

Calculation of Exchange Frequencies in bcc ^3He with the Path-Integral Monte Carlo Method

D. M. Ceperley^(a) and G. Jacucci

Department of Physics, University of Trento, I-38050 Povo, Italy

(Received 21 July 1986)

The exchange frequency in crystal ^3He is calculated from first principles with a combination of the path-integral Monte Carlo method and a method used in classical statistical mechanics to determine free-energy differences. The frequency of nearest-neighbor exchange at melting density is 0.46 mK, that of triple exchange is 0.19 mK, and that of four-particle planar exchange is 0.27 mK. These exchange frequencies are within 30% of the values obtained from the empirical multiple-exchange model and agree with measurements. Many other types of high-order cyclic exchanges make significant contributions to thermodynamic properties, showing that ^3He is more complex than previously thought.

PACS numbers: 67.80.Mg, 02.70.+d, 05.30.Fk

Crystal ^3He at millikelvin temperatures is one of the simplest and cleanest examples in nature of a lattice-spin system. This simplicity arises because atomic helium is, at those temperatures, practically a hard spherical atom with very weak bonding to other helium atoms. Also, thermal phonons and vacancies are not excited. Thus the properties of the magnetic crystal result only from atomic exchange which occurs very rarely, roughly every 10^5 atomic vibrations. Originally it was anticipated that crystal ^3He would be described by the antiferromagnetic Heisenberg spin- $\frac{1}{2}$ model since one can show that if only pairs of nearest-neighbor atoms exchange, the system in continuous space can be mapped onto this spin model. The experimental phase diagram is totally at variance with this model: For example, the symmetry of the ground state is different from that of the Heisenberg model. To fit experimental data it is necessary to assume that two-, three-, and four-atom exchanges are approximately equally frequent. This is known as the multiple-exchange model.¹ Since exchange of atoms is a tunneling process, one would expect the barriers for these different processes to be, in general, different and to have different density dependences. It therefore seems improbable that the various frequencies have equal orders of magnitude. The calculation of the exchange frequencies from first principles is necessary for this model to be finally verified.²

To define the exchange frequencies and the lattice-spin model, one assumes that most of the time the atoms are close to lattice sites.³ If there are no ground-state vacancies, there are $N!$ ways of arranging the N atoms onto N lattice sites. This degeneracy is broken by the exchange of atoms. Suppose that we allow only two ways of arranging the N atoms onto the lattice sites which we will denote as Z and PZ . Here P is a cyclic permutation of a few atoms and Z is the vector of a perfect bcc lattice $Z = \{z_1, z_2, \dots, z_N\}$. Then the ground state is split into two states ϕ_0 and ϕ_1 with even and odd symmetry and energies E_0 and E_1 . The frequency with which the system

oscillates from Z to PZ is $2J_P = E_1 - E_0$. This definition applies to any permutation, but it is expected that only for small cyclic exchanges will the frequency be significant. Then for temperatures below 10 mK, the system of spin- $\frac{1}{2}$ fermions is described by a lattice Hamiltonian³ acting only on the spins of the atoms: $\sum_p J_p (-1)^P P_\sigma$, where $(-1)^P$ is the parity of the permutation and P_σ is the spin permutation operator.

The exchange frequencies are difficult to calculate since the helium atoms have large zero-point motion and correlation. An exchange of a pair of atoms necessarily involves neighboring atoms moving out of the way, and so it is really a collective process involving on the order of twenty atoms.⁴ This explains qualitatively why the frequencies of three- and four-atom exchange are similar to that of two-atom exchange since those exchanges impinge on neighboring atoms much less.

Consider the many-body density matrix for distinguishable particles:

$$\rho(R, R'; \beta) = \sum_n e^{-\beta E_n} \phi_n(R) \phi_n(R'), \quad (1)$$

where $\beta = 1/kT$ and R represents the $3N$ spatial coordinates of the atoms. Again let us make the restriction that the atoms must be near Z or PZ . Then for temperatures well below the Debye temperature only two states will contribute to the expansion in Eq. (1). To determine the exchange frequency, consider the density matrix taken between the perfect lattice and a permutation of the perfect lattice, normalized by the diagonal density matrix

$$F_P(\beta) \equiv \frac{\rho(Z, PZ; \beta)}{\rho(Z, Z; \beta)} = \tanh[J_P(\beta - \beta_P)], \quad (2)$$

where the second equality follows from symmetry properties and $\beta_P = -\ln[\phi_1(Z)/\phi_0(Z)]/J_P$. If $F_P(\beta)$ is calculated at two values of β , the exchange frequency can be determined.

