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Quantum diffusion and pairing of *ortho*-H$_2$ impurities in *para*-H$_2$

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Pairing and clustering of o-H$_2$ impurities in solid p-H$_2$ are discussed. The anomalous temperature dependencies observed experimentally earlier are explained not only on the basis of transitions between different mechanisms of quantum diffusion, but also taking into account the large differences between diffusion trajectories associated with different mechanisms. The most interesting and important is a description of diffusion trajectories related to a two-phonon mechanism of quantum diffusion when because of strong "kinetic repulsion" the characteristic pairing trajectories are very long. The considerable decrease in pairing times at low temperatures is caused by a transition from this regime to another one with much shorter trajectories. Two major simplifications permitted to cut considerably the number of unknown (fitting) constants involved staying still within the reasonable agreement with experimental data. The concentration dependence of the pairing and clustering times is also discussed. At lower o-H$_2$ concentrations intermediate stages of clustering should be studied, taking into account a coherent motion of pairs or triads of o-H$_2$ particles.

I. INTRODUCTION

Quantum diffusion has been studied—theoretically and experimentally—for about twenty years. The word "quantum" in this context refers both to (quantum) peculiarities of diffusion and to perculiarities of (quantum) solids involved. The main objects are the helium and hydrogen crystals and hydrogen and some other light particles in metals.

In molecular hydrogen the quantum diffusion is observed as clustering of orthohydrogen impurity molecules in parahydrogen crystals[1] or pairing (with consequent recombination) of atoms of hydrogen isotopes in crystals of molecular hydrogen,[2] and in helium—in experiments on (spin) diffusion of ^{3}He impurities in solid ^{4}He. However, though the quantum anomalies of diffusion of impurity particles are to a large extent the same, the languages for description are very different for helium and hydrogen systems (see, e.g., reviews[3,4] and references therein).

Below I try to approach some features of quantum diffusion of ortho-H$_2$ impurities in para-H$_2$ crystals based on the ideas which to some extent originated from the studies of solid helium. The aim is to explain some of the experimental data[1] and to reanalyze the main diffusion characteristics based on these data. Therefore it may be important to understand some common features of helium and hydrogen systems and their major differences. This is discussed in the rest of the Introduction. In Sec. II I demonstrate that different mechanisms of quantum diffusion result in different diffusion (pairing) trajectories. The most interesting hopping mechanism and a diffusion problem lead to what is called "kinetic repulsion" with extremely long pairing trajectories (much longer than for a standard random walk). The transition from this regime to another one at low temperatures results not only in a change in a hopping rate, but also in a considerable shortening of pairing trajectories. The last circumstance is crucial (Sec. III) for understanding temperature and concentration dependences of the pairing time for o-H$_2$ impurities. In Sec. IV I explain why a coherent diffusion of pairs and triads may be important on later stages of clustering.

Quantum diffusion is studied in hcp phases of helium and hydrogen crystals. This means the same symmetry considerations for impurities, the same coordination numbers, and the same restrictions for "crablike" motion for pairs and triads (see below).

For both crystals the diffusion properties of impurities are determined only by relations between the impurity bandwidths Δ (tunneling rates) and other energy parameters for impurities. As far as one knows the value of Δ, the knowledge of an underlying tunneling mechanism becomes irrelevant for evaluation of diffusion parameters. Of course, one should understand the tunneling mechanism if one wants to calculate Δ; however, such calculations are not very accurate (Δ depends exponentially on several not very well-known parameters), and the experimental data on diffusion are usually the best source for evaluation of Δ.

In both cases the bandwidths Δ (and tunneling frequencies, $t_0 \sim \Delta/12$) are extremely small so that practically any imperfections in potential relief prevent coherent propagation of impurity waves. An "unassisted" tunneling of impurity particles to the neighbor lattice site may occur only if the energy mismatch, δE, between the energy levels for the impurity particles on these adjacent sites does not exceed the bare tunneling rate $\delta E < t_0$. As a result, the unassisted tunneling may occur only for very small mismatches. The mismatches are caused by imperfections of crystals, external fields, or interaction between impurities themselves. While the first type of mismatches is accidental and random and should be studied statistically, the last two are of more regular nature and should be approached in a different way.

