

⁹D. Amit and E. P. Gross, Phys. Rev. **145**, 130 (1966).
¹⁰The Po²¹⁰ was purchased from U. S. Radium Corp. and the activity at time of purchase was 750 $\mu\text{Ci}/\text{in.}^2$
¹¹The 170- μ grids were from 2C39A tubes and were purchased from Eimac Corp.
¹²The mesh with different size openings was purchased from Buckbee Mears Co.

¹³Model 250-3919, Microdot Corp.
¹⁴Model 610BR Electrometer, Keithley Corp.
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¹⁶A. Walraven, Phys. Rev. A **1**, 145 (1970).
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Exchange Interaction in Solid He³

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On the basis of our previous theory used to calculate the static properties of crystalline He³ and He⁴ at $T=0$, we compute the exchange interaction of the nuclear spins in bcc He³ as a function of molar volume, obtaining good agreement with experiment. Comparison with the theories of Nosanow and co-workers and of Guyer and Zane shows that the success of the theory is mainly due to the effective-force constant used in the computations.

I. INTRODUCTION

In recent years the exchange interaction J between two atoms in solid He³ has been measured by a number of workers.¹⁻⁵ The absolute value of J ranges from about⁶ 10^{-3} to 10^{-4} °K as the nearest-neighbor distance a runs from 3.7 to 3.5 Å corresponding to molar volume between 23.5 and 19.9 cm³ in the bcc phase. These values of J are large compared to what one would predict for a classical crystal because of the large zero-point motion of the relatively light He³ atoms. However, J is still very small compared to the ground-state energy E_0 which is of order 1 °K per particle and consequently the possibility of exchange may be ignored in calculations of E_0 and related thermodynamic quantities. This is done in most theories of quantum crystals and was done by us in Ref. 7 where the thermodynamic properties of crystalline He³ and He⁴ are calculated at $T=0$. In the present work we evaluate the exchange interaction as a function of molar volume on the basis of the theory and results of Ref. 7.

A theoretical determination of J was first given by Bernardes and Primakoff⁸ and subsequently by Mullin, Nosanow, and co-workers.⁹⁻¹¹ In addition, Guyer and Zane¹² have recently calculated J , basing their work on the quantum crystal theory of Guyer¹³ and Sarkissian.¹⁴

The approach that we use is similar to that of the previous theories; J is defined in terms of the energy difference between the singlet and triplet spin states of two nearest-neighbor He³ atoms. There are, however, important differences among the three approaches as regards the formalism and the approximations used in computing this energy differ-

ence; these are discussed below.

The calculation of J is an important one because J is extremely sensitive to the force constant α describing the single-particle effective potential in which each atom sits, and there is also some sensitivity of the result to the form of the two-particle correlation function. Thus J should be a good test of any quantum crystal theory. In this context it should be mentioned that there is some disagreement among experimental values of J which are obtained from several different types of experiment. In particular, the values inferred from NMR measurements are sensitive to small concentrations of impurities. Reference 5 contains a discussion of this problem.

The remainder of this paper contains (i) in Sec. II, a brief review of the formalism of Ref. 7 and construction of symmetric and antisymmetric space states for nearest neighbors; (ii) in Sec. III, the calculational details and numerical results; and (iii) in Sec. IV, a discussion of our results and a comparison of them with experiment and other theories.

II. FORMALISM

We begin by summarizing the theory of Ref. 7 in which exchange effects are ignored and the particle statistics play no role. The single-particle Green's function for the He³ localized at position \vec{R}_i is given by¹⁵

$$g_i(1, 1'; \nu) = \sum_{\rho} \phi_{i\rho}(1) \phi_{i\rho}(1') / (\omega_{\nu} - \epsilon_{\rho}) \quad (1)$$

in the frequency representation. The single-particle wave function $\phi_{i\rho}(1)$ obeys the equation

$$[-\nabla_1^2/2m + u_i(1)]\phi_{i\rho}(1) = \epsilon_\rho \phi_{i\rho}(1), \quad (2)$$

where

$$u_i(1) = u_0 + (\alpha^4/2m)(\vec{r}_1 - \vec{R}_i)^2 \equiv u_0 + V_i(1) \quad (3)$$

in the harmonic approximation; m is the atomic mass and $\omega_\nu = i\pi(2\nu + 1)T + \mu$ for fermions. Here, ν is an integer; T , the temperature; and μ , the chemical potential. The force constant α is determined from a self-consistency condition [Eq. (7)] which relates the single-particle self-energy and the two-particle Green's function $G_{ij}(12; 1'2)$. The particles are approximated as moving in a static self-consistent field in which case all multiple-particle Green's functions have the same pole as g_i in Eq. (1) when viewed as functions of ω_ν . Consequently, the two-particle Green's function for particles localized around sites i and j has the form

$$G_{ij}(12, 12; \nu) = \phi_{i0}^2(1)\phi_{j0}^2(2)\chi_{ij}(1, 2)/(\omega_\nu - \epsilon_0),$$

where the summation over ρ in Eq. (1) is omitted because we are interested only in the $T=0$ limit. This means that $\rho=0$ in what follows so we drop this subscript.

