1}), \quad (2.16)$$

where  $G(m)$  is the  $m$ th-order-correct ground-state energy, given also by

$$G(m) = G_0 + G_1 + \cdots + G_m. \quad (2.17)$$

It also follows that the conditions

$$A_\kappa |0(m)\rangle = 0(\epsilon^{m+1}), \quad C_\lambda |0(m)\rangle = 0(\epsilon^{m+1}); \quad (2.18)$$

$$\langle 0(m) | 0(m) \rangle = 1 + 0(\epsilon^{m+1}) \quad (2.19)$$

are necessarily satisfied by the normalized  $m$ th-order ground state  $|0(m)\rangle$ , and further that these conditions determine the state uniquely. In order to prove the necessity of (2.18), take the Hermitian conjugate of (2.12) to get

$$[\mathcal{H}, A_\kappa] = -\omega_\kappa A_\kappa + 0(\epsilon^{m+1}), \quad (2.20a)$$

$$[\mathcal{H}, C_\lambda] = -\omega_\lambda C_\lambda + 0(\epsilon^{m+1}). \quad (2.20b)$$

Thus to order  $\epsilon^m$ , if  $|0(m)\rangle$  is an eigenstate of  $\mathcal{H}$  with energy  $G(m)$ , then either  $A_\kappa |0(m)\rangle$  and  $C_\lambda |0(m)\rangle$  are eigenstates with energies  $G(m) - \omega_\kappa$ ,  $G(m) - \omega_\lambda$ , respectively, or else  $A_\kappa |0(m)\rangle = 0$  and  $C_\lambda |0(m)\rangle = 0$ . Since  $G(m)$  is the lowest energy and  $\omega_\kappa, \omega_\lambda$  are positive, the second alternative must hold. To show that (2.18) and (2.19) determine  $|0(m)\rangle$ , start with  $m=1$  and write the first-order-correct ground state  $|0(1)\rangle$  as  $|0(0)\rangle + |g_1\rangle$ , where  $|g_1\rangle \sim \epsilon$ . The zeroth-order equations are satisfied, according to (2.5). The first-order equations are

$$A_{0\kappa} |g_1\rangle + A_{1\kappa} |0(0)\rangle = 0, \quad (2.21a)$$

$$C_{0\lambda} |g_1\rangle + C_{1\lambda} |0(0)\rangle = 0, \quad (2.21b)$$

and for normalization

$$\langle 0(0) | g_1 \rangle + \langle g_1 | 0(0) \rangle = 0. \quad (2.22)$$

Equations (2.21) determine the product of every  $\langle \cdots n_\kappa \cdots n_\lambda \cdots (0) |$ , except  $\langle \cdots 0_\kappa \cdots 0_\lambda \cdots (0) |$ , with  $|g_1\rangle$ , in terms of the matrix elements of  $A_{1\kappa}, C_{1\lambda}$  in the zeroth-order representation. Then (2.22) determines the product of  $\langle 0(0) |$  with  $|g_1\rangle$ , so that  $|g_1\rangle$  is determined. This procedure can now be carried out for terms of order  $\epsilon^2, \cdots, \epsilon^m$ , to show that  $|0(m)\rangle$  is determined by the conditions (2.18) and (2.19).

If the problem is solved to order  $m$ , that is, if (2.12) and (2.14) are satisfied, the particle energies are of the

form

$$\omega_\kappa = \omega_{0\kappa} + \omega_{1\kappa} + \cdots + \omega_{m\kappa}, \quad (2.23a)$$

$$\omega_\lambda = \omega_{0\lambda} + \omega_{1\lambda} + \cdots + \omega_{m\lambda}, \quad (2.23b)$$

where  $\omega_{1\kappa} \sim \epsilon \omega_{0\kappa}$ ,  $\omega_{1\lambda} \sim \epsilon \omega_{0\lambda}$ , and so on. It is possible to calculate the next higher order contributions to the particle energies, namely  $\omega_{m+1,\kappa}$  and  $\omega_{m+1,\lambda}$ , without finding the  $(m+1)$ th-order contributions to the creation operators. Let us carry out this calculation first for the boson energies.

With  $A_\kappa^\dagger$  given by (2.11a), assume that  $A_{m+1,\kappa}^\dagger$  exists such that

$$\begin{aligned} [\mathcal{H}, A_\kappa^\dagger + A_{m+1,\kappa}^\dagger] \\ = (\omega_\kappa + \omega_{m+1,\kappa})(A_\kappa^\dagger + A_{m+1,\kappa}^\dagger) + 0(\epsilon^{m+2}). \end{aligned} \quad (2.24)$$

In view of (2.12a), the terms of order  $0, 1, \cdots, m$  in this equation are already satisfied; the  $(m+1)$ -order terms are

$$\begin{aligned} [\mathcal{H}_0, A_{m+1,\kappa}^\dagger] + [\mathcal{H}_1, A_{m\kappa}^\dagger] + \cdots + [\mathcal{H}_{m+1}, A_{0\kappa}^\dagger] \\ = \omega_{0\kappa} A_{m+1,\kappa}^\dagger + \omega_{1\kappa} A_{m\kappa}^\dagger + \cdots + \omega_{m+1,\kappa} A_{0\kappa}^\dagger. \end{aligned} \quad (2.25)$$

This operator equation may be evaluated in any representation; we evaluate it in the zeroth-order representation. In particular, if we take the matrix element  $\langle \cdots n_\kappa + 1 \cdots n_\lambda \cdots (0) |$  Eq. (2.25)  $| \cdots n_\kappa \cdots n_\lambda \cdots (0) \rangle$ , the terms containing  $A_{m+1,\kappa}^\dagger$  cancel. Then, treating  $\omega_{m+1,\kappa}$  as a number, we find from (2.25)

$$\begin{aligned} \langle \cdots n_\kappa + 1 \cdots n_\lambda \cdots (0) | [\mathcal{H}_1, A_{m\kappa}^\dagger] \\ + [\mathcal{H}_2, A_{m-1,\kappa}^\dagger] + \cdots + [\mathcal{H}_{m+1}, A_{0\kappa}^\dagger] \\ - \omega_{1\kappa} A_{m\kappa}^\dagger - \omega_{2\kappa} A_{m-1,\kappa}^\dagger - \cdots \\ - \omega_{m\kappa} A_{1\kappa}^\dagger | \cdots n_\kappa \cdots n_\lambda \cdots (0) \rangle \\ = (n_\kappa + 1)^{1/2} \omega_{m+1,\kappa}. \end{aligned} \quad (2.26)$$

The same procedure goes through for fermions, where the matrix elements are further restricted to

$$\langle \cdots n_\kappa \cdots 1_\lambda \cdots (0) | \text{Equation} | \cdots n_\kappa \cdots 0_\lambda \cdots (0) \rangle.$$

The result is

$$\begin{aligned} \langle \cdots n_\kappa \cdots 1_\lambda \cdots (0) | [\mathcal{H}_1, C_{m\lambda}^\dagger] \\ + [\mathcal{H}_2, C_{m-1,\lambda}^\dagger] + \cdots + [\mathcal{H}_{m+1}, C_{0\lambda}^\dagger] \\ - \omega_{1\lambda} C_{m\lambda}^\dagger - \omega_{2\lambda} C_{m-1,\lambda}^\dagger - \cdots \\ - \omega_{m\lambda} C_{1\lambda}^\dagger | \cdots n_\kappa \cdots 0_\lambda \cdots (0) \rangle \\ = (-1)^{p_\lambda} \omega_{m+1,\lambda}. \end{aligned} \quad (2.27)$$

Equations (2.26) and (2.27) are useful tools of the present theory. If the problem is solvable to order  $m+1$ , in terms of particles with the quantum numbers  $\kappa, \lambda$ , then these equations give the correct  $(m+1)$ th-order contributions to the particle energies, without requiring the  $(m+1)$ th-order solutions. If the energies so calculated are numbers, independent of the state vectors in the matrix elements, then it is probable that the problem is indeed solvable to order  $m+1$  in terms of such particles. On the other hand, if the energies so calculated depend on the state vectors in the matrix

elements, then it is certain that the operators  $A_{m+1,\kappa}^\dagger$ ,  $C_{m+1,\lambda}^\dagger$  do not exist such as to satisfy the  $(m+1)$ th-order Hamiltonian commutator equations [Eq. (2.24) and its counterpart for  $C_\lambda^\dagger$ ]. This situation is illustrated in the problems which are treated in Secs. IV and V below.

### C. Interpretation of Higher Order Energies

Regardless of the form of  $\omega_{m+1,\kappa}$ ,  $\omega_{m+1,\lambda}$ , Eqs. (2.26) and (2.27) give the same result as Rayleigh-Schrödinger perturbation theory for the  $(m+1)$ th-order contribution to the energy difference between the appropriate states. To prove this, we assume that (2.12) and (2.14) are satisfied, so that the eigenstates are given by the  $m$ th-order occupation number representation (2.13), and derive (2.26) and (2.27) from Rayleigh-Schrödinger theory. The derivation is lengthy, so we merely sketch it here for bosons only.

Let  $E(\cdots n_\kappa \cdots (m))$  be the energy of the state  $|\cdots n_\kappa \cdots (m)\rangle$ , and let  $E_{m+1}(\cdots n_\kappa \cdots)$  be the  $(m+1)$ th-order contribution to the energy of the  $(m+1)$ th-order state which is derived from  $|\cdots n_\kappa \cdots (m)\rangle$ . Then, requiring the Schrödinger equation be satisfied and requiring normalization, to order  $m+1$ , leads to the equation

$$\begin{aligned} \langle \cdots n_\kappa \cdots (m) | \mathcal{H} - E(\cdots n_\kappa \cdots (m)) | \cdots n_\kappa \cdots (m) \rangle \\ = E_{m+1}(\cdots n_\kappa \cdots) + 0(\epsilon^{m+2}). \end{aligned}$$

Now write this equation over for  $n_\kappa+1$  to give an equation for  $E_{m+1}(\cdots n_\kappa+1 \cdots) - E_{m+1}(\cdots n_\kappa \cdots)$ . Then use the properties of the  $m$ th-order solution:

$$\begin{aligned} |\cdots n_\kappa+1 \cdots (m)\rangle &= (n_\kappa+1)^{-1/2} A_\kappa^\dagger |\cdots n_\kappa \cdots (m)\rangle, \\ \langle \cdots n_\kappa \cdots (m) | &= (n_\kappa+1)^{-1/2} \langle \cdots n_\kappa+1 \cdots (m) | A_\kappa^\dagger, \\ E(\cdots n_\kappa+1 \cdots (m)) &= E(\cdots n_\kappa \cdots (m)) + \omega_\kappa, \end{aligned}$$

where  $A_\kappa^\dagger$ ,  $A_\kappa$ ,  $\omega_\kappa$  only contain terms to order  $m$ , according to (2.11) and (2.23). This leads to the equation

$$\begin{aligned} E_{m+1}(\cdots n_\kappa+1 \cdots) - E_{m+1}(\cdots n_\kappa \cdots) + 0(\epsilon^{m+2}) \\ = (n_\kappa+1)^{-1/2} \langle \cdots n_\kappa+1 \cdots (m) | [\mathcal{H}, A_\kappa^\dagger] \\ - \omega_\kappa A_\kappa^\dagger | \cdots n_\kappa \cdots (m) \rangle. \end{aligned}$$

In view of the  $m$ th-order solution, the operator in the matrix element here vanishes for terms of order  $0, 1, \dots, m$ . Thus, equating  $(m+1)$ th-order terms in this equation picks out  $(m+1)$ th-order terms in the operator and zeroth-order terms in the vectors, and establishes the relation

$$\omega_{m+1,\kappa} = E_{m+1}(\cdots n_\kappa+1 \cdots) - E_{m+1}(\cdots n_\kappa \cdots), \quad (2.28)$$

where  $\omega_{m+1,\kappa}$  is given by (2.26). Similarly, for fermions we find

$$\omega_{m+1,\lambda} = E_{m+1}(\cdots 1_\lambda \cdots) - E_{m+1}(\cdots 0_\lambda \cdots), \quad (2.29)$$

where  $\omega_{m+1,\lambda}$  is given by (2.27).