Generally, there are two main ways in which impurities tunnel through a crystal with considerable energy mismatches. The first is similar to what happens in glasses: due to the randomness (or some other peculiarities) of energy distribution, there is always some probability, $w(t_0)$, that the mismatch between impurity level for the adjacent sites is less than t_0. Then the effective tunneling rate is $t = t_0 w(t_0)$, and the problem reduces to an evaluation of $w(t_0)$. For example, when mismatches are randomly distributed in some interval Ω with constant density of states $1/\Omega$, then $w(t_0) = t_0/\Omega$, and $t = t_0^2/\Omega$.

The second possiblity involves inelastic tunneling processes (e.g., phonon assisted jumps), when the energy mismatch is compensated due to participation of some additional (quasi)particles (mainly phonons) responsible for the energy balance. In this case the tunneling process is at least of the second order with the effective rate $t = t_0^2/\Omega$, where now the energy Ω depends on t_0, mismatches δE, and characteristic parameters of other particles involved.

Of course, there are also some mixed processes when the mismatches are overcome due to some randomness in their distribution and participation of other particles.

To an extent, the thermal fluctuations (phonons) play the same dual role for quantum diffusion in hydrogen and in helium being responsible for tunneling in the case of inhomogeneous potential relief (energy difference at the adjacent lattice sites) and destroying coherence in some other cases.

The differences between quantum diffusion in hydrogen and helium are mainly caused by a difference in energy scales, while the origin and mechanism of quantum diffusion (two-, three-, or four-particle exchange, resonance conversion, etc.) are not very important; the diffusion processes are determined by and very sensitive to (even qualitatively) the value of the tunneling frequency t_0. The scales for t_0 for ortho-H_2 and ^{3}He impurities are assumed to be different: $t_H \sim 10^3$ s^{-1} (10^{-7} K), $t_{He} \sim 10^6$ s^{-1} (10^{-4} K) (here and below $\hbar = 1$). As a result, thresholds for sensitivity for inhomogeneity in potential reliefs are different. What is more, for ortho-H_2 this threshold is so low that it becomes very improbable to expect coherent tunneling through several lattice sites in a reasonable range of parameters.

The interaction between impurities is also different. For ^{3}He impurities the main interaction channel is an elastic interaction, $U(\mathbf{r}) \sim U(\mathbf{n})/r^3 [U(\mathbf{n}) \sim 10^{-2}$ K], due to a small difference in atomic volumes between host and impurity atoms, while for hydrogen the main channel (at small distances) is associated with the electric quadrupole-quadrupole (EQQ) interaction, $U(\mathbf{r}) \sim U(\mathbf{n})/r^5$, $U(\mathbf{n}) \gtrsim 1$ K. What is more, for pairs of ortho-H_2 molecules, there seems to be a large difference when particles belong to the same or different sublattices of the hcp lattice,[3] while the importance of such differences for helium impurities is unconfirmed.

Another major difference is that while for helium one usually studies the real diffusion of particles (spins) through crystal, for hydrogen the experiments[1,2] concern the pairing processes where the pairing particles usually

spend most of the time close to each other where the interaction energy is large. Therefore in helium the energy mismatches for impurities are created by all other impurity particles and are somewhat random reflecting the randomness in impurity distributions, while in hydrogen the important mismatches are due mostly to the interaction between the pairing particles and are not random. In this sense the problem of impurity pairing and clustering in hydrogen crystals is different from the random diffusion processes in helium crystals.

Of course, there are other, less significant, differences—for example, in cross sections of impurity-phonon interactions, etc.

Below I analyze the quantum diffusion of ortho-H_2 impurity molecules using some geometric considerations. I also try to demonstrate that the problem does not reduce the calculation of individual hopping rates, but should include the discussion of properties of different diffusion trajectories. It seems that a careful consideration of pairing (diffusion) trajectories may explain some of the puzzling experimental data of Ref. 1, namely, a rapid drop in the pairing time at low temperatures.

II. HOPPING RATES
AND DIFFUSION TRAJECTORIES

Diffusion, by definition, is a random process. However, the presence of anisotropic potential field for diffusing particles leads to an appearance of some preferred directions. Therefore, average velocities for diffusion in different directions may become very different, and, to some extent, the randomness is suppressed. This may happen in the process of clustering for ortho-H_2 molecules.

