

fore seem more rational to eliminate the experimentally irrelevant atoms from Eq. (2.10) and discuss a generalized master equation for the reduced field-density operator  $W_F(t) = \text{tr}_A W(t)$ . This has actually been done for the laser by Haake, Ref. 5, which in many respects parallels the present paper. However, elimination procedures are ultimately motivated not by economical considerations but rather the physically sound approximations they eventually give rise to. As may be seen from Sec. 4 of Haake's paper, the integral kernel in the generalized master equation for  $W_F(t)$  allows for a convergent expansion if  $1/T_1, 1/T_2 \gg \kappa$  (which is usually fulfilled for a laser) but does not for the superradiance limit (2.14).

<sup>12</sup>This formula has also been obtained for the far field in Ref. 2(c).

<sup>13</sup>Recall that  $\gamma_L = \gamma + \gamma^{\text{coll}}$ ; if no collision broadening, i. e., nonradiative decay is present,  $\gamma_L$  equals the natural linewidth  $\gamma$  of the atomic transition.

<sup>14</sup>F. T. Arrecchi and E. Courtens, Phys. Rev. A **2**, 1730 (1970). These authors have also obtained and discussed the values for  $l_c$  and  $N_c$  given in (6.5) and (6.7). Using arguments completely independent from ours, they show that  $N_c$  is "the maximum number of atoms that can cooperate to superradiant emission" and that  $l_c$  is the maximum distance between atoms able to cooperate.

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## Theory of Defects in Quantum Crystals

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The classical theory for mass defects in crystals is inapplicable to quantum crystals, where zero-point motion leads to a force-constant renormalization on the introduction of mass defects. We develop a variational theory for handling such problems which simplifies the renormalization so that the problem reduces to that of a single frequency-dependent mass defect, to be calculated in a self-consistent fashion. Various anomalies observed in the properties of quantum crystals are discussed in light of the present theory. The theory may also be used to calculate in a simple fashion the properties of extended defects in classical crystals.

### I. INTRODUCTION

The traditional theory of lattice dynamics<sup>1</sup> assumes that the deviations of particles about their mean positions in the crystal are small relative to the equilibrium interparticle separation, and that the ratio of these quantities is a legitimate small expansion parameter in a perturbation treatment. In isotopes of helium and hydrogen, such an approach breaks down.<sup>2</sup> Because of the small mass of the atoms and their weak attractive interaction, the zero-point kinetic energy is of the same order of magnitude as the potential energy, and the rms deviation is as large as 30% of the equilibrium interparticle separation. Since the peculiarity of these crystals is rooted in the large zero-point motion, they have been called *quantum crystals*. The work on these crystals in the past few years has resulted in a clear understanding of the theoretical framework in which these crystals ought to be regarded. From the point of view of this paper, the salient points in this development have been the following: Nosanow<sup>3</sup> clearly formulated the problem of short-range correlations in such solids and showed that the single-particle variational wave functions are approximately Gaussian. Brenig<sup>4</sup> and Fredkin and Werthamer<sup>5</sup> showed through the random-phase approximation that the elementary

excitations of even such highly anharmonic crystals are phonons. Assuming phonon wave functions (generalized Gaussians in coordinate space), Koehler<sup>6</sup> obtained a concise formula for the phonon frequencies by a variational calculation. Horner<sup>7</sup> obtained the result of Koehler through an elegant perturbation resummation and also showed how one may go beyond the noninteracting quasiparticle picture in such crystals. The result of these theoretical investigations may be summarized by saying that at least for long wavelengths, the excitations in quantum crystals are phonons, whose frequencies however should be determined self-consistently from force constants that are the thermal average of the second derivatives of some effective interparticle potential which includes the effect of short-range correlations. More precisely, the frequency  $\omega_{\vec{k}\lambda}^2$  of a mode with wave vector  $\vec{k}$  and polarization  $\lambda$  is given by

$$\omega_{\vec{k}\lambda}^2 = \frac{1}{m} \sum_{i < j, \alpha\beta} \epsilon_{\lambda\alpha}^*(\vec{k}) \epsilon_{\beta\lambda}(\vec{k}) (1 - e^{i\vec{k} \cdot \vec{R}_{ij}}) \times \langle \nabla_{i\alpha} \nabla_{j\beta} v(r_{ij}) \rangle, \quad (1.1)$$

where  $m$  is the mass of an atom;  $i, j$  label the lattice sites;  $\alpha, \beta$  label the Cartesian coordinates;  $\vec{R}_{ij}$  is the vector joining  $i$  to  $j$ ;  $\epsilon_{\lambda\alpha}(\vec{k})$  is a polarization vector;  $v(r_{ij})$  is the effective potential between

particles at a separation  $r_{ij}$ ; and  $\langle \rangle$  indicates a thermal average.

