

## Cell Model of Quantum Liquids and Solids. I. Crystalline State\*

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A second-quantized cell-model Hamiltonian is derived to provide a model for quantum crystals and liquids. The boson crystal is treated in this article. The cells are divided into two sublattices: (i) *regular*, which are usually occupied, and (ii) *interstitial*, which are usually empty. The particle hard cores are simulated by assuming Fermi commutation relations for operators referring to a single cell; this allows a discussion in terms of a spin-analog Hamiltonian which is diagonalized in the spin-wave approximation. Because the Hamiltonian includes a term which allows tunneling between regular and interstitial sites, the ground state includes a description of zero-point motion and exchange via virtual intermediate interstitial occupation. Excited states include nonlocalized vacancies, interstitials, and vacancy-interstitial pairs. Phonon states are not included in this analysis. The model exhibits a phase transition to the Bose condensed state which is examined briefly.

### I. INTRODUCTION

The names "quantum liquid" and "quantum crystal" have been given to the condensed phases of helium because they manifest such interesting quantum phenomena. The zero-point energy is so large that liquid  $^4\text{He}$  has a superfluid phase and solid  $^3\text{He}$  exhibits nuclear exchange and antiferromagnetism<sup>1</sup> and such excitations as vacancy waves<sup>2</sup> and mass fluctuation waves.<sup>3</sup> The methods which will be described here have been used before (in references quoted below) to treat these substances, especially the superfluid phase. They will be applied to quantum solids in this article. The author believes they can also be used in further studies of the liquid state.

In recent years there have been several discussions in the literature<sup>4-7</sup> of a cell model of a Bose-Einstein (BE) condensed quantum fluid. This model uses cell-creation and -destruction operators which commute like ordinary Bose operators for different sites but which anticommute when they refer to the same site. This latter property ensures that no cell is doubly occupied and so simulates the effect of a hard-core potential. The mixed Bose and Fermi commutation relations are those of Pauli matrices and allow the model to be cast into a spin-analog form. The techniques of analysis developed for spin systems such as molecular field theory, spin-wave theory, etc., are then easily adapted to this problem.

This cell model is characterized by a hopping or tunneling term in the Hamiltonian which destroys a particle on a site and creates one on a neighboring site. This term is most directly responsible for the important features, such as the BE condensation which occurs in the liquid phase of this model. Such a term also occurs in the well-known Hubbard Hamiltonian<sup>8</sup> which has been used to describe vari-

ous electron effects in solids, such as the metal-insulator transition. Recently, Hubbard-like Hamiltonians have been used<sup>9,10</sup> to provide a model of several phenomena in quantum systems (helium, especially). The hopping term is quite evidently appropriate for liquids since the atoms do a considerable amount of roaming about. However, it also proves useful in describing phenomena characteristic of solid helium.

The work on the Hubbard Hamiltonian for quantum systems has stimulated us to apply the spin analog to the crystalline phase of quantum systems. Our model of a crystal turns out to be analogous to an anisotropic Heisenberg antiferromagnet. Since a spin-up in the spin-analog system represents an occupied cell and a spin-down an empty cell, our model contains regular (or normally filled) sites and interstitials. The interstitials give the particles a chance to move off their sites and allow several interesting phenomena to be described by the model. Among these are the excited states of the system: Frenkel-like vacancy-interstitial pair waves; the vacancy waves introduced by Hetherington<sup>2</sup> which are shown to be of the Schottky variety; and interstitial waves. A vacancy is found to be accompanied by a cloud of virtual interstitials. Particle exchange takes place via vacancy-interstitial pair intermediate states and is treated by the spin-wave analysis to all orders in multiparticle exchanges.

Recently Chester<sup>11</sup> has speculated that a quantum crystal may be described by a wave function which can exhibit a BE condensation. Strongly tied to this possibility is the deduction that a quantum crystal has a finite fraction of vacancies in the ground state. A discussion of ground-state "defectons" (vacancies, interstitials, and impurities) and their BE condensation has also been given by Andreev and Lifshitz.<sup>12</sup> Since our model is an anti-

ferromagnet analog which has a deviation from perfect sublattice magnetization even in the ground state, we find vacancy-interstitial pairs in our crystal ground state. However, these are not to be interpreted as true vacancies in the ground state but merely a cell-model manifestation of zero-point motion. As a particle oscillates around its lattice site it may move from its regular cell into a neighboring interstitial cell, thus forming a short-lived vacancy-interstitial pair, and then return to its regular cell. The pair never becomes unbound and we are not surprised that we find no BE condensation in our crystalline state. However, we find our solid undergoes a phase transition to a state which we believe has a BE condensation. Whether this state (or states) corresponds to a liquid or to the "superfluid solid" is discussed only briefly in Sec. VII and will be the subject of future research.

In Sec. II we derive the model Hamiltonian and it is diagonalized in Sec. III. The ground state of the system is discussed in Sec. IV and the vacancy wave excited states are treated in Sec. V. Some numerical estimates are given in Sec. VI. In Sec. VII we present some brief speculations concerning the transition from the solid to a Bose condensed phase and a discussion is contained in Sec. VIII.

## II. MODEL HAMILTONIAN

To describe a Bose solid we begin with a second-quantized Hamiltonian

$$H = \int \Psi^\dagger(\vec{r}) [- (\hbar^2/2m)\nabla^2] \Psi(\vec{r}) d\vec{r} + \frac{1}{2} \int \Psi^\dagger(\vec{r}) \Psi^\dagger(\vec{r}') V(\vec{r} - \vec{r}') \Psi(\vec{r}') \Psi(\vec{r}) d\vec{r} d\vec{r}' . \quad (2.1)$$

We expand<sup>9,10</sup> the field operator  $\Psi^\dagger(\vec{r})$  in a set of localized orthogonal states  $\zeta_{\vec{R}}^{(n)}$  (e.g., Wannier states):

$$\Psi^\dagger(\vec{r}) = \sum_{\vec{R}, n} b_{\vec{R}}^{(n)\dagger} \zeta_{\vec{R}}^{(n)}(\vec{r}) , \quad (2.2)$$

where  $b_{\vec{R}}^{(n)\dagger}$  is an operator which creates a particle in the  $n$ th excited state localized in the cell at  $\vec{R}$ . We truncate the complete set by considering only one localized state in each cell. By making this approximation we will lose the phonon excitations of our crystal<sup>13</sup>; however, the resulting Hamiltonian is still sufficiently complicated to be interesting. The operators  $b_{\vec{R}}$  and  $b_{\vec{R}'}^\dagger$  have Bose commutation relations for  $\vec{R}, \vec{R}'$  not equal, but we simulate the effect of the hard cores by assuming *anticommutation* relations for  $\vec{R} = \vec{R}'$ .<sup>4-7</sup> Thus we have

$$\begin{aligned} [b_{\vec{R}}, b_{\vec{R}'}^\dagger] &= 0, \quad [b_{\vec{R}}, b_{\vec{R}'}] = 0, \quad \vec{R} \neq \vec{R}' \\ \{b_{\vec{R}}, b_{\vec{R}}^\dagger\} &= 1, \quad \{b_{\vec{R}}, b_{\vec{R}}\} = 0. \end{aligned} \quad (2.3)$$

These relations assure that the number operator

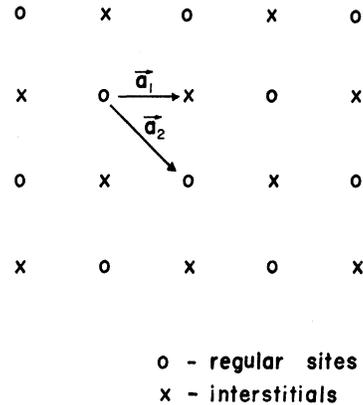


FIG. 1. Schematic representation of the two sublattices: the regular cells ( $\alpha$ ) which are occupied most of the time and the interstitial cells ( $\beta$ ) which are mostly empty. The distance between a regular cell and an interstitial is  $\vec{a}_1$ , and  $\vec{a}_2$  is the distance between two regular cells.

