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Exchange Energy of Solid ³He Obtained from Pressure Measurements*

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An argument is given which shows that there is no undetermined constant in values of the exchange energy of solid ³He obtained from pressure measurements.

In previous work[1,2] absolute values of the exchange energy J of solid ³He were obtained from observations of the effect of spin ordering on the pressure. This work extended to 13 mK, with the ordering temperature $T_c \lesssim 2$ mK. Thus the high-temperature series expansion, with the first term only, is valid for the exchange contribution to the pressure,[2]

$$P_{ex} = \frac{3R}{V}\left(\frac{J}{k}\right)^2 \frac{\partial \ln|J|}{\partial \ln V} \frac{1}{T} \; . \qquad (1)$$

In this expression R is the gas constant, k is Boltzmann's constant, and V is the molar volume. Recently, susceptibility measurements have indicated that the ordering is antiferromagnetic.[3]

Since Eq. (1) involves J and its volume derivative, a self-consistent procedure was used to obtain $J(V)$ over the volume range from 21 to 24 cm³/mole. The question has been raised as to whether the $J(V)$ found are unique. Mathematically, both J^2 and $J^2 + C$ are equivalent solutions to Eq. (1) since they have the same value of

$$\frac{J^2}{V}\frac{\partial \ln|J|}{\partial \ln V} = \frac{J\partial|J|}{\partial V} = \frac{1}{2}\frac{\partial J^2}{\partial V} \; . \qquad (2)$$

However, a simple physical argument shows that we must have $C = 0$. We will show below that if
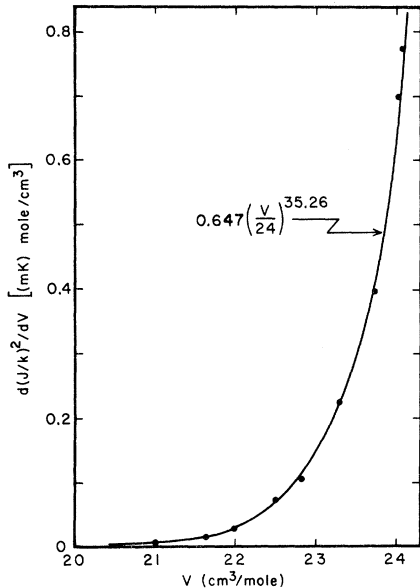
FIG. 1. Experimentally determined values of $d(J/k)^2/dV$ versus V. The solid curve, given by

$$\frac{d(J/k)^2}{dV} = 0.647 \left(\frac{V}{24} \right)^{35.26}$$

is a least-squares fit to aV^b.

TABLE I. Values of $|J/k|$ obtained from Eqs. (3) and (4) compared to those obtained previously by the self-consistent analysis.

V (cm³/mole)	$|J/k|$ (mK)	$|J/k|_{sc}$ (mK)
24	0.655	0.67
23	0.304	0.30
22	0.135	0.14
21	0.059	0.057

$J(V)$ is "well behaved" and if $J(V) = 0$ for some small V (here V may assume any mathematical value, not necessarily a physically obtainable one), then we must have $C = 0$. It is clear that if V is reduced to V_{hc} corresponding to the "hard-core" lattice spacing, then the atoms are restricted to lattice sites, there can be no exchange,[4] and $J(V_{hc}) = 0$.

That this requires $C = 0$ can be seen by integrating dJ^2/DV,

$$J^2(V) = \int_{V_0}^{V} \frac{dJ^2}{dV'} dV' + J^2(V_0), \qquad (3)$$

where V_0 is the starting point for the integration. Mathematically, Eq. (3) is an identity, with the additive term $J^2(V_0)$ strictly a constant. However, three points must be considered in determining the accuracy of the $J(V)$ obtained from it using the experimental data. Accuracy of the experimental values of dJ^2/dV is discussed in Ref. 3. (Here we are not concerned specifically with the accuracy of the results, but with evaluation of the additive constant.) The problem of evaluating $J^2(V_0)$ is just that for C above. We take $V_0 = V_{hc}$ so that $J^2(V_0) = 0$.

But we have the problem that the integrand, $d(J/k)^2/dV$, is determined experimentally only over the range from 21 to 24 cm³/mole, while $V_{hc} \approx 8$ cm³/mole.

