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Theory of the quantum diffusion of parahydrogen impurities in solid orthohydrogen

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The hopping of parahydrogen impurities in solid orthohydrogen due to resonant conversion processes of para-ortho into ortho-para pairs is investigated theoretically both in the ordered and in the disordered phase. At temperatures below the transition temperature T_0 the jump frequency is predicted to be about four times larger than for ortho impurities in solid parahydrogen at the same impurity concentration. The effect on the hopping of the distortion of the ordered state by the impurities is taken into account, and the cohesive and interaction energies of the impurities are calculated. In the disordered phase the jump frequency is about two orders of magnitude smaller than below T_0, and the quantum diffusion of the para impurities is expected to be negligible above T_0.

I. INTRODUCTION

The diffusive, hopping motion of orthohydrogen impurities in solid parahydrogen has been investigated in the temperature range $1.2 \lesssim T \lesssim 4$ K by NMR,[1] thermodynamic,[2,3] infrared,[4,5] and microwave[6] techniques, and has been interpreted[7] as due to successive conversion processes of nearest neighbor (NN) ortho-para into para-ortho pairs. These "resonant" conversion processes leave the total rotational energy of the molecules and the ortho-para concentration ratio, c, unchanged and involve no emission or absorption of phonons. The resonant conversion rate, and hence the jump frequency of an ortho excitation, is proportional to the square of the relevant matrix element of the magnetic interaction between the nuclear spins in the ortho-para pair, and falls off with the inverse tenth power of the separation of the pair.[7] The process is therefore effective only for NN pairs, the relative probability of a NN jump being 96%. Since the hopping is not due to a thermally activated process and persists down to the lowest temperatures, but is nonetheless a pure random-walk process,[7] it is called quantum diffusion.

Apart from the rotational energy an ortho impurity in solid parahydrogen has a negative energy of about 1.1 K compared to the para molecules, which arises from the polarization of the neighboring molecules by the electric quadrupole field of the impurity. Pairs of NN ortho impurities in their ground state have an additional binding energy of about 3.4 K, and the equilibrium distribution of pairs and singles therefore changes appreciably below about 4 K. In the spectroscopic experiments[4-6] the change in time in the total number of singles or pairs in the sample is measured after imposing a sudden change in the temperature, by monitoring the intensity of a spectral feature identifiable as a single or pair feature, respectively. The observed overall approach to equilibrium is accurately exponential and a reaction time constant, τ, can be defined, which has values in the range 1–10 h for the temperatures and concentrations (0.2–1.8%) used in these experiments.

Theoretically one can readily calculate from first principles the average jump frequency of an ortho excitation, but the derivation of an accurate relation between ν and τ is more difficult because of the complexity of the kinetics of the reaction and of the pair formation process which requires an exchange of energy with the lattice. From a comparison of theory and experiment one can, however, conclude that the characteristic properties of the quantum diffusion of orthohydrogen impurities in solid parahydrogen are (i) that the jump frequency is reduced as a result of the tumbling motion of the ortho molecules due to the electric quadrupole-quadrupole (EQQ) interaction between them by a factor of order 10^7, (ii) that the temperature dependence of the jump frequency is weak as long as the temperature does not fall below the width of the librational band (about 0.1 K at $c = 1\%$), and (iii) that the observed stronger temperature dependence of τ must be ascribed to the pair formation or dissociation process. Property (ii) can be expected to change if the ortho molecules become ferromagnetically aligned at low temperatures because of a phonon mediated interaction, as has recently been suggested.[8]

In the present paper the complementary problem of the quantum diffusion of parahydrogen impurities in solid orthohydrogen is studied theoretically, both in the ordered and in the disordered phase. The characteristic differences in the properties of para impurities and ortho impurities in the two concentration limits are the following. A para impurity in ordered orthohydrogen has an extra positive energy of about 11 K, compared to the host molecules, because of the broken EQQ bonds with its neighbors. A pair of NN para impurities has a binding energy of about 0.9 K, compared to 3.4 K for ortho pairs in parahydrogen in their ground state, and at a given temperature the equilibrium ratio of singles to pairs is quite different in the two cases. Above the order-disorder transition temperature T_0, which is 2.8 K in pure orthohydrogen,[9] the jump frequency of a para impurity is two orders of magnitude smaller than for ortho impurities at comparable impurity concentrations, because of the shorter orientational correlation time of the ortho molecules at $c = 100\%$ than at $c = 1\%$, and the quantum diffusion is essentially negligible. Below T_0 the tumbling motion of the ortho molecules plays a minor role and the jump frequency at vanishing impurity concentrations is determined by the precessional motion of the nuclear spins of the ortho molecules. At finite concentations the effective interaction energy of the para impurities creates an energy mismatch between the inital and final state of a hop and the jump frequency is reduced by many orders of magnitude. The resulting quantum diffusion is predicted to be about four times faster than for ortho impurities at the same impurity concentration.

In Sec. II we formulate the mean-field theory of the perturbation of the ordered state of solid orthohydrogen by the para impurities and we discuss the binding and interaction energies of the impurities and their dependence on the temperature. In Sec. III we present the calculation of the jump frequency of isolated impurities at low temperatures in terms of the nuclear-spin-correlation time and the overlap factor arising from the distortion of the orientational arrangement of the surrounding ortho molecules, and we discuss the effect of the mismatch in energy arising at finite concentrations from the interactions between the impurities. In Sec. IV we calculate the reduction of the jump frequency by the tumbling motion of the ortho molecules above the transition temperature. In Sec. V some remarks are made about the approach to equilibrium, and Sec. VI contains the main conclusions.

II. MEAN-FIELD THEORY OF THE ORDERED STATE PERTURBED BY IMPURITIES

Pure orthohydrogen in the ordered phase has the $Pa3$ structure[10–12] consisting of four simple cubic sublattices (0,1,2,3) on a fcc lattice, with the symmetry axes of the molecules aligned along the four body diagonals of the elementary cube. Here and in the following "the symmetry axis of a molecule" refers to the symmetry axis of the charge distribution of the molecule in the ground state, not to be confused with the internuclear axis of the molecule. All the molecules in the crystal occupy equivalent positions in the sense that each molecule can be transformed into any other one by an element of the space group of the crystal. Each molecule has six NN's in a plane perpendicular to its symmetry axis (plane 0) and three in each of two planes on opposite sides of plane 0 (planes 1 and −1), and those will be called in-plane (ip) and out-of-plane (op) neighbors, respectively. We choose plane 1 for all the molecules such that the view of plane 0 from plane 1 is as shown in Fig. 1, where the arrows are the projections of the symmetry axes of the molecules in plane 0 onto plane 0. The view of plane 0 from plane −1 is different, and we can therefore assign a definite sense to each symmetry axis, which we choose in the direction from plane 0 to plane 1 for each molecule. Keeping this in mind, we label the sublattices and introduce local coordinate frames in the following way. Select an arbitrary molecule 0 as "central" molecule. All the molecules with the same symmetry axis form an sc lattice which we choose as sublattice 0. Choose a "fixed" coordinate frame $S(X,Y,Z)$ with origin at the site of molecule 0 and with axes along the cubical axes of the crystal such that the symmetry axis of molecule 0 is in the [111] direction (and not in the $[\bar{1}\bar{1}\bar{1}]$ direction). The symmetry axes of the four NN's (1,2,3,4) of molecule 0 in the XY plane are then in the $[1\bar{1}\bar{1}]$ direction relative to S, and all the molecules with that same symmetry axis form sublattice 1. The four NN's (5,6,7,8) in the YZ plane have their symmetry axes along $[\bar{1}1\bar{1}]$ and belong to sublattice 2, and the four NN's (9,10,11,12) in the ZX plane are aligned along $[\bar{1}\bar{1}1]$ and belong to sublattice 3, of Figs. 2 and 3. At each site j we introduce a local frame $s_j(x_j,y_j,z_j,)$ with z_j in the direction of the oriented symmetry axis of molecule j. The x_j and y_j axes need not be specified, except that all frames are to be right handed. Finally for each pair of molecules

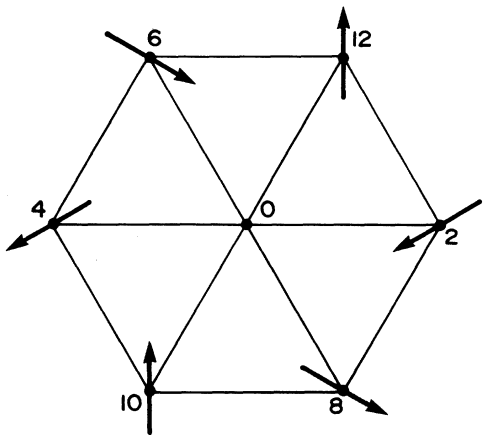

FIG. 1. The six NN's of molecule 0 in plane 0 and their symmetry axes, as seen from plane 1. The arrows all point downwards. The symmetry axis of molecule 0 is perpendicular to the plane and points upwards, cf. Fig. 3.

