

Dynamic-local-field approximation for the quantum solids

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A local-molecular-field description for the ground-state properties of the quantum solids is presented. The dynamical behavior of atoms contributing to the local field, which acts on an arbitrary pair of test particles, is incorporated by decoupling the pair correlations between these field atoms. The energy, pressure, compressibility, single-particle-distribution function, and the root-mean-square atomic deviations about the equilibrium lattice sites are calculated for H_2 , 3He , and 4He over the volume range $5 < V \leq 24.5 \text{ cm}^3/\text{mole}$. The results are in close agreement with existing Monte Carlo calculations wherever comparisons are possible. At very high pressures the results agree with simplified descriptions which depend on negligible overlap of the system wave function between neighboring lattice sites.

I. INTRODUCTION

The quantum solids have been difficult to understand analytically because of their large zero-point motion. This motion invalidates standard semiclassical approaches and those quantum-mechanical calculations which do not account for the short-ranged pair correlations between atoms.

Perhaps the most reliable theoretical description of the ground-state properties of quantum solids are the Monte Carlo calculations of Hansen and co-workers^{1,2} on helium and Bruce³ on hydrogen. This method is a quantum-mechanical analog of the biased random-walk procedure described by Wood and Parker.⁴ Classically, the bias is established by the Boltzmann-probability distribution; whereas, quantum mechanically, it is given by the absolute square of the ground-state wave function $|\Phi|^2$. A parametrized form is generally chosen for Φ and the parameters are determined variationally by minimizing the ground-state energy.

A form for the N -particle wave function which satisfies the gross requirements of the system is

$$\Phi(\vec{r}_1, \dots, \vec{r}_N) = \prod_{i=1}^N \varphi(\vec{r}_i) \prod_{j < k}^N f(r_{jk}), \quad (1)$$

where the $\varphi(\vec{r}_i) \equiv \varphi(\vec{r}_i - \vec{R}_i)$ are single-particle functions localized about the equilibrium lattice sites \vec{R}_i . They exhibit spatial order characteristic of the solid. The $\frac{1}{2}N(N-1)$ functions $f(r_{jk})$ correlate the motion of all pairs of particles. The limiting behavior for $f(r)$ is $\lim_{r \rightarrow 0} f(r) = 0$, $\lim_{r \rightarrow \infty} f(r) = 1$. Hence, these functions lower the probability of finding two molecules close together and they have no effect at large separations.

Although there are a number of aspects of the Monte Carlo method which can lead to significant

error,⁴ it is generally believed that this approach is fairly reliable. For this reason, the results of our approximate theory are closely compared with the Monte Carlo calculations. Of course, comparisons with experiment are also made but it is difficult to draw definite conclusions from this information. The difficulty is that the semiphenomenological interaction potential, incorporated into the calculation, is of uncertain quality.⁵ As pointed out by Hansen⁶ and others, small differences in presently acceptable descriptions of the helium pair potential, significantly alter calculated results.

An important objective of this work is to provide an approximate yet accurate description of quantum solids. The detailed nature of these approximations are expected to give insight into the systems dynamical character by pinpointing those particular aspects of the many-body behavior which must be accurately described and those which are of lesser importance.

II. MOLECULAR-FIELD DESCRIPTION

A. General development

The expectation value of the Hamiltonian for an N -particle system is

$$\langle H \rangle = \langle \Phi | \Phi \rangle^{-1} \langle \Phi | -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i < j} V(r_{ij}) | \Phi \rangle, \quad (2)$$

where $V(r)$ is the pair potential and $\langle \Phi | \Phi \rangle$ is the normalization integral. To facilitate comparisons with other work, $V(r)$ is represented by the Lennard-Jones (6-12) potential:

$$V(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad (3)$$

where $\sigma = 2.556 \text{ \AA}$, $\epsilon = 10.22 \text{ K}$ for helium⁷ and σ

= 2.958 Å, $\epsilon = 36.7$ K for molecular hydrogen.⁸ The ground-state wave function Φ is given by Eq. (1), where

$$\varphi(\vec{r}_i) = (\beta/\pi)^{3/4} e^{-(\beta/2)(\vec{r}_i - \vec{r}_i)^2}, \quad (4)$$

$$f(r) = e^{-(\kappa/r)^{5/2}}. \quad (5)$$

The quantities β and κ are variational parameters to be determined. These forms for φ and f are used extensively in other related works where they appear to have sufficient flexibility to adequately represent the ground state of the system.¹⁻³ They are also adopted here partially because of the stated objective to compare this approximate theory with other calculations.