In deriving (2.28) and (2.29), we have assumed that  $\mathcal{H}$  can be diagonalized to order  $m$ , *but not necessarily to order  $m+1$* , in terms of particles with quantum numbers  $\kappa, \lambda$ . These equations thus provide the interpretation that  $\omega_\kappa, \omega_\lambda$  are creation energies for fundamental excitations of the system to one order higher than the order to which interactions can be removed between these excitations. This is, of course, equivalent to diagonalizing  $\mathcal{H}$  to order  $m$  and using first-order perturbation to calculate  $(m+1)$ th-order energy differences.

Now if (2.12) and (2.14) are satisfied, with  $\omega_\kappa, \omega_\lambda$  real to order  $m$ , then (2.28) and (2.29) show that  $\omega_{m+1,\kappa}$  and  $\omega_{m+1,\lambda}$  are real and the states are stationary to order  $m+1$ . However, in carrying out the renormalization procedure in real problems, we have to introduce complex energies to avoid certain divergences (see Secs. IV and V below). Indeed, we find, as one would expect, that if the interactions between particles cannot be removed in order  $m+1$ , then  $\omega_{m+1,\kappa}, \omega_{m+1,\lambda}$  are complex. Let us take  $\mathcal{H}$  to be independent of time, set  $\hbar=1$ , and use the Heisenberg equation of motion to calculate the time derivative of the  $m$ th-order propagation operators.

$$(d/dt)A_\kappa(t)A_\kappa^\dagger(0) = i[\mathcal{H}, A_\kappa(t)]A_\kappa^\dagger(0), \quad (2.30)$$

where the time argument is in parentheses. Diagonal elements of (2.30) can be evaluated to order  $m+1$  in the  $(m+1)$ th-order representation by using (2.20a) and (2.26); the result is

$$\begin{aligned} i[\mathcal{H}, A_\kappa(t)]A_\kappa^\dagger(0) \\ = -i(\omega_\kappa + \omega_{m+1,\kappa}^*)A_\kappa(t)A_\kappa^\dagger(0) + 0(\epsilon^{m+2}). \end{aligned} \quad (2.31)$$

Integration of (2.30) then gives, to order  $m+1$ ,

$$\begin{aligned} A_\kappa(t)A_\kappa^\dagger(0) \\ = \exp[-i(\omega_\kappa + \omega_{m+1,\kappa}^*)t]A_\kappa(0)A_\kappa^\dagger(0). \end{aligned} \quad (2.32)$$

The same procedure goes for the fermion operators:

$$C_\lambda(t)C_\lambda^\dagger(0) = \exp[-i(\omega_\lambda + \omega_{m+1,\lambda}^*)t]C_\lambda(0)C_\lambda^\dagger(0). \quad (2.33)$$

Thus if a particle is created at  $t=0$ , the state has an attenuation constant of  $-\text{Im}\omega_{m+1,\kappa}^*$  or  $-\text{Im}\omega_{m+1,\lambda}^*$ . Similarly, if a particle is destroyed at  $t=0$ , the state has an attenuation constant of  $\text{Im}\omega_{m+1,\kappa}$  or  $\text{Im}\omega_{m+1,\lambda}$ .

Note that (2.32) and (2.33) are *diagonal* representations; this is appropriate for calculating state lifetimes.

A final remark is in order here. It is a well-known result of Rayleigh-Schrödinger perturbation theory that if the eigenvectors of  $\mathcal{H}$  are found to  $\epsilon^m$ , the eigenvalues of  $\mathcal{H}$  can be calculated to order  $\epsilon^{2m+1}$ . It is not our intention to use this result in the present work; we simply wish to calculate the particle-creation energies to one order higher than we find the particle-creation operators.

### D. Statistical Mechanics

We wish to obtain an expression for the partition function  $Z$  which is correct to order  $m+1$ , if the problem is solved to order  $m$ . Thus we evaluate

$$Z = \text{Tr} e^{-\beta \mathcal{H}} \quad (2.34)$$

in the  $(m+1)$ th-order representation of  $\mathcal{H}$ ; here  $\beta = (KT)^{-1}$ . The eigenvalues of  $\mathcal{H}$  follow from the  $m$ th-order solution as discussed above:

$$E(\cdots n_\kappa \cdots n_\lambda \cdots) = G(m) + \sum_\kappa n_\kappa \omega_\kappa + \sum_\lambda n_\lambda \omega_\lambda + E_{m+1}(\cdots n_\kappa \cdots n_\lambda \cdots) + O(\epsilon^{m+2}). \quad (2.35)$$

Here  $E(\cdots n_\kappa \cdots n_\lambda \cdots)$  is the energy of the state which is derived from the zeroth-order state  $|\cdots n_\kappa \cdots n_\lambda \cdots(0)\rangle$ ;  $G(m)$  is the  $m$ th-order-correct ground-state energy;  $\omega_\kappa$  and  $\omega_\lambda$  are the  $m$ th-order-correct creation energies of the form of (2.23), and  $E_{m+1}(\cdots n_\kappa \cdots n_\lambda \cdots)$  is the  $(m+1)$ th-order contribution to the energy of the state.  $E_{m+1}$  is a function of the  $\omega_{m+1,\kappa}$  and  $\omega_{m+1,\lambda}$ , but is not necessarily of the form  $\sum_\kappa n_\kappa \omega_{m+1,\kappa} + \sum_\lambda n_\lambda \omega_{m+1,\lambda}$ ; this circumstance is made clear in the examples of Secs. IV and V. The partition function is conveniently calculated by expanding the exponential for  $E_{m+1}$  contributions small compared to  $E(m)$  contributions; the result is

$$Z = Z(m)[1 - \beta \bar{E}_{m+1}] + O(\epsilon^{m+2}), \quad (2.36)$$

where  $Z(m)$  is the  $m$ th-order-correct partition function, calculated from the  $m$ th-order-correct energies  $E(m)$ , and  $\bar{E}_{m+1}$  is the statistical average of the  $(m+1)$ th-order contributions to the system energy levels.

The Helmholtz free energy is defined by

$$F = -\beta^{-1} \ln Z. \quad (2.37)$$

From (2.36),  $F$  is given correct to order  $m+1$  according to

$$F = F(m) + \bar{E}_{m+1}. \quad (2.38)$$

Finally, let us add  $G_{m+1}$ , the  $(m+1)$ th-order contribution to the ground-state energy, to  $F(m)$ , subtract the same from  $\bar{E}_{m+1}$ , and write out the boson and fermion contributions to  $F(m)$ .

$$F = G(m+1) + \beta^{-1} \sum_\kappa \ln[1 - \exp(-\beta \omega_\kappa)] - \beta^{-1} \sum_\lambda \ln[1 + \exp(-\beta \omega_\lambda)] + (\bar{E}_{m+1} - G_{m+1}). \quad (2.39)$$

This is a particularly useful form to use in conjunction with the present theory. The renormalization procedure gives directly the excitation energies, and hence  $\omega_\kappa$ ,  $\omega_\lambda$ , and contributions to  $(E_{m+1} - G_{m+1})$  in the form of  $\omega_{m+1,\kappa}$ ,  $\omega_{m+1,\lambda}$ . Thus the temperature-dependent part of the free energy is easily calculated. In addition, since  $(\bar{E}_{m+1} - G_{m+1})$  is of order  $m+1$ , a zeroth-order average may be used in computing this quantity to order  $m+1$ .

### III. ILLUSTRATIVE FIRST-ORDER CALCULATIONS

#### A. Many-Boson System

The problem is defined by the Hamiltonian and the boson commutators:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \cdots; \quad \mathcal{H}_0 = G_0 + \sum_\kappa \omega_{0\kappa} A_{0\kappa}^\dagger A_{0\kappa}; \quad (3.1)$$

$$[A_{0\kappa}, A_{0\kappa'}] = 0, \quad [A_{0\kappa}, A_{0\kappa'}^\dagger] = \delta_{\kappa\kappa'}. \quad (3.2)$$

The form of  $\mathcal{H}_1$  need not be specified here, except that  $\mathcal{H}_1^\dagger = \mathcal{H}_1$ .

From (2.26), the first-order energy corrections are given by

$$\langle \cdots n_\kappa + 1 \cdots(0) | [\mathcal{H}_1, A_{0\kappa}^\dagger] | \cdots n_\kappa \cdots(0) \rangle = (n_\kappa + 1)^{1/2} \omega_{1\kappa}. \quad (3.3)$$

With  $\omega_{1\kappa}$  given by (3.3), assume that we can find first-order operators  $A_{1\kappa}^\dagger$  such that the Hamiltonian commutator equations and the boson commutator equations are satisfied to first order. That is,

$$[\mathcal{H}, A_{1\kappa}^\dagger] = \omega_{1\kappa} A_{1\kappa}^\dagger + O(\epsilon^2); \quad (3.4)$$

$$[A_{1\kappa}, A_{1\kappa'}] = 0, \quad [A_{1\kappa}, A_{1\kappa'}^\dagger] = \delta_{\kappa\kappa'} + O(\epsilon^2), \quad (3.5)$$

with

$$A_{1\kappa}^\dagger = A_{0\kappa}^\dagger + A_{1\kappa}^\dagger, \quad \omega_{1\kappa} = \omega_{0\kappa} + \omega_{1\kappa}. \quad (3.6)$$

The zeroth-order terms in (3.4), (3.5) are satisfied; equating first-order terms gives the following requirements for  $A_{1\kappa}^\dagger$ :

$$[\mathcal{H}_0, A_{1\kappa}^\dagger] + [\mathcal{H}_1, A_{0\kappa}^\dagger] = \omega_{0\kappa} A_{1\kappa}^\dagger + \omega_{1\kappa} A_{0\kappa}^\dagger; \quad (3.7)$$

$$[A_{0\kappa}, A_{1\kappa'}] + [A_{1\kappa}, A_{0\kappa'}] = 0,$$

$$[A_{0\kappa}, A_{1\kappa'}^\dagger] + [A_{1\kappa}, A_{0\kappa'}^\dagger] = 0. \quad (3.8)$$

If (3.7) and (3.8) are satisfied, then  $\mathcal{H}$  is diagonal to first order in terms of the renormalized creation and annihilation operators. We can carry out a direct proof as follows. Define  $\tilde{\mathcal{H}}$  as

$$\tilde{\mathcal{H}} = G_0 + \sum_\kappa (\omega_{0\kappa} + \omega_{1\kappa}) (A_{0\kappa}^\dagger + A_{1\kappa}^\dagger) (A_{0\kappa} + A_{1\kappa}). \quad (3.9)$$