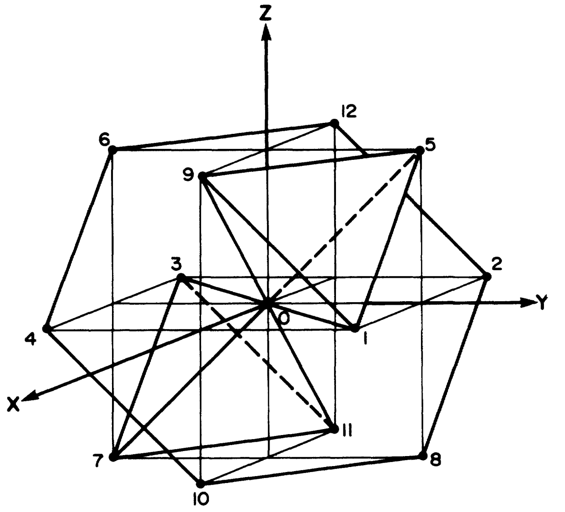

FIG. 2. The 12 NN's of molecule 0, and plane 0 (even molecules), plane 1 (molecules 1,5,9) and plane 1 (molecules 3,7,11). The symmetry axis of molecule 0 is perpendicular to these planes and along the [111] direction.

j,k we introduce an "intermolecular" frame s_{jk} with z axis along the line from j to k.

The polar angles of the internuclear axis of molecule j relative to an intermolecular frame are denoted by $(\theta_j, \phi_j) \equiv \vec{\omega}_j$, in the local frame at j by $\vec{\omega}_j'$, and in S by Ω_j. Primes generally indicate quantities referring to local frames, $|10'\rangle_j$ for example being the rotational state of molecule j with wave function $Y_{10}(\vec{\omega}_j')$. The orientation of molecule j will also be denoted simply by j, as in $\psi(j)$, whenever convenient. The polar angles of the symmetry axes of molecules j and k in s_{jk} are denoted by β_j, α_j and β_k, α_k, respectively, and for the 12 NN's of molecule 0 corresponding to $j=0$ and $k=1, \ldots, 12$ these are given in Table I.

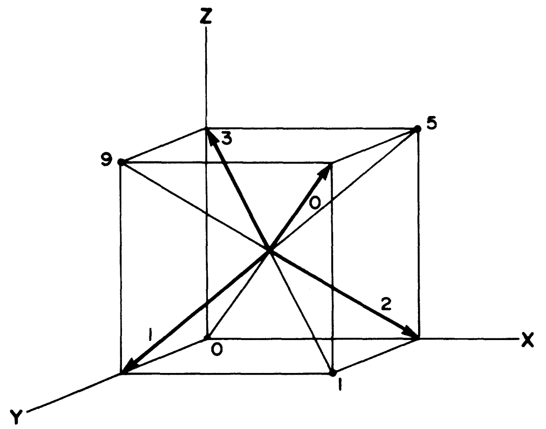

FIG. 3. Symmetry axes 0,1,2,3 assigned to the sublattices 0,1,2,3. The molecules 0,1,5,9 belong to the sublattices 0,1,2,3, respectively. Cyclic permutations of 1,2,3 yield identical structures, but noncyclic ones do not.

For the anisotropic intermolecular interaction we assume the EQQ interaction, averaged over the zero-point lattice vibrations but neglecting the nonaxiality of the pair distribution function, which is given by[13]

$$H_{jk} = c_{jk} \sum_{m=-2}^{+2} a_m Y_{2m}(\vec{\omega}_j) Y_{2m}^*(\vec{\omega}_k) \ , \tag{1}$$

where

$$c_{jk} = \frac{10}{3} \pi \Gamma_0 \xi(R_{jk}) (R_0/R_{jk})^5 \ . \tag{2}$$

R_0 being the NN separation, $\xi(R_{jk})$ the phonon renormalization factor, $\Gamma_0 = (6Q^2/25R_0^5)$, and $a_0 = 6$, $a_{\pm 1} = -4$, $a_{\pm 2} = 1$. For the various parameters we adopt the most recent values,[13] $R_0 = 3.784$ Å, $\Gamma_0 = 0.6634$ cm^{-1}, $\xi(R_0) \equiv \xi_{54} = 0.899$, and $\xi(R_{jk}) = 1$ for $R_{jk} > R_0$, so that the renormalized NN coupling constant is

$$\Gamma \equiv \xi_{54}\Gamma_0 = 0.5964 \text{ cm}^{-1} = 0.8581 \text{ K} \ . \tag{3}$$

The neglected anisotropic interactions are of the order of a few percent of the interaction (1) and may be neglected in the present context. For example, if the anisotropic Van der Waals interaction between NN's is included, a term $\frac{6}{5}\epsilon_4$ must be added[13] to Γ which then changes in value from Eq. (3) to 0.5743 cm^{-1}.

We first consider $T = 0$ K. In the mean-field theory[11] the rotational wave functions of a crystal of

TABLE I. Polar angles of the symmetry axes of the NN molecules 0 and j in Fig. 2 in the intermolecular frames. $\cos(\alpha_j - \alpha_0) = -(\frac{1}{3})^{1/2}$ for all j.

NN type	j	$(\frac{3}{2})^{1/2}\cos\beta_0$	$(\frac{3}{2})^{1/2}\cos\beta_j$	$(\frac{3}{2})^{1/2}\sin(\alpha_j - \alpha_0)$
	1	+1	0	+1
+1	5	+1	0	+1
	9	+1	0	+1
	2	0	−1	+1
+0	6	0	−1	+1
	10	0	−1	+1
	4	0	+1	−1
−0	8	0	+1	−1
	12	0	+1	−1
	3	−1	0	−1
−1	7	−1	0	−1
	11	−1	0	−1

N orthohydrogen molecules are assumed to be products of the form

$$\Psi^{(0)}=\prod_{j=1}^{N}\psi_{\mu_j}^{(0)}(j) \ , \tag{4}$$

where

$$[K+U^{(0)}(j)]\psi_{\mu_j}^{(0)}(j)=E^{(0)}\psi_{\mu_j}^{(0)}(j) \ . \tag{5}$$

K is the (constant) rotational energy and $U^{(0)}(j)$ the mean potential energy of molecule j,

$$U^{(0)}(j)=\sum_{k}\langle\psi_{\mu_k}^{(0)}(k)|H_{jk}|\psi_{\mu_k}^{(0)}(k)\rangle \ , \tag{6}$$

where $H_{jj}=0$ and H_{jk} is the EQQ interaction (1). The self-consistent solutions of Eqs. (5) and (6) are[11]

$$\psi_{\mu}^{(0)}(j)=Y_{1\mu}(\vec{\omega}_j') \ . \tag{7}$$

The ground state corresponds to all $\mu_j=0$. Using the result that for any intermolecular axis one has

$$\begin{aligned}\langle 10'|2m|10'\rangle &= \langle Y_{10}(\vec{\omega}_j')|Y_{2m}(\vec{\omega}_j)|Y_{10}(\vec{\omega}_j')\rangle \\ &= \tfrac{2}{5}Y_{2m}(\beta_j,\alpha_j) \ ,\end{aligned} \tag{8}$$

one easily verifies the well-known property[11] that the energy of the pair jk in the ground state is equal to $\frac{4}{25}$ times the energy of classical quadrupoles aligned along the symmetry axes of the molecules,

$$\begin{aligned}&\langle 10',10'|H_{jk}|10',10'\rangle \\ &\qquad = \tfrac{4}{25}c_{jk}\sum_{m}a_m Y_{2m}(\beta_j,\alpha_j)Y_{2m}^{*}(\beta_k,\alpha_k) \ .\end{aligned} \tag{9}$$

In the first excited state one of the molecules is in the state (7) with $\mu=\pm 1$, and this state is $2N$-fold degenerate. From Eq. (9) and the fact that $\mathrm{tr}H_{jk}=0$, one finds that the excitation energy is equal to

$$\Delta E=19\Gamma+\tfrac{7}{4}\sqrt{2}\Gamma_0+\cdots=21.75\Gamma \ . \tag{10}$$

The third- and higher-order shells together contribute only about 1% to ΔE, and will be neglected throughout.