$n_{\vec{R}} = b_{\vec{R}}^\dagger b_{\vec{R}}$  will have eigenvalues 0 or 1 as expected for hard-core particles. The mixed commutation relations are those obeyed by Pauli matrices.

One new feature we wish to introduce in our treatment is the inclusion of interstitial lattice sites. We divide the lattice into two interpenetrating sublattices  $\alpha$  and  $\beta$  as illustrated in Fig. 1. It is assumed that in a crystalline phase most particles will occupy the *regular* sites  $\vec{R}_\alpha$  and very few will be found on the *interstitial* sites  $\vec{R}_\beta$ . Each regular site has, as its nearest neighbors,  $z_1$  interstitial sites at distances  $\vec{a}_1$ , and, as its second neighbors,  $z_2$  regular sites at distances  $\vec{a}_2$ .

Under these assumptions and upon substitution of (1.2), the kinetic energy becomes

$$KE = \sum_{\vec{R}} t_{\vec{R}} b_{\vec{R}}^\dagger b_{\vec{R}} - \tau \sum_{\vec{R}, \vec{a}_1} b_{\vec{R} + \vec{a}_1}^\dagger b_{\vec{R}} , \quad (2.4)$$

with

$$t_{\vec{R}} = (\hbar^2/2m) \int \zeta_{\vec{R}}^*(\vec{r}) \nabla^2 \zeta_{\vec{R}}(\vec{r}) d\vec{r} , \quad (2.5)$$

$$\tau = (\hbar^2/2m) \int \zeta_{\vec{R} + \vec{a}_1}^*(\vec{r}) \nabla^2 \zeta_{\vec{R}}(\vec{r}) d\vec{r} . \quad (2.6)$$

The first term in (2.4) is a kinetic energy associated with the localization of particles on cells. We will allow for the possibility that the value that this energy of localization has for regular sites,

$$t = t_{R_\alpha} ,$$

may differ from its value for interstitial sites,

$$t' = t_{R_\beta} .$$

The second term in Eq. (2.4) allows a particle to tunnel from a site at  $\vec{R}$  to one at  $\vec{R} + \vec{a}_1$ . We neglect any tunneling between sites separated by more than the nearest-neighbor distance  $\vec{a}_1$ . It is this tunneling term which gives rise to the effects we consider in this article.

If we insert our cell representation, Eq. (2.2), into the potential energy, we find a variety of types of terms, but we retain only the following interaction terms:

$$PE = \frac{1}{2} \sum_{\vec{R} \neq \vec{R}'} \phi(\vec{R} - \vec{R}') (b_{\vec{R}}^\dagger b_{\vec{R}}) (b_{\vec{R}'}^\dagger b_{\vec{R}'}), \quad (2.7)$$

where

$$\begin{aligned} \phi(\vec{R} - \vec{R}') = & \int \zeta_{\vec{R}}^*(\vec{r}) \zeta_{\vec{R}'}(\vec{r}') V(\vec{r} - \vec{r}') \\ & \times \zeta_{\vec{R}}(\vec{r}') \zeta_{\vec{R}'}(\vec{r}) d\vec{r} d\vec{r}'. \end{aligned} \quad (2.8)$$

The terms involving  $\vec{R} = \vec{R}'$  do not appear because of the commutation relations. Terms which have been dropped include the tunneling form containing  $(b_{\vec{R}}^\dagger b_{\vec{R}}) b_{\vec{R}_1}^\dagger b_{\vec{R}_2}$  and the double-tunneling form containing  $b_{\vec{R}_1}^\dagger b_{\vec{R}_2} b_{\vec{R}_3}^\dagger b_{\vec{R}_4}$ . The first type involves the interaction of a particle with one which is tunneling and should not produce any physical effect significantly different from those produced by the second term in Eq. (2.4). Since we are not attempting a first-principles derivation of the coefficients of the Hamiltonian, such as  $\tau$ , we can consider all tunneling factors as lumped in  $\tau$ . Also since double tunneling will occur in second order in the  $\tau$  term, we neglect such a term in the PE. We also neglect as small an additional exchange correction to  $\phi(\vec{R} - \vec{R}')$ . Our philosophy in these simplifications is that we are not striving for rigor but we want to arrive at a Hamiltonian representing the appropriate physical effects of a quantum crystal. There is an alternative derivation<sup>9,14</sup> of our Hamiltonian based on using nonoverlapping functions  $\zeta_{\vec{R}}$  and in replacing the  $\nabla^2$  operator by a finite-differences formula. In that derivation one finds  $t = \hbar^2 z_1 / 2ma_1^2$  and  $\tau = t/z_1$ .

Putting our results together we arrive at a model Hamiltonian similar to that used previously by other workers<sup>4-10</sup> to describe crystalline and liquid phases, but now containing a regular-site-Interstitial-site structure:

$$\begin{aligned} H = & t \sum_{\vec{R}_\alpha} n_{\vec{R}_\alpha} + t' \sum_{\vec{R}_\beta} n_{\vec{R}_\beta} \\ & - \tau \left( \sum_{\vec{R}_\alpha, \vec{a}_1} b_{\vec{R}_\alpha, \vec{a}_1}^\dagger b_{\vec{R}_\alpha} + \sum_{\vec{R}_\beta, \vec{a}_1} b_{\vec{R}_\beta, \vec{a}_1}^\dagger b_{\vec{R}_\beta} \right) \\ & + \phi_1 \sum_{\vec{R}_\alpha, \vec{a}_1} n_{\vec{R}_\alpha, \vec{a}_1} n_{\vec{R}_\alpha} - \frac{1}{2} \phi_2 \sum_{\vec{R}_\alpha, \vec{a}_2} n_{\vec{R}_\alpha, \vec{a}_2} n_{\vec{R}_\alpha} \\ & - \frac{1}{2} \phi_2 \sum_{\vec{R}_\beta, \vec{a}_2} n_{\vec{R}_\beta, \vec{a}_2} n_{\vec{R}_\beta}, \end{aligned} \quad (2.9)$$

with

$$n_{\vec{R}} = b_{\vec{R}}^\dagger b_{\vec{R}}, \quad (2.10)$$

$$\phi_1 = \phi(\vec{a}_1), \quad \phi_2 = -\phi(\vec{a}_2). \quad (2.11)$$

By the choice of signs in Eq. (2.11) we indicate our assumption that a particle on a regular ( $\alpha$ ) site has a repulsive interaction  $+\phi_1$  with a particle on a neighboring interstitial ( $\beta$ ) site, and that it has an

attractive interaction  $-\phi_2$  with a particle on the nearest regular (second-neighbor) site. Also two particles on two second-neighboring  $\beta$  sites are attracted according to  $-\phi_2$ .