To evaluate these density matrices, $M-1$ intermediate points R_1, R_2, \dots, R_{M-1} are inserted by use of the product property of density matrices giving

$$F_P(\beta) = \frac{\int dR_1 \cdots dR_{M-1} \rho(Z, R_1; \tau) \rho(R_1, R_2; \tau) \cdots \rho(R_{M-1}, PZ; \tau)}{\int dR_1 \cdots dR_{M-1} \rho(Z, R_1; \tau) \rho(R_1, R_2; \tau) \cdots \rho(R_{M-1}, Z; \tau)}, \quad (3)$$

where $\tau = \beta/M$. The path-integral Monte Carlo method is based on making M large enough so that an accurate expression can be written down for $\rho(R, R'; \tau)$. We have used for $\rho(R, R'; \tau)$ the product of two-atom density matrices⁵ and its most important correction term, and $\tau = 0.025/\text{K}$ where it was assumed that the helium atoms interact with a pair potential derived from theory and atom-atom scattering data.⁶ This high-temperature density matrix gives the low-temperature properties of liquid and solid ⁴He to an accuracy of 0.1 K/atom.⁵

There has been considerable development in classical statistical mechanics of methods for the computation of such ratios with the Monte Carlo method and, as suggested by one of us,⁷ such methods are useful for quantum problems. First let us review the Metropolis Monte Carlo method⁸ for sampling from an arbitrary probability distribution function, $\pi(s)$, where s represents the state of some system. The sampling is achieved by the construction of a Markovian random walk where at each step of the walk the state of the system is moved to a nearby state based on a transition probability $T(s \rightarrow s')$ chosen so that detailed balance applies. This guarantees that the probability of the walk visiting the state s is $\pi(s)$. Rejections, which mean that the state is not always changed at each step, are used to satisfy the detailed-balance condition.

To calculate $F_P(\beta)$ we define the state of the walk to consist not only of the path but also of a discrete variable called σ which takes two values, I or P . When $\sigma = I$ we set $R_M = Z$ and when $\sigma = P$ then $R_M = PZ$; the paths either close on themselves or are cross linked. Thus the state is $\{R_1, R_2, \dots, R_{M-1}, \sigma\}$. Now the Metropolis method is used to sample the distribution function, $\pi(s) = \rho(Z, R_1; \tau) \cdots \rho(R_{M-1}, R_M; \tau)$, allowing, of course, for transitions between the two states I and P . Then the average number of steps the walk spends in the state P divided by the average number in the state I equals $F_P(\beta)$.

The success of the method clearly depends on the ability to make many transitions between the two states. Luckily this problem has been studied⁵ since it arises in calculations of the lambda transition in Bose ⁴He. Our procedure for making a transition from I to P is to choose a section of the path as likely to allow an exchange. The total path is divided into three parts. The coordinates R_1, \dots, R_k are left unchanged. The coordinates R_{k+j}, \dots, R_M are reflected into PR_{k+j}, \dots, PR_M which by definition changes the state from I to P . Since the Hamiltonian is symmetric this does not change $\pi(s)$. Finally, a new section of the path is sampled to connect R_k onto PR_{k+j} . The coordinates of the atoms not involved in the exchange are left unchanged while those exchanging are chosen according to the bisection algorithm where first the midpoint between R_k and PR_{k+j} is sampled, then midpoints of the two resulting segments are chosen, etc., until the entire segment is sampled.

There is an optimal size, j , for this collective move of the path from state I to P . If j is too small the springs of the polymers will be stretched too much in going from R_k to PR_{k+j} . If j is too large rejections will occur because of the accumulation of small errors in the sampling procedures. The parameter β_P gives the amount of imaginary time needed for the exchange to take place and it is about 0.3/K for most of the exchanges examined. We have found that the optimal value of j is approximately $\beta_P/(2\tau)$. For an exchange of four atoms the optimal elementary Monte Carlo move from state I to P turns out to involve changing 84 coordinates.

A similar method has been optimized for classical statistical mechanics by Bennett.⁹ The relative time the system spends in the two states is equal to the rate for making transitions from I to P divided by the reverse rate. Thus it is not actually necessary to make the transitions from one state to the other but only necessary to compute the rates that one could have made the transitions. This combination of classical and quantum techniques has the important property that its accuracy is independent of the actual tunneling frequency. The exchange frequency is expressed as the ratio of rates, not as the very small difference between two eigenvalues. Computer time is only weakly dependent on the number of atoms in the system and on temperature. Our computer runs have involved 16, 54, and 128 atoms. Calculations have been performed down to 0.25 K but most are for 1 K.