Then

$$\mathcal{H} - \tilde{\mathcal{H}} = \mathcal{H}_1 - \tilde{\mathcal{H}}_1 + O(\epsilon^2), \quad (3.10)$$

where

$$\tilde{\mathcal{H}}_1 = \sum_\kappa [\omega_{1\kappa} A_{0\kappa}^\dagger A_{0\kappa} + \omega_{0\kappa} (A_{0\kappa}^\dagger A_{1\kappa} + A_{1\kappa}^\dagger A_{0\kappa})]. \quad (3.11)$$

A short calculation, with the aid of (3.1), (3.2), and (3.8), yields

$$[\mathcal{H}_1 - \tilde{\mathcal{H}}_1, A_{0\kappa}^\dagger] = [\mathcal{H}_1, A_{0\kappa}^\dagger] + [\mathcal{H}_0, A_{1\kappa}^\dagger] - \omega_{1\kappa} A_{0\kappa}^\dagger - \omega_{0\kappa} A_{1\kappa}^\dagger.$$

But this vanishes by (3.7). Similarly, since  $\mathcal{H}_1$  and  $\tilde{\mathcal{H}}_1$  are Hermitian,  $[\mathcal{H}_1 - \tilde{\mathcal{H}}_1, A_{0\kappa}]$  vanishes. Thus, by the lemma of Sec. IIA above,  $\mathcal{H}_1 - \tilde{\mathcal{H}}_1$  is a number; this number is of order  $\epsilon$  and is presumably  $G_1$ , the first-order contribution to the ground-state energy. We can then write

$$\mathcal{H} = \tilde{\mathcal{H}} + G_1 + O(\epsilon^2). \quad (3.12)$$

There is still some arbitrariness in the  $A_{1\kappa}^\dagger$  operators. Any operator  $B_{1\kappa}^\dagger$  can be added to  $A_{1\kappa}^\dagger$ , and (3.7) and (3.8) will still be satisfied if

$$\begin{aligned} [\mathcal{H}_0, B_{1\kappa}^\dagger] &= \omega_{0\kappa} B_{1\kappa}^\dagger; \\ [A_{0\kappa}, B_{1\kappa'}^\dagger] + [B_{1\kappa}, A_{0\kappa'}] &= 0, \\ [A_{0\kappa}, B_{1\kappa'}^\dagger] + [B_{1\kappa}, A_{0\kappa'}^\dagger] &= 0. \end{aligned} \quad (3.13)$$

The conditions (3.13) are satisfied by  $B_{1\kappa}^\dagger$  of the forms

$$\begin{aligned} B_{1\kappa}^\dagger &= i\bar{b}_\kappa A_{0\kappa}^\dagger, \\ B_{1\kappa}^\dagger &= iA_{0\kappa}^\dagger \sum_{\kappa'} \bar{b}_{\kappa\kappa'} A_{0\kappa'}^\dagger, \end{aligned} \quad (3.14)$$

and so forth, where  $\bar{b}_\kappa, \bar{b}_{\kappa\kappa'}$  are real numbers of order  $\epsilon$ , with  $\bar{b}_{\kappa\kappa'} = \bar{b}_{\kappa'\kappa}$ . Such arbitrariness in the first-order creation operators does not affect the  $\omega_{1\kappa}$ , of course, since  $\omega_{1\kappa}$  is independent of  $A_{1\kappa}^\dagger$  according to (3.3). In addition, the operators  $B_{1\kappa}^\dagger$  of the forms (3.14) give zero contribution to  $\mathcal{H}_1$  of (3.11), and hence give no contribution to the ground-state energy and do not change the relation (3.12).

### B. Many-Fermion System

The problem is defined by the Hamiltonian and the fermion anticommutators:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \dots; \quad \mathcal{H}_0 = G_0 + \sum_\lambda \omega_{0\lambda} C_{0\lambda}^\dagger C_{0\lambda}; \quad (3.15)$$

$$[C_{0\lambda}, C_{0\lambda'}]_+ = 0, \quad [C_{0\lambda}, C_{0\lambda'}^\dagger]_+ = \delta_{\lambda\lambda'}. \quad (3.16)$$

The first-order energy corrections are given by

$$\begin{aligned} \langle \dots 1_\lambda \dots (0) | [\mathcal{H}_1, C_{0\lambda}^\dagger] | \dots 0_\lambda \dots (0) \rangle \\ = (-1)^{p_\lambda} \omega_{1\lambda}. \end{aligned} \quad (3.17)$$

The first-order operators  $C_{1\lambda}^\dagger$  are now required to satisfy the counterparts of (3.7) and (3.8):

$$[\mathcal{H}_0, C_{1\lambda}^\dagger] + [\mathcal{H}_1, C_{0\lambda}^\dagger] = \omega_{0\lambda} C_{1\lambda}^\dagger + \omega_{1\lambda} C_{0\lambda}^\dagger; \quad (3.18)$$

$$\begin{aligned} [C_{0\lambda}, C_{1\lambda'}^\dagger] + [C_{1\lambda}, C_{0\lambda'}] &= 0, \\ [C_{0\lambda}, C_{1\lambda'}^\dagger] + [C_{1\lambda}, C_{0\lambda'}^\dagger] &= 0. \end{aligned} \quad (3.19)$$

With the aid of these equations we can show that  $\mathcal{H} - \mathcal{H}_0$  commutes, to order  $\epsilon$ , with all the  $C_{0\lambda}, C_{0\lambda}^\dagger$ , where  $\mathcal{H}$  is analogous to (3.9). Thus  $\mathcal{H} - \mathcal{H}_0$  is a number of order  $\epsilon$ , and  $\mathcal{H}$  can be written

$$\begin{aligned} \mathcal{H} &= (G_0 + G_1) + \sum_\lambda (\omega_{0\lambda} + \omega_{1\lambda}) \\ &\quad \times (C_{0\lambda}^\dagger + C_{1\lambda}^\dagger)(C_{0\lambda} + C_{1\lambda}) + O(\epsilon^2). \end{aligned} \quad (3.20)$$

Also the  $C_{1\lambda}^\dagger$  are arbitrary to an additive operator of the form  $i d_\lambda C_{0\lambda}^\dagger$  with  $d_\lambda$  a real number of order  $\epsilon$ ; this arbitrariness is merely an eigenvector phase factor.

### C. Comparison with Other Methods

#### Rayleigh-Schrödinger Perturbation Theory

In any problem where perturbation theory is valid, any method must reproduce the Rayleigh-Schrödinger energy levels. We have already shown in Sec. IIC that the present method gives the same result as Rayleigh-

Schrödinger for the difference between system energy levels. A particularly simple illustration of this theorem is the first-order examples treated above. Operating with the  $A_{0\kappa}^\dagger$  in (3.3), or with the  $C_{0\lambda}^\dagger$  in (3.17), gives the ordinary first-order equations for energy differences:

$$\begin{aligned} \omega_{1\kappa} &= \langle \dots n_\kappa + 1 \dots (0) | \mathcal{H}_1 | \dots n_\kappa + 1 \dots (0) \rangle \\ &\quad - \langle \dots n_\kappa \dots (0) | \mathcal{H}_1 | \dots n_\kappa \dots (0) \rangle, \end{aligned} \quad (3.21a)$$

$$\begin{aligned} \omega_{1\lambda} &= \langle \dots 1_\lambda \dots (0) | \mathcal{H}_1 | \dots 1_\lambda \dots (0) \rangle \\ &\quad - \langle \dots 0_\lambda \dots (0) | \mathcal{H}_1 | \dots 0_\lambda \dots (0) \rangle. \end{aligned} \quad (3.21b)$$

We have also shown that the conditions (2.18), (2.19) determine the  $m$ th-order ground state uniquely. Let us take the many-boson example and show that the first-order ground state so determined is just the Rayleigh-Schrödinger first-order ground state. The conditions (2.18) are

$$(A_{0\kappa} + A_{1\kappa}) | 0(1) \rangle = 0(\epsilon^2). \quad (3.22)$$

Write the first-order-correct ground state  $| 0(1) \rangle$  as  $| 0(0) \rangle + | g_1 \rangle$ ; the zeroth-order conditions  $A_{0\kappa} | 0(0) \rangle = 0$  are presumed to be satisfied and the first-order terms in (3.22) are

$$A_{0\kappa} | g_1 \rangle + A_{1\kappa} | 0(0) \rangle = 0. \quad (3.23)$$

Now take the Hermitian conjugate of (3.7) to get

$$[\mathcal{H}_0, A_{1\kappa}] + [\mathcal{H}_1, A_{0\kappa}] = -\omega_{0\kappa} A_{1\kappa} - \omega_{1\kappa} A_{0\kappa}. \quad (3.24)$$

Operate with (3.24) on  $| 0(0) \rangle$ , use (3.23), and take the product with  $\langle \dots n_\kappa \dots (0) |$  to get

$$\begin{aligned} \langle \dots n_\kappa \dots (0) | (G_0 - \omega_{0\kappa} - \mathcal{H}_0) A_{0\kappa} | g_1 \rangle \\ = \langle \dots n_\kappa \dots (0) | A_{0\kappa} \mathcal{H}_1 | 0(0) \rangle. \end{aligned} \quad (3.25)$$

Then operate with  $\mathcal{H}_0$  and  $A_{0\kappa}$  on  $\langle \dots n_\kappa \dots (0) |$  to produce  $\langle \dots n_\kappa + 1 \dots (0) |$ , and finally obtain the equation

$$\begin{aligned} \langle \dots n_\kappa + 1 \dots (0) | g_1 \rangle \\ = \frac{\langle \dots n_\kappa + 1 \dots (0) | \mathcal{H}_1 | 0(0) \rangle}{G_0 - E(\dots n_\kappa + 1 \dots (0))}. \end{aligned} \quad (3.26)$$

Equations (3.26) for all  $\langle \dots n_\kappa + 1 \dots (0) |$ , along with the normalization conditions, determine  $| g_1 \rangle$  to be just the Rayleigh-Schrödinger first-order correction to the ground state.<sup>7</sup>

#### Random-Phase Approximation

In this method<sup>1-4</sup> the procedure is to linearize the equation of motion for a creation operator, say  $A_{0\kappa}^\dagger$ . In the Heisenberg picture, with  $\hbar = 1$ , this equation is

$$(d/dt) A_{0\kappa}^\dagger = i[\mathcal{H}, A_{0\kappa}^\dagger]. \quad (3.27)$$

For a perturbation problem we have  $[\mathcal{H}_0, A_{0\kappa}^\dagger] = \omega_{0\kappa} A_{0\kappa}^\dagger$ , and (3.27) to first order is

$$(d/dt) A_{0\kappa}^\dagger = i\omega_{0\kappa} A_{0\kappa}^\dagger + i[\mathcal{H}_1, A_{0\kappa}^\dagger]. \quad (3.28)$$

<sup>7</sup> See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed.

Now the linearization procedure consists of picking terms out of the right-hand side which contain an  $A_{0\kappa}^\dagger$ , and replacing the operators which multiply the  $A_{0\kappa}^\dagger$  by an expectation value (matrix element or statistical average). This is equivalent to calculating  $\omega_{1\kappa}$  according to (3.3), or  $\omega_{1\lambda}$  according to (3.17). We remark that, for perturbation problems, the present work provides a derivation of this linearization procedure, and also provides detailed interpretation of the creation energies so obtained.