Though the quantum crystals were of much use to the many-body theorists, much of their effort may be characterized as an attempt to understand why the crystals display routine classical behavior in most macroscopic properties (while they display in the liquid state very bizarre phenomena). However, on introduction of defects in such crystals they display several anomalies not observed in classical systems. Briefly, some of them are the following: The thermal resistivity in crystals with isotopic defects<sup>8,9</sup> is much larger than can be explained on the basis of Rayleigh scattering due to the mass difference; the intermediate-bath specific heat deduced in spin-lattice relaxation measurements in <sup>3</sup>He depends dramatically on <sup>4</sup>He concentration,<sup>10-12</sup> leading to the belief that the <sup>4</sup>He atoms locally enhance the exchange frequency among the <sup>3</sup>He atoms by more than an order of magnitude; there are effects on the magnitude and the temperature dependence of the spin-lattice relaxation times<sup>11</sup> for impurities as few as 1 in 10<sup>5</sup>, and mixtures of <sup>3</sup>He and <sup>4</sup>He are perhaps the only isotopic mixtures to undergo phase separation in laboratory times.<sup>13,14</sup>

In the present work, we develop a theory of defects<sup>15</sup> which is applicable to quantum crystals. We have borrowed from the elegant theory of defects in crystals developed<sup>16</sup> by Lifshitz and by Montroll and from Koehler's formulation<sup>6</sup> of the theory of perfect quantum crystals. We state here the theoretical problem, which precludes the application of the Lifshitz-Montroll theory to quantum crystals. Accepting that self-consistent phonons are the quasiparticles for perfect quantum crystals, the introduction of a mass defect produces a shift in the eigenfrequencies and the eigenvectors, which in turn produces a change in the force constant in the quantum crystals of the same order as the mass defect. The simple mass-defect theory is then no longer valid, and one requires a self-consistent treatment of the whole mass-force-constant defect complex.

Our method is also applicable to the calculation of the properties of extended defects (a strong mass defect and rapidly decreasing force-constant defects its vicinity).

In Sec. II we briefly review the classical theory of defects, and in Sec. III this theory is generalized by a variational method to be applicable to quantum crystals. In Sec. IV we discuss the results and review previous work on this problem.

## II. "CLASSICAL" TREATMENT OF DEFECT PROBLEMS

Let the pure crystal be composed of particles of mass  $M$  arranged in a Bravais lattice and interact-

ing with harmonic force constants  $A_{\alpha\beta}(l, l')$ . For the pure crystal the  $3N$  equations of motion for the displacements  $u_\alpha(l)$  in the direction  $\alpha$  of a particle whose mean position is  $\vec{R}_l$  are

$$M \ddot{u}_\alpha(l) + \sum_{l' \neq l} A_{\alpha\beta}(l, l') u_\beta(l') = 0. \quad (2.1)$$

The eigenvalues  $\omega_\lambda^2(\vec{k})$  and the eigenvectors  $\epsilon_{\lambda\alpha}(\vec{k})$  pertain to the dynamical matrix

$$D_{\alpha\beta}(\vec{k}) = \frac{1}{M} \sum_{l < l'} A_{\alpha\beta}(l, l') e^{i\vec{k} \cdot (\vec{R}_l - \vec{R}_{l'})}. \quad (2.2)$$

The eigenvectors are orthogonal and may be normalized so that

$$\begin{aligned} \sum_\alpha \epsilon_{\alpha\lambda}^*(\vec{k}) \epsilon_{\alpha\lambda'}(\vec{k}) &= \delta_{\lambda\lambda'}, \\ \sum_\lambda \epsilon_{\alpha\lambda}^*(\vec{k}) \epsilon_{\lambda\beta}(\vec{k}) &= \delta_{\alpha\beta}. \end{aligned} \quad (2.3)$$