### III. DIAGONALIZATION

The Hamiltonian can be transformed into a very familiar form by using the fact that the commutation relations are those of Pauli matrices. We can make the identification

$$b_{\vec{R}}^\dagger = \sigma_{\vec{R}}^{(+)}, \quad b_{\vec{R}} = \sigma_{\vec{R}}^{(-)}, \quad (3.1)$$

$$n_{\vec{R}} = b_{\vec{R}}^\dagger b_{\vec{R}} = \frac{1}{2} (1 + \sigma_{\vec{R}}^{(z)}). \quad (3.2)$$

In this spin-analog picture, an up-spin corresponds to an occupied site and a down-spin to an unoccupied one. The Hamiltonian becomes that of an anisotropic Heisenberg *antiferromagnet* because of the nearest-neighbor repulsion and the second-neighbor attraction on the regular-interstitial arrangement of sites. There are also effective external magnetic fields in the spin analog. We find

$$\begin{aligned} H = & \mathcal{G} - B \sum_{\vec{R}_\alpha} \sigma_{\vec{R}_\alpha}^{(z)} - B' \sum_{\vec{R}_\beta} \sigma_{\vec{R}_\beta}^{(z)} \\ & - \frac{\tau}{2} \sum_{\vec{R}, \vec{a}_1} (\sigma_{\vec{R}, \vec{a}_1}^{(+)} \sigma_{\vec{R}}^{(-)} + \sigma_{\vec{R}, \vec{a}_1}^{(-)} \sigma_{\vec{R}}^{(+)}) \\ & + \frac{1}{8} \phi_1 \sum_{\vec{R}, \vec{a}_1} \sigma_{\vec{R}, \vec{a}_1}^{(z)} \sigma_{\vec{R}}^{(z)} - \frac{1}{8} \phi_2 \sum_{\vec{R}, \vec{a}_2} \sigma_{\vec{R}, \vec{a}_2}^{(z)} \sigma_{\vec{R}}^{(z)}, \end{aligned} \quad (3.3)$$

with

$$\mathcal{G} = M(t + \frac{1}{4} z_1 \phi_1 - \frac{1}{4} z_2 \phi_2). \quad (3.4)$$

$M$  is the number of  $\alpha$  sites. (There are also  $M$   $\beta$  sites.) The analog external magnetic fields are

$$B = -\frac{1}{2}(t + \frac{1}{2} z_1 \phi_1 - \frac{1}{2} z_2 \phi_2), \quad (3.5)$$

$$B' = -\frac{1}{2}(t' + \frac{1}{2} z_1 \phi_1 - \frac{1}{2} z_2 \phi_2).$$

The particle number is, from Eq. (3.2),

$$N = M + \frac{1}{2} \sum_{\vec{R}} \sigma_{\vec{R}}^{(z)}. \quad (3.6)$$

To diagonalize  $H$  using this spin analogy one applies the usual spin-wave analysis.<sup>15</sup> We introduce boson spin deviation operators in reciprocal space,  $c_{\vec{k}}$  for deviations on the  $\alpha$  lattice and  $d_{\vec{k}}$  for those on the  $\beta$  lattice. These are defined by

$$\begin{aligned} \sigma_{\vec{R}_\alpha}^{(+)} & \simeq (1/\sqrt{M}) \sum_{\vec{k}} e^{-i\vec{k} \cdot \vec{R}_\alpha} c_{\vec{k}}, \\ \sigma_{\vec{R}_\beta}^{(+)} & \simeq (1/\sqrt{M}) \sum_{\vec{k}} e^{-i\vec{k} \cdot \vec{R}_\beta} d_{\vec{k}}^\dagger, \end{aligned} \quad (3.7)$$

$$\sigma_{\vec{R}_\alpha}^{(z)} = 1 - \frac{2}{M} \sum_{\vec{k}, \vec{k}'} e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_\alpha} c_{\vec{k}}^\dagger c_{\vec{k}'},$$

$$\sigma_{\vec{R}_\beta}^{(z)} = -1 + \frac{2}{M} \sum_{\vec{k}, \vec{k}'} e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_\beta} d_{\vec{k}}^\dagger d_{\vec{k}'},$$

The usual situation is for an  $\alpha$  site to be occupied by a particle and a  $\beta$  site (interstitial) to be empty, so  $c_{\mathbf{k}}^\dagger$  creates a vacancy wave of vector  $\mathbf{k}$ , and  $d_{\mathbf{k}}^\dagger$  creates an interstitial wave. This is easily seen by examination of the number operator in this representation, which is

$$N = M - \sum_{\mathbf{k}'} c_{\mathbf{k}'}^\dagger c_{\mathbf{k}'} + \sum_{\mathbf{k}} d_{\mathbf{k}}^\dagger d_{\mathbf{k}}. \quad (3.8)$$

Since  $\sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}$  is the number of vacancies in the system, it subtracts from the usual number of particles  $M$ ; similarly,  $\sum_{\mathbf{k}} d_{\mathbf{k}}^\dagger d_{\mathbf{k}}$  is the number of interstitial particles and adds to  $M$ .

If we introduce these boson operators in the usual way we find the approximate Hamiltonian

$$H = E_0 - \tau \sum_{\mathbf{k}} \gamma_{\mathbf{k}} (d_{\mathbf{k}}^\dagger c_{\mathbf{k}}^\dagger + d_{\mathbf{k}} c_{\mathbf{k}}) + (W + 2B) \sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + (W - 2B') \sum_{\mathbf{k}} d_{\mathbf{k}}^\dagger d_{\mathbf{k}}, \quad (3.9)$$

where

$$E_0 = M(t - \frac{1}{2}z_2\phi_2), \quad (3.10)$$

$$W = \frac{1}{2}(z_1\phi_1 + z_2\phi_2), \quad (3.11)$$

$$\gamma_{\mathbf{k}} = \sum_{\mathbf{a}_1} e^{i\mathbf{k}\cdot\mathbf{a}_1}. \quad (3.12)$$

Equation (3.9) has a simple interpretation:  $E_0$  is the Hartree-like energy that  $M$  particles have if all are localized on regular sites. However, a "spin deviation" on a regular site (i.e., a vacancy, with  $\langle \sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \rangle = 1$ ) costs an energy

$$\mu_v \equiv W + 2B = -t + z_2\phi_2. \quad (3.13)$$

One gains the kinetic energy  $t$  but must break  $z_2$  attractive bonds of strength  $\phi_2$  in making the vacancy. Similarly, the energy to make an interstitial is

$$\mu_I \equiv W - 2B' = t' + z_1\phi_1. \quad (3.14)$$

The added energy is the interstitial cell kinetic energy  $t'$  and the interstitial-regular-site potential energy  $z_1\phi_1$ .