One of the major calculated and observed characteristics is the time of the formation of a nearest-neighbor (NN) pair of ortho-H_2 molecules or a NN pair of impurity atoms in a parahydrogen crystal. This time depends on (i) initial distance between particles; (ii) the hopping frequency which is a function of the energy mismatches and, consequently, of the current distance between the pairing particles; (iii) the length of characteristic trajectory (number of jumps) including the degree of randomness of the trajectory. Since the tunneling probability crucially depends on the energy mismatch for the adjacent sites, the last factor—the diffusion trajectories— is also very sensitive to the temperature and the interaction.

Generally, the effective hopping frequency for quantum diffusion in the crystal with considerable energy mismatches is

$$t = t_0^2/\Omega , \tag{1}$$

where Ω is some characteristic energy related to the energy mismatch on adjacent sites and to the most effective way to overcome this mismatch. The different hopping mechanisms lead not only to the different hopping rates (1), but also to different diffusion (pairing) trajectories.

Let us illustrate it on the example of four limiting cases.

(a) The first one occurs either when the mismatches δE

are small in comparison with the bare tunneling frequency t_0 (the effective hopping frequency $t = t_0$), or when the hopping is restricted by two-phonon processes[4−7] while the thermal fluctuations are strong in comparison with potential shifts [high temperatures, $T \geq T_0 = \Theta(T/\Theta\xi)^\beta \gg \delta E$, Θ is the Debye temperature, the index β is equal—depending on the situation—to 7 or 9, and ξ is an unknown constant, $1 > \xi > 0.1$]:

$$t = t_0^2/T_0 . \tag{2}$$

Then the pairing time is equal for the initial spacing $R = N_0 a$ (a is the interatomic distance) to $\tau \sim N_0^2/t$. Here we have a real random diffusion.

(b) The second case corresponds to low temperatures and relatively high mismatches when the two-phonon processes are ineffective, and the diffusion is accompanied by spontaneous emission of phonons.[5] Since the probability of such jumps rapidly increases with energy shifts δE between adjacent sites (proportionally to δE^3),

$$t = t_0^2 (\delta E/\zeta\Theta)^3/\Theta , \tag{3}$$

the pairing takes place not due to the random diffusion motion, but as a result of consequently irreversible jumps along the energy gradient (see Fig. 1):

$$\tau \sim (\Theta/t_0^2)(\zeta\Theta)^3 \sum_i \delta E_i^{-3} \tag{4}$$

with the summation along the trajectory 1 in Fig. 1. The deviations from the trajectory of Fig. 1 are small as far as the values of δE differ considerably for different directions of the jump. Usually it is true only on the last stages of pairing when the pairing particles are already very close to each other (at large distances between parti-
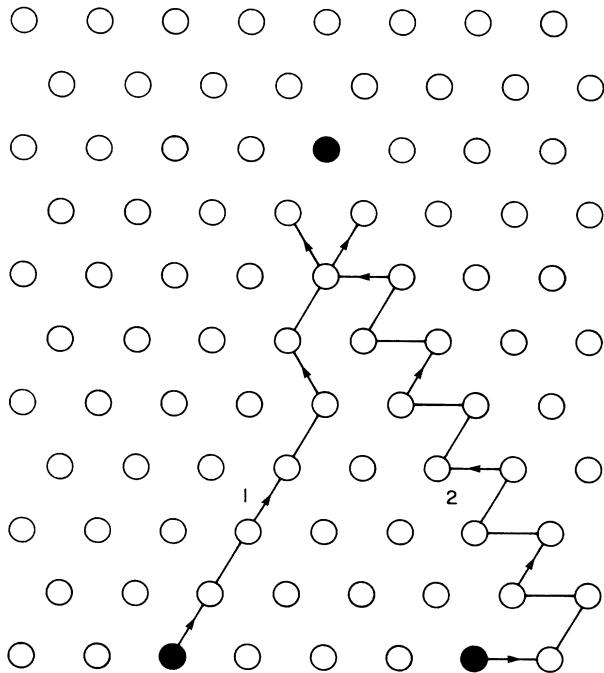
cles this mechanism is not interesting anyway). Since for hydrogen

$$\delta E_i = a^5 U(\mathbf{n})[R_i^{-5} - (R_i + a)^{-5}] , \tag{5}$$

the summation along the trajectory would lead to a peculiar dependence on the initial distance N_0, i.e., impurity concentration $x \sim N_0^{-3}$,

$$\tau = a^{-15} \left[\frac{\Theta}{t_0^2} \right] \left[\frac{\zeta\Theta}{U(\mathbf{n})} \right]^3 \sum_k (R_k^{-5} - R_{k+1}^{-5})^- . \tag{6}$$