The normal coordinates of the problem are

$$q_\lambda(\vec{k}) = \sum_{\alpha, l} T_{\lambda\alpha}^*(\vec{k}l) u_\alpha(l), \quad (2.4)$$

where

$$T_{\alpha\lambda}(\vec{k}, l) = (NM)^{-1/2} \epsilon_{\alpha\lambda}^*(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_l}. \quad (2.5)$$

The elements of  $T$  satisfy the equation

$$\sum_{\beta, l'} A_{\alpha\beta}(l, l') T_{\beta\lambda}(\vec{k}, l') = M \omega_\lambda^2(\vec{k}) T_{\alpha\lambda}(\vec{k}, l'), \quad (2.6)$$

this being the definition of a diagonalizing operator. The eigenvectors  $T_{\alpha\lambda}(\vec{k}, l)$  are normalized,

$$\sum_{\alpha, l} M(l) |T_{\alpha\lambda}(\vec{k}, l)|^2 = 1. \quad (2.7)$$

In the presence of defects,  $M$  will depend on  $l$ , and  $A_{\alpha\beta}(l, l')$  will not depend only on  $l - l'$ ; as a consequence  $\vec{k}$  cannot be used to characterize the modes. The equation of motion for the particles in a defective crystal may be written in terms of that for a pure crystal as

$$-M \omega_\alpha^2 u_\alpha(l) + \sum_{\beta, l'} A_{\alpha\beta}(l, l') u_\beta(l') = \sum_{\beta, l'} C_{\alpha\beta}(l, l') u_\beta(l'), \quad (2.8)$$

where  $C_{\alpha\beta}(l, l')$  is the defect matrix

$$C_{\alpha\beta}(l, l') = -\Delta M(l) \omega_\alpha^2 \delta_{\alpha\beta}(l, l') + \Delta A_{\alpha\beta}(l, l') \quad (2.9)$$

and  $\Delta M(l)$  and  $\Delta A_{\alpha\beta}(l, l')$  are the deviations. Now we introduce new normal modes for the lattice with defects, in analogy to (2.4):

$$u_\alpha(l) = \sum_\nu T_\alpha(\nu, l) q(\nu), \quad (2.10)$$

where  $\nu$  labels the  $3N$  normal modes just as  $\vec{k}, \lambda$  do for the perfect crystal.

By definition  $T_\alpha(\nu, l)$  satisfy

$$\begin{aligned} -\omega_\nu^2 M T_\alpha(\nu, l) + \sum_{\beta, l'} A_{\alpha\beta}(\nu, l') T_\beta(\nu, l') \\ = \sum_{\beta, l'} C_{\alpha\beta}(\nu, l') T_\beta(\nu, l'). \end{aligned} \quad (2.11)$$

The solution of (2.11) may be written in terms of the Green's function  $g_{\alpha\beta}^\nu(l, l')$  which satisfies the

equation

$$-\omega_\nu^2 M g_{\alpha\gamma}^\nu(l, l'') + \sum_{\beta l'} A_{\alpha\beta}(l, l') g_{\beta\gamma}^\nu(l', l'') = \delta_{\alpha\gamma} \delta(l, l''). \quad (2.12)$$

Using (2.6), we obtain

$$g_{\alpha\beta}^\nu(l, l') = \sum_{\vec{k}\lambda} \frac{T_{\alpha\lambda}(\vec{k}l) T_{\lambda\beta}^*(\vec{k}l')}{\omega_\lambda^2(\vec{k}) - \omega_\nu^2}. \quad (2.13)$$

The solution of (2.11) is

$$T_\alpha(\nu, l) = \sum_{\beta l'} \sum_{\gamma l''} g_{\alpha\beta}^\nu(l, l') C_{\beta\gamma}(l'' l') T_\gamma(\nu, l''), \quad (2.14)$$

and since the new  $T_\alpha(\nu, l)$  are normalized as

$$\sum_{\alpha, l} M(l) |T_\alpha(\nu, l)|^2 = 1, \quad (2.15)$$

they are completely determined.