#### Thermodynamic Green's-Function Method

Perhaps the most direct procedure is to compare our renormalized energies with the self-energies of the Green's-function method. For a perturbation problem, the  $\omega_{1\kappa}$  and  $\omega_{1\lambda}$  of (3.3) and (3.17), respectively, are the same as first-order Hartree-Fock results.<sup>4</sup> But the first-order Hartree-Fock energies have been shown to be the same as the first-order contribution to the temperature-independent self-energies,<sup>8</sup> and the statistical averages of the first-order Hartree-Fock energies have been shown to be the same as the first-order contribution to the temperature-dependent self-energies.<sup>9</sup> Thus in first-order we recover the temperature-dependent energy shifts of the thermodynamic Green's-function method by taking statistical averages of  $\omega_{1\kappa}$ ,  $\omega_{1\lambda}$ .

In the following two sections we give detailed calculations of renormalized energies to second order; in each case the statistical average of the renormalized energies agrees with the thermodynamic Green's-function self-energies.

### IV. APPLICATION TO ANHARMONIC LATTICE DYNAMICS

#### A. Definition of the Problem

The Hamiltonian is the sum of the kinetic energy KE and the potential energy  $U$ , which are given in terms of the positions and velocities of the ions as follows:

$$\text{KE} = \frac{1}{2} \sum_{n,\rho} M_j (\dot{u}_{n\rho})^2, \quad (4.1)$$

$$U = U_0 + U_2 + U_3 + U_4, \quad (4.2)$$

$$U_2 = \frac{1}{2} \sum_{nn',\rho\rho'} A_{n\rho,n'\rho'} u_{n\rho} u_{n'\rho'}, \quad (4.3)$$

$$U_3 = (1/3!) \sum_{\substack{nn'n'' \\ \rho\rho'\rho''}} B_{n\rho,n'\rho',n''\rho''} u_{n\rho} u_{n'\rho'} u_{n''\rho''}, \quad (4.4)$$

$$U_4 = (1/4!) \sum_{\substack{n \dots n'''' \\ \rho \dots \rho''''}} C_{n\rho,n'\rho',n''\rho'',n'''\rho'''} \times u_{n\rho} u_{n'\rho'} u_{n''\rho''} u_{n'''\rho'''} \quad (4.5)$$

Here  $n$  labels a unit cell,  $j$  an ion in the unit cell,  $i$  is a Cartesian coordinate,  $\rho$  stands for a pair  $(j,i)$ ,  $M_j$  is the mass of an ion of type  $j$ ,  $\mathbf{u}_{nj}$  is the displacement of ion  $(n,j)$  from its equilibrium position, and  $\dot{\mathbf{u}}_{nj}$  is the time derivative of  $\mathbf{u}_{nj}$ . There are  $N$  unit cells in the crystal and  $J$  ions per unit cell.  $U_0$  is the static lattice potential energy, and the  $A$ ,  $B$ , and  $C$  coefficients are defined by (4.3)–(4.5). The definition of the problem is completed by the commutators

$$[M_j \dot{u}_{n\rho}, u_{n'\rho'}] = -i\hbar \delta_{nn'} \delta_{\rho\rho'}, \quad (4.6)$$

$$[u_{n\rho}, u_{n'\rho'}] = [\dot{u}_{n\rho}, \dot{u}_{n'\rho'}] = 0. \quad (4.7)$$

We have taken the trouble to express the problem in the primitive form (4.1)–(4.7) so as to make clear our definitions. Detailed discussion of the diagonalization of  $\mathcal{H}$ , to second order in displacements, may be found in any standard text<sup>10,11</sup>; we outline the transformations below. The traveling-wave operators  $q_{\mathbf{k}s}$  are introduced by the Fourier transform

$$u_{n\rho} = N^{-1/2} \sum_{\mathbf{k},s} q_{\mathbf{k}s} v_{\mathbf{k},\rho s} \exp(i\mathbf{k} \cdot \mathbf{r}_{nj}), \quad (4.8)$$

where  $\mathbf{k}$  are the wave vectors,  $s$  is the polarization index,  $\mathbf{r}_{nj}$  is the equilibrium position of ion  $(n,j)$ , and  $v_{\mathbf{k},\rho s}$  are components of the eigenvectors of the secular equation.<sup>12</sup> The creation and annihilation operators are then defined by

$$q_{\mathbf{k}s} = (\hbar/2M_c \omega_{\mathbf{k}s})^{1/2} (A_{\mathbf{k}s} + A_{-\mathbf{k}s}^\dagger), \quad (4.9)$$

$$\dot{q}_{\mathbf{k}s} = i(\hbar\omega_{\mathbf{k}s}/2M_c)^{1/2} (A_{-\mathbf{k}s}^\dagger - A_{\mathbf{k}s}), \quad (4.10)$$

where  $M_c = \sum_j M_j$ , i.e., the total mass of one unit cell, and  $\omega_{\mathbf{k}s}$  are the traveling-wave frequencies. As a final step we introduce the abbreviation  $\kappa$  for  $(\mathbf{k},s)$ , with  $-\kappa$  for  $(-\mathbf{k},s)$ , and define the following Fourier transforms of the  $B$ ,  $C$  coefficients.

$$\begin{aligned} B_{\kappa\kappa'\kappa''} &= [(1/3!)(\hbar/2NM_c)^{3/2}(\omega_\kappa\omega_{\kappa'}\omega_{\kappa''})^{-1/2}] \\ &\times \sum_{\substack{nn'n'' \\ \rho\rho'\rho''}} B_{n\rho,n'\rho',n''\rho''} v_{\mathbf{k},\rho s} v_{\mathbf{k}',\rho' s'} v_{\mathbf{k}'',\rho'' s''} \\ &\times \exp[i(\mathbf{k} \cdot \mathbf{r}_{nj} + \mathbf{k}' \cdot \mathbf{r}_{n'j'} + \mathbf{k}'' \cdot \mathbf{r}_{n''j''})]; \quad (4.11) \\ C_{\kappa\kappa'\kappa''\kappa'''} &= [(1/4!)(\hbar/2NM_c)^2(\omega_\kappa\omega_{\kappa'}\omega_{\kappa''}\omega_{\kappa'''})^{-1/2}] \\ &\times \sum_{\substack{n \dots n'''' \\ \rho \dots \rho''''}} C_{n\rho,n'\rho',n''\rho'',n'''\rho'''} \\ &\times v_{\mathbf{k},\rho s} v_{\mathbf{k}',\rho' s'} v_{\mathbf{k}'',\rho'' s''} v_{\mathbf{k}''',\rho''' s'''} \\ &\times \exp[i(\mathbf{k} \cdot \mathbf{r}_{nj} + \mathbf{k}' \cdot \mathbf{r}_{n'j'} + \mathbf{k}'' \cdot \mathbf{r}_{n''j''} \\ &\quad + \mathbf{k}''' \cdot \mathbf{r}_{n'''j'''})]. \quad (4.12) \end{aligned}$$

We now introduce a subscript 0 to denote unrenormalized energies  $\hbar\omega_{0\kappa}$  and operators  $A_{0\kappa}^\dagger$  and write

<sup>8</sup> D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

<sup>9</sup> L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

<sup>10</sup> M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Ltd., Oxford, England, 1954).

<sup>11</sup> R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, England, 1955).

<sup>12</sup> See, e.g., D. C. Wallace, *Phys. Rev.* **131**, 2046 (1963).



the statement of the problem in final form

$$\begin{aligned}
\mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2, \\
\mathcal{H}_0 &= G_0 + \sum_{\mathbf{k}} \hbar \omega_{0\mathbf{k}} A_{0\mathbf{k}}^\dagger A_{0\mathbf{k}}, \\
G_0 &= U_0 + \frac{1}{2} \sum_{\mathbf{k}} \hbar \omega_{0\mathbf{k}}, \\
\mathcal{H}_1 &= \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} B_{\mathbf{k}\mathbf{k}'\mathbf{k}''} (A_{0\mathbf{k}} + A_{0-\mathbf{k}}^\dagger) \\
&\quad \times (A_{0\mathbf{k}'} + A_{0-\mathbf{k}'}^\dagger) (A_{0\mathbf{k}''} + A_{0-\mathbf{k}''}^\dagger), \\
\mathcal{H}_2 &= \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} C_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} (A_{0\mathbf{k}} + A_{0-\mathbf{k}}^\dagger) (A_{0\mathbf{k}'} + A_{0-\mathbf{k}'}^\dagger) \\
&\quad \times (A_{0\mathbf{k}''} + A_{0-\mathbf{k}''}^\dagger) (A_{0\mathbf{k}'''} + A_{0-\mathbf{k}'''}^\dagger).
\end{aligned} \tag{4.13}$$

The phonon commutators are

$$\begin{aligned}
[A_{0\mathbf{k}}, A_{0\mathbf{k}'}] &= 0, \\
[A_{0\mathbf{k}}, A_{0\mathbf{k}'}^\dagger] &= \delta_{\mathbf{k}\mathbf{k}'}.
\end{aligned} \tag{4.14}$$

From the derivation of (4.13), it follows that  $\mathcal{H}_0$ ,  $\mathcal{H}_1$ ,  $\mathcal{H}_2$  are each Hermitian, that  $\omega_{0\mathbf{k}} = \omega_{0-\mathbf{k}}$ , and that  $B_{\mathbf{k}\mathbf{k}'\mathbf{k}''}$ ,  $C_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}$  are completely symmetric in their indices, and  $B_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^* = B_{-\mathbf{k}, -\mathbf{k}', -\mathbf{k}''}$ ,  $C_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}^* = C_{-\mathbf{k}, -\mathbf{k}', -\mathbf{k}'', -\mathbf{k}'''}$ . We also note that  $B_{\mathbf{k}\mathbf{k}'\mathbf{k}''}$  contains a  $\delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'')$  and  $C_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}$  contains a  $\delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'' + \mathbf{k}''')$ .

The expansion parameter in this problem is a root-mean-square displacement divided by a lattice parameter.<sup>13</sup> Denoting this by  $\epsilon$ , we have the following orders of magnitude

$$\begin{aligned}
A_{0\mathbf{k}}, A_{0\mathbf{k}}^\dagger &\sim 1, \\
\sum_{\mathbf{k}'\mathbf{k}''} B_{\mathbf{k}\mathbf{k}'\mathbf{k}''} &\sim \epsilon \hbar \omega_{0\mathbf{k}}, \\
\sum_{\mathbf{k}'\mathbf{k}''\mathbf{k}'''} C_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} &\sim \epsilon^2 \hbar \omega_{0\mathbf{k}}.
\end{aligned} \tag{4.15}$$

Thus, compared to the phonon operator term in  $\mathcal{H}_0$ ,  $\mathcal{H}_1$  is of order  $\epsilon$  and  $\mathcal{H}_2$  is of order  $\epsilon^2$ ; this is the basis for our perturbation treatment. The static lattice binding energy  $U_0$  is of course large compared to  $N\hbar\omega_{0\mathbf{k}}$ .

