THEORY OF CRYSTALLINE He^3 AT 0°K[†]

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In recent years there has been considerable theoretical interest in the properties of crystalline He^3.[1-4] Because of its small mass, the zero-point energy of crystalline He^3 is very large relative to its potential energy. Thus, it is intuitively clear that the effect of correlations is very important in determining the properties of this system. Bernardes and Primakoff[1] used a correlation function which was calculated in a phenomenological way. Saunders[3] used a Jastrow-type wave function[5] and derived an approximate differential equation for the correlation function. Recently, Mullin[6] has studied the effect of correlations in crystalline Ne.

In this note we study anew the effect of pair correlations in crystalline He^3 by means of a variational calculation with Jastrow-type wave functions. Our main purpose is to derive a systematic cluster expansion of the ground-state energy E_0 and show that this expansion converges rapidly for crystalline He^3. We present a calculation of E_0 using the first term in this expansion and estimate the first correction. We find that this correction is sufficiently small so that the first term is accurate to within a few percent. In addition, we present a calculation of the exchange integral J using this approach.

The Hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_{i<j} v_{ij}, \tag{1}$$

where $v_{ij} = v(|\vec{r}_i - \vec{r}_j|)$ is the potential energy of interaction between two atoms. The He-He potential is well approximated by the Lennard-Jones form[7]

$$v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{2}$$

where $\epsilon = 10.2$°K and $\sigma = 2.56$ Å. Our trial wave function is assumed to be real and of the form[5,8]

$$\Psi = \prod_i \varphi_i \prod_{j<k} f_{jk}, \tag{3}$$

where $\varphi_i = \varphi(|\vec{r}_i - \vec{R}_i|)$, $f_{jk} = f(|\vec{r}_j - \vec{r}_k|)$, and $\vec{R}_i$ is the coordinate of the ith lattice site. Using (3), we may write

$$E_0 = \{\sum_i (\Psi, P_i \Psi) + \sum_{i<j} (\Psi, V_{ij} \Psi)\}/(\Psi, \Psi), \tag{4}$$

where

$$P_i = -(\hbar^2/4m\varphi_i^2)(\varphi_i \nabla_i^2 \varphi_i - \nabla_i \varphi_i \cdot \nabla_i \varphi_i), \tag{5}$$

$$V_{ij} = v_{ij} - (\hbar^2/2mf_{ij}^2)(f_{ij} \nabla_i^2 f_{ij} - \nabla_i f_{ij} \cdot \nabla_i f_{ij}). \tag{6}$$

To obtain (4) we have used integration by parts (see Jackson and Feenberg[9] for details).

We shall now make a cluster development[10] of (4). To do this, define

$$\omega \equiv \int d\vec{r}\, \varphi^2(\vec{r}),$$

$$Y(\gamma) \equiv (\Psi, \exp(\gamma \textstyle\sum_i P_i)\Psi)\omega^N, \tag{7}$$

and

$$Z(\gamma) \equiv (\Psi, \exp(\gamma \sum_{i<j} V_{ij})\Psi)/\omega^N, \tag{8}$$

from which it follows that

$$E_0 = (\partial/\partial\gamma) \log\{Y(\gamma)Z(\gamma)\}|_{\gamma=0}. \tag{9}$$

If we now define the averaging process

$$\langle g(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n)\rangle \equiv \int \frac{d\vec{r}_1}{\omega}\varphi_1^2 \int \frac{d\vec{r}_2}{\omega}\varphi_2^2 \cdots \int \frac{d\vec{r}_n}{\omega}\varphi_n^2 \times g(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n),$$

it is a straightforward application of van Kampen's method[11] to show that

$$\begin{aligned} E_0 = {} & \{\sum_i \langle P_i\rangle + \tfrac{1}{2}\sum_{i,j}{}'(\langle V_{ij} f_{ij}^2\rangle/\langle f_{ij}^2\rangle)\} \\ & + \{\sum_{i,j}{}'[(\langle P_i f_{ij}^2\rangle/\langle f_{ij}^2\rangle) - \langle P_i\rangle] \\ & + \tfrac{1}{2}\sum_{i,j,k}{}' [(\langle V_{ij} f_{ij}^2 f_{ik}^2 f_{jk}^2\rangle/\langle f_{ij}^2 f_{ik}^2 f_{jk}^2\rangle) \\ & - (\langle V_{ij} f_{ij}^2\rangle/\langle f_{ij}^2\rangle)]\} + \cdots. \end{aligned} \tag{10}$$