The correlation function $\chi_{ij}(1, 2)$ is found in Ref. 7 to obey the equation

$$\begin{aligned} &[-\nabla_1^2/2m - \nabla_2^2/2m + V(1, 2) + \sum'_k \int \phi_k^2(3) \\ &\times [V(1, 3)\chi_{ik}(1, 3) + V(2, 3)\chi_{jk}(2, 3)]d^3r_3 + \Delta_{ij}(1, 2)] \\ &\times \phi_i(1)\phi_j(2)\chi_{ij}(1, 2) = \lambda_0\phi_i(1)\phi_j(2)\chi_{ij}(1, 2), \quad (4) \end{aligned}$$

where the prime on the summation indicates summation over positions $k \neq i, j$ and V is the interatomic potential $V(1, 3) = v(\vec{r}_1, \vec{r}_3)$. The choice of λ_0 in Eq. (4) determines the asymptotic behavior of $\chi_{ij}(1, 2)$ for large separation of \vec{r}_1 and \vec{r}_2 . The function $\Delta_{ij}(1, 2)$ is given by

$$\begin{aligned} \Delta_{ij}(1, 2) = &\sum'_k \int \phi_k^2(3) \{V(1, 3)[\chi_{jk}(2, 3) - 1]\chi_{ik}(1, 3) \\ &+ V(2, 3)[\chi_{ik}(1, 3) - 1]\chi_{jk}(2, 3)\} d^3r_3. \quad (5) \end{aligned}$$

Equations (4) and (5) are derived by writing down the equation of motion for the two-particle Green's function and approximating the three-particle Green's function as

$$\phi_i^2(1)\phi_j^2(2)\phi_k^2(3)\chi_{ij}(1, 2)\chi_{jk}(2, 3)\chi_{ik}(1, 3)(\omega_\nu - \epsilon_0)^{-1}.$$

The normalization condition on $\chi_{ij}(1, 2)$ is

$$\int \chi_{ij}(1, 2)\phi_i^2(1)\phi_j^2(2)d^3r_1d^3r_2 = 1. \quad (6)$$

The self-consistency condition for $u_i(1)$ is

$$u_i(1)\phi_i^2(1) = \sum'_j \int V(1, 2)\phi_i^2(1)\phi_j^2(2)\chi_{ij}(1, 2)d^3r_2, \quad (7)$$

where the sum on j excludes the term $j=i$; this relation may be substituted into Eq. (4) with the result

$$\begin{aligned} &\{-\nabla_1^2/2m - (\nabla_2^3/2m) + u_i(1) + u_j(2) + V(1, 2) \\ &- [\int \phi_j^2(\bar{2})V(1, \bar{2})\chi_{ij}(1, \bar{2})d^2\bar{r}_2 \\ &+ \int \phi_i^2(\bar{1})V(\bar{1}, 2)\chi_{ij}(\bar{1}, 2)d^3\bar{r}_1] + \Delta_{ij}(1, 2)\} \\ &\times \phi_i(1)\phi_j(2)\chi_{ij}(1, 2) \\ &= \lambda_0\phi_i(1)\phi_j(2)\chi_{ij}(1, 2). \quad (8) \end{aligned}$$

Equations (2), (5), (7), and (8) form the basis of the theory used in Ref. 7 to calculate the static properties of solid helium. Because of the complexity of Eq. (5), we use the simple approximation

$$\Delta_{ij}(1, 2) = \Delta_0 + p(r_{12} - R_{ij}), \quad (9)$$

where $R_{ij} = |\vec{R}_i - \vec{R}_j|$ and the constant Δ_0 may be adsorbed into λ_0 . The parameter p is chosen such that the physically reasonable condition

$$\int (\vec{r}_{12} - \vec{R}_{ij}) \cdot \vec{R}_{ij}\chi_{ij}(1, 2)\phi_i^2(1)\phi_j^2(2)d^3r_1d^3r_2 = 0 \quad (10)$$

is satisfied. The value of p determined in this way is compatible⁷ with that which is obtained by expanding Eq. (5), given the final result for $\chi_{ij}(1, 2)$. We want to emphasize that this simple approximate procedure is used for $\Delta_{ij}(1, 2)$ only because of the large expenditure of computer time that would be required to treat it more exactly.

In the present work, we wish to construct states which are symmetric and antisymmetric under the exchange of the particles localized around \vec{R}_i and \vec{R}_j . The difference in energy of the two lowest lying states of different symmetry may be related to the exchange constant J which appears in the Heisenberg model Hamiltonian $H_{ex} = -2J\sum_{i>j}(\vec{S}_i \cdot \vec{S}_j)$; for particles of spin $\frac{1}{2}$, \vec{S}_i is such that $\langle S_i^2 \rangle = \frac{3}{4}$. The singlet and triplet states are eigenstates of the two-spin operators in H_{ex}

$$-2J(\vec{S}_i \cdot \vec{S}_j)|t_{ij}\rangle = -\frac{1}{2}J|t_{ij}\rangle$$

and

$$-2J(\vec{S}_i \cdot \vec{S}_j)|s_{ij}\rangle = \frac{2}{3}J|s_{ij}\rangle,$$

where $|s_{ij}\rangle$ and $|t_{ij}\rangle$ are triplet and singlet spin states of particles i and j . The former corresponds to a symmetric space state, the energy of which we denote ϵ^+ ; the latter, to an antisymmetric space state with energy ϵ^- . If the Heisenberg Hamiltonian is to account for this energy difference, we must have

$$\epsilon^+ - \epsilon^- = \frac{3}{2}J - (-\frac{1}{2}J) = 2J. \quad (11)$$

As pointed out in Ref. 1, Eq. (11) is a result of the convention used in H_{ex} . When comparing experimental or theoretical values of J , one should check the conventions used by the different authors which are not always the same as that used here and in Ref. 1.