In (2.14) only those  $T_\gamma(\nu, l)$  appear in the right-hand side that are affected by the defect. Using these in the left-hand side, we obtain a set of homogeneous equations that have a solution if and only if

$$\det \left| \sum_{\beta l''} g_{\alpha\beta}^\nu(l, l'') C_{\beta\gamma}(l'' l') - \delta_{\alpha\gamma} \delta(l, l') \right| = 0. \quad (2.16)$$

This determinant has the same dimensions as the number of coordinates affected by the defect, and this is what makes this procedure workable in determining the properties of a crystal with a small concentration of defects.

We now specialize the above treatment to a single defect mass  $M'$  at the origin. If  $\epsilon = (M - M')/M$ ,

$$C_{\alpha\beta}(l, l') = -\epsilon M \omega^2 \delta_{\alpha\beta}(l, 0) \delta(l', 0).$$

Equation (2.14) now reduces to

$$T_\alpha(\nu, l) = -\epsilon M \omega_\nu^2 \sum_\beta g_{\alpha\beta}^\nu(l, 0) T_\beta(\nu, 0) \quad (2.17)$$

and (2.16) reduces to a  $3 \times 3$  determinant,

$$|\epsilon M \omega_\nu^2 g_{\alpha\beta}^\nu(0, 0) + \delta_{\alpha\beta}| = 0. \quad (2.18)$$

For Bravais cubic lattices,  $g_{\alpha\beta}^\nu(0, 0) = \delta_{\alpha\beta} g^\nu(0, 0)$ , and hence from (2.17) we have the threefold degenerate solutions

$$1 + \frac{\epsilon \omega_\nu^2}{3N} \sum_{\vec{k}, \lambda} \frac{1}{\omega_\lambda^2(\vec{k}) - \omega_\nu^2} = 0, \quad (2.19)$$

which we may write more concisely as

$$\epsilon \omega_\nu^2 g^\nu(0, 0) = -1, \quad (2.20)$$

where

$$g^\nu(0, 0) = \frac{1}{3N} \sum_{\vec{k}, \lambda} \frac{1}{\omega_\lambda^2(\vec{k}) - \omega_\nu^2}.$$

Equation (2.19) provides the new eigenfrequencies for the problem and (2.14) and (2.15) give the new eigenvectors.

We briefly discuss the characteristics of the solutions obtained from Eqs. (2.19) and (2.20). If the

defect mass is heavier than the host mass ( $\epsilon < 0$ ), the frequencies given by (2.19) are decreased from their unperturbed values, but by no more than the difference between the unperturbed frequencies. Thus the  $\omega_\nu$  are different from  $\omega_{\vec{k}\lambda}$  by  $O(1/N)$ ; however, any physical property which is a function of the sum over all frequencies is affected to  $O(1)$ . The frequency dependence of the amplitude of the defect atom,  $|T(\nu 0)|^2$ , is altered from that of the perfect crystal, which is a constant (in the Debye approximation). There is a low-frequency resonance, in the amplitude, which shifts to lower frequencies as  $|\epsilon|$  increases. This resonance behavior often gives rise to a pronounced dip in the thermal conductivity as a function of temperature at high temperatures.

If the mass defect is lighter, all the frequencies are increased, but again by no more than the difference between adjacent unperturbed frequencies; also a new mode is generated at a frequency higher than that of the perfect crystal and which decays exponentially away from the defect site. The introduction of defects changes the optical properties of ionic crystals. It changes the velocity and mean square displacement; the change in velocity is seen in Mössbauer experiments. The presence of local modes gives rise to an exponential temperature dependence in the spin-lattice relaxation times in some substances. There are various other observable effects; these have been reviewed by Maradudin.<sup>17</sup>

### III. ISOTOPE DEFECTS IN QUANTUM CRYSTALS

Since the interatomic potentials between different isotopes of helium are the same, one may expect that the simple mass-defect theory reviewed in Sec. II would ideally apply to them. As was pointed out in the Introduction, it is, in fact, quite inapplicable because of the large zero-point motion in such crystals, which necessitates the use of a re-normalized theory for the excitations. A simple isotope defect which changes the eigenfrequencies and eigenvectors also produces a change in the effective force constants for the defect and its neighbors of the same order. The eigenfrequencies and the eigenvectors must now be calculated anew. Thus a single mass defect leads to a multidefect problem because of the many-body effects. Now a multidefect problem in which the defect has to be determined self-consistently is a hopeless task. The approach to the problem we adopt here is to reduce the problem to that of a single defect, and yet take care of the self-consistent force changes in the best possible fashion. As we show below, this approach leads to an effective mass which is frequency dependent.