Moreover, since most of the time (6) is spent on the first jump, a good estimate for (6) is

$$\tau \sim \left[\frac{\Theta}{t_0^2} \right] \left[\frac{\zeta\Theta}{U(\mathbf{n})} \right]^3 / [(N_0 - 1)^{-5} - N_0^{-5}]^3 . \tag{7}$$

For example, at ultralow temperatures and concentrations the characteristic time of the pair formation,

$$\tau = \sigma(5\Theta/t_0^2)(\zeta\Theta/U)^3 x^{-6} , \tag{8}$$

should be temperature independent and strongly dependent on impurity concentration (σ is a dimensionless geometric factor). Except for a few first jumps, this regime does not have any randomness. The larger the energy mismatches, the closer is the real "diffusion" trajectory to curve 1 (Fig. 1) consisting of motion along straight upward trajectory along the principal axis (till the intersection with the vertical axis) with consequent zigzag motion along the vertical axis.

Note that Eq. (3) corresponds to an attraction between the pairing particles (motion along potential field with emission of phonons). Otherwise the jumps should be accompanied by absorption of phonons, and in Eq. (3) one should substitute one of δE by T.[6]

(c) The third limiting case corresponds to the two-phonon process with $T_0 \ll \delta E$, when[5,6]

$$t = t_0^2 T_0/\delta E^2 , \tag{9}$$

and the characteristic pairing trajectory tends to be perpendicular to the energy gradient, and, as a result, is much longer than in previous cases (see curve 2 in Fig. 1). Of course, Eqs. (2) and (9) correspond to different limiting cases of a more general expression for the hopping rate

$$t = t_0^2 T_0/(\delta E^2 + T_0^2) . $$

The minimal pairing time estimate for this mechanism of quantum diffusion is

$$\tau_{min} \sim (1/t_0^2 T_0) \sum_i (\delta E_i)^2 , \tag{10}$$

where the summation should be performed along the trajectory 2 in Fig. 1. However, unlike case (b) when the trajectory 1 in Fig. 1 represented a real pairing trajectory (at least in the limiting case of rapidly increasing mismatches), the trajectory 2 is only the optimal pairing trajectory for the hopping mechanism (c): the real pairing never corresponds to the steady approach along this trajectory, and the pairing time is much longer than (10). Needless to say that the trajectory 2 (and the real pairing

FIG. 1. Pairing trajectories. Curve 1, hopping mechanism (b); curve 2, hopping mechanism (c).

trajectory) is now always much longer than the trajectory 1 for case (b). The understanding of the pairing trajectories in this case is crucial for interpretation of data.[1]

Since t strongly depends on δE, Eq. (9), it is usually assumed that the good estimate of the diffusion time in this regime corresponds to the time of the longest individual jump with the largest δE. It is absolutely wrong, and Eq. (10) does not describe the pairing of ortho-H$_2$ impurities even qualitatively.

In this case, the situation is not so transparent as in the case (b). Even if one neglects all random diffusion deviations from the optimal trajectory (curve 2 in Fig. 1), still the diffusion walk along it is not simple: the problem is that, in most parts of the trajectory, the probability of turning back is much higher (δE for the backward jump is much smaller) than for the pairing ascent. This kinetic repulsion occurs if the mismatch δE_L for the step L is larger than for the backward step $L-1$. Such repulsion always takes palce since the probability of getting on the next "step" of the staircase—or stepping down—is much smaller than the probability of going back and forth along the same step (see Fig. 1). What is more, the real pattern strongly deviates from the "optimal" one from Fig. 1: the particle tends to walk along each step rather than to jump to the next one or to step down. As a result, the particle stays for a very long time on each step (the closer to the second particle—the longer). And the total pairing time is much longer than the bare time of the less probable (i.e., the last) jump.