We have not yet diagonalized  $H$  since we still have the tunneling terms containing the factor  $\gamma_{\mathbf{k}}$ . To complete the diagonalization we make the necessary Bogoliubov transformation<sup>15</sup>

$$\alpha_{\mathbf{k}} = u_{\mathbf{k}} c_{\mathbf{k}} - v_{\mathbf{k}} d_{\mathbf{k}}^\dagger, \quad \beta_{\mathbf{k}} = u_{\mathbf{k}} d_{\mathbf{k}} - v_{\mathbf{k}} c_{\mathbf{k}}^\dagger, \quad (3.15)$$

with

$$u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2 = 1. \quad (3.16)$$

The Hamiltonian is diagonalized if

$$u_{\mathbf{k}}^2 = \frac{1}{2} \{ [1 - (\tau \gamma_{\mathbf{k}}/D)^2]^{-1/2} + 1 \}, \quad (3.17)$$

$$v_{\mathbf{k}}^2 = \frac{1}{2} \{ [1 - (\tau \gamma_{\mathbf{k}}/D)^2]^{-1/2} - 1 \},$$

where

$$D = W + B - B' = \frac{1}{2}(t' - t + z_1\phi_1 + z_2\phi_2). \quad (3.18)$$

The energy spectrum is

$$E = E_0 + E_1 + \sum_{\mathbf{k}} (\omega_{\mathbf{k}}^{(\alpha)} n_{\mathbf{k}} + \omega_{\mathbf{k}}^{(\beta)} m_{\mathbf{k}}), \quad (3.19)$$

where

$$E_1 = \sum_{\mathbf{k}} D \{ [1 - (\tau \gamma_{\mathbf{k}}/D)^2]^{1/2} - 1 \}, \quad (3.20)$$

$$\omega_{\mathbf{k}}^{(\alpha)} = D [1 - (\tau \gamma_{\mathbf{k}}/D)^2]^{1/2} + B + B', \quad (3.21)$$

$$\omega_{\mathbf{k}}^{(\beta)} = D [1 - (\tau \gamma_{\mathbf{k}}/D)^2]^{1/2} - B - B', \quad (3.22)$$

and  $n_{\mathbf{k}}$  and  $m_{\mathbf{k}}$  are non-negative integers.

#### IV. GROUND STATE

The ground state is  $E = E_0 + E_1$ . We have already seen that  $E_0$  is the Hartree-like energy for  $M$  particles on  $M$  regular sites. The energy  $E_1$  arises from the tunneling part of  $H$  and corresponds to the zero-point energy of vacancy-interstitial pairs. Its nature is best understood if we assume, as is valid in most of the crystalline phase (even for solid helium), that  $\tau/D \ll 1$ . Then, since

$$\sum_{\mathbf{k}} \gamma_{\mathbf{k}}^2 = Mz_1, \quad (4.1)$$

we find the following expansion in  $\tau/D$ :

$$E_1 = -\frac{1}{2}Mz_1(\tau^2/D) - \frac{1}{8}(\tau^4/D^3) \sum_{\mathbf{k}} \gamma_{\mathbf{k}}^4 + \dots \quad (4.2)$$

The two terms shown in this series could be derived by using perturbation theory up to fourth order in the tunneling term with the rest of the Hamiltonian as the unperturbed part [see Eq. (2.9)]. The first term is the energy associated with a particle moving from a regular site to an interstitial and back again. To see this, look at the second-order perturbation formula (first order vanishes)

$$\Delta E_2 = \frac{\langle 0 | H_1 | p \rangle \langle p | H_1 | 0 \rangle}{E_0 - E_p}, \quad (4.3)$$

where

$$H_1 = -\tau \sum_{\mathbf{R}, \mathbf{a}_1} b_{\mathbf{R}, \mathbf{a}_1}^\dagger b_{\mathbf{R}}. \quad (4.4)$$

The ground state  $|0\rangle$  has particles on all  $\alpha$  sites and all  $\beta$  sites are empty, so that the  $H_1$  on the right of  $\Delta E_2$  creates one vacancy and one interstitial on a pair of neighboring  $\alpha$  and  $\beta$  sites. The second  $H_1$  returns the system to the ground state. The energy denominator is

$$E_0 - E_p = \mu_I + \mu_v = t' + z_1\phi_1 - t + z_2\phi_2 = 2D. \quad (4.5)$$

Thus, we have

$$\Delta E_2 = - \sum_{\mathbf{R}, \mathbf{a}_1}^{(-\tau)} \frac{1}{2D} (-\tau) = - \frac{Mz_1\tau^2}{2D}, \quad (4.6)$$

as in Eq. (4.2). This motion of a particle into an interstitial site and then back again to its regular site is simply the cell-model representation of zero-point motion. When tunneling is possible, the state of the system with all particles on regular sites is not the ground state. This effect also oc-

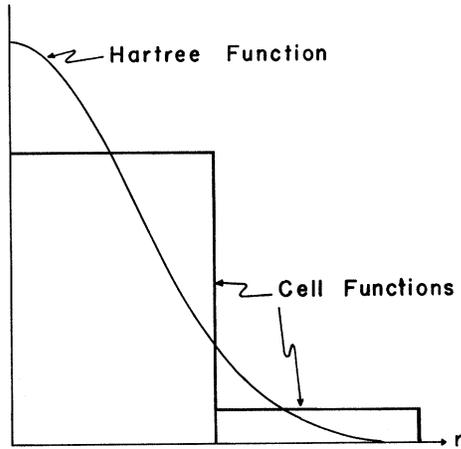


FIG. 2. Comparison of the cell model with a Hartree theory. The cell functions in this example are step functions. The large cell function gives the probability of finding a particle on a regular lattice, the small one gives the probability of occupation of an interstitial. In a Hartree theory this probability is given by a single continuous function as shown.

curs in the spin analog: The ground state of an antiferromagnet does not have complete spin alignment on each of the two sublattices. The number of these "ground-state vacancies" (or interstitials) is

$$\begin{aligned}
 N_V &= \sum_{\mathbf{R}_\beta} \langle 0 | b_{\mathbf{R}_\beta}^\dagger b_{\mathbf{R}_\beta} | 0 \rangle = \sum_{\mathbf{k}} v_{\mathbf{k}}^2 \\
 &= \frac{1}{2} \sum_{\mathbf{k}} \{ [1 - (\tau \gamma_{\mathbf{k}}/D)^2]^{-1/2} - 1 \} \\
 &\approx M z_1 \tau^2 / 4D^2 \quad \text{for } \tau/D \ll 1. \quad (4.7)
 \end{aligned}$$

This result means that any particle spends  $N_V/M$  of its time in neighboring cells because of zero-point motion, as it would in a non-cell-model description by a Hartree single-particle function (see Fig. 2).