#### A. Variational Solution of Defect Problem in Quantum Crystals

Our method is variational; we choose the wave

function (or equivalently the eigenvectors) of a model problem and use the variational principle to determine the parameters in it. The parameters will be chosen to be the new frequencies (or equivalently the elements of the force-constant matrix). This part of our work is similar to Koehler's.<sup>6</sup> We will also have to determine the force-constant defects self-consistently.

As the variational wave function, we choose the wave function for a specified set of defects within the harmonic approximation:

$$\varphi_0 = \eta \exp\left(-\sum_{i,j} \frac{1}{2} (m_i m_j)^{1/2} u_i G_{ij} u_j\right). \quad (3.1)$$

The force-constant matrix  $\overline{G}$  is determined variationally with the restriction that it be diagonalized by the eigenvectors (2.14) to yield the frequencies, which in turn affect the eigenvectors. The norm  $\eta$  in (3.1) is given by

$$\eta^2 = (\hbar \pi)^{-3N/2} |G|^{1/2}. \quad (3.2)$$

We write the Hamiltonian for the defect problem under consideration as the sum of a kinetic-energy part  $H_0$  and a potential-energy part  $H_1$ :

$$H = H_0 + H_1.$$

The expectation value of  $H$  in the state  $\varphi_0$  is

$$E = \langle \varphi_0, (H_0 + H_1) \varphi_0 \rangle, \quad (3.3)$$

$$\langle \varphi_0, H_0 \varphi_0 \rangle = -\frac{1}{2} \sum_i \int \varphi_0 (\nabla_i^2 / m_i) \varphi_0 = \frac{1}{4} \sum_i G_{ii}.$$

Thus we have

$$E = \frac{1}{4} \sum_i G_{ii} + \int H_1 \varphi_0^2. \quad (3.4)$$

We use the elements of  $G$  as the variational parameters, so that by the variational principle

$$\frac{\partial}{\partial G_{kl}} E = 0 = \frac{1}{4} \delta_{kl} + \int H_1 \frac{\partial}{\partial G_{kl}} \varphi_0^2.$$

Now we have

$$\frac{\partial}{\partial G_{kl}} \eta^2 = \frac{1}{2|G|} \eta^2 G_{kl}^c,$$

where  $G_{kl}^c$  is the cofactor of the element  $G_{kl}$  and

$$|G| = \sum_i G_{ia} G_{ia}^c = \sum_i G_{ai} G_{ai}^c.$$

Thus we have

$$\frac{\partial}{\partial G_{kl}} \varphi_0^2 = \frac{1}{2|G|} G_{kl}^c \varphi_0^2 - (m_k m_l)^{1/2} u_k u_l \varphi_0^2,$$

so that

$$\begin{aligned} 0 &= \frac{1}{4} \delta_{kl} + \int H_1 \left( \frac{1}{2|G|} G_{kl}^c \varphi_0^2 - (m_k m_l)^{1/2} u_k u_l \varphi_0^2 \right) \\ &= \frac{\partial}{\partial G_{kl}} E. \end{aligned} \quad (3.5)$$

Next we note that

$$\begin{aligned} \frac{\partial^2}{\partial u_k \partial u_l} \varphi_0^2 &= \frac{\partial}{\partial u_k} \left[ -2 \left( \sum_r (m_r m_r)^{1/2} G_{lr} u_r \right) \varphi_0^2 \right] \\ &= -2(m_l m_r)^{1/2} G_{kl} \varphi_0^2 + 4(m_l m_k)^{1/2} \\ &\quad \times \sum_{r,s} [(m_r)^{1/2} G_{lr} u_r] [(m_s)^{1/2} G_{rs} u_s] \varphi_0^2. \end{aligned} \quad (3.6)$$

Now multiplying (3.5) by  $G$  on both sides, and using (3.6), we get

$$0 = \frac{1}{4} \sum_k G_{ik} G_{kj} - \frac{1}{4(m_i m_j)^{1/2}} \frac{\partial^2}{\partial u_i \partial u_j} \varphi_0^2. \quad (3.7)$$