The picture of random jumps along the trajectory with decreasing probability (increasing time) of jump on each step is not trivial. Let us discus it, in the beginning, for the one-dimensional (1D) case. If the ratio of corresponding probabilities is very large, it seems, at first glance, that the total time scale of the diffusion is determined by the probability t_N of the last jump $\tau \simeq 1/t_N$. It is not true. Suppose we calculate the time τ for the particle to travel from site 1 to site $N+1$ (N steps) with the hopping frequencies for each step $t_{i+1} \ll t_i$. The total time τ consists of the time of the final jump, $\tau_N = 1/t_N$, plus the time needed to come to the site N. However, to jump to the site $N+1$ from N, the particle has to come to the site N t_{N-1}/t_N times since the probability to go back to the site $N-1$ from N is much larger than to continue to $N+1$. Therefore, the particle has to make $t_{N-1}/t_N \gg 1$ jumps from $N-1$ to N. The time it takes is equal to $\tau_{N-1} t_{N-1}/t_N = \tau_N$ and is much longer than the bare time τ_{N-1}. To come to the site $N-1$ t_{N-1}/t_N times the particle has to come to $N-2$ $(t_{N-1}/t_N)(t_{N-2}/t_{N-1}) = t_{N-2}/t_N$ times, and to spend time equal to $\tau_{N-2} t_{N-2}/t_N = \tau_N$, and not τ_{N-2}, on jumps $N-2 \to N-1$. As a result the effective time spent on each jump is equal to τ_N and not to much shorter bare time τ_i, and the total time

$$\tau = N\tau_N \gg \tau_N \ . \tag{11}$$

If the total pairing way is determined by this mechanism, then $\tau > x^{-1/3}\tau_N$ [one should keep in mind that the effective length N in Eq. (11) is much longer—see the trajectory 2 in Fig. 1—than the initial "bare" distance be-

tween the pairing particles $N_0 \approx x^{-1/3}$].

If one allows the condition $t_{i+1} \ll t_i$ to relax, then instead of Eq. (11) one gets

$$\tau = \sum_{i=1}^{N} \frac{1}{t_i} \prod_{j=i-1}^{N-1} \left[1 + \frac{t_j}{t_{j+1}} \right] \ .$$

However, above we did not take into account a possible stochastization of the path with deviations from, for example, trajectory 2 in Fig. 1. The corresponding result for the 3D diffusion problem differs considerably from the 1D result (11) even in the simplest situation of the large ratios of hopping probabilities in different directions. It is difficult to give a general form for a dependence of the pairing time, τ, on an initial distance between pairing particles N_0; the corresponding index is not universal and should be computed for each lattice, concentration, and interaction separately. One may only estimate a range of variation for this index.

There are two limiting cases. The first one corresponds to a spherical representation of the 3D problem when the real lattice is substituted by a system of lattice sites located on a set of concentric spherical shells centered on one of the pairing particles. Then one may assume that the hopping probabilities along the radius of the sphere, i.e., for jumps between the shells, depend only on the radii of the spherical shells involved, rapidly decrease with the increasing radius (with the decreasing distance between the pairing particles), and do not depend on particle coordinates on the shells and on the possibilities of jumps (regardless of their probabilities) along the shells. In this case the jumps along the shells do not affect the pairing process at all, the problem still is—effectively—one dimensional, and the pairing time is given by Eq. (11) with N equal to the number of the shells involved.

Though the hexagonal lattice is very symmetrical, such a spherical model is oversimplified especially at small distances between particles when such isotropic spherical shells cannot be introduced. The opposite limiting case corresponds to extremely large differences in hopping probabilities in all nonequivalent directions. Generally, the probabilities of jumps from shell to shell are much lower than the jump rates along the shells and strongly depend on the particles coordinates on the shells. Then (see, e.g., Fig. 1) the jumps onto a different shell may be effectively performed only from some definite position on another shell, and a possibility of a nearly free walk along each shell leads to a significant decrease of effective probability of jumps from shell to shell thus increasing the total pairing time. Therefore the effective time for jumps from shell to shell (actually, the times $\tau_i = 1/t_i$ above) should depend on the length of each step, i.e., on the index i. This dependence may be either linear or quadratic, and the resulting pairing time τ is not a linear function of N as in Eq. (11), but should be given by the equation