In the presence of a single parahydrogen impurity at site i, the wave function will be

$$\Psi=Y_{00}(i)\prod_{j\neq i}\psi_i(j) \ , \tag{11}$$

where

$$\psi_i(j)=\sum_{\mu=-1}^{+1}a_{\mu i}Y_{1\mu}(\vec{\omega}_j') \tag{12}$$

is a solution of the equation

$$[K+U_i(j)]\psi_i(j)=E\psi_i(j) \quad (j\neq i) \tag{13}$$

and

$$U_i(j)=\sum_{k\neq i}\langle\psi_i(k)|H_{jk}|\psi_i(k)\rangle \ . \tag{14}$$

Introducing an auxiliary ortho wave function for molecule i of the form

$$\psi_i(i)=\sum_{\mu}c_{\mu}Y_{1\mu}(\vec{\omega}_i') \ , \tag{15}$$

we can write Eq. (14) in the form

$$U_i(j)=\sum_{k}\langle\psi_i(k)|H_{jk}|\psi_i(k)\rangle-\langle\psi_i(i)|H_{ji}|\psi_i(i)\rangle \ , \tag{16}$$

which is independent of the choice of the coefficients c_{μ} in the definition (15). Choosing $c_{\pm 1}=0$, we get

$$U_i(j)=U(j)+V_i(j) \ , \tag{17}$$

where

$$U(j)=\sum_{k}\langle\psi_i(k)|H_{jk}|\psi_i(k)\rangle \ , \quad \psi_i(i)=\psi_0^{(0)}(i) \ , \tag{18}$$

and

$$V_i(j)=-\langle\psi_0^{(0)}(i)|H_{ji}|\psi_0^{(0)}(i)\rangle \ , \tag{19}$$

and Eq. (10) then becomes

$$[K+U(j)+V_i(j)]\psi_i(j)=E\psi_i(j) \ . \tag{20}$$

If the term $V_i(j)$ is neglected, Eq. (20) reduces to Eq. (13), and the ground-state solutions are then given by Eq. (7) with $\mu=0$. The perturbation of the surrounding molecules by the para impurity is actually very small, and $V_i(j)$ may be treated as a small perturbation term. One easily sees that the term $U(j)$ in Eq. (20) differs from $U^{(0)}(j)$ at most by second-order terms, and Eq. (20) may hence be approximated by

$$[K+U^{(0)}(j)+V_i(j)]\psi_i(j)=E\psi_i(j) \quad (j\neq i) \ . \tag{21}$$

These equations no longer present a self-consistency problem, since $U^{(0)}$ and V_i are *known* functions of the orientation of molecule j, and we can therefore solve Eq. (21) by ordinary perturbation methods.

The first-order change in the energy of molecule j in the presence of an impurity at i is

$$\begin{aligned}E_{ij}^{(1)} &= \langle\psi_0^{(0)}(j)|V_i(j)|\psi_0^{(0)}(j)\rangle \\ &= -\langle 10',10'|H_{ij}|10',10'\rangle \ ,\end{aligned} \tag{22}$$

and the values of this quantity for the molecules in the first two shells around i are

$$E_{\mathrm{NN}}^{(1)}=\tfrac{19}{18}\Gamma, \quad E_{\mathrm{NNN}}^{(1)}=\tfrac{7}{36}\sqrt{2}\Gamma_0 \ . \tag{23}$$

The second-order change in the energy of molecule j due to the perturbation $V_i(j)$ is

$$E_{ij}^{(2)}=-\left(\frac{1}{\Delta E}\right)\sum_{\mu=\pm 1}|\langle 10',10'|H_{ij}|10',1\mu'\rangle|^2 \ , \tag{24}$$

where ΔE is given by Eq. (10). The sum in Eq. (24)

is most easily evaluated by adding and subtracting the term corresponding to $\mu=0$ and using the invariance of $\sum_{\mu} |1\mu'\rangle \langle 1\mu'|$ under a change of axes. For the NN's we get in this way

$$E_{ij}^{(2)} = -\left[\frac{1}{\Delta E}\right] \sum_{\mu=-1}^{+1} |\langle 10', 10'|H_{ij}|10', 1\mu\rangle|^2 + \left[\frac{19}{18}\right]^2 \left[\frac{\Gamma^2}{\Delta E}\right] \quad . \tag{25}$$

Letting μ refer to the intermolecular frame s_{ij}, we have

$$\langle 10', 10'|H_{ij}|10', 1\mu\rangle = -\tfrac{2}{5}\left[\frac{2}{3}\right]^{1/2} \sum_{mn} C(211;mn\mu)\, Y_{2m}(\beta_i, \alpha_i)\, Y_{1n}(\beta_j, \alpha_j) \quad . \tag{26}$$

This quantity has a different value for the ip and op neighbors of molecule i, and from Eqs. (25) and (26) we get

$$E_{\mathrm{NN}}^{(2)}(\mathrm{ip}) = -\frac{301}{162}\frac{\Gamma^2}{\Delta E}, \quad E_{\mathrm{NN}}^{(2)}(\mathrm{op}) = -\frac{196}{162}\frac{\Gamma^2}{\Delta E} \quad . \tag{27}$$

Assuming that the isotropic interaction between ortho-para and para-para pairs is the same, the excess energy, ϵ_i, of a para impurity in solid orthohydrogen at $T=0$ K is

$$\begin{aligned} \epsilon_i &= 12E_{\mathrm{NN}}^{(1)} + 6E_{\mathrm{NNN}}^{(1)} + 6E_{\mathrm{NN}}^{(2)}(\mathrm{ip}) + 6E_{\mathrm{NN}}^{(2)}(\mathrm{op}) \\ &= \tfrac{38}{3}\Gamma + \frac{7\sqrt{2}}{6}\Gamma_0 - \frac{497}{27}\frac{\Gamma^2}{\Delta E} \quad . \end{aligned} \tag{28}$$

Using Eqs. (3) and (10) we obtain from Eq. (28) the value $\epsilon_i = 8.14\ \mathrm{cm}^{-1} = 11.7$ K for the excess energy in the mean-field approximation.

When one goes beyond the mean-field theory, the excited level corresponding to $\mu = \pm 1$ broadens into a librational band,[14–18] and this effect tends to decrease the effective value of ΔE in Eq. (24). Reducing ΔE by as much as a factor of 2, changes the value of ϵ_i to 11.0 K, and the true value of ϵ_i at $T=0$ K can hence be expected to lie between 11.0 and 11.7 K. The broadening of the excited level is accompanied by a slight lowering of the ground-state energy and an admixing into the ground state of excited states containing two or more librational excitations.[19] This "zero-point" effect, familiar from the theory of antiferromagnetism, reduces the long-range order parameter, defined in Fig. 4, at $T=0$ K by about 2%.[19] Miyagi[20] has also calculated the binding and interaction energies of the parahydrogen impurities including the zero-point effect which he finds to be important for pairs of impurities at larger separations. However, for our present purposes we may neglect these effects and confine ourselves to the mean-field theory.

When a pair of para impurities is present at the sites i and i', we assume a wave function of the form

$$\Psi = Y_{00}(i)\, Y_{00}(i') \prod_{j \neq i,i'} \psi_{ii'}(j) \quad . \tag{29}$$

Proceeding as for a single impurity, we find that the first-order change in the energy of molecule $j \neq i,i'$ is equal to the sum of two terms of the form (22),

$$E_{ii'j}^{(1)} = E_{ij}^{(1)} + E_{i'j}^{(1)} \quad , \tag{30}$$

and that the second-order change is given by

$$E_{ii'j}^{(2)} = E_{ij}^{(2)} + E_{i'j}^{(2)} - \frac{2}{\Delta E} \sum_{\mu=\pm 1} \mathrm{Re}[a_{i'j}^{*}(\mu)\, a_{ij}(\mu)] \quad , \tag{31}$$

where

$$a_{ij}(\mu) = \langle 1\mu', 10'|H_{ij}|10', 10'\rangle \quad . \tag{32}$$

The sum in Eq. (31) is not simplified by adding the term $\mu=0$, and the quantities (32) must therefore be calculated explicitly, which is most easily done by transforming all the wave functions to the intermolecular frame. The quantity of greatest interest is the effective interaction energy of the impurities, which is equal to the total energy of the crystal minus the energy when the two impurities are far apart.

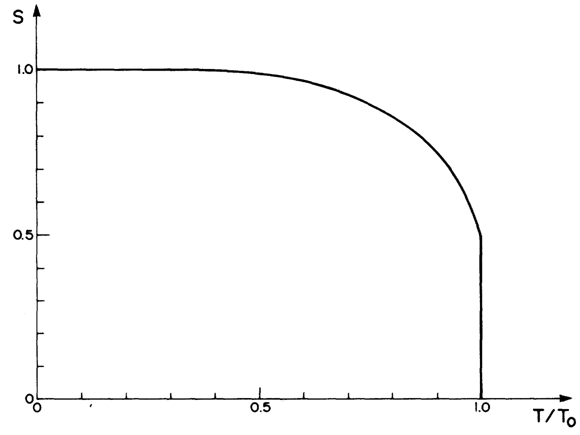

FIG. 4. Long-range order parameter $s = \langle 1 - \frac{3}{2}J_{z'}^2 \rangle$ as a function of T/T_0 according to the mean-field theory (Ref. 11).