### B. First-Order Phonon Operators

From (4.13) and (4.14), a direct calculation shows that the zeroth-order Hamiltonian commutator equations are satisfied.

$$[\mathcal{H}_0, A_{0\mathbf{k}}^\dagger] = \hbar \omega_{0\mathbf{k}} A_{0\mathbf{k}}^\dagger. \tag{4.16}$$

For first-order energies we need the commutators  $[\mathcal{H}_1, A_{0\mathbf{k}}^\dagger]$ ; with the aid of the symmetry of the  $B_{\mathbf{k}\mathbf{k}'\mathbf{k}''}$  this is

$$\begin{aligned}
[\mathcal{H}_1, A_{0\mathbf{k}}^\dagger] &= 3 \sum_{\mathbf{k}'\mathbf{k}''} B_{\mathbf{k}\mathbf{k}'\mathbf{k}''} \\
&\quad \times (A_{0\mathbf{k}'} + A_{0-\mathbf{k}'}^\dagger) (A_{0\mathbf{k}''} + A_{0-\mathbf{k}''}^\dagger).
\end{aligned} \tag{4.17}$$

The right-hand side of (4.17) gives no contribution to the matrix elements in (2.26) for the first-order energies [see also (3.3) for the many-boson case in first order]. Thus

$$\hbar \omega_{1\mathbf{k}} = 0. \tag{4.18}$$

We now wish to find  $A_{1\mathbf{k}}^\dagger$  so as to satisfy the Hamiltonian commutator equations (2.12a) to first order

<sup>13</sup> L. Van Hove, Solid-State and Molecular Theory Group Technical Report No. 11, 1959 (unpublished).

[see also (3.7)]. In view of (4.18), these equations are

$$[\mathcal{H}_0, A_{1\mathbf{k}}^\dagger] + [\mathcal{H}_1, A_{0\mathbf{k}}^\dagger] = \hbar \omega_{0\mathbf{k}} A_{1\mathbf{k}}^\dagger. \tag{4.19}$$

From (4.17) we expect  $A_{1\mathbf{k}}^\dagger$  to be of second order in the  $A_{0\mathbf{k}}, A_{0\mathbf{k}}^\dagger$  operators; indeed if  $A_{1\mathbf{k}}^\dagger$  is of second order in  $A_{0\mathbf{k}}, A_{0\mathbf{k}}^\dagger$ , then each term in (4.19) is of second order in the operators. We therefore take the general form

$$\begin{aligned}
A_{1\mathbf{k}}^\dagger &= \sum_{\mathbf{k}'\mathbf{k}''} B_{\mathbf{k}\mathbf{k}'\mathbf{k}''} (\alpha_{\mathbf{k}\mathbf{k}'\mathbf{k}''} A_{0\mathbf{k}'} A_{0\mathbf{k}''} \\
&\quad + \beta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} A_{0\mathbf{k}'} A_{0-\mathbf{k}'}^\dagger + \eta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} A_{0-\mathbf{k}'}^\dagger A_{0\mathbf{k}''} \\
&\quad + \zeta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} A_{0-\mathbf{k}'}^\dagger A_{0-\mathbf{k}''}^\dagger),
\end{aligned} \tag{4.20}$$

where the  $\alpha, \beta, \eta, \zeta$  are coefficients to be determined. It is more convenient here not to put all the operators in normal order, although it would not affect the results to do so. Now the commutator  $[\mathcal{H}_0, A_{1\mathbf{k}}^\dagger]$  is found to be

$$\begin{aligned}
[\mathcal{H}_0, A_{1\mathbf{k}}^\dagger] &= \sum_{\mathbf{k}'\mathbf{k}''} B_{\mathbf{k}\mathbf{k}'\mathbf{k}''} \\
&\quad \times [-\alpha_{\mathbf{k}\mathbf{k}'\mathbf{k}''} (\hbar \omega_{0\mathbf{k}'} + \hbar \omega_{0\mathbf{k}''}) A_{0\mathbf{k}'} A_{0\mathbf{k}''} \\
&\quad - \beta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} (\hbar \omega_{0\mathbf{k}'} - \hbar \omega_{0\mathbf{k}'}^\dagger) A_{0\mathbf{k}'} A_{0-\mathbf{k}'}^\dagger \\
&\quad + \eta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} (\hbar \omega_{0\mathbf{k}'} - \hbar \omega_{0\mathbf{k}''}) A_{0-\mathbf{k}'}^\dagger A_{0\mathbf{k}''} \\
&\quad + \zeta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} (\hbar \omega_{0\mathbf{k}'} + \hbar \omega_{0\mathbf{k}''}) A_{0-\mathbf{k}'}^\dagger A_{0-\mathbf{k}''}^\dagger].
\end{aligned} \tag{4.21}$$

In order to satisfy (4.19), the coefficients of like operators must be equated; this gives equations for the  $\alpha, \beta, \eta, \zeta$  coefficients. Because of vanishing denominators, however, certain of these coefficients cannot be defined. We avoid this difficulty by introducing the positive real infinitesimals  $\gamma_{\mathbf{k}}$ , and satisfying, instead of (4.19), the following equation:

$$[\mathcal{H}_0, A_{1\mathbf{k}}^\dagger] + [\mathcal{H}_1, A_{0\mathbf{k}}^\dagger] = (\hbar \omega_{0\mathbf{k}} - i\gamma_{\mathbf{k}}) A_{1\mathbf{k}}^\dagger. \tag{4.22}$$

Then, with the aid of (4.17), (4.20), and (4.21), the conditions (4.22) lead directly to the following results:

$$\begin{aligned}
\alpha_{\mathbf{k}\mathbf{k}'\mathbf{k}''} &= 3(\hbar \omega_{0\mathbf{k}} + \hbar \omega_{0\mathbf{k}'} + \hbar \omega_{0\mathbf{k}''} - i\gamma_{\mathbf{k}})^{-1}, \\
\beta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} &= 3(\hbar \omega_{0\mathbf{k}} + \hbar \omega_{0\mathbf{k}'} - \hbar \omega_{0\mathbf{k}'}^\dagger - i\gamma_{\mathbf{k}})^{-1}, \\
\eta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} &= 3(\hbar \omega_{0\mathbf{k}} - \hbar \omega_{0\mathbf{k}'} + \hbar \omega_{0\mathbf{k}''} - i\gamma_{\mathbf{k}})^{-1}, \\
\zeta_{\mathbf{k}\mathbf{k}'\mathbf{k}''} &= 3(\hbar \omega_{0\mathbf{k}} - \hbar \omega_{0\mathbf{k}'} - \hbar \omega_{0\mathbf{k}''} - i\gamma_{\mathbf{k}})^{-1}.
\end{aligned} \tag{4.23}$$

Some remarks concerning this procedure are in order. It is generally not possible to take the limit  $\gamma_{\mathbf{k}} \rightarrow 0$  in operator expressions, such as  $A_{1\mathbf{k}}^\dagger$ , on account of the highly singular nature of the creation and annihilation operators. However, omitting consideration of the modes for which  $\omega_{0\mathbf{k}} = 0$  (uniform translation of the entire crystal), then  $\gamma_{\mathbf{k}}$  in the numerator on the right-hand side of (4.22) can be taken to be arbitrarily small compared to  $\hbar \omega_{0\mathbf{k}}$ . Our rationale is that we have satisfied (4.19) to a degree of approximation which is better than any order of perturbation which we will consider. After statistical averages are taken, when all operators are replaced by smoothly varying functions of the wave vectors, the limit  $\gamma_{\mathbf{k}} \rightarrow 0$  can be taken. Finally, we point out that the sign chosen here for  $\gamma_{\mathbf{k}}$  is such as to produce decaying states from the (complex) second-order energies.

Let us now investigate the first-order phonon commutators to see if the renormalized operators are good boson operators. In view of the zeroth-order commutators (4.14), the first-order requirements are

$$\begin{aligned} [A_{0\kappa}, A_{1\kappa'}] + [A_{1\kappa}, A_{0\kappa'}] &= 0, \\ [A_{0\kappa}, A_{1\kappa'}^\dagger] + [A_{1\kappa}, A_{0\kappa'}^\dagger] &= 0. \end{aligned} \quad (4.24)$$

These commutators are linear in the  $A_{0\kappa}$ ,  $A_{0\kappa}^\dagger$  operators; the first equation of (4.24) is satisfied if and only if

$$\begin{aligned} \alpha_{\kappa'\kappa\kappa'}^* + \alpha_{\kappa'\kappa'\kappa}^* - \alpha_{\kappa\kappa'\kappa'}^* - \alpha_{\kappa\kappa'\kappa}^* &= 0, \\ \beta_{\kappa'\kappa\kappa'}^* + \eta_{\kappa'\kappa\kappa'}^* - \beta_{\kappa\kappa'\kappa'}^* - \eta_{\kappa\kappa'\kappa'}^* &= 0. \end{aligned} \quad (4.25)$$

The second of (4.24) is satisfied if and only if

$$\begin{aligned} \beta_{\kappa'\kappa'\kappa} + \eta_{\kappa'\kappa\kappa'} + \zeta_{\kappa\kappa'\kappa'}^* + \zeta_{\kappa'\kappa'\kappa}^* &= 0, \\ \zeta_{\kappa'\kappa'\kappa} + \zeta_{\kappa\kappa'\kappa'} + \eta_{\kappa\kappa'\kappa'}^* + \beta_{\kappa\kappa'\kappa}^* &= 0. \end{aligned} \quad (4.26)$$

Conditions (4.25), (4.26) are all satisfied if and only if  $\gamma_\kappa$  is independent of  $\kappa$ . Thus take

$$\gamma_\kappa = \gamma, \quad \text{all } \kappa. \quad (4.27)$$

The first-order commutator conditions (4.24) are satisfied by (4.27) for arbitrary  $\gamma$ , and hence in the limit  $\gamma \rightarrow 0$ .

It is of interest to check the form of  $\mathfrak{H}$  in terms of the renormalized phonon operators. For this purpose define  $\mathfrak{H}$  according to

$$\mathfrak{H} = G_0 + \sum_\kappa \hbar\omega_{0\kappa} (A_{0\kappa}^\dagger + A_{1\kappa}^\dagger) (A_{0\kappa} + A_{1\kappa}). \quad (4.28)$$

The zeroth-order terms of  $\mathfrak{H}$  are equal to  $\mathfrak{H}_0$ ; we denote the first-order terms of  $\mathfrak{H}$  by  $\mathfrak{H}_1$ . A direct but lengthy calculation gives the following result:

$$\begin{aligned} \mathfrak{H}_1 - \mathfrak{H}_1 = i\gamma \sum_{\kappa\kappa'\kappa''} B_{\kappa\kappa'\kappa''} (\beta_{\kappa\kappa'\kappa''}^* A_{0-\kappa'}^\dagger A_{0-\kappa''}^\dagger A_{0\kappa'} \\ - \beta_{\kappa\kappa'\kappa''} A_{0-\kappa'}^\dagger A_{0\kappa} A_{0\kappa'}). \end{aligned} \quad (4.29)$$

To obtain (4.29), we have dropped a number of terms which are of relative order  $N^{-1}$  and have taken  $\gamma \rightarrow 0$  in some terms whose denominator never vanishes. Thus the Hamiltonian is not diagonal to first order, in terms of the renormalized phonon operators, on account of those terms in (4.29) for which the energy part of the denominator vanishes. This causes no difficulties in the remaining calculations. We note that the statistical average of  $\mathfrak{H}_1 - \mathfrak{H}_1$  vanishes when  $\gamma \rightarrow 0$ . Also, since there is no constant term in (4.29), there is no first-order correction to the ground-state energy.