The theory of Ref. 7 may be generalized to include the proper symmetrization of the various Green's functions and effective field. In the prior work, we assume at the outset that particles 1 and 2 are localized at the positions \vec{R}_i and \vec{R}_j . In order to compute ϵ^+ and ϵ^- , the duct joining lattice sites i and j should be opened (to use Thouless's¹⁶ words); consequently, we write the creation operators ψ^\dagger corresponding to placing a particle on sites i and j as

$$\psi^\dagger(1) = (1/\sqrt{2})[\psi_i^\dagger(1) + e^{i\theta}\psi_j^\dagger(1)] \quad (12a)$$

and

$$\psi^\dagger(2) = (1/\sqrt{2})[\psi_i^\dagger(2) + e^{i\theta'}\psi_j^\dagger(2)], \quad (12b)$$

where ψ_i^\dagger and ψ_j^\dagger are the operators used in Ref. 7 for placing particles on the individual sites i and j . Also, $e^{i\theta}$ and $e^{i\theta'}$ are phase factors chosen to produce the required symmetry of the Green's functions. The single-particle Green's function is defined in the usual way,

$$\begin{aligned} g(1, 1') &\equiv (1/i) \langle T(\psi(1)\psi^\dagger(1')) \rangle \\ &= \frac{1}{2}[g_{ii}(1, 1') + g_{jj}(1, 1') \\ &\quad + e^{i\theta}g_{ij}(1, 1') + e^{-i\theta}g_{ji}(1, 1')], \quad (13) \end{aligned}$$

where

$$g_{ij}(1, 1') \equiv (1/i) \langle T(\psi_i(1)\psi_j^\dagger(1')) \rangle.$$

On the assumption that the particles are localized, the Green's function is calculated as in Ref. (7) where $g_{ij} = 0$ is assumed. Thus we have

$$g(1, 1') \approx \frac{1}{2}[g_{ii}(1, 1') + g_{jj}(1, 1')]. \quad (14)$$

Equation (14) is not very accurate for arguments near $\frac{1}{2}(\vec{R}_i + \vec{R}_j)$ where the harmonic approximation to $u_i(1)$ is also not very accurate. In this sense, Eq. (14) is consistent with the approximation used in Ref. 7.

Next, in the unsymmetrized theory, we find the two-particle equal-time Green's function

$$\begin{aligned} G_{ij}(12, 1'2') \Big|_{t_2=t_1, t'_2=t'_1} \\ = \frac{1}{2} \langle T(\psi_i(1)\psi_j(2)\psi_j^\dagger(2')\psi_i^\dagger(1')) \Big|_{t_2=t_1, t'_2=t'_1} \\ = \chi_{ij}(1, 2)\phi_i(1)\phi_j(2)\phi_i(1')\phi_j(2'), \quad (15) \end{aligned}$$

where the function $\chi_{ij}(1, 2)$ is normalized such that

$$\int G_{ij}(12; 12') \Big|_{t_2=t_1} d^3r_1 d^3r_2 = 1.$$

In the present case, the appropriate generalization

$$\begin{aligned} G_{ij}(12; 1'2') &= (1/i^2) \langle T(\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')) \rangle \\ &\sim [\phi_i(1)\phi_j(2)\phi_i(1')\phi_j(2')\chi_{ij}(1, 2) \\ &\quad + \phi_j(1)\phi_i(2)\phi_j(1')\phi_i(2')\chi_{ji}(1, 2) \\ &\quad + \phi_i(1)\phi_j(2)\phi_j(1')\phi_i(2')\chi_{ij}(1, 2)e^{i(\theta-\theta')} \\ &\quad + \phi_j(1)\phi_i(2)\phi_i(1')\phi_j(2')\chi_{ji}(1, 2)e^{i(\theta'-\theta)}]. \quad (16) \end{aligned}$$

In order to arrive at Eq. (16), it is necessary to assume no double occupancy of either site,

$$\psi_i(1)\psi_i(2) \equiv 0 \equiv \psi_j(1)\psi_j(2).$$

The phase factor is now chosen to symmetrize the Green's function in a way appropriate for the singlet or triplet spin state

$$\begin{aligned} G_{ij}^\pm(12; 1'2') &= (1/2N_\pm) [\phi_i(1)\phi_j(2)\phi_i(1')\phi_j(2')\chi_{ij}(1, 2) \\ &\quad + \phi_j(1)\phi_i(2)\phi_j(1')\phi_i(2')\chi_{ji}(1, 2) \\ &\quad \pm \phi_i(1)\phi_j(2)\phi_j(1')\phi_i(2')\chi_{ij}(1, 2) \\ &\quad \pm \phi_j(1)\phi_i(2)\phi_i(1')\phi_j(2')\chi_{ji}(1, 2)] \\ &= (1/2N_\pm) \{ [\phi_i(1)\phi_j(2)\chi_{ij}(1, 2) \pm \phi_j(1)\phi_i(2) \\ &\quad \times \chi_{ji}(1, 2)] [\phi_i(1')\phi_j(2') \pm \phi_j(1')\phi_i(2')] \}. \quad (17) \end{aligned}$$

The normalization constant $N_\pm = 1 \pm x$ where

$$x = \int \phi_i(1)\phi_j(2)\phi_j(1)\phi_i(2)\chi_{ij}(1, 2)d^3r_1d^3r_2. \quad (18)$$