This quantity has the same value for all NN pairs and is given by

$$\begin{aligned}\epsilon_{ii'}(a) &= E_{ii'}(a) - E_{ii'}(\infty) \\ &= -E_{\mathrm{NN}}^{(1)} - E_{\mathrm{NN}}^{(2)}(\mathrm{ip}) - E_{\mathrm{NN}}^{(2)}(\mathrm{op}) \\ &\quad - \frac{2}{\Delta E} \sum_{j \neq i,i'} \sum_{\mu = \pm 1} \mathrm{Re}[a_{i'j}^{*}(\mu) a_{ij}(\mu)] \ . \qquad (33)\end{aligned}$$

Restricting the sum over j to the four common NN's of i and i' ($j = 6, 7, 9, 10$ for $i = 0, i' = 4$), we find that the last term in Eq. (33) almost cancels the second and third terms [note the difference in sign of the cross term relative to the direct second-order terms in Eqs. (31) and (33), respectively]. Using Eqs. (23) and (27), we get from Eq. (33)

$$\epsilon_{ii'}(a) = -\tfrac{19}{18}\Gamma + \tfrac{41}{81}\Gamma^2/\Delta E \ . \qquad (34)$$

For the mean-field value (10) of ΔE this yields $\epsilon_{ii'}(a) = -0.87$ K, and reducing ΔE by a factor of 2 gives -0.85 K, so that the true value is close to -0.86 K.

We now consider the temperature dependence of the energies (28) and (33) in the mean-field theory. According to James and Raich[11] the self-consistent states for pure orthohydrogen at a finite temperature are still given by $|1\mu'\rangle$, $\mu = 0, \pm 1$, but these states are now occupied with probabilities $P_0 = 1 - \rho$ and $P_1 = P_{-1} = \frac{1}{2}\rho$, where $\rho(T)$ is obtained by minimizing the free energy. The resulting long-range order parameter $s = 1 - \frac{3}{2}\rho$ is shown in Fig. 4 as a function of T/T_0, where T_0 is the transition temperature which experimentally has the value $T_0 = 2.8$ K.[9] It is seen that s is practically constant up to $T \simeq \frac{1}{2}T_0$ and then falls rapidly to $s = \frac{1}{2}$ at $T = T_0$, where a first-order transition occurs.[11] In the mean-field theory the energies per molecule and per bond are proportional to s^2. As far as the first-order contributions are concerned, the energies (28) and (33) are also proportional to s^2. In first approximation the excess energy (28) of a para impurity, and the interaction energy (33) between two NN impurities, are thus constant up to about $T = \frac{1}{2}T_0$ and then fall to one-fourth of their values as T increases to T_0. These estimates suffice for our present purpose, and we shall not attempt to calculate the temperature dependence of the second-order terms.

III. CALCULATION OF THE JUMP FREQUENCY IN THE ORDERED PHASE

We first consider a single para impurity in a crystal of orthohydrogen at temperatures ($T \lesssim 1.4$ K) which are effectively zero as far as the orientational motion of the molecules is concerned but infinite as compared to the interaction energy of the nuclear spins in neighboring molecules. The probability of a resonant conversion process, in which the para molecule converts into an ortho molecule and one of the neighboring ortho molecules into a para molecule, is determined by three factors, viz. (a) the matrix element of the relevant part of the magnetic interaction between the nuclear spins in the two molecules, (b) the overlap factor arising from the change in position of the impurity, and (c) the reduction factor due to the finite correlation time characterizing the precessional motion of the nuclear spins. The calculation of these factors is presented in Secs. III A, III B, and III C.

At finite impurity concentrations the energy of the crystal is different before and after a jump of one of the impurities because of the change in the total interaction energy of the impurities caused by the jump. The resulting jump frequency depends strongly on the configuration of the surrounding impurities. At an impurity concentration of 1% the average jump frequency is reduced by this energy mismatch by many orders of magnitude and becomes independent of the nuclear-spin-correlation time. These effects are discussed in Sec. III D.

A. Conversion matrix element

The interaction responsible for the transition of a pair of NN molecules 1,2 from a para-ortho to an ortho-para state is given by

$$V = 12\pi\epsilon_1 \sum_{m \cdots n'} d_{mm'nn'} Y_{1m}(\vec{\omega}_1) Y_{1m'}(\vec{\omega}_2) K_{1n} K_{2n'} \ , \qquad (35)$$

where

$$\epsilon_1 = (70)^{1/2}(\xi_{54}\gamma^2\hbar^2 r_0^2/12R_0^5) \ . \qquad (36)$$

We use the same notation as in I (Ref. 7) except for the replacements $\zeta_{12} \rightarrow \xi_{54}$ and $a \rightarrow R_0$, and the fact that the initial and final states are interchanged. In the present case the initial and final rotational states of the converting pair are

$$|i\rangle = |00\rangle_1 |10'\rangle_2, \quad |f\rangle = |10'\rangle_1 |00\rangle_2 \ . \qquad (37)$$

We neglect the perturbations in the states $|10'\rangle_2$ and $|10'\rangle_1$ due to the presence of the impurity and we take these perturbations into account only in the overlap factors arising from the surrounding molecules. Transforming the states (37) from the local frames to the intermolecular frame, we obtain

$$K_{12} \equiv \langle f | V | i \rangle = \sum_{nn'} d_{nn'} K_{1n} K_{2n'} \ , \qquad (38)$$

where

$$d_{nn'} = 4\pi\epsilon_1 \sum_{mm'} d_{mm'nn'} Y_{1m}(\beta_1, \alpha_1) Y_{1m'}(\beta_2, \alpha_2) \ . \qquad (39)$$

When the nuclear-spin states of molecule 2 are equally populated with random phases, the quantity appearing in the calculation of the jump frequency is

$$W_0=\frac{1}{3}\sum_{n_1 n_2}|\langle 1n_1,00|K_{12}|00,1n_2\rangle|^2 \ . \tag{40}$$

Using Eq. (39) and the expression (I.18)[7] for $d_{mm'nn'}$, we find that W_0 has the value

$$W_0=\frac{1}{3}\sum_{nn'}|d_{nn'}|^2=\frac{37}{35}\epsilon_1^2 \tag{41}$$

for all NN pairs. For NNN pairs the value of Eq. (40) is a factor 2^5 smaller than Eq. (41) and may be neglected.

B. Overlap factor

When the impurity hops from site i to a NN site i', the orientations of the surrounding ortho molecules change by small amounts, and we now calculate the total overlap factor involved in such a transition. The perturbation in the orientational states of the ortho molecules surrounding an impurity are different for the ip and op neighbors of the impurity, and the question arises whether the probabilities of hopping to the 12 NN's are the same. That this is indeed true can be seen using the time reversal and space symmetries, as we now show. As is evident from Table I, there are four different types of NN jumps which we label in the same way as the NN's. For example, a jump from $j=0$ to 1 will be called of type +1. Because of time-reversal invariance the jump probability from $j=1$ to 0 which is a jump of type +0 is equal to that from $j=0$ to 1. The square of the matrix element of the nuclear magnetic interaction is the same for these two jumps, because the corresponding operator is Hermitian, and the total overlap factors for jumps of the type +1 and +0 must therefore be equal. Because the site $j=0$ is a center of inversion symmetry of the crystal, the jump probability from $j=0$ to 1 is equal to that from $j=0$ to 3 which is a jump of type −1, and both the square of the matrix element and the overlap factor must be equal for jumps of the type +1 and −1, and similarly for jumps of the type +0 and −0. The squares of the matrix elements and the overlap factors are therefore the same for all 12 NN's.