In (10) we have retained only the first two terms in the cluster development; it is a straightforward, but tedious, problem to write down the general term. The expansions given here are an improvement over the previous work[12] since all of the corrections referring to a cluster of a given size are grouped together.

We have calculated E_0 for a nearest-neighbor distance of 3.75 Å in the approximation that only the first term in (10) is retained and $\langle f_{ij}^2\rangle \simeq 1$ for all i and j. Then we have explicitly

$$H_0 = -\frac{\hbar^2}{2m}\sum_i \int \frac{d\vec{r}_i}{\omega}\varphi_i \nabla_i^2 \varphi_i + \frac{1}{2}\sum_{i,j}{}' \int \frac{d\vec{r}_i}{\omega}\int \frac{d\vec{r}_j}{\omega}\varphi_i^2 \varphi_j^2 f_{ij}^2 V_{ij}. \tag{11}$$

Further, we choose the analytic form

$$f(r) = \exp\{-K[(\sigma/r)^{10} - (\sigma/r)^4]\}, \tag{12}$$

which vanishes exponentially for $r \to 0$ and approaches unity for $r \to \infty$ as the usual forms do.[3,5,9] However, (12) also has a maximum at about the same value of r for which $v(r)$ has a minimum. Hence this form should be an improvement over previous forms, since it enables the kinetic energy and potential energy to be lowered simultaneously.

For each value of K, the minimum of (11) can be found by solving the Hartree equations[4] with an effective interaction $f_{ij}^2 V_{ij}$. The result is shown in Fig. 1; the minimum occurs for $K \simeq 0.32$. The energy is given in Table I along with other values for comparison. We find that the calculated $\varphi(r)$ is approximated to two significant figures by the analytic form $\exp(-\frac{1}{2}Ar^2)$, except for $r > 2$ Å, where φ is very small. The value of A is also given in Table I.

To study the error in our calculations we have estimated the correction terms in (10) by using the analytic approximation for φ. We find

$$\langle P_i f_{ij}^2\rangle / \langle f_{ij}^2\rangle = \langle P_i\rangle \text{ (identically)}, \tag{13}$$

$$\frac{\langle V_{ij} f_{ij}^2 f_{ik}^2 f_{jk}^2\rangle}{\langle f_{ij}^2 f_{ik}^2 f_{jk}^2\rangle} \simeq \frac{\langle V_{ij} f_{ij}^2\rangle}{\langle f_{ij}^2\rangle}, \tag{14}$$

where (14) follows from the fact that φ_i is fairly well localized about $\vec{R}_i$ and $f^2(r)$ varies slowly when r is greater than or about equal to the nearest-neighbor distance. Thus to the approximation that $\varphi = \exp(-\frac{1}{2}Ar^2)$, the first term in (10) is essentially exact. We therefore feel that it is safe to say that it is correct to within a few percent and it may even be much more accurate.

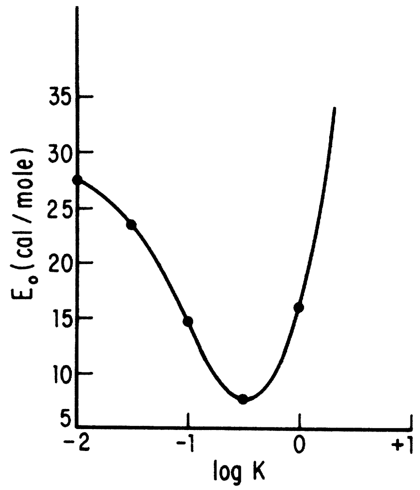

FIG. 1. Plot of E_0 vs log K as calculated from (11) for a nearest-neighbor distance of 3.75 Å.