Next, in the unsymmetrized theory, the self-consistent effective potential $u_i(1)$ is given by Eqs. (4) and (8) of Ref. 7,

$$u_i(1)g_i(1, 1') = \sum_j \int V(1, 2)G_{ij}(12; 1'2') \Big|_{t_2=t_1} d^3r_2. \quad (19)$$

In the present symmetrized scheme, this equation must be modified according to Eqs. (14) and (16), leading to

$$\begin{aligned} V_{ij}^\pm(1)(\phi_i^2(1) + \phi_j^2(1)) &= \sum_k \int V(1, 2)[\phi_i^2(1)\phi_k^2(2)\chi_{ik}(1, 2) \\ &\quad + \phi_j^2(1)\phi_k^2(2)\chi_{jk}(1, 2)] d^3r_2 \pm \phi_i(1)\phi_j(1)\bar{V}_{ij}(1). \quad (20) \end{aligned}$$

The second term on the right-hand side involves a $\bar{V}_{ij} \sim J$, the exchange interaction. The existence of this term means that the effective-force constant depends on the symmetry of the state, with the dif-

ference being of relative order $J/(\alpha^2/2m)$. Taking this difference into account in the calculation of J itself leads to a correction of the order $J^2/(\alpha^2/2m)$ and we shall ignore it. Then Eq. (20) gives $V_{ij}^\pm(1) = V_{ij}(1)$ where

$$V_{ij}(1) \approx \begin{cases} u_i(1) & \text{for } \vec{r}_1 \approx \vec{R}_i \\ u_j(1) & \text{for } \vec{r}_1 \approx \vec{R}_j \end{cases}.$$

For $\vec{r}_1 \approx \frac{1}{2}(\vec{R}_i + \vec{R}_j)$, $V_{ij}(1)$ cannot be obtained accurately within the harmonic approximation. Consequently, we shall simply use

$$\begin{aligned} V_{ij}(1) &= u_i(1) = u_0 + (\alpha^4/2m) (\vec{r}_1 - \vec{R}_i)^2, \\ &|\vec{r}_1 - \vec{R}_i| < |\vec{r}_1 - \vec{R}_j| \\ &= u_j(1) = u_0 + (\alpha^4/2m) (\vec{r}_1 - \vec{R}_j)^2, \\ &|\vec{r}_1 - \vec{R}_i| > |\vec{r}_1 - \vec{R}_j|. \end{aligned} \quad (21)$$

$$H_{ij}(1, 2)\phi_i(1)\phi_j(2)\chi_{ij}(1, 2) = H(\xi, \eta, \vec{X})\phi_i(1)\phi_j(2)\chi_{ij}(1, 2)$$

$$\begin{aligned} &= \left(\frac{\alpha^2}{\pi}\right)^3 \left[\frac{3}{2} \frac{\alpha^2}{m} - \frac{1}{m} \frac{1}{\xi} \frac{\partial^2}{\partial \xi^2} \xi + v(\xi) + \frac{\alpha^2}{2m} \frac{\eta^2 + \xi^2 - R_{ii}^2}{\xi} \frac{\partial}{\partial \xi} - W_{ij}(\xi, \eta, \vec{X}) + p(\xi - R_{ij}) \right] e^{-\alpha^2 \eta^2/4 - \alpha^2 x^2} \chi_{ij}(\xi, \eta, \vec{X}) \\ &= \lambda_0 \left(\frac{\alpha^2}{\pi}\right)^3 e^{-\alpha^2 \eta^2/4 - \alpha^2 x^2} \chi_{ij}(\xi, \eta, \vec{X}) \equiv \lambda_0 \phi_i(1)\phi_j(2)\chi_{ij}(1, 2), \end{aligned} \quad (24)$$

where $\xi = |\vec{r}_1 - \vec{r}_2|$, $\eta = |(\vec{r}_1 - \vec{r}_2) - (\vec{R}_i - \vec{R}_j)|$, and $\vec{X} = \frac{1}{2}[(\vec{r}_1 + \vec{r}_2) - (\vec{R}_i + \vec{R}_j)]$. When $H_{ij}(1, 2)$ operates on $\phi_i(1)\phi_j(2)\chi_{ij}(2, 1)$, it is more convenient to express it in terms of $\bar{\eta} = |(\vec{r}_1 - \vec{r}_2) - (\vec{R}_j - \vec{R}_i)|$ which leads to the same functional form of H_{ij} with $\bar{\eta}$ in place of η ,

$$H_{ij}(\xi, \bar{\eta}, \vec{X})\phi_j(1)\phi_i(2)\chi_{ij}(2, 1) = \lambda_0 \phi_j(1)\phi_i(2)\chi_{ij}(2, 1), \quad (25)$$

with

$$\phi_j(1)\phi_i(2)\chi_{ij}(2, 1) = (\alpha^2/\pi) e^{-\alpha^2 \bar{\eta}^2/4 - \alpha^2 x^2} \chi_{ij}(\xi, \bar{\eta}, \vec{X}).$$

If Eqs. (24) and (25) are both solved in the same way, they will lead to the same value of λ_0 , as they are formally identical.¹⁸

Next, we multiply Eq. (23) from the left-hand side by $\phi_i(1)\phi_j(2) \pm \phi_j(1)\phi_i(2)$ and integrate over all \vec{r}_1 and \vec{r}_2 to obtain¹⁹

$$\begin{aligned} \epsilon^\pm &= \frac{1}{2} \int [\phi_i(1)\phi_j(2) \pm \phi_j(1)\phi_i(2)] [V_{ij}(1) + V_{ij}(2) \\ &- u_i(1) - u_j(2) + H_{ij}(1, 2)] [\phi_i(1)\phi_j(2)\chi_{ij}(1, 2) \\ &\pm \phi_j(1)\phi_i(2)\chi_{ij}(2, 1)] d^3 r_1 d^3 r_2 / (1 \pm x). \end{aligned} \quad (26)$$

This approximation is equivalent to assuming that the "duct" described by Thouless¹⁶ is small. We note that $V_{ij}(1)$ is similar to the effective field used in Ref. 12.