The state of molecule j perturbed by the impurity at i is given by

$$|\psi_i(j)\rangle=N_{ij}\left[|10'\rangle_j+\alpha\sum_{\mu=\pm 1}a_{ij}(\mu)|1\mu'\rangle_j\right] \ , \tag{42}$$

where $\alpha=1/\Delta E$, and $a_{ij}(\mu)$ is defined by Eq. (32). Using Eq. (24) we can express the normalization constants N_{ij} in terms of the second-order energies,

$$N_{ij}=\left[1+\alpha^2\sum_{\mu=\pm 1}|a_{ij}(\mu)|^2\right]^{-1/2}=(1-\alpha E_{ij}^{(2)})^{-1/2} \ , \tag{43}$$

and for the ip and op NN pairs we therefore get from Eq. (27)

$$N_{\rm ip}=\left[1+\frac{301}{162}\frac{\Gamma^2}{\Delta E}\right]^{-1/2} \ , \quad N_{\rm op}=\left[1+\frac{196}{162}\frac{\Gamma^2}{\Delta E}\right]^{-1/2} \ . \tag{44}$$

The total overlap factor is given by

$$F=\prod_{j\neq i,i'}\langle\psi_{i'}(j)|\psi_i(j)\rangle=\prod_j N_{ij}N_{i'j}f_j \ , \tag{45}$$

where

$$f_j=1+\alpha^2\sum_{\mu=\pm 1}a_{i'j}^*(\mu)a_{ij}(\mu) \ . \tag{46}$$

These quantities are appreciably different from 1 only for the four common NN's of i and i', and labeling these by k, we get from Eq. (45)

$$F=(N_{\rm ip}N_{\rm op})^{12}\prod_k f_k \ . \tag{47}$$

For the four different types of NN pairs, the amplitudes $a_{ij}(\mu)$ have the values

$$a_{ij}(1)=-a_{ij}^*(-1)=-\frac{1}{9}\Gamma\left(\frac{17}{2}\pm i\sqrt{3}\right)\exp(i\gamma_j^{ij}) \ , \tag{48}$$

when j is an ip NN of i of the type −0 or +0, respectively, and

$$a_{ij}(1)=-a_{ij}^*(-1)=\pm\frac{1}{9}\Gamma(4\sqrt{3}+i)\exp(i\gamma_j^{ij}) \ , \tag{49}$$

when j is an op NN of i of the type +1 or −1, respectively, and $\gamma_j^{ij}-\gamma_j^{i'j}=\gamma_j^{ii'}$ is the angle of rotation around z_j from z_{ij} to $z_{i'j}$. Taking $i=0$ and $i'=4$, we have $k=6,7,9,10$, cf. Fig. 2, and using Eqs. (48) and (51) we obtain

$$f_k=1+c_k(\Gamma/\Delta E)^2 \ , \tag{50}$$

where

$$c_6=\frac{217}{162}, \quad c_7=\frac{239}{162}, \quad c_9=-\frac{49}{81}, \quad c_{10}=-\frac{301}{324} \ , \tag{51}$$

and these results have also been used to obtain Eq. (34). Using Eq. (10) we obtain $F^2=0.93$ and reducing ΔE by a factor of 2 gives $F^2=0.77$. The reduction of the jump frequency of a para impurity in ordered orthohydrogen due to the overlap factor is proportional to F^2 and hence amounts to about 15%.

C. Reduction effect due to the nuclear precessional motion

The ground rotational state of solid orthohydrogen is nondegenerate and at low temperatures the random-walk nature of the hopping of a para impurity and the time proportionality of the transition probability arise from the precessional motion of the nuclear spins of the ortho molecules, which broadens the ground state into a narrow nuclear-spin energy band.

Let α be the arrangement in which the impurity is on site $i=1$, and α' the one in which the impurity is on a NN site $i'=2$. The Hamiltonian of the spin systems of the ortho molecules in the arrangements α and α' are given by

$$H_\alpha=\tfrac{1}{2}\sum_{jk\neq 1} M_{jk},\quad H_{\alpha'}=\tfrac{1}{2}\sum_{jk\neq 2} M_{jk}\ , \tag{52}$$

where

$$M_{jk}=\sum_{\mu\mu'} M_{jk}^{\mu\mu'} I_{j\mu} I_{k\mu'} \tag{53}$$

is the magnetic dipole-dipole interaction between the total nuclear spins $\vec{\mathrm{I}}_j$ and $\vec{\mathrm{I}}_k$ of molecules j and k, and[7]

$$M_{jk}^{\mu\mu'}=-\mu_0^2 C(112;\mu\mu')\,Y^*_{2,\mu+\mu'}(\vec{\Omega}_{jk})/R_{jk}^3\ . \tag{54}$$

In terms of the eigenstates $|\alpha\nu\rangle$ and $|\alpha'\nu'\rangle$ of H_α and $H_{\alpha'}$, respectively, the total probability per unit time for transitions between α and α' is given by

$$\begin{aligned} W_{\alpha\alpha'}&=2\pi\hbar^{-1}\sum_{\nu\nu'} P_{\alpha\nu}|\langle\alpha'\nu'|K_{12}|\alpha\nu\rangle|^2\,\delta(E_{\alpha'\nu'}-E_{\alpha\nu})\\ &=\hbar^{-2}\int_{-\infty}^{+\infty} K_{\alpha\alpha'}(t)\,dt\ , \end{aligned} \tag{55}$$

where $P_{\alpha\nu}=3^{-N+1}$, K_{12} is the spin-conversion operator (38), and

$$\begin{aligned} K_{\alpha\alpha'}(t)=3^{-N+1}&\sum_{\nu\nu'}\langle\alpha\nu|K_{12}|\alpha'\nu'\rangle\\ &\times\langle\alpha'\nu'|e^{iH_{\alpha'}t}K_{12}e^{-H_{\alpha}t}|\alpha\nu\rangle\ . \end{aligned} \tag{56}$$

It is clear that in this expression we may put

$$\begin{aligned} |\alpha\nu\rangle&=|00,1n_2,1n_3,\ldots\rangle\ ,\\ |\alpha'\nu'\rangle&=|1n_1',00,1n_3',\ldots\rangle\ . \end{aligned} \tag{57}$$

We assume that the correlation function (57) is Gaussian,

$$K_{\alpha\alpha'}(t)=K_{\alpha\alpha'}(0)e^{-(t/\tau_0)^2/2}\ , \tag{58}$$

which is a natural assumption for a spin system of this kind, and we then get

$$W_{\alpha\alpha'}=(2\pi)^{1/2}\hbar^{-2}K_{\alpha\alpha'}(0)\tau_0 \tag{59}$$

and

$$\tau_0=[-\ddot{K}_{\alpha\alpha'}(0)/K_{\alpha\alpha'}(0)]^{-1/2}\ . \tag{60}$$

From Eqs. (56) and (57) we obtain

$$K_{\alpha\alpha'}(0)=W_0=\tfrac{37}{35}\epsilon_1^2\ , \tag{61}$$

and

$$-\hbar^2\ddot{K}_{\alpha\alpha'}(0)=\tfrac{1}{3}\sum_{nn'}(-1)^n d_{\bar{n}n'}\langle 1n,00|\{F_{12}\}|00,1n'\rangle\ , \tag{62}$$

where

$$F_{12}=H_{\alpha'}^2K_{12}-2H_{\alpha'}K_{12}H_\alpha+K_{12}H_\alpha^2\ , \tag{63}$$

and the curly brackets indicate an averaging over all orientations of the spins of molecules 3 ,. . ., N,

$$\{A\}=3^{-N+2}\sum_{n_3\cdots n_N}\langle 1n_3,\ldots,1n_N|A|1n_3,\ldots,1n_N\rangle \tag{64}$$

Using Eq. (52) and

$$\{I_{j\mu}I_{j\bar{\nu}}\}=\tfrac{2}{3}(-1)^\mu\delta_{\mu\nu}\ , \tag{65}$$

we get

$$-\hbar^2\ddot{K}_{\alpha\alpha'}(0)=\frac{4}{9}\sum_{n\cdots\nu}(-1)^{n+m'}d_{nn'}d_{m\bar{m}}[\tfrac{1}{2}(S_{11}^{\mu\nu}+S_{22}^{\mu\nu})\langle 1n|I_\mu I_\nu|1m\rangle\langle 1m'|1n'\rangle-S_{12}^{\mu\nu}\langle 1n|I_\mu|1m\rangle\langle 1m'|I_\nu|1n'\rangle]\ , \tag{66}$$

where

$$S_{ii'}^{\mu\nu}=\sum_{j=3}^{N}\sum_{\mu'}(-1)^{\mu'}M_{ij}^{\mu\mu'}M_{i'j}^{\nu\mu'}\ . \tag{67}$$

For $i=i'$ we obtain from Eqs. (54) and (67),

$$S_{11}^{\mu\nu}=S_{22}^{\mu\nu}=-\left(\frac{5\mu_0^2}{R_0^3}\right)^2\sum_l\frac{C(22l,000)}{[4\pi(2l+1)]^{1/2}}\begin{Bmatrix}1&1&l\\2&2&1\end{Bmatrix}C(111;\mu\nu)S^*_{l,\mu+\nu}\ , \tag{68}$$

where

$$S_{lm}=\sum_{j=2}^{\infty}\left(\frac{R_0}{R_{ij}}\right)^6 Y_{lm}(\vec{\Omega}_{ij})-Y_{lm}(\vec{\Omega}_{12})\ . \tag{69}$$