The second term in (4.2) corresponds to the exchange of pairs of particles and can be derived in fourth-order perturbation theory. Two particles on regular  $\alpha$  sites a distance  $\tilde{a}_2$  apart move into an interstitial and then, instead of moving back into their original sites, they move into each other's sites and so end up exchanged (see Fig. 3). The factor  $\sum_{\mathbf{k}} \gamma_{\mathbf{k}}^4$  is the number of sets of two regular sites and two interstitials in the lattice such that near-neighbor exchange can take place. One can show that

$$\sum_{\mathbf{k}} \gamma_{\mathbf{k}}^4 = M \sum_{\tilde{\mathbf{a}}_1, \tilde{\mathbf{a}}_1', \tilde{\mathbf{a}}_1'', \tilde{\mathbf{a}}_1'''} \delta_{\tilde{\mathbf{a}}_1 + \tilde{\mathbf{a}}_1' + \tilde{\mathbf{a}}_1'' + \tilde{\mathbf{a}}_1''', 0} \approx 12M, \quad (4.8)$$

where the last equality is exact if the  $\alpha$  and  $\beta$  sublattices are each face-centered cubic interpenetrating to form a simple cubic lattice. This model of

exchange is very similar to that proposed by Guyer and Zane<sup>16</sup> (cf. their Fig. 9), in which particles must move out of line to interstitial positions, because of their hard cores, in order to exchange with one another. Higher-order terms in Eq. (4.2) represent multiparticle exchange energies.

## V. EXCITED STATES

The frequencies  $\omega_{\mathbf{k}}^{(\alpha)}$  and  $\omega_{\mathbf{k}}^{(\beta)}$  in Eqs. (3.21) and (3.22) are the energies of the states of nonlocalized vacancies and interstitials, respectively, with  $n_{\mathbf{k}}$  and  $m_{\mathbf{k}}$  as their occupation numbers. We can expand these frequencies in powers of  $\tau/D$  as done for the ground state. We find

$$\omega_{\mathbf{k}}^{(\alpha)} \approx \mu_V - \frac{1}{2} \frac{\tau^2}{D} \left( \sum_{\tilde{\mathbf{a}}_1} \cos \tilde{\mathbf{k}} \cdot \tilde{\mathbf{a}}_1 \right)^2, \quad (5.1)$$

$$\omega_{\mathbf{k}}^{(\beta)} \approx \mu_I - \frac{1}{2} \frac{\tau^2}{D} \left( \sum_{\tilde{\mathbf{a}}_1} \cos \tilde{\mathbf{k}} \cdot \tilde{\mathbf{a}}_1 \right)^2,$$

where energies  $\mu_V$  and  $\mu_I$  were defined in Eqs. (3.13) and (3.14) as the Hartree-like energies necessary to destroy a particle on a regular site and to add a particle to an interstitial, respectively. Including the tunneling effects by means of the Bogoliubov transformation has spread these energies into bands.

In Fig. 4 we illustrate the qualitative form for  $\omega_{\mathbf{k}}^{(\alpha)}$ . Note that for  $\tilde{\mathbf{k}}$  small,  $\omega_{\mathbf{k}}^{(\alpha)} - \mu_V \sim k^2$  with a positive effective mass given by

$$m^* = m \left( \frac{\hbar^2}{2m\tilde{a}_1^2} \frac{6D}{z_1^2 \tau^2} \right). \quad (5.2)$$

This positive effective mass is simply a result of the symmetry of the wave function. The  $\tilde{\mathbf{k}}=0$  one-vacancy state is the completely symmetric state for  $M-1$  particles in  $M$  regular sites. Having no nodes, it is the lowest energy state of all the system. In this state the particles are able to spread

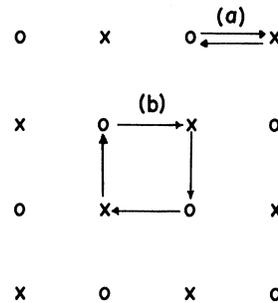


FIG. 3. Two processes which illustrate the first terms in the expansion of Eq. (4.2): Process (a) represents zero-point motion, in which a particle moves from a regular cell to an interstitial and back; process (b) represents exchange, in which two particles move off regular sites to interstitials and, instead of returning to their original cells, exchange places.

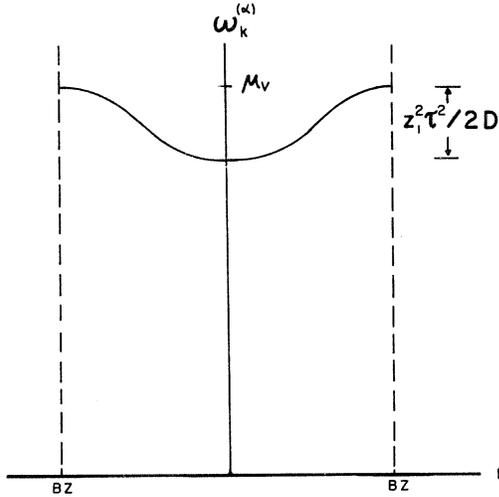


FIG. 4. A qualitative illustration of the form of the excitation frequency  $\omega_k^{(\alpha)}$ . The largest value is  $\mu_V$  and the bandwidth is  $z_1^2 \tau^2 / 2D$ . BZ is the Brillouin zone boundary.

out most effectively and lower their kinetic energy. The spectrum is not inverted (with a negative  $m^*$ ) like a "hole" state, as in the case in the theory of Guyer and Zane.<sup>17</sup>

One interesting feature of the vacancy-wave state is the "cloud" of additional virtual interstitials associated with it. The total number of interstitials in the vacancy-wave state  $|\alpha_{\vec{k}}^\dagger\rangle$  is

$$\sum_{\vec{R}_\beta} \langle \alpha_{\vec{k}}^\dagger | b_{\vec{R}_\beta}^\dagger b_{\vec{R}_\beta} | \alpha_{\vec{k}}^\dagger \rangle = \sum_{\vec{k}'} v_{\vec{k}'}^2 + v_{\vec{k}}^2, \quad (5.3)$$

The first term is the average number of ground-state interstitials as computed in Eq. (4.7). The second term gives the small number of additional interstitials which occur because of the vacancy. In order for a vacancy to leave its original site a particle must move into that site by tunneling through an interstitial position. Thus it is the *motion* of the vacancy which gives rise to the extra interstitial number  $v_{\vec{k}'}^2$ , and we might call them "dynamic" virtual interstitials. If we had a stationary vacancy we might expect to find a lattice distortion, i.e., particles spending some time in interstitials around the vacancy in order to lower their energy. These might be called "static" virtual interstitials. By studying vacancy-vacancy correlation functions one can show that such a static lattice distortion effect is not present in our spin-wave approximate theory. A more accurate analysis would include them by considering a vacancy-vacancy interaction. We will show later that our numerical results for vacancy excitations disagree with experiment because of this lack.

For  $\vec{k}$  near the zone boundary the effective mass becomes negative and the number of virtual inter-

stitials diminishes to zero. In this state a node occurs on each interstitial site. One can also show that an interstitial wave gives rise to a cloud of virtual vacancies.