Given Eq. (21) for the effective potential, the operator in the brackets, $\{H_{ij}(1, 2)\}$, on the left-hand side of Eq. (4) becomes

$$\bar{H}_{ij}(1, 2) = H_{ij}(1, 2) + [V_{ij}(1) + V_{ij}(2) - u_i(1) - u_j(2)], \quad (22)$$

and a similar alteration appears in Eq. (8). We are interested in the two-body eigenvalue $\lambda_0 \rightarrow \epsilon^\pm$ in Eq. (4) for symmetrical and antisymmetrical space states, in which case it has the form

$$\begin{aligned} \bar{H}_{ij}(1, 2) [\chi_{ij}(1, 2)\phi_i(1)\phi_j(2) \pm \chi_{ij}(2, 1)\phi_j(1)\phi_i(2)] \\ = \epsilon^\pm [\chi_{ij}(1, 2)\phi_i(1)\phi_j(2) \pm \chi_{ij}(2, 1)\phi_j(1)\phi_i(2)]. \end{aligned} \quad (23)$$

To determine the effect of operating with $\bar{H}_{ij}(1, 2)$, it is useful to take advantage of the unsymmetrized equation which can be written in the form^{7,17}

Equations (24) and (25) tell us that the result of operating with $H_{ij}(1, 2)$ to the right-hand side is just λ_0 times the symmetrized function. Consequently, when we take $\epsilon^+ - \epsilon^-$ to form J , this part vanishes identically. Also, we make use of the fact $x \ll 1$ and keep only the first order term in x :

$$\begin{aligned} J &= \frac{1}{2}(\epsilon^+ - \epsilon^-) = \int \phi_i(1)\phi_j(2)\chi_{ij}(1, 2) \\ &\times [V_{ij}(1) + V_{ij}(2) - u_i(1) - u_j(2)] \\ &\times [\phi_j(1)\phi_i(2) - x\phi_i(1)\phi_j(2)] d^3 r_1 d^3 r_2. \end{aligned} \quad (27)$$

In writing Eq. (27) we have used the symmetry property $\chi_{ij}(1, 2) = \chi_{ij}(2, 1)$ which is true of the approximate correlation functions found in Ref. 7.

This result differs from those of previous theories. Although our starting point is essentially the same as in Ref. 10, the numerical simplifications employed make direct comparison of the final answer difficult. It is true, however, that insofar as the numerical results are concerned, the form of the operator $[V_{ij}(1) + V_{ij}(2) - u_i(1) - u_j(2)]$ which enters Eq. (27) is unimportant compared to the force constant α which appears not only in [] but also

in $\phi_i(1) = (\alpha^2/\pi)^{3/4} e^{-\alpha^2(\vec{r}_1 - \vec{R}_i)^2/2}$. Thus the choice of α has a very large effect on the calculated J whereas the form of the operator [] will, if it is determined in a physically reasonable way, not affect the result by more than about a factor of 2.

Equation (27) is similar to the "tunnelling" term found by Guyer and Zane,¹² but in our formalism we do not find their "interaction" term.¹⁸

Finally, we wish to mention the importance of using the equation of motion (4) for $\chi_{ij}(1, 2)$ to eliminate the contribution from $H_{ij}(1, 2)$ in Eq. (26). If this is not done, an inaccuracy in $\chi_{ij}(1, 2)$ which

has a small effect on the ground-state energy E_0 can have a large effect on J . This can happen, for example, if one uses a variational approach to solve Eq. (24) as we in fact did before settling upon the present method of calculation.

Finally, we wish to mention another approach due to Thouless^{16,19} in which J is expressed as a surface integral. In this approach, the equation for $\chi_{ij}(1, 2)[\phi_i(1)\phi_j(2) \pm \phi_j(1)\phi_i(2)]$ is multiplied from the left-hand side by $\psi_{\mp}(1, 2) \equiv [\phi_i(1)\phi_j(2) \pm \phi_j(1)\phi_i(2)]$ rather than by $\psi_{\pm}(1, 2)$. Then the difference of the energies is

$$\begin{aligned} 2J = \epsilon^+ - \epsilon^- &= \left[\int \psi_-(1, 2) \left(-\frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} \right) \chi_{ij}(1, 2) \psi_+(1, 2) d^3r_1 d^3r_2 - \int \psi_+(1, 2) \left(-\frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} \right) \chi_{ij}(1, 2) \psi_-(1, 2) d^3r_1 d^3r_2 \right] \\ &\quad \times \left[\int \psi_+(1, 2) \chi_{ij}(1, 2) \psi_-(1, 2) d^3r_1 d^3r_2 \right]^{-1} \\ &= -(1/2m) \left\{ \int \nabla \cdot [\psi_-(1, 2) \nabla \psi_{ij}(1, 2) \psi_+(1, 2) - \psi_+(1, 2) \nabla \chi_{ij}(1, 2) \psi_-(1, 2)] d^3r_1 d^3r_2 \right. \\ &\quad \left. - \int [\psi_+(1, 2) \nabla \psi_-(1, 2) \nabla \chi_{ij}(1, 2) - \psi_-(1, 2) \nabla \psi_+(1, 2) \nabla \chi_{ij}(1, 2)] d^3r_1 d^3r_2 \right\} \\ &\quad \times \left[\int \psi_+(1, 2) \chi_{ij}(1, 2) \psi_-(1, 2) d^3r_1 d^3r_2 \right]^{-1}. \end{aligned}$$