### C. Second-Order Energies

The second-order contributions to the phonon energies are given by (2.26); since the first-order contributions are zero, this becomes

$$\begin{aligned} \langle \dots n_\kappa + 1 \dots (0) | [\mathfrak{H}_2, A_{1\kappa}^\dagger] \\ + [\mathfrak{H}_2, A_{0\kappa}^\dagger] | \dots n_\kappa \dots (0) \rangle \\ = (n_\kappa + 1)^{1/2} \hbar\omega_{2\kappa}. \end{aligned} \quad (4.30)$$

The calculation of the commutators in (4.30) is straightforward. After evaluating the matrix element, and using the symmetries of  $B_{\kappa\kappa'\kappa''}$ ,  $C_{\kappa\kappa'\kappa''}$ , the result is

$$\begin{aligned} \hbar\omega_{2\kappa} = 12 \sum_{\kappa'} C_{\kappa, -\kappa, \kappa', -\kappa'} (n_{\kappa'} + n_{-\kappa'} + 1) \\ - 6 \sum_{\kappa'\kappa''} \{ B_{\kappa\kappa'\kappa''} B_{-\kappa, -\kappa', -\kappa''} [\alpha_{\kappa\kappa'\kappa''} (n_{\kappa'} + n_{\kappa''} + 1) \\ + \beta_{\kappa\kappa'\kappa''} (n_{-\kappa'} - n_{\kappa'}) + \eta_{\kappa\kappa'\kappa''} (n_{-\kappa'} - n_{\kappa'}) \\ - \zeta_{\kappa\kappa'\kappa''} (n_{-\kappa'} + n_{-\kappa''} + 1)] + B_{\kappa, -\kappa, \kappa'} B_{\kappa', -\kappa', -\kappa''} \\ \times (\eta_{\kappa\kappa\kappa'} - \zeta_{\kappa\kappa\kappa'}) (n_{\kappa'} + n_{-\kappa'} + 1) \}. \end{aligned} \quad (4.31)$$

In deriving (4.31) we have dropped a number of terms which are of relative order  $N^{-1}$ . It is customary (see, e.g., the references discussed in Sec. IVD below) to omit the term containing  $B_{\kappa, -\kappa, \kappa'} B_{\kappa', -\kappa', -\kappa''}$ . Since  $B_{\kappa\kappa'\kappa''}$  contains a  $\delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'')$ , this term contains a  $\delta(\mathbf{k}')$ , and hence should be dropped for acoustic modes; thus the  $\Sigma_{\kappa'}$  contained in  $\Sigma_{\kappa'}$  is only over optic modes for this last term in  $\hbar\omega_{2\kappa}$ .

From the form of  $\hbar\omega_{2\kappa}$  it is obvious that we have gone as far as we can with the renormalization procedure. According to the comments at the end of Sec. IIB, the interactions between phonons cannot be removed in second order. In other words, true normal modes for this problem, at least correct to second order, cannot belong to the simple quantum numbers  $\kappa$ .

Before proceeding to take the statistical average of the phonon energies, let us calculate the system energy levels. In view of (4.13) and (4.14) the system energies, correct to order  $\hbar\omega_{0\kappa}$ , are simply

$$E(\dots n_\kappa \dots (0)) = G_0 + \sum_\kappa n_\kappa \hbar\omega_{0\kappa}. \quad (4.32)$$

Now since the  $\hbar\omega_{2\kappa}$  depend on all the  $n_{\kappa'}$ , the second-order contributions to the system energies are not simply  $\sum_\kappa n_\kappa \hbar\omega_{2\kappa}$ . In particular, for a term in  $\hbar\omega_{2\kappa}$  of the form  $\sum_{\kappa'} S_{\kappa\kappa'} n_{\kappa'}$ , where  $S_{\kappa\kappa'}$  are numbers, the contribution to the system energy is  $\frac{1}{2} \sum_{\kappa\kappa'} S_{\kappa\kappa'} n_\kappa n_{\kappa'}$ ; the  $\frac{1}{2}$  avoids counting each particle contribution twice. Note that this does not give the diagonal terms ( $n_\kappa n_\kappa$  terms) correctly, but such terms are of relative order  $N^{-1}$ . In general, for a term which is summed over  $r$  different occupation numbers, one needs a factor  $(r!)^{-1}$ . Thus, because of the interactions between the renormalized particles, the system energies are not simply the sum of the particle energies. The system energies, correct to second order, are thus

$$\begin{aligned} E(\dots n_\kappa \dots (2)) = (G_0 + G_2) + \sum_\kappa n_\kappa \hbar\omega_{0\kappa} \\ + 6 \sum_{\kappa\kappa'} C_{\kappa, -\kappa, \kappa', -\kappa'} (n_{\kappa'} + n_{-\kappa'} + 2) n_\kappa \\ - 3 \sum_{\kappa\kappa'\kappa''} \{ B_{\kappa\kappa'\kappa''} B_{-\kappa, -\kappa', -\kappa''} [\alpha_{\kappa\kappa'\kappa''} (n_{\kappa'} + n_{\kappa''} + 2) n_\kappa \\ + \beta_{\kappa\kappa'\kappa''} (n_{-\kappa'} - n_{\kappa'}) n_\kappa + \eta_{\kappa\kappa'\kappa''} (n_{-\kappa'} - n_{\kappa'}) n_\kappa \\ - \zeta_{\kappa\kappa'\kappa''} (n_{-\kappa'} + n_{-\kappa''} + 2) n_\kappa] + B_{\kappa, -\kappa, \kappa'} B_{\kappa', -\kappa', -\kappa''} \\ \times (\eta_{\kappa\kappa\kappa'} - \zeta_{\kappa\kappa\kappa'}) (n_{\kappa'} + n_{-\kappa'} + 2) n_\kappa \}. \end{aligned} \quad (4.33)$$

Here  $G_2$  is the second-order contribution to the ground-state energy; we do not calculate this here.

### D. Statistical Mechanics

#### Phonon Energies

In order to calculate  $\hbar\bar{\omega}_{2\kappa}$  correct to second order, it is only necessary to use a zeroth-order average. This means replacing each  $n_\kappa$  by  $\bar{n}_\kappa$ , where

$$\bar{n}_\kappa = [\exp(\beta\hbar\omega_{0\kappa}) - 1]^{-1}. \quad (4.34)$$

It is also useful to note  $\bar{n}_\kappa = \bar{n}_{-\kappa}$ . We can now take the

$$\hbar\Delta_\kappa = 12\Sigma_{\kappa'} C_{\kappa, -\kappa, \kappa', -\kappa'} (2\bar{n}_{\kappa'} + 1) - 18\hbar^{-1}\Sigma_{\kappa' \kappa''} B_{\kappa \kappa' \kappa''} B_{-\kappa, -\kappa', -\kappa''}$$

$$\times \left[ \frac{(\bar{n}_{\kappa'} + \bar{n}_{\kappa''} + 1)}{(\omega_{0\kappa} + \omega_{0\kappa'} + \omega_{0\kappa''})_p} + \frac{(\bar{n}_{\kappa''} - \bar{n}_{\kappa'})}{(\omega_{0\kappa} + \omega_{0\kappa'} - \omega_{0\kappa''})_p} + \frac{(\bar{n}_{\kappa'} - \bar{n}_{\kappa''})}{(\omega_{0\kappa} - \omega_{0\kappa'} + \omega_{0\kappa''})_p} - \frac{(\bar{n}_{\kappa'} + \bar{n}_{\kappa''} + 1)}{(\omega_{0\kappa} - \omega_{0\kappa'} - \omega_{0\kappa''})_p} \right] - 36\hbar^{-1}\Sigma_{\kappa' \kappa''} B_{\kappa, -\kappa, \kappa'} B_{\kappa', -\kappa', -\kappa''} (2\bar{n}_{\kappa''} + 1) (\omega_{0\kappa'})^{-1}; \quad (4.37)$$

$$\hbar\Gamma_\kappa = 18\pi\hbar^{-1}\Sigma_{\kappa' \kappa''} B_{\kappa \kappa' \kappa''} B_{-\kappa, -\kappa', -\kappa''}$$

$$\times \{ (\bar{n}_{\kappa'} + \bar{n}_{\kappa''} + 1) [\delta(\omega_{0\kappa} - \omega_{0\kappa'} - \omega_{0\kappa''}) - \delta(\omega_{0\kappa} + \omega_{0\kappa'} + \omega_{0\kappa''})] + (\bar{n}_{\kappa'} - \bar{n}_{\kappa''}) [\delta(\omega_{0\kappa} + \omega_{0\kappa'} - \omega_{0\kappa''}) - \delta(\omega_{0\kappa} - \omega_{0\kappa'} + \omega_{0\kappa''})] \}. \quad (4.38)$$

The statistical averages of the second-order phonon energies are naturally interpreted in terms of inelastic neutron scattering experiments. Since this experiment sees a statistical average, the neutrons will create (or destroy) renormalized phonons with energy  $\hbar(\omega_{0\kappa} + \Delta_\kappa)$  and with lifetime  $\Gamma_\kappa^{-1}$ .

#### Helmholtz Free Energy

From the general equation (2.39) above, the free energy is given to second order by

$$F = (G_0 + G_2) + \beta^{-1}\Sigma_\kappa \ln[1 - \exp(-\beta\hbar\omega_{0\kappa})] + (\bar{E}_2 - G_2). \quad (4.39)$$

Here  $(\bar{E}_2 - G_2)$  is the statistical average of the second-order contribution to the excitation energy of the system and hence, correct to second order, is just the zeroth-order statistical average of the double- and triple-sum terms on the right-hand side of (4.33). After replacing all  $n_\kappa$  by  $\bar{n}_\kappa$ , we take the limit  $\gamma \rightarrow 0$  and calculate the real part as the anharmonic contribution to the temperature dependent part of the free energy; the result is

$$\text{Re}(\bar{E}_2 - G_2) = 12\Sigma_{\kappa \kappa'} C_{\kappa, -\kappa, \kappa', -\kappa'} (\bar{n}_\kappa \bar{n}_{\kappa'} + \bar{n}_\kappa) - 18\hbar^{-1}\Sigma_{\kappa \kappa' \kappa''} B_{\kappa \kappa' \kappa''} B_{-\kappa, -\kappa', -\kappa''} \times \left[ \frac{(\bar{n}_\kappa \bar{n}_{\kappa'} + \bar{n}_\kappa)}{(\omega_{0\kappa} + \omega_{0\kappa'} + \omega_{0\kappa''})_p} + \frac{(\bar{n}_\kappa \bar{n}_{\kappa''} + \bar{n}_{\kappa'} \bar{n}_{\kappa''} - \bar{n}_\kappa \bar{n}_{\kappa'} + \bar{n}_{\kappa''})}{(\omega_{0\kappa} + \omega_{0\kappa'} - \omega_{0\kappa''})_p} \right] - 36\hbar^{-1}\Sigma_{\kappa \kappa' \kappa''} B_{\kappa, -\kappa, \kappa'} B_{\kappa', -\kappa', -\kappa''} (\bar{n}_\kappa \bar{n}_{\kappa''} + \bar{n}_\kappa) (\omega_{0\kappa'})^{-1}. \quad (4.40)$$

#### Comparison with Previous Work

With regard to the statistical average phonon energies, the expressions (4.37), (4.38) above for  $\hbar\Delta_\kappa$ ,  $\hbar\Gamma_\kappa$  agree with the diagonal elements of the self-energy terms calculated by Kokkedee<sup>14</sup> by diagram-summation techniques. They also agree with the phonon energy shifts and lifetimes calculated by Maradudin and Fein<sup>15</sup> by phonon propagators. Finally, the present results agree with the diagonal elements of the self-energy terms calculated by Cowley<sup>16</sup> by thermodynamic Green's functions.

<sup>14</sup> J. J. Kokkedee, *Physica* 268, 374 (192).

<sup>15</sup> A. A. Maradudin and A. E. Fein, *Phys. Rev.* 128, 2589 (1962).