The values of l in Eq. (68) are restricted to 0 and 2, and because of the cubic symmetry the lattice sum in the right-hand side of Eq. (69) vanishes for $l=2$. Choosing the z axis along $\vec{\mathbf{R}}_{12}$, we therefore get

$$S_{11'}^{\mu\nu}=\frac{5\mu_0^4}{12\pi R_0^6}[(S_6-1)(-1)^{\mu}\delta_{\mu\bar{\nu}} -(\tfrac{3}{2})^{1/2}C(112;\mu\nu 0)] \ , \qquad (70)$$

where

$$S_6=\sum_{j=2}^{\infty}\left(\frac{R_0}{R_{ij}}\right)^6=14.454 \ . \qquad (71)$$

Using the results

$$\langle 1m|I_\mu|1n\rangle=2^{1/2}C(111;n\mu m) \qquad (72)$$

and

$$\sum_{nn'}C(121;n0n)|d_{nn'}|^2=-(\tfrac{2}{5})^{1/2}\tfrac{57}{74}W_0 \ , \qquad (73)$$

we obtain

$$-\hbar^2\ddot{K}_{\alpha\alpha'}(0)=\frac{5\mu_0^4}{9\pi R_0^6}[2(S_6-1)+\tfrac{19}{74}-C_{12}]W_0 \ , \qquad (74)$$

where C_{12} is the contribution from the last term in Eq. (66). The sum in Eq. (67) for $i\neq i'$ is difficult to evaluate and we have calculated only the contribution from the four common NN's of $i=1$ and $i'=2$ to this sum. The resulting value, $C_{12}=1.4$, contributes about 5% to Eq. (74) and may hence be neglected. Neglecting also the even smaller second term in Eq. (74) we arrive at the final expression

$$\tau_0=[16\gamma^4\hbar^2(S_6-1)/3R_0^6]^{-1/2} \ , \qquad (75)$$

for the relaxation time (60).

Following I, we write the transition probability (59) in the form

$$W_{\alpha\alpha'}=2(2\pi)^{1/2}(\nu_0\tau_0)\nu_0 \ , \qquad (76)$$

where

$$\nu_0=[K_{\alpha\alpha'}(0)/2\hbar^2]^{1/2} \qquad (77)$$

is the transition probability in the absence of the nuclear precessional motion, and $2(2\pi)^{1/2}\nu_0\tau_0$ is the reduction factor due to this motion. Including finally the overlap factor F^2 calculated in Sec. III B, we obtain for the probability per unit time of a jump of the para impurity to a definite NN site the expression

$$\nu=2(2\pi)^{1/2}(\nu_0\tau_0)\nu_0F^2 \ . \qquad (78)$$

This quantity will be called the jump frequency, to be distinguished from the total jump frequency which is equal to 12ν. Neglecting the contribution of about 3% from the jumps to more distant than nearest neighbors, the average time the impurity spends on a given lattice site is $t_1=(12\nu)^{-1}$. Using Eqs. (61) and (75) we obtain

$$\nu_0=2.43\times 10^2\ \text{s}^{-1} \ ,$$
$$2(2\pi)^{1/2}\nu_0\tau_0=1.04\times 10^{-2} \ , \qquad (79)$$
$$\nu=2.53F^2\ \text{s}^{-1} \ ,$$

where F^2 lies in the range 0.8–0.9. The quantities (79) refer to the hypothetical case of a single para impurity in otherwise pure orthohydrogen, i.e., to noninteracting impurities. The effect of the interaction between the impurities is discussed in Sec. III D.

Thus far we have considered temperatures ($T\lesssim\frac{1}{2}T_0$) for which the orientations of the molecules may be assumed to be fixed, i.e., all the molecules to be in the state $|10'\rangle$, and the transition probability $W_{\alpha\alpha'}$ is then determined by the nuclear correlation function $K_{\alpha\alpha'}(t)$, cf. Eq. (55). At higher temperatures in the ordered phase ($T\leq T_0$), we must consider the total correlation function, $G_{\alpha\alpha'}(t)$, involving the nuclear spins and the orientations of the molecules, and $W_{\alpha\alpha'}$ is then given by Eq. (I.25) of Ref. 7,

$$W_{\alpha\alpha'}=\hbar^{-2}\int_{-\infty}^{+\infty}G_{\alpha\alpha'}(t)\,dt \ , \qquad (80)$$

where

$$G_{\alpha\alpha'}(t)=\langle V_{\alpha\alpha'}(0)V_{\alpha'\alpha}(t)\rangle \ , \qquad (81)$$

and V is given by Eq. (35). At low temperatures, $G_{\alpha\alpha'}(t)$ decays from its initial value $G_{\alpha\alpha'}(0)$ to zero with a relaxation time τ_0 determined by the nuclear magnetic interaction. At finite temperatures $T\leq T_0$, the orientations of the molecules are characterized by a long-range order parameter, $s(T)$, shown in Fig. 4 as a function of T/T_0 according to the mean-field theory. The correlation function $G_{\alpha\alpha'}(t)$ decays from its initial value $G_{\alpha\alpha'}(0)$ to the value $s(T)^2G_{\alpha\alpha'}(0)$ in a time $\tau_Q \ll \tau_0$ determined by the EQQ interaction between the molecules and then to zero in the nuclear relaxation time τ_0 given by Eq. (60). In the expression (80) for the jump frequency, we may neglect the contribution from the spike around $t=0$ of width τ_Q and in the ordered state the jump frequency is therefore equal to

$$\nu(T)=s(T)^2\nu(0) \ , \qquad (82)$$

where $\nu(0)\equiv\nu$ is given by Eq. (78).

D. Jump frequency at finite concentrations

We first consider $T=0$ K. The effective interaction energy between NN impurities was calculated in Sec. II, cf. Eq. (33). At the relatively large separations realized at low impurity concentrations, we may neglect the second-order contributions and the interaction energy between these impurities (which will now be called i and j) is then given by

$$\epsilon_{ij} = \langle 10', 10' | H_{ij} | 10', 10' \rangle \equiv \langle H_{ij} \rangle \quad . \tag{83}$$

When the impurity i jumps to a NN site i', the change in the total energy is equal to

$$\hbar \omega_{\alpha\alpha'} = \sum_{j \neq i,i'} (\langle H_{i'j} \rangle - \langle H_{ij} \rangle) \quad , \tag{84}$$

where j runs over all the impurities common to the configurations α and α', and the jump frequency is given by

$$\begin{aligned} W_{\alpha\alpha'} &= \hbar^{-2} \int_{-\infty}^{+\infty} K_{\alpha\alpha'}(t) e^{i\omega_{\alpha\alpha'} t} dt \\ &= (2\pi)^{1/2} \hbar^{-2} W_0 \tau_0 e^{-\omega^2_{\alpha\alpha'} \tau_0^2/2} \quad , \end{aligned} \tag{85}$$

rather than by Eq. (55). The quantity of interest is the average jump frequency obtained by averaging Eq. (85) over a suitable class of configurations α, which also implies an averaging over the 12 NN sites i',

$$\nu = \{ W_{\alpha\alpha'} \}_\alpha \quad . \tag{86}$$

At any finite concentration the width of Eq. (85) is very small compared to the width of the distribution, $P(\omega_{\alpha\alpha'})$, of $\omega_{\alpha\alpha'}$ and assuming the latter to be Gaussian we obtain from Eqs. (85) and (86),

$$\nu = (2\pi)^{1/2} \hbar^{-2} W_0 / \omega_{1/2} = 2(2\pi)^{1/2} (\nu_0/\omega_{1/2}) \nu_0 \quad , \tag{87}$$

where

$$(\omega_{1/2})^2 = \{ \omega^2_{\alpha\alpha'} \}_\alpha \quad . \tag{88}$$

At low impurity concentrations, $c \lesssim 5\%$, the cross terms arising when Eq. (84) is substituted into Eq. (88) give a small contribution when averaged over α, and we get

$$(\hbar \omega_{1/2})^2 = \sum_{j \neq i,i'} \{ \langle H_{i'j} \rangle^2 + \langle H_{ij} \rangle^2 - 2 \langle H_{i'j} \rangle \langle H_{ij} \rangle \}_\alpha \quad . \tag{89}$$

The first two terms are equal after averaging over α, and the last term may be estimated by neglecting the difference in the directions of $\vec{R}_{ij}$ and $\vec{R}_{i'j}$. In this way we obtain, using Eq. (9),

$$(\hbar \omega_{1/2})^2 = \left\{ \sum_j \langle H_{ij} \rangle^2 \right\}_\alpha = \tfrac{56}{45} \Gamma_0^2 \left\{ \sum_j \xi(R_{ij})^2 \left(\frac{R_0}{R_{ij}} \right)^{10} \right\}_\alpha \quad . \tag{90}$$