We have also calculated $\langle f_{ij}^2\rangle$ when i and j are nearest, second, and third neighbors; we find $\langle f_{ij}^2\rangle = 1.08$, 1.07, and 1.01, respectively. Therefore the approximation $\langle f_{ij}^2\rangle \simeq 1$ causes an error of about 7% in the potential energy since the nearest neighbors make the largest contribution. Since we find that $\sum_i P_i = 35.6$ cal/mole and $\frac{1}{2}\sum_{i,j}{}'\langle f_{ij}^2 V_{ij}\rangle = -28.0$ cal/mole, we conclude that our value of E_0 is about 2 cal too low. However, this error does not affect the rapid convergence of the cluster expansion and will be remedied in future calculations.

We have also calculated the exchange integral J on the basis of the Gaussian approximation [we use Eq. (11) of BP]; the result is given in Table I. Needless to say, this calculation cannot be relied upon since J is very sensitive to the "tail" of φ, and it is well known that such "tails" are not well determined by variational calculations.

We wish to point out that (11) looks very much like the equation for E_0 used by BP. The main difference is that they do not have the terms which contain derivatives of f. It is just the absence of these terms which enables them to obtain a nega-

Table I. The values of E_0 (in cal/mole), A (in Å^{-2}) and J (in °K). All results are for a nearest-neighbor distance of 3.75 Å.

	B-P	Saunders[b]	This work	Experiment[b,c]
E_0	-5.3	5.5	7.6	$\simeq -4$
A	0.81	1.7	1.5	...
J	$\simeq 2 \times 10^{-2}$	$\simeq 3 \times 10^{-3}$	$\simeq 2 \times 10^{-3}$	order of 10^{-3}

[a] See reference 1.
[b] See reference 3.
[c] See reference 4.

tive value for E_0; to obtain this result they seriously underestimate the kinetic energy. Thus they obtain a single-particle wave function which is too "wide" (this can be seen from their small value of A), and this is the reason why they obtain too large a value for J.

In conclusion, we wish to point out that it is quite possible for this approach to yield a much better value of E_0 than we have reported here. We have only used an analytic form for $f(r)$, although it is quite feasible to derive and solve a differential equation for f. In this way one might obtain a 10% improvement in both the kinetic and potential energies. Since E_0 is an order of magnitude smaller than either of these, a significant improvement is possible.

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EVIDENCE FOR FIELD-DEPENDENT ZERO-POINT SPIN-WAVE EFFECTS IN ANTIFERROMAGNETS*

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In this note we report the observation and analysis of nonlinear behavior in the low-temperature magnetic field dependence of the transverse magnetization, and corresponding magnetic field dependence of the perpendicular differential susceptibility, of antiferromagnetic EuTe and $CoCl_2$. We feel that these effects arise primarily from the zero-point spin-wave contribution to the free energy in accord with the theory of Kanamori and Yosida.[1]

A method in common use for the estimation of exchange parameters[2] utilizes the initial perpendicular susceptibility and presumes it to be a constant up to the saturation field, in accord with molecular field theory. However, a nonlinearity in the magnetization curve reduces the accuracy of this method; e.g., such a procedure overestimates the saturation field by about 10% in the case of EuTe. A zero-point correction to the initial susceptibility, in the evaluation of exchange parameters, has occasionally been considered but its magnitude is not precisely known.[3]

The magnetization[4] and the differential susceptibility[5] were examined to 200 kOe. EuTe powders were used because the anisotropy field [presumably in the (111) layer planes[6] of the fcc structure] is extremely low, i.e., about 200 Oe.[7] Above 4 kOe, all crystallites are magnetizing in the transverse mode. Monocrystals of $CoCl_2$ were measured with the field perpendicular to the c axis. Here, the transverse mode is obtained above 2 kOe.[8]

In Fig. 1 we present the magnetization and differential susceptibility for a EuTe powder sphere at 2.1°K. The magnetization curve is similar to one published by Busch et al.[9] during our study. Of principal interest is the upward concavity from the dashed line drawn to fit the