The exchange frequency is given by the slope of $F_P(\beta)$ with respect to β [see Eq. (2) and Fig. 1]. One can

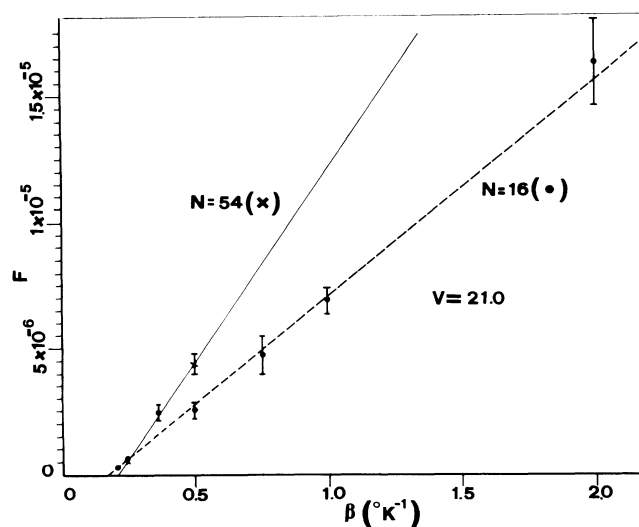


FIG. 1. $F_P(\beta)$ for pair nearest-neighbor exchange. The dots are for 16 atoms and the crosses are for 54 atoms. The solid line represents the least-squares fit of Eq. (2) through the crosses and the dashed line that through the dots. The slope is the exchange frequency J_P and the intercept is the imaginary time of the exchange β_P .

TABLE I. Exchange frequencies at two densities. The semiempirical values from the multiple-exchange model (MEM) are in the last column.^a The type of exchange is determined (Ref. 10) by the set of $p(p-1)/2$ pair distances amongst the p atoms exchanging where 1 refers to a nearest-neighbor (nn) distance, 2 a next-nearest-neighbor (nnn), etc. The first set of numbers specify the distances of adjacent atoms on the cycle, the next set the second neighbors, etc.

Volume (cm ³ /mole) p type	20.07 J_P (MC) (μ K)	24.12 J_P (MC) (mK)	24.12 J_P (MEM) (mK)
2(1) nn	15 ($\pm 13\%$)	0.46 ($\pm 7\%$)	0.35
2(2) nnn		0.065 ($\pm 10\%$)	
3(112) triplet	4 ($\pm 20\%$)	0.19 ($\pm 10\%$)	0.14
4(1 ⁴ ;23) planar	6 ($\pm 30\%$)	0.27 ($\pm 10\%$)	0.30
4(1 ⁴ ;22) folded		0.027 ($\pm 18\%$)	
4(1122;31)		0.006 ($\pm 25\%$)	
4(1212;11)		0.0005 ($\pm 45\%$)	
4(1212;14)		0.011 ($\pm 30\%$)	
4(2 ⁴ ;33) square		0.0019 ($\pm 30\%$)	
6(1 ⁶ ;3 ⁶ ;4 ³)		0.36 ($\pm 30\%$)	
6(1 ⁶ ;523 523;417)		0.022 ($\pm 35\%$)	

^aD. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer-Verlag, New York, 1977).

determine the slope with a single calculation since the exchange takes only a finite amount of imaginary time; it is an instanton. Define the time T_e when the exchange occurs for a given path in the state P as the value in imaginary time when the path is equidistant from Z and PZ . Now Eq. (2) implies that T_e can assume $(\beta - \beta_P)$ different values; that is an extra degree of freedom the P state has that the I state lacks. Suppose that we demand that the path in the P state have its exchange time in the middle of the path: $|\beta/2 - T_e| < \bar{\beta}/2$ where $\bar{\beta}$ is a constant less than $\beta - \beta_P$. Now that the exchange is confined to a known portion of imaginary time in the middle of the path T_e can assume exactly $\bar{\beta}$ different values and for this new distribution $F_P(\beta) = \tanh(\bar{\beta}J_P)$. We have checked that this method gives the same value of J_P .

We have calculated a variety of two-, three-, four-, and six-particle exchange frequencies at two densities: near melting ($v=24.12$ cm³/mole), and near the high-pressure limit of the bcc solid ($v=20.07$ cm³/mole). These are given in Table I. We have tested that the exchange frequencies are not sensitive to β , $\bar{\beta}$, the number of particles, and time step τ , to the 10% accuracy level of our calculations. We find that pair exchange is most frequent, but this is followed closely by planar four-atom exchange and triplet exchange. Thus, the multiple-exchange model is strongly supported. The semiempirical exchange frequencies, also in Table I, from the Monte Carlo (MC) frequencies by 30%. We do not expect perfect agreement since, first, many other types of exchanges are significant and, second, the semiempirical frequencies are partly determined by approximate

mean-field calculations¹ on the lattice model. The ordering of exchange frequencies is correctly predicted by high-density semiclassical calculations⁴ with a purely repulsive interaction, but those calculations have not yielded absolute magnitudes. Also we find that the largest exchange frequencies scale with density as the (20 ± 1) th power, in agreement with experiment.^{1,2}