The volume of integration may be chosen as $z_1 < 0$ and $z_2 > 0$ where $\vec{R}_j - \vec{R}_i$ is the polar axis and $\frac{1}{2}(\vec{R}_i + \vec{R}_j)$ is the origin of coordinates. Then the first integral in the preceding equation can be converted to a surface integral. The physical assumptions used in this approach are not much different from ours.

III. NUMERICAL PROCEDURE

By substituting Eqs. (3) and (21) into (27) and rearranging the terms, we find

$$\begin{aligned} J &= -(2\alpha^4/2m) \int \phi_i(1)\phi_j(2)\chi_{ij}(1, 2) \\ &\quad \times [\phi_i(2)\phi_j(2) - x\phi_i(1)\phi_j(2)] \\ &\quad \times [(\vec{r}_1 - \vec{R}_i)^2 - (\vec{r}_1 - \vec{R}_j)^2] d^3r_1 d^3r_2, \quad (28) \end{aligned}$$

where the integration over \vec{r}_1 is restricted to the region of space $|\vec{r}_1 - \vec{R}_i| > |\vec{r}_1 - \vec{R}_j|$. We next transform variables, choosing as origin of coordinates the point $\frac{1}{2}(\vec{R}_i + \vec{R}_j)$, with $\vec{X} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$ and $\vec{r} = \vec{r}_2 - \vec{r}_1$. Then

$$\begin{aligned} J &= -\left(\frac{\alpha^2}{\pi}\right)^3 \frac{2\alpha^4}{m} \int d^3r d^3X e^{-2\alpha^2 X^2 - \alpha^2 r^2/2 - \alpha^2 a^2/2} \\ &\quad \times \chi(\vec{r}, \vec{X}) [(\vec{X} - \frac{1}{2}\vec{r}) \cdot \vec{a}] [1 - x e^{\alpha^2 \vec{a} \cdot \vec{r}}], \quad (29) \end{aligned}$$

where $\vec{a} = \vec{R}_j - \vec{R}_i$. The region of integration is such that the inequality $X \cos \theta_X - \frac{1}{2}r \cos \theta_r > 0$ is satisfied; $\theta_X(\theta_r)$ is the angle between $\vec{X}(\vec{r})$ and \vec{a} .

We use the approximate correlation function of Ref. 7 which is a function of r alone; in this case the integration may be partially completed analytically. As a result of the restriction on the range of integration, the term $\sim x$ in Eq. (29) turns out to be of order $e^{-\alpha^2 a^2/4} \sim 10^{-2}$ relative to the leading term and so may be dropped. Equation (29) then becomes

$$\begin{aligned} J &\cong -\frac{8\alpha^{10}}{\pi m} a e^{-\alpha^2 a^2/2} \int_0^\infty r^2 dr \chi(r) e^{-\alpha^2 r^2/2} \\ &\quad \times \left[\int_0^{r/2} X^2 dX \left(\frac{2}{3} \frac{X^2}{r} + \frac{r}{2} \right) e^{-2\alpha^2 X^2} \right. \\ &\quad \left. + \int_{r/2}^\infty X^2 dX \left(X + \frac{1}{12} \frac{r^2}{X} \right) e^{-2\alpha^2 X^2} \right]. \quad (30) \end{aligned}$$

From this point the integration is completed numerically using functions and force constants computed in Ref. 7. They were determined using as interatomic potential both the Lennard-Jones 6-12 interaction (LJ) $v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, $\epsilon = 10.2^\circ \text{K}$, and $\sigma = 2.556 \text{ \AA}$, and the Yntema-Schneider interaction (YS) $v(r) = (1200 e^{-4.72r} - 1.24/r^6 - 1.89/r^8) \times 10^{-12} \text{ erg}$, where r is in Angstroms.

In Figs. 1 and 2 we plot the exchange interaction J as a function of volume. The curve marked A in Fig. 2 is the same as that marked PT in Fig. 1 and results from using the LJ interaction to deter-

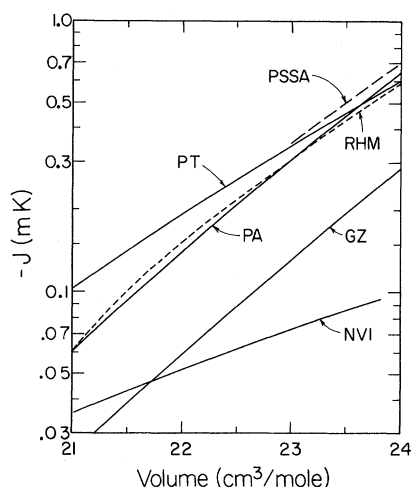


FIG. 1. The exchange integral $|J|$ (m°K) vs molar volume (cm^3/mole). The curve marked PT is the present theory while GZ is from Ref. 12 and NVI from Ref. 11; the experimental curves are from Refs. 1 (PA), 3 (PSSA), and 4 (RHM).