<sup>16</sup> R. A. Cowley, *Advan. Phys.* 12, 421 (1963).

limit  $\gamma \rightarrow 0$  with the aid of the symbolic identity

$$\lim_{\gamma \rightarrow 0^+} \frac{1}{x \pm i\gamma} = \frac{1}{(x)_p} \mp i\pi\delta(x). \quad (4.35)$$

The subscript  $p$  means to take the principal part of the integral (or sum) in which this function appears. The result of this calculation is as follows:

$$\hbar\bar{\omega}_{2\kappa} = \hbar\Delta_\kappa + i\hbar\Gamma_\kappa, \quad (4.36)$$

where  $\Delta_\kappa$ ,  $\Gamma_\kappa$  are real.

The expression (4.40) for the temperature-dependent part of the anharmonic free energy agrees with the previous calculations<sup>16-20</sup>; in most of these references the last term in (4.40) is omitted.

Cowley<sup>16</sup> gives considerable discussion to the fact that his quasiharmonic calculation does not give the correct answer. Since his quasiharmonic calculation consists of adding the second-order term  $\Sigma_\kappa (\bar{n}_\kappa + \frac{1}{2})\hbar\Delta_\kappa$  to the harmonic free energy, it is immediately obvious

<sup>17</sup> W. Ludwig, *J. Phys. Chem. Solids* 4, 283 (1958).

<sup>18</sup> A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, *Ann. Phys. (N. Y.)* 15, 337 (1961).

<sup>19</sup> J. M. Keller and D. C. Wallace, *Phys. Rev.* 126, 1275 (1962).

<sup>20</sup> D. C. Wallace, *Phys. Rev.* 133, A153 (1964).

in view of the discussion following (4.32) why this procedure does not give the right answer. We strongly caution against the use of such temperature-dependent energy levels, along with the customary statistics, in calculating the partition function or quantities derived from it. Such procedure is not within the scope of ordinary statistical-mechanics derivations. The present method obtains the appropriate quantum-mechanical energies, and hence avoids difficulties associated with temperature-dependent energy levels.

## V. APPLICATION TO ELECTRON-PHONON INTERACTIONS

### A. Definition of the Problem

Let us consider normal metals and treat the electron-phonon interactions as a perturbation. The Hamiltonian for this problem is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \quad (5.1)$$

$$\mathcal{H}_0 = \sum_{\mathbf{q}, \sigma} \epsilon_{\mathbf{q}\sigma} C_{\mathbf{q}\sigma}^\dagger C_{\mathbf{q}\sigma} + \sum_{\mathbf{k}, s} \hbar\omega_{\mathbf{k}s} A_{\mathbf{k}s}^\dagger A_{\mathbf{k}s}, \quad (5.2)$$

$$\mathcal{H}_1 = \sum_{\mathbf{k}, s} V_{\mathbf{k}s} (A_{\mathbf{k}s} + A_{-\mathbf{k}s}^\dagger) \sum_{\mathbf{q}, \sigma} C_{\mathbf{q}+\mathbf{k}, \sigma}^\dagger C_{\mathbf{q}\sigma}. \quad (5.3)$$

Here  $\mathbf{q}$  is the electron wave vector, which takes on all values,  $\sigma$  is the electron spin,  $\mathbf{k}$  is the phonon wave vector, which lies in the first zone, and  $s$  is the phonon polarization. The electron energies are  $\epsilon_{\mathbf{q}\sigma}$ , the phonon energies are  $\hbar\omega_{\mathbf{k}s}$ , and the interaction potential coefficients are  $V_{\mathbf{k}s}$ . The creation and annihilation operators are all of order 1, while the perturbation parameter is contained in the small coefficients  $V_{\mathbf{k}s}$ .

This Hamiltonian is the same as that used by Pines.<sup>4</sup> Also, the present Hamiltonian reduces to the one used by Fröhlich<sup>21</sup> if we take free-electron energies for  $\epsilon_{\mathbf{q}\sigma}$ , restrict phonon polarizations to longitudinal acoustic modes, and take elastic wave energies for  $\hbar\omega_{\mathbf{k}s}$ . The above Hamiltonian is also the same as Migdal's,<sup>22</sup> except that he omits the  $\Sigma_\sigma$  in  $\mathcal{H}_0$  and  $\mathcal{H}_1$ . Finally, this Hamiltonian is the same as that used by Nakajima and Watabe.<sup>23</sup>

Umklapp processes are included (implicitly) by allowing the  $\Sigma_{\mathbf{k}}$  in  $\mathcal{H}_1$  to go over all values, i.e., extended zones. Such processes can be separated out explicitly at any time in the following calculations. In addition, we generalize the usual treatments by allowing an arbitrary number of atoms per unit cell, so that the index  $s$  includes optic modes. The present method encounters no difficulty from this generalization. In this

<sup>21</sup> H. Fröhlich, Proc. Roy. Soc. (London) **A215**, 291 (1952).

<sup>22</sup> A. B. Migdal, Zh. Eksperim. i Teor. Fiz. **34**, 1438 (1958) [English transl.: Soviet Phys.—JETP **7**, 996 (1958)]. Migdal claims the problem cannot be treated by perturbation methods. However, Migdal decouples the Dyson equation on the basis of the smallness of the inverse nuclear mass which appears in the interaction coefficients  $V_{\mathbf{k}s}$ ; this procedure is then equivalent to the present perturbation treatment and to the other treatments referred to here.

<sup>23</sup> S. Nakajima and M. Watabe, Progr. Theoret. Phys. (Kyoto) **29**, 341 (1963).

connection, Bardeen's<sup>24</sup> derivation of the interaction coefficients shows that for longitudinal acoustic modes  $V_{\mathbf{k}s} \rightarrow 0$  as  $\mathbf{k} \rightarrow 0$ . Also, the requirement  $\mathcal{H}_1$  is Hermitian leads to  $V_{\mathbf{k}s} = V_{-\mathbf{k}s}^*$ .

It is convenient to use the following abbreviations:

$$\begin{aligned} \kappa &= (\mathbf{k}, s), \quad \text{with} \quad -\kappa = (-\mathbf{k}, s); \\ \lambda &= (\mathbf{q}, \sigma), \quad \text{with} \quad -\lambda = (-\mathbf{q}, \sigma); \\ \lambda + \kappa &= (\mathbf{q} + \mathbf{k}, \sigma). \end{aligned} \quad (5.4)$$

After abbreviating this way, care is required in using indices such as  $\lambda + \kappa$ , especially in a Kronecker delta such as  $\delta_{\lambda+\kappa, \lambda'}$ . Generally, this delta can be used to eliminate a sum over  $\lambda$  or  $\lambda'$ , but not  $\kappa$ . In other words, as indicated by (5.4),  $\lambda + \kappa$  means only the  $\mathbf{k}$  from  $\kappa$ ; in the following calculations this  $\mathbf{k}$  is usually in the extended zone scheme since it arises from  $\mathcal{H}_1$ . Introducing a subscript 0 for unrenormalized energies and operators, the problem is defined as follows:

$$\mathcal{H}_0 = \sum_{\lambda} \epsilon_{0\lambda} C_{0\lambda}^\dagger C_{0\lambda} + \sum_{\kappa} \hbar\omega_{0\kappa} A_{0\kappa}^\dagger A_{0\kappa}; \quad (5.5)$$

$$\mathcal{H}_1 = \sum_{\kappa} V_{\kappa} (A_{0\kappa} + A_{0-\kappa}^\dagger) \sum_{\lambda} C_{0\lambda+\kappa}^\dagger C_{0\lambda}; \quad (5.6)$$

$$\begin{aligned} [A_{0\kappa}, A_{0\kappa'}] &= [A_{0\kappa}, C_{0\lambda}] = [A_{0\kappa}, C_{0\lambda}^\dagger] = [C_{0\lambda}, C_{0\lambda'}]_+ = 0, \\ [A_{0\kappa}, A_{0\kappa'}^\dagger] &= \delta_{\kappa\kappa'}, \quad [C_{0\lambda}, C_{0\lambda'}^\dagger]_+ = \delta_{\lambda\lambda'}. \end{aligned} \quad (5.7)$$

### B. Renormalization

From (5.5) and (5.7), the zeroth-order Hamiltonian commutator equations are found to be satisfied:

$$[\mathcal{H}_0, A_{0\kappa}^\dagger] = \hbar\omega_{0\kappa} A_{0\kappa}^\dagger, \quad (5.8)$$

$$[\mathcal{H}_0, C_{0\lambda}^\dagger] = \epsilon_{0\lambda} C_{0\lambda}^\dagger. \quad (5.9)$$

The commutators of  $\mathcal{H}_1$  with the zeroth-order creation operators are

$$[\mathcal{H}_1, A_{0\kappa}^\dagger] = V_{\kappa} \sum_{\lambda} C_{0\lambda+\kappa}^\dagger C_{0\lambda}, \quad (5.10)$$

$$[\mathcal{H}_1, C_{0\lambda}^\dagger] = \sum_{\kappa} V_{\kappa} (A_{0\kappa} + A_{0-\kappa}^\dagger) C_{0\lambda+\kappa}^\dagger. \quad (5.11)$$

From the general equations (2.26) and (2.27), we see that the first-order contributions to the phonon energies and electron energies are all zero for the commutators (5.10) and (5.11)

$$\hbar\omega_{1\kappa} = \epsilon_{1\lambda} = 0. \quad (5.12)$$

Just as in the case of lattice dynamics above, we take general forms for the first-order contributions to the creation operators which contain operators like those which appear on the right-hand side of (5.10) and (5.11).

$$A_{1\kappa}^\dagger = V_{\kappa} \sum_{\lambda} \alpha_{\lambda\kappa} C_{0\lambda+\kappa}^\dagger C_{0\lambda}, \quad (5.13)$$

$$C_{1\lambda}^\dagger = \sum_{\kappa} V_{\kappa} (\eta_{\kappa\lambda} A_{0\kappa} + \zeta_{\kappa\lambda} A_{0-\kappa}^\dagger) C_{0\lambda+\kappa}^\dagger, \quad (5.14)$$

where  $\alpha_{\lambda\kappa}$ ,  $\eta_{\kappa\lambda}$ ,  $\zeta_{\kappa\lambda}$  are coefficients to be determined.

<sup>24</sup> J. Bardeen, Phys. Rev. **52**, 688 (1937).