Thus we have

$$(G^2)_{ij} = \frac{1}{(m_i m_j)^{1/2}} \int H_1 \frac{\partial^2}{\partial u_i \partial u_j} \varphi_0^2 \equiv \frac{\langle P_{ij} \rangle}{(m_i m_j)^{1/2}}. \quad (3.8)$$

Using the fact that  $T_\alpha(\nu, i)$  are eigenvectors of  $\overline{G}$ , we obtain

$$\omega_\nu^2 = \sum_{i\alpha, j\beta} T_\alpha(\nu, i) \langle P_{i\alpha, j\beta} \rangle T_\beta^*(\nu, j). \quad (3.9)$$

#### B. Single Mass-Defect Variational Solution

We now specialize (3.9) for the case when  $\varphi_0$  is the wave function of the problem with a single mass defect at the origin. We therefore use the eigenvectors  $T$  of the single-defect problem:

$$T_\alpha(\nu, l) = -\epsilon M \omega_\nu^2 \sum_\beta g_{\alpha\beta}^\nu(l, 0) T_\beta(\nu, 0). \quad (3.10)$$

Substituting (3.10) in (3.9) and using the properties of a Bravais lattice, we obtain

$$\begin{aligned} (\epsilon M \omega_\nu)^{-2} &= -\sum_\gamma T_\gamma(\nu, 0) T_\gamma^*(\nu, 0) \\ &\quad \times \sum_{i\alpha, j\beta} \langle P_{i\alpha, j\beta} \rangle g_{\alpha\gamma}^\nu(i, 0) g_{\beta\gamma}^{\nu*}(j, 0). \end{aligned} \quad (3.11)$$

The normalization condition (2.15) may be written

$$\sum_{\alpha, l} M |T_\alpha(\nu, l)|^2 - \sum_\alpha \epsilon M |T_\alpha(\nu, 0)|^2 = 1. \quad (3.12)$$

Using (3.10), contracting with (2.3) and using the symmetry of a cubic Bravais lattice, we obtain

$$|T_\alpha(\nu, 0)|^2 = \frac{1}{3\epsilon M} \left( \frac{\epsilon \omega_\nu^4}{3N} \sum_{\vec{k}\lambda} \frac{1}{[\omega_\lambda^2(\vec{k}) - \omega_\nu^2]^2} - 1 \right)^{-1}. \quad (3.13)$$

Now we write

$$\langle P_{i\alpha, j\beta} \rangle = \langle P_{i\alpha, j\beta}^0 \rangle + \langle \Delta P_{i\alpha, j\beta} \rangle,$$

where  $\langle P_{i\alpha, j\beta}^0 \rangle$  is the value for a perfect crystal and  $\langle \Delta P_{i\alpha, j\beta} \rangle$  is the change introduced by the defect.

We use the fact that

$$\sum_{i\alpha, j\beta} T_{\alpha\lambda}^*(\vec{k}, i) \langle P_{i\alpha, j\beta}^0 \rangle T_{\beta\lambda}(\vec{k}, j) = \omega_{\vec{k}\lambda}^2 \quad (3.14)$$

to get

$$\sum_{i\alpha, j\beta} \langle P_{i\alpha, j\beta} \rangle g_{\alpha\gamma}^\nu(i, 0) g_{\beta\gamma}^{\nu*}(j, 0)$$

$$= \frac{1}{NM} \sum_{\vec{k}\lambda} \frac{\omega_\lambda^2(\vec{k})}{[\omega_\lambda^2(\vec{k}) - \omega_\nu^2]^2} + \sum_{i\alpha, j\beta} \langle \Delta P_{i\alpha, j\beta} \rangle g_{\alpha\gamma}^\nu(i, 0) g_{\beta\gamma}^{\nu*}(j, 0) . \quad (3.15)$$

Using (3.15) in (3.11) we get

$$-1 = \epsilon M \omega_\nu^2 \left( \frac{1}{3NM} \sum_{\vec{k}\lambda} \frac{1}{\omega_\lambda^2(\vec{k}) - \omega_\nu^2} + \frac{1}{3} \sum_{i\alpha, j\beta} g_{\alpha\gamma}^\nu(i, 0) \langle \Delta P_{i\alpha, j\beta} \rangle g_{\beta\gamma}^{\nu*}(j, 0) \right) . \quad (3.16)$$

In "classical" crystals with a single mass defect,  $\langle \Delta P_{i\alpha, j\beta} \rangle = 0$  and we get the old result (2.19).