mine the force constant and correlation function. Also in Fig. 1 are several experimental curves and the theoretical results of Nosanow and Varma (NVI) and Guyer and Zane (GZ). Both of these theoretical groups also use the LJ interatomic potential. Curve B in Fig. 2 results from using the YS interaction but otherwise maintaining the conditions under which A is obtained. Curves C and D, on the other hand, are found using the LJ interaction but differ from A in the following respects: The effect of three-body correlations is not included when calculating C; this is accomplished by setting $p=0$ in Eq. (9) and ignoring Eq. (10). In the case of D, the effect of changing the boundary condition satisfied by $\chi_{ij}(1, 2)$ at large $|\vec{r}_1 - \vec{r}_2|$ is investigated. Specifically, we arbitrarily choose λ_0 such that $\chi_{ij}(r)=0$ at $r=1.6a$ and set $\chi_{ij}(r)\equiv 0$ for all $r > 1.6a$. This is to be contrasted with the procedure used in Ref. 7 which was to choose λ_0 so that $\chi(r)$ is finite at infinity. The latter procedure was used in calculating curves A, B, and C.

IV. DISCUSSION

In Fig. 1, the results of the present theory (PT) are compared with the experimental work of Refs. 1 (PA), 3 (PSSA), and 4 (RHM); we note that agreement of theory and experiment is within a factor of 2 over the entire range of the experimental data and is particularly good at high molar volumes.

The rapid variation of J as a function of volume can be traced to the behavior of $\alpha^2 a^2$; Eq. (30) has the general behavior $J \sim \alpha^3 a e^{-\alpha^2(a^2 + \sigma^2)/2}$, where σ is the hard-core radius of the interaction. The detailed behavior of the correlation function or of the

effective field directly affects J by perhaps a factor of 2. The effect of the field on the true one-particle function $\phi(1)$ is probably a good deal more important and may well change this function appreciably from the Gaussian form in the interstitial region.

There is an additional point that should be made concerning the effect of α on J . Equation (7) for $u_i(1)$ cannot be exactly satisfied when the harmonic approximation, Eq. (3), is used for $u_i(1)$. This means there is some arbitrariness in the way u_0 and α are found from Eq. (7). In Ref. 7, we examine two methods of choosing u_0 and α . In the first, the right-hand side of Eq. (7) is expanded and the zero-order and quadratic terms in $(\vec{r}_1 - \vec{R}_i)^2$ are identified as the two terms in the harmonic potential. The results of this method were used in determining the theoretical curves of Figs. 1 and 2.

This expansion is not obviously valid, however, and higher order terms could be important. We have examined this possibility by first choosing u_0 according to the expansion and then integrating Eq. (7) over all \vec{r}_1 , using Eq. (3) for $u_i(1)$. The α determined in this way will contain the effects of higher-order terms. If it is much different from the previous force constant, this will be a sign that higher-order terms are important. It turns out⁷ that the second method gives only slightly larger α , producing a ground-state energy per particle $\sim 1.5^\circ\text{K}$ larger in bcc ^3He than the first method. The exchange integral J is more sensitive to α and is reduced by a factor of ≈ 0.75 independent of molar volume. This means, for example, that according to the second method of choosing α , the curve marked PT in Fig. 1 should be translated downward so that it crosses the experimental curves at about $V = 22 \text{ cm}^3$ rather than near $24 \text{ cm}^3/\text{mole}$.

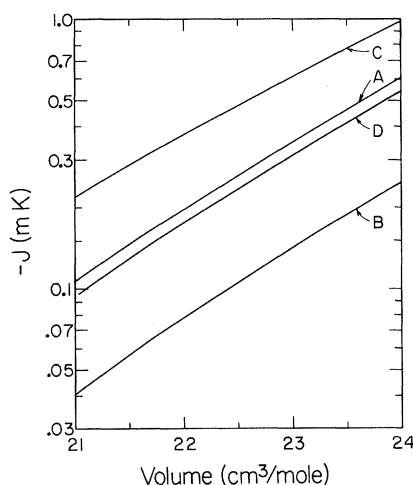


FIG. 2. Theoretical curves of $|J|$ (m°K) vs molar volume (cm^3/mole). The conditions under which these results were determined are described in the text.

The rather large difference in the slopes of the theoretical curves PT and NVI is a direct consequence of the difference in the behavior of α^2 here and the corresponding quantity A in Nosanow's theory. For example, in going from $V=24$ to 20 cm³ per mole, we find that α^2 increases by a factor of 1.42 whereas A changes by a factor 1.3.¹⁰ In Guyer's theory on the other hand, α^2 changes by a factor of 1.44 and is slightly larger in magnitude than the values we find.

Despite the relatively good agreement with experiment of the present theory, we cannot claim that it is necessarily correct because of the many approximations made in order to obtain simple single-particle and correlation functions. The effect on the calculated J should be investigated. We note, for example, that a change in α of 5% will alter J by about a factor of 2. A potentially important correction that should be made is to go beyond the harmonic approximation to the self-consistent field. The next term could alter considerably the behavior of u and of ϕ in the interstitial region between \bar{R}_i and \bar{R}_j , which is important in the calculation of J .