The specific heat and the magnetic susceptibility at zero magnetic field and at temperatures above the ordering transition can be expanded in powers of the inverse temperature:

$$C_V \propto e_2\beta^2 - e_3\beta^3, \quad \chi^{-1} \propto \beta^{-1} - \theta + \beta B, \quad (4)$$

where the coefficients are products of the exchange frequencies.¹ Also the value of the magnetic field when ³He becomes ferromagnetic at zero temperature is a linear combination of the exchange frequencies. The calculation of the coefficients and magnetic field has been done in two ways: first, by use of the three largest frequencies, and second, by use of all frequencies in Table I. The results, in Table II, show the importance of many types of exchange in crystal ³He. Even though the frequencies of some of the exchanges are small, they are numerous. The most important frequencies are determined to better than 10%, but because of large cancellations the resulting coefficients are very inaccurate. With the present results we cannot rule out the possibility that even more types of exchanges are important. It is also possible that the interatomic potential is inaccurate. But since our results give the measured properties of ³He within the errors, it is unlikely that other proposed exchange mechanisms,² such as ground-state vacancies or

TABLE II. High-temperature thermodynamic-expansion coefficients, as defined in Eq. (4) at melting ($v=24.12$ cm³/mole) and the zero-temperature critical magnetic field for the transition into the ferromagnetic phase. The first column was obtained by our using only the three largest exchange processes (nn, t , and planar), the second column uses all calculated frequencies.

Property	Three frequencies	All frequencies	Experiment ^a
θ (mK)	0.1 ± 1.0	-2.2 ± 1.0	-1.7 ± 0.1
e_2 (mK ²)	5.0 ± 0.8	5.9 ± 1.6	5.9
e_3 (mK ³)	2.0 ± 4.0		<2.4
B (mK ²)	0.7 ± 0.8		0.0 ± 1
H_{c2} (T)	9.7 ± 2.1	19.0 ± 2.2	...

^aReference 11.

the coupling to phonons are relevant. The importance of so many types of exchange complicates the already difficult process of our determining from the exchange Hamiltonian such properties as the transition temperature and spin-wave velocities.

In conclusion, a first-principles method of calculating exchange frequencies in quantum crystals has been developed and tested. This calculation has verified the multiple-exchange model for ³He. Three types of exchange are dominant but many others produce significant effects showing that ³He is more complex than previously thought. We anticipate that the development of this accurate computational technique will lead to a much deeper understanding of exchange in quantum crystals.

We wish to thank E. L. Pollock for useful discussions, B. J. Alder for suggesting improvements on the manuscript, and the Aspen Institute for Physics (Aspen, CO), where this research was initiated. This work was partially supported by Consiglio Nazionale delle Ricerche (Italy) through the Center of Studies in Trento.

(a)Permanent address: Lawrence Livermore National Laboratory, Livermore, Ca 94550.

¹M. Roger, J. Hetherington, and J. M. Delrieu, *Rev. Mod. Phys.* **55**, 1 (1983).

²M. C. Cross and D. S. Fisher, *Rev. Mod. Phys.* **57**, 881 (1985).

³D. J. Thouless, *Proc. Phys. Soc. London* **86**, 893 (1965).

⁴M. Roger, *Phys. Rev. B* **30**, 6432 (1984).

⁵E. L. Pollock and D. M. Ceperley, *Phys. Rev. B* **30**, 2555 (1984); D. M. Ceperley and E. L. Pollock, *Phys. Rev. Lett.* **56**, 351 (1986).

⁶R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, *J. Chem. Phys.* **70**, 4330 (1979); D. M. Ceperley and H. Partridge, *J. Chem. Phys.* **81**, 5833 (1984).

⁷G. Jacucci, in *Monte Carlo Methods in Quantum Problems*, edited by M. H. Kalos (Reidel, Dordrecht, The Netherlands, 1984).

⁸N. Metropolis, A. W. Rosenbluth, M. H. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).

⁹C. H. Bennett, *J. Comput. Phys.* **22**, 245 (1976).

¹⁰A. K. McMahan and R. A. Guyer, *Phys. Rev. A* **7**, 1105 (1973).

¹¹H. L. Stipdonk, G. Frossati, and J. H. Hetherington, *J. Low. Temp. Phys.* **61**, 185 (1985).