We are interested in the hopping frequency of single impurities before pair formation, and we must therefore assume that the sites i and i' have no NN impurities,[7] so that the jump we are considering is not the last jump. From Eq. (90) we then obtain[7]

$$(\hbar \omega_{1/2})^2 = \tfrac{56}{45} \Gamma^2 (0.231) c \quad , \tag{91}$$

and using Eq. (79) we get

$$2(2\pi)^{1/2} (\nu_0/\omega_{1/2}) = 0.73 \times 10^{-7} c^{-1/2} \quad . \tag{92}$$

At $c = 1\%$ the average jump frequency (87) is then equal to

$$\nu = 1.76 \times 10^{-4} \text{ s}^{-1} \quad . \tag{93}$$

The corresponding values of these quantities for ortho impurities in solid parahydrogen at an ortho concentration of 1%, obtained in I, but recalculated here with the present best values of the various constants, given above Eq. (3), are

$$\begin{aligned} &\nu_0 = 4.73 \times 10^2 \text{ s}^{-1} \quad , \\ &2(2\pi)^{1/2} \nu_0 \tau_Q = 1.02 \times 10^{-7} \quad , \\ &\nu = 2(2\pi)^{1/2} (\nu_0 \tau_Q) \nu_0 = 0.48 \times 10^{-4} \text{ s}^{-1} \quad . \end{aligned} \tag{94}$$

The jump frequency of para impurities in the ordered phase is thus expected to be a factor of about 3 to 4 larger than for ortho impurities in parahydrogen at the same impurity concentration. We remark that the processes involved in these two cases are rather different. For the ortho impurities the EQQ interaction is dynamic in the sense that in the initial and final configurations, α and α', the rotational level of the crystal is spread out into an energy band. In α all the states of the band are equally populated (except at very low temperatures) and within the Heisenberg uncertainty only horizontal transitions are possible. This means that a hop occurs, for given α and α', only when the randomly fluctuating orientations of the ortho molecules are such that the hop will result in no change in the total EQQ interaction energy. This effect is described by the factor $\nu_0 \tau_Q$ in Eq. (94), where τ_Q is the orientational correlation time of the ortho impurities. On the other hand, for the para impurities at low temperatures ($T \lesssim \frac{1}{2} T_0$), the interaction (83) between the impurities is purely static. A given hop occurs only when, because of hops of other impurities, the resulting configurations α and α' have zero energy mismatch within the Heisenberg uncertainty, and this effect is reflected in the factor $\nu_0/\omega_{1/2}$ in Eq. (87), where $\hbar\omega_{1/2}$ is the mean-square static energy difference between α and α'.

At a finite temperature below T_0, the interaction energy (83) is reduced by a factor $s(T)^2$, in the mean-field theory to which we restrict ourselves here. However, the quantity (85) can be shown in the same approximation to be reduced by the same factor, and the jump frequency (87) is therefore expected to be roughly independent of the temperature throughout the ordered phase. The mean-field theory is, of course, not a very good approximation for calculating interaction energies, and a more reliable calculation of the temperature dependence of the various quantities determining the jump frequency would require us to go beyond the mean-field theory.

IV. CALCULATION OF THE JUMP FREQUENCY IN THE DISORDERED PHASE

Above the transition temperature T_0, the long-range order disappears and the calculation of the expression (80) for the jump frequency is then similar to that for ortho impurities in parahydrogen except for the difference in the arrangement of the ortho molecules. We give only an outline of the calculation and we refer to I[7] for the details.

In the initial and final configurations α and α', defined in Sec. III C, the Hamiltonians governing the orientational motion of the molecules are equal to the total EQQ interaction energies between the $N-1$ ortho molecules,

$$H_\alpha = \frac{1}{2} \sum_{jk \neq 1} H_{jk}, \quad H_{\alpha'} = \frac{1}{2} \sum_{jk \neq 2} H_{jk} , \tag{95}$$

where H_{jk} is given by Eq. (1). The correlation function $G_{\alpha\alpha'}(t)$ is given by Eq. (81) with

$$V_{\alpha\alpha'}(t) = P_{\alpha'} e^{iH_{\alpha'}t} V e^{-iH_\alpha t} P_\alpha , \tag{96}$$

where V is the resonant conversion interaction (35). At high temperatures ($T >> T_0$), we obtain from Eqs. (81) and (96),

$$G_{\alpha\alpha'}(0) = \epsilon_1^2 \sum_{m \cdots n'} |d_{mm'nn'}|^2 = 4\epsilon_1^2 , \tag{97}$$

and

$$-\hbar^2 \ddot{G}_{\alpha\alpha'}(0) = (A_{\alpha\alpha'} - 2B_{\alpha\alpha'})\epsilon_1^2 , \tag{98}$$

where

$$A_{\alpha\alpha'} = \frac{280}{9} \Gamma_0^2 \sum_{i=1}^{2} \sum_{j} \xi(R_{ij}) \left(\frac{R_0}{R_{ij}} \right)^{10} \times [1 + \tfrac{25}{196}(3\cos^2\theta_{ij} - 1)] , \tag{99}$$

and $B_{\alpha\alpha'}$ may be neglected.[7] The sum over j extends over all the ortho molecules common to the arrangements α and α', which in this case implies $j = 3, \ldots, N$. The two terms corresponding to $i = 1$ and 2 in Eq. (99) are equal and can easily be evaluated with the result

$$\sum_{j=3}^{\infty} \xi(R_{ij}) \left(\frac{R_0}{R_{ij}} \right)^{10} = 11\xi_{54}^2 + (S_{10} - 12) \tag{100}$$

and

$$\sum_{j=3}^{\infty} \xi(R_{ij}) \left(\frac{R_0}{R_{ij}} \right)^{10} (3\cos^2\theta_{ij} - 1) = -\xi_{54}^2(3\cos^2\theta_{12} - 1) = -2\xi_{54}^2 , \tag{101}$$

since the sum over all $j \neq i$ vanishes because of the cubic symmetry. Hence we get from Eq. (99)

$$A_{\alpha\alpha'} = \frac{560}{9} \left[\frac{1053}{98} \xi_{54}^2 + (S_{10} - 12)\Gamma_0^2 \right] . \tag{102}$$

In the present problem where all the sites except the impurity site are occupied by ortho molecules, it is natural to assume that the correlation function (81) is Gaussian. Denoting the resulting correlation time by τ_∞,

$$\tau_\infty = [-\ddot{G}_{\alpha\alpha'}(0)/G_{\alpha\alpha'}(0)]^{1/2} , \tag{103}$$

we obtain the following results in the high-temperature limit ($T >> T_0$),

$$\begin{aligned} \nu_0 &= 4.73 \times 10^2\,\mathrm{s}^{-1} , \\ 2(2\pi)^{1/2}\nu_0\tau_\infty &= 1.59 \times 10^{-9} , \end{aligned} \tag{104}$$

$$\nu(\infty) = 0.752 \times 10^{-6}\,\mathrm{s}^{-1}, \quad t_1(\infty) = 31\ \mathrm{h} . \tag{105}$$

The jump frequency in the absence of the EQQ interaction, ν_0, is of course the same as in Eq. (94), but the reduction factor is seen to be two orders of magnitude smaller than at 1% ortho concentration, as was to be expected. As T approaches T_0 from above, the jump frequency can be expected to increase from the value $\nu(\infty)$ by perhaps as much as a factor of 2. We have not calculated the temperature dependence of ν above T_0, but we can conclude that the quantum diffusion of para impurities in orthohydrogen is essentially negligible at all temperatures above T_0.

V. CALCULATION OF THE RELAXATION-TIME CONSTANTS

In the experiments on the quantum diffusion of ortho impurities in parahydrogen described in Sec. I, one measures the time evolution of the system after a sudden change in the temperature. The main questions one would like to answer in this connection are (i) what is the true thermodynamic equilibrium state for given temperature and concentration, assuming that ordinary ortho-para conversion does not take place, (ii) what are the processes by which the system reaches this equilibrium state, and (iii) what are the values of the time constants characterizing these relaxation processes and how do they depend on the temperature and the concentration. We will not discuss these questions in detail here but confine ourselves to the following remarks stressing the differences between the ortho impurities and the para impurities.