In Fig. 2 we plot four calculated curves of J vs molar volume, each of which is obtained under slightly different conditions. First, curve A is found using the LJ potential and the three-particle correlation term $\Delta_{ij}(1, 2)$ in Eq. (8). Also, λ_0 is chosen so that $\chi_{ij}(r)$ remains finite at large $r \rightarrow \infty$. Curve B is computed under the same conditions except that the YS potential is used. Even as this potential leads to a large ground-state energy in

Ref. 7, so does it produce a smaller J . This result is principally a consequence of the larger force constant α that it gives. Curve C is calculated using the LJ potential once again but neglecting the term $\Delta_{ij}(1, 2)$ entirely and discarding the condition Eq. (9). The resulting curve for J is less sensitive to molar volume, just as the ground-state energy computed this way in Ref. 7 is relatively insensitive to molar volume. Finally, curve D is obtained in the same way as A except that λ_0 is chosen (somewhat arbitrarily) so that $\chi(r)=0$ at $r=1.6a$ and is taken equal to zero for all larger r . This was done to alter the behavior of $\chi(r)$ for $r>a$ fairly drastically. This hardly affects J at all, from which we may conclude that the behavior of $\chi(r)$ at large r is not very important to the calculation of J or, equivalently, that the choice of λ_0 is not important.

In conclusion, we wish to emphasize that theoretical values of J are likely to be a good test of calculated force constants α because of the extreme sensitivity of the exchange interaction to this parameter. Similarly, the phonon dispersion relation is strongly dependent on α , at least for small wave numbers, and should also be a good test of a theory in this respect. Calculations of this property are in progress.

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¹⁸We show here that although the potential $V_{ij}(1)$ used in the calculation is very similar to that of Ref. 12, the interaction term does not appear in our model. By transforming the Laplacian operator according to Eq. (24), the difference between this equation and the *formally identical* corresponding equation with $1 \leftrightarrow 2$ or $\eta \rightarrow \bar{\eta}$ is such that no extra term appears. In Ref. 12 the exact Laplacian operator is used in taking the derivative of the wave function whereas only the angle independent part is used for the correlation function. This gives rise to the interaction term. Note too that we integrate over the entire space in contrast to the half-space used for the term in Ref. 12. If we have to choose some restricted space of integration in this model, and we do not see any

reason to do so, then our arguments would not be valid and there will be an addition term involving a derivative of χ .

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Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Potassium Ions and Positive Nitric Oxide Ions in Nitric Oxide†

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We have measured in a drift-tube mass spectrometer the mobilities of NO⁺, NO⁺·NO, and K⁺ ions in NO at 300 °K. The measurements were made over a substantial range of E/N , where E is the drift field intensity and N is the gas number density. The zero-field reduced mobilities were found to be 1.91 ± 0.06 , 1.78 ± 0.05 , and 2.245 ± 0.067 cm²/Vsec, respectively. Measurements were also made of the longitudinal diffusion coefficients of NO⁺ and K⁺ ions in nitric oxide at 300 °K as a function of E/N . Our results are in fair agreement with those predicted by the Einstein equation from the experimental zero-field mobilities.

I. INTRODUCTION

Recent investigations of ions¹⁻⁷ in H₂, D₂, N₂, and O₂ utilizing the drift-tube mass spectrometer of this laboratory have been extended to positive ions in nitric oxide at room temperature. The ions studied are NO⁺, NO⁺·NO, and K⁺. The present work includes the only direct measurements known to the authors of positive-ion mobilities in nitric oxide, although mobility measurements of NO⁺ in other gases have been performed elsewhere.⁸ The low-field mobilities of NO⁺ and NO⁺·NO in nitric oxide can also be calculated from ambipolar diffusion coefficients measured in recent stationary-afterglow experiments,⁹⁻¹¹ and these mobilities are compared with the present results. In addition, the longitudinal diffusion coefficients of NO⁺ and K⁺ in NO have been obtained in our laboratory. No other data are available for comparison with our diffusion coefficients.

II. APPARATUS

The drift-tube mass spectrometer employed in the present measurements has already been described in detail,¹⁻⁷ so only a brief description will be given here. From an electron-bombardment ion source which is movable over almost the entire length of the cylindrical drift tube (44 cm), short bursts of ions formed from NO can be gated into the drift region on the axis. Potassium ions can also be generated inside the ion source from a platinum-gauze filament coated with Kingman feldspar. Each ion swarm gated into the drift region subsequently diffuses and in some cases undergoes ion-molecule

reactions as it drifts down the tube under the influence of the uniform axial electric field. A sample of the ions reaching the far end of the drift region passes through a small aperture (0.035 cm diam, located on the axis) into a differentially pumped region, and thence to an rf quadrupole mass filter. Ions of the particular species which the filter is set to pass are detected by a capillary electron multiplier. Voltage pulses generated by the detection of single ions are time-sorted by a 256-channel time-of-flight analyzer that is triggered by the ion source burst. The accumulation of sorted counts from many thousands of identical source bursts produces a histogram of the ion transit times through the apparatus for a particular drift distance, gas pressure, and drift field intensity. Such "arrival time spectra" are obtained successively for each species of ions present in the drift tube over a wide range of the experimental variables, and the drift velocities and longitudinal diffusion coefficients are calculated from these spectra by methods to be discussed later in this paper.

Both Air Products "chemically pure" and Matheson "technical grade" nitric oxide were used in the present experiment. The purity of both gases was nominally 98.5%. Gas pressures ranging from 0.02-1.0 Torr were employed in the drift tube. Mass scans made throughout the experiment showed the dominant ions to have masses of 30 and 60 amu, which correspond to NO⁺ and NO⁺·NO, respectively. Masses of 48, 90, and 105 amu were also observed. Only traces of the latter two masses were present, but mass 48 (identified as NO⁺·H₂O) fluctuated in abundance. As in earlier work,⁹ this impurity ion was