The use of the inverse relations of Eqs. (3.15) in Eq. (3.8) gives

$$N = \sum_{\vec{R}} \langle b_{\vec{R}}^\dagger b_{\vec{R}} \rangle = M + \sum_{\vec{k}} m_{\vec{k}} - \sum_{\vec{k}} n_{\vec{k}}. \quad (5.4)$$

If we wish to have as many particles  $N$  as regular sites  $M$  then the last two terms of Eq. (5.4) must cancel; i.e., there are as many interstitials as vacancies. Applying this condition we get the excitation energy of a Frenkel-pair wave separated from the ground state by a gap

$$\begin{aligned} \Delta_F &= \omega_0^{(\alpha)} + \omega_0^{(\beta)} = 2D [1 - (z_1 \tau / D)^2]^{1/2} \\ &\approx t' - t + z_1 \phi_1 + z_2 \phi_2 - (z_1 \tau)^2 / D \quad \text{for } \tau \ll D, \end{aligned} \quad (5.5)$$

with the band of pair states of width

$$\delta_F = (z_1 \tau)^2 / D. \quad (5.6)$$

To evaluate the gap for forming a Schottky-type vacancy wave (i.e., with no real interstitial present) we must use the fact that the quantities  $t$ ,  $\phi_1$ , and  $\phi_2$  are dependent on the volume per particle,  $v = V/N$ . We form a single Schottky vacancy wave by requiring  $M = N + 1$  and any one of the  $n_{\vec{k}} \neq 0$  with all  $m_{\vec{k}} = 0$  in the energy [Eq. (3.19)]. At constant molar volume  $V$  the volume per particle goes from  $v_0 = V/N$  to  $v = V/(N + 1)$  in making a vacancy, so the gap forming a Schottky vacancy is

$$\begin{aligned} \Delta_S &= E_0(N + 1, v) + E_1(N + 1, v) + \omega_0^{(\alpha)} \\ &\quad - E_0(N, v_0) - E_1(N, v_0) \\ &\approx t - \frac{1}{2} z_2 \phi_2 + (1/M) \sum_{\vec{k}} D [1 - (\tau \gamma_{\vec{k}} / D)^2]^{1/2} - 1 \\ &\quad + D [1 - (\tau \gamma_0 / D)^2]^{1/2} + B + B' + P v_0. \end{aligned} \quad (5.7)$$

The last term comes from expanding the energy when evaluated at  $v = V/(N + 1) \approx v_0 - v_0/N$  in powers of  $v_0/N$ . The term in  $(1/M) \sum_{\vec{k}}$  arises from the increased density of  $\vec{k}$  states if  $M \rightarrow N + 1$ . If  $\tau/D \ll 1$ , the gap becomes

$$\Delta_S \approx \frac{1}{2} z_2 \phi_2 - \frac{z_1}{2} \frac{\tau^2}{D} - \frac{z_1^2}{2} \frac{\tau^2}{D} + P v_0, \quad (5.8)$$

with a bandwidth

$$\delta_S = (z_1 \tau)^2 / 2D. \quad (5.9)$$

It is also possible to have an interstitial wave. We can find the gap for creation of one of these by considering  $M = N - 1$  and  $m_0 = 1$ ,  $m_{\vec{k}} = 0$  ( $\vec{k} \neq 0$ ), and all  $n_{\vec{k}} = 0$ . At constant molar volume  $V$ , the volume per particle is increased to  $V/(N - 1)$ . Thus we have

$$\begin{aligned} \Delta_I = & -t + \frac{1}{2} z_2 \phi_2 - (1/M) \sum_{\vec{r}} \{ [1 - (\tau \gamma_{\vec{r}}/D)^2]^{1/2} - 1 \} \\ & + D [1 - (\tau \gamma_0/D)^2]^{1/2} - 2B - P v_0 \\ \simeq & t' - t + z_1 \phi_1 + \frac{1}{2} z_2 \phi_2 + \frac{z_1}{2} \frac{\tau^2}{D} - \frac{z_1^2}{2} \frac{\tau^2}{D} - P v_0, \end{aligned} \quad (5.10)$$

where the last approximation holds for  $\tau/D \ll 1$ . The bandwidth is also  $(z_1 \tau)^2/2D$ . Note that  $\Delta_S + \Delta_I = \Delta_F$ , as it should.

One can qualitatively understand the terms in  $\Delta_S$  and  $\Delta_I$ , Eqs. (5.8) and (5.10), as follows<sup>2</sup>: To form a vacancy, remove a particle from a site internal to the crystal, which raises the energy  $z_2 \phi_2$ ; place the particle on the surface which lowers the energy by  $\frac{1}{2} z_2 \phi_2$  and gives the crystal a volume  $v_0$  larger than the original  $V$ ; finally, let the external pressure do work  $P v_0$  to reduce the volume back to  $V$ . Together with the small lowering of energy due to the band structure we get a gap  $\Delta_S$ . A similar analysis can be given for  $\Delta_I$ .

#### VI. NUMERICAL EXAMPLE

The theory outlined above is based on expanding the field operator in a set of localized functions  $\zeta_{\vec{R}}(\vec{r})$ . We arrive at results dependent on the coefficients  $t$ ,  $t'$ ,  $\tau$ ,  $\phi_1$ ,  $\phi_2$  which are expressed in terms of the  $\zeta_{\vec{R}}$ 's. Since the  $\zeta_{\vec{R}}$ 's are unknown we might determine the coefficients by comparison with experiment. However, there are too many of them to carry out this procedure. Fortunately, it is possible to invent an *ad hoc* analysis which relates the constants to one another and allows us to get an order of magnitude idea of the size of various effects. This analysis is not to be taken too seriously and the coefficient values are subject to change if they become susceptible to measurement.

Although the theory has been carried out for bosons, we would expect many similarities, in low order in the tunneling term, if we were to treat fermions. Many of the basic properties of vacancy waves, zero-point motion, and the magnitude of the exchange energy should be the same for fermions and bosons. We find that, except for very near to melting, low order in tunneling [i.e.,  $(\tau z_1/D)^2 \ll 1$ ] is adequate for treating crystalline helium. Thus we apply the theory to solid <sup>3</sup>He for which there is detailed experimental information on cohesive energies, exchange, and specific heat.

The ground-state energy is  $E_0 + E_1$  as given in Eqs. (3.10) and (3.20). If we neglect  $E_1$  for the moment, we can determine the kinetic energy and therefore  $t$  by using the relation between it and the zero-point energy expressed in terms of the Debye temperature  $\Theta_D$ . We have

$$t \simeq \frac{3}{4} k_B \Theta_D, \quad (6.1)$$

where  $k_B$  is the Boltzmann constant. At an interparticle distance  $a_2 = 3.75 \text{ \AA}$  (molar volume  $\sim 24 \text{ cm}^3$ ) in bcc <sup>3</sup>He,  $\Theta_D \simeq 15 \text{ K}^{18-20}$  and we find

$$t \simeq 11 \text{ K}. \quad (6.2)$$

The cohesive energy<sup>19</sup> is  $E_0 \simeq -1 \text{ K}$ , so that we find

$$z_2 \phi_2 \simeq 24 \text{ K}. \quad (6.3)$$

In Fig. 2 we related the relative occupancy of regular and interstitial sites to a Hartree-type single-particle function. Such a correspondence allows us to get an idea of the values of the other coefficients of the theory. A Hartree wave function  $\eta(\vec{r} - \vec{R})$ , for single-particle motion about a lattice site at  $\vec{R}$ , has a behavior in the regular cell and in the interstitial cells about  $\vec{R}$  which we assume can be written as a Gaussian

$$\eta(r) \sim e^{-Ar^2/2}, \quad (6.4)$$

where  $A$  is constant. This form is obviously suggested by the successful use of a Gaussian by Nosanow and co-workers.<sup>21</sup>

The probability of finding a particle from a particular regular site on a given neighboring interstitial site is

$$(\tau/2D)^2 \approx e^{-Aa_1^2}, \quad (6.5)$$

where the left-hand side is from Eq. (4.7) and the right-hand side from the Hartree function of Eq. (6.4).