The next problem is to determine  $\langle \Delta P_{ij} \rangle$ . The problem of the hard core in the potential may be handled as by Nosanow.<sup>3</sup> If  $v_{ij}$  is the effective nonsingular potential obtained from the first two terms of the cluster expansion, we have that

$$\begin{aligned} \langle P_{ij}^0 \rangle &= \int H_1 \frac{\partial^2}{\partial u_i \partial u_j} \varphi_0^2 \\ &= \int \varphi_0^2 \frac{\partial^2}{\partial u_i \partial u_j} v_{ij} , \quad i \neq j \\ &= \sum_k \int \varphi_0^2 \frac{\partial^2}{\partial u_i^2} v_{ik} , \quad i = j \end{aligned} \quad (3.17)$$

where  $\varphi_0$  is the ground-state wave function for the perfect crystal. Koehler<sup>6</sup> has shown that it is possible to reduce (3.17) to integration over a single variable to get

$$\begin{aligned} \langle P_{ij}^0 \rangle &= \int e^{-\vec{u}_{ij} \cdot \vec{F}_{ij}^0} \frac{\partial^2}{\partial u_i \partial u_j} v_{ij} , \quad i \neq j \\ &= \int e^{-\vec{u}_{ij} \cdot \vec{F}_{ij}^0} \sum_k \frac{\partial^2}{\partial u_i^2} v_{ik} , \quad i = j \end{aligned} \quad (3.18)$$

where  $\vec{F}^0$  is given by

$$(F_{ij}^0)^{-1} = \sum_{\vec{k}\lambda} \omega_{\vec{k}\lambda}^{-1} (1 - T_{\vec{k}\lambda}^* T_{\vec{k}\lambda}) . \quad (3.19)$$

In an analogous fashion it can be proved that

$$\begin{aligned} \langle P_{ij} \rangle &= \int e^{-\vec{u}_{ij} \cdot \vec{F}_{ij}} \frac{\partial^2}{\partial u_i \partial u_j} v_{ij} , \quad i \neq j \\ &= \int e^{-\vec{u}_{ij} \cdot \vec{F}_{ij}} \sum_k \frac{\partial^2}{\partial u_i^2} v_{ik} , \quad i = j \end{aligned} \quad (3.20)$$

where  $\vec{F}$  is given by

$$(F_{ij})_{\alpha\beta}^{-1} = \sum_\nu [ |\vec{T}_{i\alpha}(\nu)|^2 + |T_{j\beta}(\nu)|^2 - 2T_{i\alpha}^* T_{j\beta}(\nu) ] \omega_\nu^{-1} . \quad (3.21)$$

Due to the altered effective potential between the particles, there will, in general, be a distortion around the defect. We may determine the distortion by varying  $\langle \varphi_0 | H | \varphi_0 \rangle$  with respect to the average distance between particles  $R_{ll'}$  to obtain

$$\sum_{l'} \left\langle \frac{\partial}{\partial R_{l'}} v_{ll'} \right\rangle = 0 \text{ for each } l . \quad (3.22)$$

#### IV. DISCUSSION

Equations (3.16), (3.20), and (3.22) give the complete solution to the problem in our variational ansatz. Comparing the form of (3.16) with (2.19) it is apparent that the defect problem in quantum crystals has been reduced to that of a single frequency-dependent mass. Our method is applicable also for the calculation of the properties of extended defects in "classical" crystals with a strong mass defect and weaker force-constant defects around it. In this case, one may use (3.16) to calculate the properties of the defect complex with  $\Delta P_{i\alpha, j\beta}$  taken as given. The advantage again would be that if the defect is indeed well localized, good approximate answers may be obtained from the solution of a determinantal equation of at the most three dimensions rather than solving in as many coordinates as are affected by the defect. This could serve as an alternate method to that devised by Oitmaa and Maradudin<sup>18</sup> to handle the same difficulty.