Using Green's theorem and with Eqs. (1), (4), and (5), Eq. (2) becomes

$$\langle H \rangle = \frac{3N\hbar^2\beta}{4m} + \langle \Phi | \Phi \rangle^{-1} \sum_{i < j} \int \Phi^2 v(r_{ij}) d\vec{r}_1 \cdots d\vec{r}_N, \quad (6)$$

where

$$v(r_{ij}) = V(r_{ij}) - (\hbar^2/2m) \nabla_i^2 \ln f(r_{ij}). \quad (7)$$

For the purposes of this calculation, it is convenient to rewrite Eq. (6) in the following form:

$$\langle H \rangle = \frac{3N\hbar^2\beta}{4m} + \langle \Phi | \Phi \rangle^{-1} \sum_{\lambda < \kappa} \int \varphi^2(\vec{r}_\lambda) \varphi^2(\vec{r}_\kappa) \times f^2(\vec{r}_{\lambda\kappa}) v(\vec{r}_{\lambda\kappa}) G(\vec{r}_\lambda, \vec{r}_\kappa) d\vec{r}_\lambda d\vec{r}_\kappa, \quad (8)$$

where

$$G(\vec{r}_\lambda, \vec{r}_\kappa) = \int \prod_{i < j \neq (\lambda, \kappa)}^N f^2(\vec{r}_{ij}) \times \prod_{s \neq \lambda, \kappa}^N |\varphi(\vec{r}_s)|^2 d\vec{r}_1 \cdots (d\vec{r}_\lambda d\vec{r}_\kappa)^{-1} \cdots d\vec{r}_N. \quad (9)$$

The parentheses around the term $(d\vec{r}_\lambda d\vec{r}_\kappa)^{-1}$ indicate that integrals over the enclosed variables are deleted. At this point the calculation is exact and it is here that different theoretical descriptions diverge. An examination of Eq. (9) shows that each particle in the system is dynamically coupled to every other particle through the pair-correlation functions $f(r_{ij})$. It is therefore obvious that a drastic approximation is necessary to reduce this coupled N -body problem to a tractable form.

In the Nosanow cluster-expansion approximation,⁹ evaluated to second order, the approximation is very drastic. It is assumed that $G(\vec{r}_\lambda, \vec{r}_\kappa) \approx 1$. The supporting argument is that the $f(r)$ in Eq. (9) have already reached their asymptotic values of unity for values of \vec{r} where the integrand in Eq. (8) is large. Under these conditions, the volume in-

tegration of $\Pi_s |\varphi(r_s)|^2$ terms in Eq. (9) give unity. This was the first approximate calculation to yield reasonable results for solid helium even though, by present standards, the results are not very good. A serious flaw in the cluster expansion as an ultimate theoretical description was pointed out by Guyer.¹⁰ He showed that the only possible wavefunction resulting from an internally self-consistent solution was a nonlocalized liquid-state function.

In view of the deficiencies in the cluster-expansion method and other approximate theories, it is apparent that the behavior of each molecule depends strongly on the influence of large numbers of neighboring molecules. Equations (8) and (9) show that the effect of all $N-2$ other molecules on an arbitrary dynamical pair, hereafter labeled (λ, κ) , is embodied in $G(\vec{r}_\lambda, \vec{r}_\kappa)$. The work presented in this article is directed at accounting for this local molecular field acting on each pair (λ, κ) and produced by the presence of the $N-2$ other molecules. The major approximation underlying this calculation is contained in the expression

$$G(\vec{r}_\lambda, \vec{r}_\kappa) \approx \prod_{s \neq \lambda, \kappa}^N \int [f^2(r_{\lambda s}) f^2(r_{\kappa s}) \varphi^2(\vec{r}_s - \vec{R}_s) d\vec{r}_s]. \quad (10)$$

This expression for $G(\vec{r}_\lambda, \vec{r}_\kappa)$ differs from Eq. (9) in that it contains no direct correlations between the $N-2$ atoms comprising the molecular field which acts on (λ, κ) . That is, the $f(r_{ij})$ which connect molecular-field atoms to one another are missing in Eq. (10). Only those pair correlations which directly link the $N-2$ atoms of the molecular field to the dynamical pair (λ, κ) are considered. This approximation is essential in that it simplifies the problem to the extent that a tractable solution is possible which still preserves the important features of the system's behavior.

B. Static-field approximation

The lowest-order approximation which takes into account the local field acting on a pair (λ, κ) , due to the $N-2$ other molecules, is a static field. That is, all $N-2$ contributing molecules are fixed at their equilibrium lattice sites. This is operationally accomplished by taking the limit

$$\lim_{B \rightarrow \infty} |\varphi(\vec{r}_i - \vec{R}_i)|^2 \rightarrow \delta(\vec{r}_i - \vec{R}_i)$$

for all $i \neq \lambda, \kappa$ in Eq. (9). Then

$$G(\vec{r}_\lambda, \vec{r}_\kappa) = \prod_{i \neq \lambda, \kappa}^N f^2(\vec{r}_i - \vec{R}_i) \prod_{j \neq \lambda, \kappa}^N f^2(\vec{r}_j - \vec{R}_j). \quad (11)$$

In an earlier work¹¹ this expression was further simplified by limiting the products over (i, j) to