The commutators with  $\mathcal{H}_0$  are then given by

$$[\mathcal{H}_0, A_{1\kappa}^\dagger] = V_\kappa \sum_\lambda \alpha_{\lambda\kappa} (\epsilon_{0\lambda+\kappa} - \epsilon_{0\lambda}) C_{0\lambda+\kappa}^\dagger C_{0\lambda}, \quad (5.15)$$

$$[\mathcal{H}_0, C_{1\lambda}^\dagger] = \sum_\kappa V_\kappa [(\epsilon_{0\lambda+\kappa} - \hbar\omega_{0\kappa}) \eta_{\kappa\lambda} A_{0\kappa} + (\epsilon_{0\lambda+\kappa} + \hbar\omega_{0\kappa}) \zeta_{\kappa\lambda} A_{0-\kappa}^\dagger] C_{0\lambda+\kappa}^\dagger. \quad (5.16)$$

We now write down the first-order terms in the Hamiltonian commutator equations (2.12). It is again necessary to introduce positive infinitesimal numbers  $\gamma_\kappa, \gamma_\lambda$ , just as in the lattice dynamics case, so that all the  $\alpha, \eta, \zeta$  coefficients are defined. In other words, we write the first-order Hamiltonian commutator equations in the form

$$[\mathcal{H}_1, A_{0\kappa}^\dagger] + [\mathcal{H}_0, A_{1\kappa}^\dagger] = (\hbar\omega_{0\kappa} - i\gamma_\kappa) A_{1\kappa}^\dagger, \quad (5.17)$$

$$[\mathcal{H}_1, C_{0\lambda}^\dagger] + [\mathcal{H}_0, C_{1\lambda}^\dagger] = (\epsilon_{0\lambda} - i\gamma_\lambda) C_{1\lambda}^\dagger, \quad (5.18)$$

where the terms involving first-order energies do not appear because of (5.12). In order to satisfy these equations, the coefficients of like operators are equated; with the aid of the commutators from (5.10), (5.11) and (5.15), (5.16), and the definitions (5.13), (5.14), this leads to the equations for the  $\alpha, \eta, \zeta$  coefficients

$$\begin{aligned} \alpha_{\lambda\kappa} &= (\hbar\omega_{0\kappa} + \epsilon_{0\lambda} - \epsilon_{0\lambda+\kappa} - i\gamma_\kappa)^{-1}, \\ \eta_{\kappa\lambda} &= (\epsilon_{0\lambda} + \hbar\omega_{0\kappa} - \epsilon_{0\lambda+\kappa} - i\gamma_\lambda)^{-1}, \\ \zeta_{\kappa\lambda} &= (\epsilon_{0\lambda} - \hbar\omega_{0\kappa} - \epsilon_{0\lambda+\kappa} - i\gamma_\lambda)^{-1}. \end{aligned} \quad (5.19)$$

It is now necessary to satisfy the particle commutators and anticommutators, Eqs. (2.14), to first order. The zeroth-order terms are given by (5.7). For the phonons, the first-order requirements are

$$\begin{aligned} [A_{0\kappa}, A_{1\kappa'}] + [A_{1\kappa}, A_{0\kappa'}] &= 0, \\ [A_{0\kappa}, A_{1\kappa'}^\dagger] + [A_{1\kappa}, A_{0\kappa'}^\dagger] &= 0. \end{aligned} \quad (5.20)$$

The commutators in (5.20) are all zero since  $A_{1\kappa}, A_{1\kappa}^\dagger$  contain only zeroth-order electron operators. The first-order electron anticommutator requirements are

$$\begin{aligned} [C_{0\lambda}, C_{1\lambda'}]_+ + [C_{1\lambda}, C_{0\lambda'}]_+ &= 0, \\ [C_{0\lambda}, C_{1\lambda'}^\dagger]_+ + [C_{1\lambda}, C_{0\lambda'}^\dagger]_+ &= 0. \end{aligned} \quad (5.21)$$

A direct calculation shows that (5.21) are satisfied if and only if  $\gamma_\lambda$  are independent of  $\lambda$ . Finally, the first-order conditions for the phonon-electron commutators are

$$\begin{aligned} [A_{0\kappa}, C_{1\lambda}] + [A_{1\kappa}, C_{0\lambda}] &= 0, \\ [A_{0\kappa}, C_{1\lambda}^\dagger] + [A_{1\kappa}, C_{0\lambda}^\dagger] &= 0. \end{aligned} \quad (5.22)$$

These conditions are satisfied if and only if all  $\gamma_\kappa = \gamma_\lambda = \gamma$ ; henceforth we take

$$\gamma_\kappa = \gamma_\lambda = \gamma. \quad (5.23)$$

Now the renormalized phonons and electrons have good commutators and anticommutators to first order. This is true for any  $\gamma$ , and hence for  $\gamma \rightarrow 0$ .

The last step in our renormalization program for this problem is to calculate the second-order energies according to the general equations (2.26) and (2.27).

For this purpose it is only necessary to calculate  $[\mathcal{H}_1, A_{1\kappa}^\dagger]$  and  $[\mathcal{H}_1, C_{1\lambda}^\dagger]$ , and take the indicated matrix elements. To avoid confusion, we use  $f_\lambda$  for the number of electrons with quantum number  $\lambda$  in a given state of the system, and continue to use  $n_\kappa$  for the number of phonons. The results are as follows:

$$\hbar\omega_{2\kappa} = V_\kappa V_{-\kappa} \sum_\lambda \alpha_{\lambda\kappa} (f_\lambda - f_{\lambda+\kappa}), \quad (5.24)$$

$$\begin{aligned} \epsilon_{2\lambda} &= \sum_\kappa V_\kappa V_{-\kappa} [\eta_{\kappa\lambda} (n_\kappa + f_{\lambda+\kappa}) + \zeta_{\kappa\lambda} (n_{-\kappa} + 1 - f_{\lambda+\kappa}) \\ &\quad + (\zeta_{\kappa\lambda} - \eta_{\kappa\lambda}) \delta(\mathbf{k}) \sum_{\lambda'} f_{\lambda'}]. \end{aligned} \quad (5.25)$$

Note that if umklapp processes are included, the  $\Sigma_{\mathbf{k}}$  contained in the  $\Sigma_\kappa$  must be over all possible  $\mathbf{k}$  (extended zones). Of particular interest is the last term in  $\epsilon_{2\lambda}$ , the term containing  $\delta(\mathbf{k})$ . It is reasonable to take  $V_\kappa = 0$  for  $\mathbf{k} = 0$  acoustic modes, and hence this term contributes only for optic modes. Also  $\sum_{\lambda'} f_{\lambda'} = N_e$ , the total number of electrons in the system; this will be used to replace  $\sum_{\lambda'} f_{\lambda'}$  in the following.

Let us pause for a moment to see what has been accomplished. The renormalized phonons and electrons have creation operators  $A_{0\kappa}^\dagger + A_{1\kappa}^\dagger$  and  $C_{0\lambda}^\dagger + C_{1\lambda}^\dagger$ , respectively. According to (5.13), a dressed phonon is accompanied by a set of electron-hole pairs; in each pair the electron-hole momentum difference (wave-vector difference) is the same as the momentum of the phonon. According to (5.14), a dressed electron is accompanied by two sets of particle pairs. One type of pair consists of an electron plus an added phonon, the total momentum of the pair being the same as that of the electron; the second type of pair consists of an electron plus a removed phonon, the momentum difference of the pair being the same as that of the electron. These dressed particles are the first-order-correct non-interacting particles of the system. In addition, the creation energies of these phonons and electrons are  $\hbar\omega_{0\kappa} + \hbar\omega_{2\kappa}$  and  $\epsilon_{0\lambda} + \epsilon_{2\lambda}$ , correct to second order. If the system is in a given quantum state, this is the energy required to create one such particle. Since from (5.24) and (5.25) the second-order creation energy contributions depend on the quantum state, i.e., depend on all the  $n_\kappa, f_\lambda$ , then we know that the interactions among the particles cannot be removed in second order. Thus we have gone as far as we can with the renormalization procedure for the particles with quantum numbers  $\kappa, \lambda$ .

### C. Statistical Averages

The statistical averages of  $\hbar\omega_{2\kappa}$  and  $\epsilon_{2\lambda}$  are obtained correct to second order by using zeroth-order averages. Thus with

$$\begin{aligned} \bar{n}_\kappa &= [\exp(\beta\hbar\omega_{0\kappa}) - 1]^{-1}, \\ \bar{f}_\lambda &= [\exp(\beta\epsilon_{0\lambda}) + 1]^{-1}, \end{aligned} \quad (5.26)$$

the averages of (5.24) and (5.25) are simply

$$\hbar\bar{\omega}_{2\kappa} = V_\kappa V_{-\kappa} \sum_\lambda \alpha_{\lambda\kappa} (\bar{f}_\lambda - \bar{f}_{\lambda+\kappa}), \quad (5.27)$$

$$\begin{aligned} \bar{\epsilon}_{2\lambda} &= \sum_\kappa V_\kappa V_{-\kappa} [\eta_{\kappa\lambda} (\bar{n}_\kappa + \bar{f}_{\lambda+\kappa}) + \zeta_{\kappa\lambda} (\bar{n}_{-\kappa} + 1 - \bar{f}_{\lambda+\kappa}) \\ &\quad + (\zeta_{\kappa\lambda} - \eta_{\kappa\lambda}) \delta(\mathbf{k}) N_e]. \end{aligned} \quad (5.28)$$

It is now possible to take the limit  $\gamma \rightarrow 0$  and obtain the real and imaginary parts, and thus the energy shifts and particle lifetimes. This is not necessary here.

We now compare these results with previous calculations. For the special case considered by Fröhlich,<sup>21</sup> namely longitudinal-acoustic phonons with energy proportional to wave vector, the real part of  $\hbar\bar{\omega}_{2k}$  agrees with his Eq. (2.36) for the correction to the sound velocity. (To get this agreement it is necessary to take his parameter  $\Gamma_w=0$  and use the principal part of his sum.) Note that our (5.27), as well as Fröhlich's expression, contains a sum over spins. The phonon self-energy terms which Migdal<sup>22</sup> has calculated by thermodynamic Green's functions are the same as (5.27) above, except that he omits the sum over spins. More specifically, the sign of the self-energy is the opposite of  $\hbar\bar{\omega}_{2k}$ , but the interpretation leads to the same energy shifts and lifetimes. Nakajima and Watabe<sup>23</sup> have calculated electron self-energies by the thermodynamic Green's-function method; if we drop the last term in (5.28) for  $\bar{\epsilon}_{2\lambda}$ , namely the optic-mode term, then  $\bar{\epsilon}_{2\lambda}$  agrees with their self-energy. Actually, the imaginary parts of  $\bar{\epsilon}_{2\lambda}$  and their self-energies have opposite signs, but again the interpretations are such as to give the same energy shifts and lifetimes.

## VI. CONCLUDING REMARKS

The present method of treating many-particle perturbation problems is recommended because it gives more information than any currently available method, and also because of its extreme simplicity. We shall elaborate on these two points.

To begin with, the procedure we have developed gives renormalized single-particle creation and annihilation operators. These operators represent the true normal modes of the system up to the order to which the operators can be determined. In addition they have a simple physical interpretation in terms of dressed particles. The procedure also gives the energy required to create (or destroy) a single particle when the system is in a given quantum state. This information is more

fundamental than the statistical averages of the particle-creation energies; it is the statistical averages which are found by the thermodynamic Green's-function method. We stress this point by noting that one can always take the statistical average of the particle energies of the present theory, but these energies cannot be found in general from the statistical averages. Furthermore, with the aid of the present particle-creation energies, the system energy levels can be found correctly, and there is no difficulty with temperature-dependent energy levels in the statistical mechanics. Finally, the present method shows directly to what order of perturbation the interactions can be removed between renormalized particles which are characterized by the zeroth-order quantum numbers.

The present method is not only simple, it is extremely simple. The renormalized operators and energies are obtained by direct and short calculations. In addition, after the problem is solved to order  $m$  ( $m$  includes 0), statistical functions are obtained to order  $m+1$  by procedures which are essentially first-order-perturbation procedures. After having calculated the free energy for an anharmonic crystal to second order by ordinary perturbation expansions to second order,<sup>20</sup> and also by the present method in Sec. IV above, we are able to say that the present calculation is simpler by an order of magnitude.

The value of the present method is amply illustrated by the calculations of Secs. IV and V above. We expect that the renormalized particles are also useful in the treatment of transport problems, although such applications are not considered here. In the following paper we try to develop the Hamiltonian commutator equations into a method for treating more difficult non-perturbation problems.

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