The tunneling coefficient  $\tau$  is given by Eq. (2.6) in terms of the kinetic-energy overlap of the Wannier functions of a regular site and an interstitial. In terms of our Hartree function we might then assume

$$\tau \approx t e^{-A(a_1/2)^2}, \quad (6.6)$$

where the latter factor is the value of the Hartree function evaluated at the point where the two Wannier functions would overlap, halfway between the two sites.

The parameter  $\tau$  may be eliminated from Eqs. (6.5) and (6.6) to give a value for  $2D$ :

$$2D = t e^{A a_1^2/4}. \quad (6.7)$$

The value of  $A a_1^2$  can be determined by using the experimental value<sup>1</sup> of the exchange energy, which at the density in question is  $\sim 10^{-3} \text{ K}$ . From Eqs. (4.2), (4.8), (6.5), and (6.7) we have

$$E_{\text{exchange}}/M \simeq 12 (2D) (\tau/2D)^4 = 12t e^{-7A a_1^2/4} \simeq 10^{-3} \text{ K}. \quad (6.8)$$

This gives

$$A a_1^2 \simeq 6.7. \quad (6.9)$$

Putting this back in Eqs. (6.6) and (6.7) we find

$$\tau \simeq 2 \text{ K}, \quad 2D \simeq 58 \text{ K}. \quad (6.10)$$

The consistency of this *ad hoc* technique can be checked by calculating the average kinetic energy per particle in the Gaussian state (6.4). If we take  $a_1 = a_2/\sqrt{2}$  as an appropriate distance to an interstitial, then  $A$  is determined and this kinetic energy turns out to be

$$\text{KE} = \frac{3}{4} \frac{\hbar^2}{m} A \approx 12 \text{ K}, \quad (6.11)$$

in remarkable agreement with our  $t$  value Eq. (6.2). We also note that the value of  $\tau$  predicted by a previous form of this theory<sup>9,14</sup> based on approximating the kinetic-energy operator by a finite difference formula was  $t/z_1$ , which agrees well with Eq. (6.10) if  $z_1 \approx 6$ . The above procedures also give consistent results for higher density. While the procedures used in arriving at numerical values of the coefficients are questionable, we suspect that the values themselves are reasonable and we will use them to evaluate the remaining physical parameters of the theory.

Since the parameters  $t'$  and  $\phi_1$  occur only in the combination  $t' + z_1 \phi_1$  in the results of the theory, our values of  $t$ ,  $z_2 \phi_2$ ,  $\tau$  and  $D$  are sufficient. We find

$$\mu_I = t' + z_1 \phi_1 = 2D + t - z_2 \phi_2 = 45 \text{ K}. \quad (6.12)$$

With these values we find the following results.

(i) The lowering of the energy per particle due to zero-point motion into the interstitial site [first term in Eq. (4.2)] is  $-z_1 \tau^2/2D = -0.4 \text{ K}$ .

(ii) The number of ground-state interstitials per regular site or the probability of finding a particle on an interstitial site [Eq. (4.7)] is  $z_1 (\tau/2D)^2 = 8 \times 10^{-3}$ .

(iii) The gap for forming a Frenkel vacancy-interstitial pair wave [Eq. (5.5)] is

$$\Delta_F = 53 \text{ K}, \quad (6.13)$$

with a bandwidth

$$\delta_F = 6 \text{ K}. \quad (6.14)$$

(iv) The gap for forming a Schottky vacancy wave [Eq. (5.8)] is

$$\Delta_S = 17 \text{ K}, \quad (6.15)$$

with a bandwidth

$$\delta_S = 3 \text{ K}. \quad (6.16)$$

(v) The gap for forming an interstitial wave is

$$\Delta_I = 36 \text{ K}, \quad (6.17)$$

with a bandwidth

$$\delta_I = 3 \text{ K}. \quad (6.18)$$

(vi) A vacancy wave or an interstitial wave for  $\vec{k}$  near zero has a positive effective mass which, by Eq. (5.2), is

$$m^* \approx 2m \quad (6.19)$$

for the density we have been considering.

The smallest of the energy gaps is  $\Delta_S \approx 17 \text{ K}$ . We assume then that the anomalous specific heat<sup>18</sup> and the NMR results<sup>22</sup> in bcc  $^3\text{He}$  are explained by assuming the formation of Schottky vacancy waves. The value of  $\Delta_S$  is larger than the experimental gap<sup>18,22</sup> of 6 K and the theoretical value of Hetherington<sup>2</sup> of 9 K because our theory does not include the effects of static lattice distortion as we discussed in Sec. V. The result that it is easier to form a Schottky vacancy than a Frenkel pair in  $^3\text{He}$  has been suggested previously by Hetherington<sup>2</sup> and is certainly in accord with our results. We see also that a vacancy is easier to form than a simple interstitial.

## VII. TRANSITION TO BOSE CONDENSED PHASE

The Hubbard Hamiltonian has been used to describe a metal-insulator transition.<sup>8</sup> Gersch and co-workers<sup>9</sup> have used such a Hamiltonian to describe a helium solid-superfluid phase transition. Our Hamiltonian also provides a phase transition. To see this note from Eqs. (3.21) and (3.22) that if

$$(z_1 \tau/D) \geq 1, \quad (7.1)$$

the frequencies  $\omega_{\vec{k}}^{(\alpha)}$  and  $\omega_{\vec{k}}^{(\beta)}$  become imaginary for  $\vec{k} \approx 0$ . Thus the solid phase is surely not stable beyond this point. As the pressure is lowered,  $\tau$  changes relatively slowly, but  $D$  which depends on  $t' + z_1 \phi_1$ , will decrease rapidly. As in helium we get a solid-liquid phase transition by lowering the pressure.

As the pressure is decreased it is likely that, before the point characterized by Eq. (7.1) is reached, one or both of the gaps  $\Delta_S$  or  $\Delta_I$  will vanish and the system will melt because it becomes unstable to the formation of vacancies or interstitials. Even before this happens it is possible that the liquid state may become energetically favored and melting will begin. If we had more detailed information concerning the liquid phase of the model we could specify the nature of the transition but we leave precise discussion to future work.

There are some qualitative statements which can be made, however. It has been shown [e.g., Eq. (4.2)] that the various powers of  $(\tau z_1/D)$  correspond to various orders of exchange. Thus the characterization (7.1) indicates that melting occurs because all orders of exchange begin to happen with nearly equal frequency. It is not surprising that such a situation would lead to a loss of long-range crystalline order. The disappearance of vacancy or interstitial gaps should bring on melting since all particles could then run freely through the crystal.