Single ortho impurities in parahydrogen have a negative energy, $\epsilon_1 = -1.1$ K, relative to the host molecules due to the quadrupolar polarization energy. When the interaction between the impurities is neglected, the minimum free energy corresponds to a random distribution of the impurities over the lattice and no phase separation occurs. The EQQ interaction between two NN impurities splits the nine-fold-degenerate rotational level of the pair into four levels. The interaction energy in the resulting ground state is $-4\Gamma = -3.4$ K, but the average energy over all the levels is zero. If a Boltzmann distribution exists over these levels, the effective interaction energy of the pair is therefore zero at high temperatures and approaches -4Γ at low temperatures. Below about 4 K the equilibrium ratio of pairs to singles therefore increases with decreasing temperatures and at low concentrations this ratio can be calculated by standard methods.[2,3,21] The energy levels of triangles of impurities with at least two sides equal to the NN separation have also been calculated.[2,22] For a triangle of three NN pairs the energy in the ground state per NN bond is -2.4Γ and is considerably less than for an isolated NN pair because of a reduced effect of resonance and a frustration in the orientational alignment. The effective interaction of the ortho impurities is therefore strongly nonadditive and in large clusters the binding energy at low temperatures per NN bond approaches the value $-\frac{19}{18}\Gamma$ characteristic of the bulk ordered phase (we ignore the small difference in this value for the hcp and fcc structures), where the resonance has completely disappeared and the orientational frustration has reduced the ground-state energy by a further factor $\frac{19}{36}$. It is clear that at $T = 0$ K the true equilibrium state corresponds to separated phases and that the average cluster size, $\langle n \rangle$, is infinite for all concentrations. It is not clear whether $\langle n \rangle$ diverges at a finite temperature for any concentration less than the critical percolation concentration of about 20%, and this question merits further investigation.

A single para impurity in ordered orthohydrogen has a positive energy which according to the mean-field theory varies from $\epsilon_1 = 11.4$ K at $T = 0$ K to $\frac{1}{4}\epsilon_1$ at the order-disorder transition temperature T_0 and vanishes above T_0. Even when the interaction between the impurities is neglected, a phase separation therefore occurs at a finite temperature, T_1, which can be calculated by equating the free energies of the random and the separated phases. For $T \lesssim \frac{1}{2}T_0$ we may put $s = 1$, cf. Fig. 4, and the energy of each broken bond is then equal to $\frac{19}{18}\Gamma$. Neglecting surface effects, the difference between the free energies per molecule of the two phases is given by

$$F_1 - F_2 = 12\tfrac{19}{18}\Gamma c + kT[c \ln c + (1-c)\ln(1-c)] - 6\tfrac{19}{18}\Gamma c \ . \tag{106}$$

Putting $F_1 - F_2 = 0$ we obtain $T_1 = 1.0-1.3$ K for c in the range 1–5%. Pairs of NN para impurities have an interaction energy (34) which varies from -0.86 K at $T = 0$ K to one-fourth of this value at $T = T_0$, and the presence of this interaction will increase the values of T_1 at higher concentrations. Finally we remark that, in contrast to the ortho impurities, the para impurities show a very nearly additive interaction in triples and higher-order clusters. From these remarks it is clear that the para impurities should show a strong tendency to clustering below T_0. Whether a complete phase separation will occur depends on the mobility of larger clusters or on their rate of dissociation, but we will not investigate these questions here.

At low para concentrations the first step in the approach to equilibrium after a lowering of the temperature is the formation of NN pairs of impurities. We can estimate the relaxation time, τ, by means of the following simple models.[23] In the diffusion model one replaces the master equation

$$\dot{P}(\vec{R}_i,t) = \nu \sum_j P(\vec{R}_j,t) - 12\nu P(\vec{R}_i,t) \ , \tag{107}$$

for the probability of finding the impurity at time t on the lattice site $\vec{R}_i$ by the diffusion equation. For a close-packed lattice the resulting diffusion coefficient is given by

$$D = 2R_0^2 \nu \ , \tag{108}$$

where R_0 is the lattice constant. If we assume that the impurities at $t = 0$ from a close-packed superlattice on the host fcc lattice, their NN separation is equal to $d = R_0 c^{-1/3}$. After a time t the probability distribution for each impurity around its position at $t = 0$ is given by

$$P(\vec{R},t) = (4\pi D t)^{-3/2} \exp(-|\vec{R}|^2/4Dt) \ . \tag{109}$$

This distribution falls to half its value at a radius $R_{1/2} = (4Dt \ln 2)^{1/2}$, and one way of arriving at an estimate of the reaction time constant τ is to put $R_{1/2} = \frac{1}{2}d$, giving

$$\tau^{-1} = A c^{2/3} \nu(T) \ , \tag{110}$$

where $A = 32 \ln 2 = 22.2$. One can also use the mean-square displacement, $R_1 = (6Dt)^{1/2}$, for which $P(R_1) = 0.22P(0)$. It is then reasonable to obtain τ by putting $R_1 = d$, and this leads to Eq. (110) with $A = 12$. It is clear that all one can conclude on the basis of the diffusion model is that τ is given by Eq. (110) where $A = 20 \pm 10$. The average number of steps of the impurities in the time τ is $\bar{n} = 12\nu\tau$ and using (110) with $A = 20$ gives $\bar{n} = 13$ at $c = 1\%$. Thus for $c \lesssim 1\%$ the diffusion model which is based on the assumption of a large number of steps, is reasonable. For $c \gtrsim 1\%$ it is more appropriate to use a kinetic model. First consider the random walk of one impurity in the cloud of fixed but randomly distributed remaining impurities.. After one step the impurity comes into contact with seven new NN sites, viz. 12 minus the original site minus the four common NN sites of the original and final site. The probability that a pair is formed after the first step is therefore $P_1 = 7c$. Neglecting retracing of steps in the random walk, the probability that a pair is formed after two steps is $P_2 = 7c \times (1-c)^7$, and after n steps $P_n = 7c(1-c)^{7(n-1)}$. When all the impurities are hopping, the average number of steps till pair formation is given by

$$\bar{n} = \left| \sum_n nP_n/2 \sum_n P_n \right| \quad . \tag{111}$$

To lowest order in c this gives

$$\tau^{-1} = 12\nu/\bar{n} = 168c\nu(T) \quad . \tag{112}$$

Because the retracing of steps has been neglected in this simple treatment, the expression (111) is a lower bound for $\bar{n}$. For $c = 1\%$ we obtain from Eq. (111) $\bar{n} = 7$, in rough agreement with the diffusion model. If the frequency of the last step is equal to $r\nu$ instead of ν, one easily sees that Eq. (112) should be replaced by

$$\tau^{-1} = \frac{168c\nu(T)}{1 + 7c(r-1)} \quad , \tag{113}$$

but we will not try to calculate the quantity r in the present paper.

Applying these results to the quantum diffusion of para impurities in ordered orthohydrogen at 1% impurity concentration, we obtain from Eq. (93), assuming $\bar{n} = 10$, the value $\tau = 0.5 \times 10^4$ s. Applying the same estimate, $\bar{n} = 10$, to the quantum diffusion of ortho impurities in parahydrogen at $c = 1\%$, we obtain from Eq. (94) the value $\tau = 1.7 \times 10^4$ s $= 4.7$ h, in reasonable agreement with the experimental values. This gives some support to our estimate of the reaction time constant, $\tau = 1$ h, for the establishment of equilibrium in the system of para impurities in ordered orthohydrogen. Above T_0 we obtain in the same way the estimate $\tau = 400$ h and the quantum diffusion in the disordered state is therefore essentially negligible.

VI. CONCLUSIONS

This paper describes a theoretical investigation of the quantum diffusion of parahydrogen impurities in solid orthohydrogen due to resonant conversion processes of para-ortho into ortho-para pairs. The main results of our calculations are:

(i) Above the order-disorder transition temperature T_0 which is 2.8 K in pure orthohydrogen, the hopping frequency of a parahydrogen impurity is proportional to the correlation time characterizing the orientational motion of the rotational angular momenta of the ortho molecules. The resulting hopping frequency is two orders of magnitude smaller than for orthohydrogen impurities in solid parahydrogen at an ortho concentration of 1%. The quantum diffusion of parahydrogen impurities in disordered orthohydrogen is characterized by a time constant of the order of 400 h and is therefore negligible for all practical purposes. Because of the weakness of the effective interaction between the parahydrogen impurities, the equilibrium distribution of these impurities over the lattice at all temperatures $T > T_0$ is in any case a random one.

(ii) In the ordered phase the hopping frequency of the para impurities is determined by the difference in the total interaction energy between the impurities before and after a hop. The resulting reaction time constant for the establishment of equilibrium is estimated to be about 1 h at 1% impurity concentration, and to vary as $c^{-1/2}$.

(iii) The distortion of the orientational order of the ortho molecules surrounding a parahydrogen impurity contributes an overlap factor to the transition element determining the hopping probability, which reduces the hopping frequency by about 15%.

(iv) The para impurities in ordered orthohydrogen have an excess energy relative to the host molecules, arising from the broken EQQ bonds, which varies from $\epsilon_1 = 11.4$ K at very low temperatures to $\frac{1}{4}\epsilon_1$ at $T = T_0$, according to the mean-field theory. Even if the attractive interaction of about 0.9 K between NN para impurities is neglected, a phase separation therefore tends to occur at a temperature which we estimate to be in the range 1.0–1.3 K for para concentrations in the range 1–5%.

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