Some numerical results of a calculation for <sup>4</sup>He defects in solid <sup>3</sup>He were presented earlier.<sup>15</sup> Detailed calculations with application to thermal conductivity will be presented later. For completeness we shall merely summarize here the conclusions arrived at earlier<sup>15,19</sup>:

(a) The force constants around the defect are changed significantly up to the third nearest neighbor. The force constants change in such a manner that for equilibrium properties the "defectiveness" is reduced. For example, the mean square displacement of the <sup>4</sup>He atom is brought closer to that of the <sup>3</sup>He atoms, and the lattice distortion around the <sup>4</sup>He atom is reduced by the force-constant re-normalization. Thus the force-constant changes act to "screen" the impurity.

(b) There is very little lattice distortion around the defect. For all densities of <sup>3</sup>He in the bcc phase it was found to be less than 1.5%. The large effect on thermal conductivity on addition of defects is thus not due to strains as has been believed.<sup>8,9</sup> Also, there is negligible change in the exchange frequency of the <sup>3</sup>He atoms around the <sup>4</sup>He defect. We calculated the change in the exchange frequency and found it to be less than 10%.

(c) The thermal conductivity change is accounted for by the force-constant changes.<sup>15</sup> This point needs further study however, since different methods<sup>8,9</sup> of analyzing the thermal conductivity data yield different results for the effect of defects. The difference in the analysis lies in the different frequency dependence used for the normal process relaxation rate  $\tau_N(\omega)$ . The data in Ref. 8 are generally for higher temperatures than in Ref. 9 (although there is an overlapping region) and the choice for  $\tau_N(\omega)$  of Ref. 8 did not fit the data of Ref. 9 and vice versa. We suggest that the same  $\tau_N(\omega)$

should be used throughout the temperature range of Refs. 8 and 9 and that the additional frequency dependence is in the effective mass of the impurity. The two sets of data can then be reconciled. As we mentioned earlier, our results are equivalent to having a frequency-dependent effective mass.

(d) The low-frequency amplitude of the  $^3\text{He}$  atoms around the defect is enhanced. In other words, there is a change in the local low-frequency density of states. The effect is significant as far as the third neighbor. We can in principle understand the variation of the temperature dependence of the spin-lattice relaxation rates  $T_1$  with  $^4\text{He}$  concentration on this basis. Formally, the calculation of  $T_1$  involves a (double) integral over the frequency spectrum, and its temperature dependence is determined by the power to which the frequency appears in the integral.

(e) The enhanced exchange frequency around the defect has been deduced from measurements of the intermediate-bath heat capacity in NMR measurements. As already mentioned by us and in calculations performed by Glyde, there is, in fact, no enhancement of the exchange frequency. We have proposed<sup>19</sup> that the increased heat capacity arises due to the hopping motion of  $^4\text{He}$  in the lattice, which contributes to the intermediate-bath heat capacity. In NMR theory this motion may be represented by a separate bath which couples strongly to the exchange bath of the  $^3\text{He}$  atoms in a temperature-independent fashion. It also couples to the phonon bath through the scattering of phonons in the hopping process and relaxes to it at a rate determined by the Raman process.

Now we briefly comment upon the work done on defects in quantum crystals by other workers. Most of the work has been done using an Einstein spectrum for the solid. This is quite appropriate for properties which depend upon the total energy or strain in the crystal. Thus Mullin<sup>20</sup> obtained excellent results in his calculations of the phase-separation of the  $^3\text{He}$ - $^4\text{He}$  mixtures, and Glyde<sup>21</sup> concluded that there is no enhancement of exchange frequency around the defect. Guyer's<sup>22</sup> work on phase separation suffered from using an inappropriate criterion for phase separation. The Einstein picture of the crystal is however quite inappropriate for calculating any frequency-dependent properties like thermal conductivity or spin-lattice relaxation rates.

There has been an attempt made by Jones<sup>23</sup> concurrently with ours to develop a theory of defects in quantum crystals with a reasonable spectrum for the solid. The starting point, Eq. (3.1), is the same. However instead of using a variational principle throughout as we have, the author uses perturbation theory in the parameter  $\epsilon$ . This leads to difficulties since the problem is nonperturbative in nature. Thus the results of Jones do not give the usual results in the "classical" limit, and he obtains an unphysical divergence of the strain due to the defect.

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