In the spin analog the transition occurring when

(7.1) is satisfied is a spin-flop<sup>7</sup> in which the magnetization changes from being exclusively in the  $z$  direction to having a component  $M_{\perp}$  in the  $x$ - $y$  plane. This  $x$ - $y$  magnetization implies the system has a Bose condensate because the order parameter<sup>23</sup> is

$$\langle \Psi^{\dagger}(\vec{r}) \rangle \sim \langle b_{\vec{R}}^{\dagger} \rangle = \langle \sigma_{\vec{R}}^{(s)} \rangle \sim M_{\perp}, \quad (7.2)$$

where  $\vec{r} \approx \vec{R}$ . Clearly the antiferromagnetic state we have been studying has no Bose condensate, but we expect the transition to describe the solid-supersolid transition. At high temperatures the spin analog will undergo another transition in which  $M_{\perp}$  goes to zero and the normal fluid becomes the stable phase. This transition has been studied previously.<sup>4</sup>

Since the  $z$  magnetization is related to the density by Eq. (3.2) we assume that a spin analog state with a  $\langle \sigma_{\vec{R}}^{(s)} \rangle$  that does not vary from cell to cell is that of a liquid, since the density is uniform. (The state described in this paper is crystalline because  $\langle \sigma_{\vec{R}}^{(s)} \rangle$  does vary as one moves from regular site to interstitial.) However, the spin analog suggests the possibility of other Bose condensed states. Suppose the coupling constants in the effective Hamiltonian (3.3) were such that a helical spin arrangement was possible. If the axis of the helix were in the  $x$  direction there would be a non-vanishing  $x$  magnetization and hence a Bose condensation. Furthermore, the  $z$  component of magnetization would be periodic and function of  $\vec{R}$  along the axis of the helix which implies a periodic density variation. Since long-range order in the density variation is characteristic of a crystal we therefore would have a Bose condensed crystalline phase. The characteristics of this Bose condensed solid phase would seem quite different from those suggested previously,<sup>11,12</sup> which involve ground-state vacancies or other defects. We do not know whether this helical state can ever occur in a real system or not, but it deserves further investigation.<sup>24</sup>

### VIII. DISCUSSION

We have presented a model which provides a fairly complete qualitative description of a quantum crystal. The coefficients occurring in the theory are not determined by the theory and so it was necessary to find them by a combined use of experiment and an *ad hoc* theoretical procedure. Nevertheless we believe the values so determined to be fairly reasonable. Some interesting theoretical descriptions result. Zero-point motion and exchange are described in terms of virtual vacancy-interstitial pair formation in the ground state; and the excited states are shown to consist of vacancy, interstitial, or vacancy-interstitial pair wave states.

Presumably the vacancy waves account for the high-temperature excess specific heat observed in solid <sup>3</sup>He.<sup>18</sup> Unless the interstitial wave gap  $\Delta_I$  is much lower than the estimate of Eq. (6.16), we suspect that it will be impossible to observe it, especially since it is superimposed on the vacancy contribution. An even stronger statement holds for the pair wave state, of course. The vacancies have a positive effective mass which gives them a spectrum as shown in Fig. 4. The theory of Guyer and Zane<sup>17</sup> yields a vacancy spectrum with a negative effective mass at  $\vec{k}=0$  (that of Fig. 4 flipped over). Perhaps it might be possible to distinguish experimentally between these two types of spectra.

We feel that the work described in this article provides techniques which may be useful in a good deal of further work. The theory can be applied to fermions<sup>25</sup>; phonons can be considered by including excited Wannier states in each cell; and, as we have already mentioned, further analysis of the Bose condensed states of the present Hamiltonian may lead to other interesting results.

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## New Derivation of the Second Virial Coefficient\*

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We present a new, completely rigorous way of proving the relation between the second virial coefficient and the  $S$  matrix. The method involves the use of the  $U_{2,\infty}$  function introduced by Lee and Yang and proceeds in the most straightforward manner. Although difficulties are encountered for virial coefficients of higher order, there is hope that this type of approach might shed some light on the question of the connection between the virial series and the scattering matrix.

### I. INTRODUCTION

It has been known for a long time<sup>1</sup> that the second virial coefficient is related in a simple manner to the two-body  $S$  matrix (or, equivalently, to the scattering amplitude).

The usual method proceeds through the study of how the interaction affects the spectrum of the two-body Hamiltonian. The system is placed in a hollow hard-wall sphere of radius large compared to the wavelength involved. By imposing the boundary conditions on the asymptotic form of the wave function, one can relate the change in density of states to the  $S$  matrix. Finally, the radius of the sphere is made to go to infinity and, in the limit, one obtains the result<sup>2</sup>

$$b_2 - b_2^{(0)} = \frac{\sqrt{2}}{(2\pi\lambda)^3} \int \frac{d^3k}{k^2} e^{-2\beta k^2} \left[ 2\pi \frac{\partial}{\partial k} \operatorname{Re} f_{\Theta\Phi}(\Theta, \Phi) - \int d\Omega_{\Theta\Phi} \operatorname{Im} \left( f_{\Theta\Phi}(\theta, \phi) \frac{\partial f_{\Theta\Phi}^*(\theta, \phi)}{\partial k} \right) \right]. \quad (1)$$

We have taken units such that  $m = \frac{1}{2}$ ,  $\hbar = 1$ .

The symbols in (1) are defined as follows:  $b_2(b_2^{(0)})$  is the second virial coefficient in the presence (absence) of interaction;  $\beta = 1/KT$ , where  $K$  is Boltzmann's constant,  $\lambda = (4\pi\beta)^{1/2}$ ;  $f_{\Theta\Phi}(\theta, \phi)$  is the scat-

tering amplitude corresponding to incoming wave vector; and  $\vec{k} = (k, \Theta, \Phi)$  and outgoing direction defined by the polar angles  $(\theta, \phi)$ . (We leave it understood that  $f$  depends also on the energy  $k^2$ .)

Another feature of the usual derivation is that the potential is taken to be spherically symmetric and essential use is made of separation of the angular and radial coordinates. Goldberger<sup>3</sup> has produced a proof of the connection between  $b_2 - b_2^{(0)}$  and the  $S$  matrix without using any particular symmetry of the potential, but still making use of energy-shift arguments.

The aim of our research is to reinvestigate and perhaps clarify the relation between the virial coefficients and the  $S$  matrix.<sup>4</sup> The virial coefficient  $b_l$  is perhaps best defined as the spacial integral, in a  $3(l-1)$ -dimensional space of the  $U_{l,\infty}$  function of Lee and Yang.<sup>5</sup> Using the theorem of Appendix A, one can convert the spacial integral into the integral over a  $(3l-4)$ -dimensional surface that is then let tend to infinity.

On the other hand the  $S$  matrix specifies the leading asymptotic behavior of the wave function along any given ray.<sup>6</sup> The nontrivial question then arises whether the limit of the surface integral is completely determined by the  $S$  matrix only. We shall provide a positive answer for  $b_2$ .