We can see that this presents no particular difficulty by referring to Fig. 1, which shows experimental values of $d(J/k)^2/dV$ versus V. The values of $d(J/k)^2/dV$ cover two orders of magnitude for V between 21 and 24 cm³/mole. The solid line is given by

$$\frac{d(J/k)^2}{dV} = 0.647 \left(\frac{V}{24} \right)^{35.26}, \qquad (4)$$

and is the result of a least-squares fit to the form aV^b. As is obvious from Fig. 1, this form fits the data quite well. From Eq. (3), $J^2(V)$ is the area under this curve between V_{hc} and V. Now, unless some rather unphysical behavior is supposed, this area will be essentially independent of how the curve is extrapolated from 21 to V_{hc}. Therefore the additive constant is zero, and $J(V)$ is uniquely determined (within the accuracy of the experiment as discussed in Ref. 3). The argument concerning areas would break down for $V \approx 21$, but once it has been established that there is no additive constant for larger V's, the self-consistent procedure can be applied with confidence.

A few values of $|J/k|$, obtained from Eqs. (3) and (4), are given in Table I. For comparison, values obtained previously by the self-consistent analysis, $|J/k|_{sc}$, are also shown. The results obtained by the two methods of analysis are seen to be in very close agreement, differing by less than 4% in all cases. This slight difference is because the self-consistent procedure permits $\partial \ln|J|/\partial \ln V$ to be volume dependent and the individual points used in this procedure do not lie exactly on the fitted curve.

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Relativistic Self-Consistent-Field Theory for Open-Shell Atoms. I

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The formulation of a relativistic restricted multiconfigurational self-consistent-field theory for open-shell atoms is given. The relativistic Hamiltonian is the sum of the one-electron Dirac-Hamiltonian and the two-electron Coulomb-repulsion terms. The total wave function is assumed to consist of a linear combination of eigenfunctions of total operators J^2 and J_z, which are themselves assumed to be known linear combinations of Slater determinants of four-component one-electron orbitals. The applicability of the formulation derived in this first paper is limited to wave functions expanded in terms of a set of distinct Slater determinants D_i, which obey the three conditions. (i) Two or more "core shells" may belong to a same symmetry specy k but their occupations must be similar. (ii) Distinct "peel shells" must belong to different symmetry species k. (iii) The symmetry species of the peel shells must be different from the symmetry species of the core shells. The most important cases are the calculations using wave functions expanded in terms of the distinct Slater determinants which arise from the $(2\bar{p})^n (2p)$, $(3\bar{d})^n (3d)^{n'}$, and $(4\bar{f})^n (4f)^{n'}$ configurations.

I. INTRODUCTION

The calculations of nonrelativistic wave functions of many-electron systems (atoms or molecules) have made, in these last years, significant progress. The self-consistent-field theory,[1] with or without interaction of configurations, and the multiconfigurational self-consistent-field theory[2] are now used in many calculations for closed-shell and open-shell systems.

More recently, the calculations of relativistic wave functions[3] have made important advances for closed-shell systems.

The object of this paper is the formulation of a relativistic restricted multiconfigurational self-consistent-field theory for open-shell atoms. Following Kim, we use a Hamiltonian which is the sum of the one-electron Dirac-Hamiltonian and the two-electron Coulomb-repulsion terms.[4] The n-electron wave function is assumed to consist of a linear combination of eigenfunctions of n-electron operators J^2 and J_z (hereafter called "configurations"), which are themselves assumed to be known linear combinations of Slater determinants of four-component one-electron orbitals. The variational principle must be applied to the corresponding expression of the energy, while the one-electron or-

bitals and the coefficients of the configurations are both varying. The practical procedure consists in deriving the self-consistent-field equations for the one-electron orbitals with invariable configuration-mixing coefficients. Having determined a set of one-electron orbitals in this way, the configuration-mixing coefficients are chosen to minimize the energy. These two calculations are repeated successively until self-consistent one-electron orbitals and configuration-mixing coefficients are obtained. Since the second phase of each iteration is identical to an interaction of configurations, we derive hereafter only the equations for the first phase of each iteration (hereafter called relativistic self-consistent-field equations).

II. HAMILTONIAN, WAVE FUNCTION, AND EXPRESSION OF THE ENERGY

A. Hamiltonian

The Hamiltonian H for an n-electron atom is

$$H = \sum_{\mu=1}^{n} H^{(D)}(\mu) + \sum_{\substack{\mu,\nu \\ \mu < \nu}} e^2/r_{\mu\nu} \ ,$$

where $r_{\mu\nu}$ is the distance between the μth and the