$$\tau \approx N^{3\alpha}\tau_N \approx Cx^{-\alpha}\tau_N \ , \tag{12}$$

where the exact value of the nonuniversal index $\alpha, \frac{1}{3} \leq \alpha \leq 1$, depends on distribution of t_i along and around the optimal path (Fig. 1), and should be estimated numerically for each case separately. The dimensionless

parameter $C > 1$ in Eq. (12) reflects the fact that the trajectory length N in Eqs. (11) and (12) is not a bare initial distance between the pairing particles, N_0, but is a length of the optimal pairing trajectory, $N > N_0$.

(d) The above descriptions assume that only the interaction with the nearest other orthomolecule is important for the diffusion of o-H$_2$. In reality, the energy mismatches on the surrounding sites are caused by interactions with all orthoparticles. However, EQQ is rapidly decreasing at large distances as $1/r^5$, and the interaction with the nearest particle becomes more important than with all other particles as soon as the distance between them, r, becomes smaller than the average distance between particles $N_0 \approx 1/x^{1/3}$. Therefore, only the initial stages of pairing correspond to the diffusion in the random potential field created by all other impurities. (In solid helium the situation is different: the interaction is proportional to $1/r^3$, and the corresponding integral may diverge at large distances. In principle, for o-H$_2$ particles, there should also be an elastic interaction channel with $1/r^3$,[7] but the corresponding coefficient is supposed to be small in comparison with an EQQ contribution.)

In such a "statistical" regime, the energy mismatches on the neighbor lattice sites are spread, due to the interaction with all impurities, within some energy interval,[1,3] $\omega_Q > T_0$ (according to Ref. 3, ω_Q is either $2x^{5/3}$ K, or $0.2x^{1/2}$ K). If the density of states within ω_Q is constant, then the resulting diffusion rate does not depend on a type of possible two-phonon processes (a) and (b): in case (a) the tunneling occurs only through the "windows" with the widths t_0 or T_0, and the effective hopping rates are $t_0(t_0/\omega_Q)$ or $(t_0^2/T_0)(T_0/\omega_Q) = t_0^2/\omega_Q$. In the case of regime (c), the effective rate is again the same,

$$ t \approx \int_{T_0}^{\omega_Q} t_0^2 \frac{T_0}{E^2} \frac{dE}{\omega_Q} \approx \frac{t_0^2}{\omega_Q} . \tag{13} $$

The effective rate of processes (b) with phonon emission is different,

$$ t \sim \int_0^{\omega_Q} \frac{t_0^2}{\Theta} \left[\frac{\delta E}{\zeta \Theta} \right]^3 \frac{d\delta E}{\omega_Q} = \frac{t_0^2}{4\Theta} \left[\frac{\omega_Q}{\zeta \Theta} \right]^3 \tag{14} $$

and is much smaller than the two-phonon and bare rates t_0^2/ω_Q as far as $\omega_Q/\zeta^{3/4}\Theta \ll 1$. Therefore in the region dominated by many-particle interaction, the pairing process always goes with the rate t_0^2/ω_Q and seems to be a random process with the time estimate given in Ref. 3.

The major problem with the statistical regime (d) is that the distance, where the energy mismatches stop to be determined by the interaction with other impurities and are dominated by the interaction within the same pair, is not a well-defined quantity. Therefore it is difficult to give a proper analytical description for a crossover from (d) to other regimes.

III. PAIRING TIME τ

In this section I deal mostly with an anomalous temperature dependence $\tau(T)$ observed[1] for the pairing time τ at rather low impurity concentrations, $x < 1\%$, namely, with a rapid decrease in the pairing time at temperatures

below 0.3 K. It is possible to explain this rapid drop in τ without involving any new diffusion mechanisms with an increasing hopping rate which one would probably not expect to find at such low temperatures. In the end of the section I explain why at higher concentrations the temperature dependence is different.

None of the above hopping regimes may occur in its pure form and be responsible for impurity pairing as a whole except for the high concentrations. One should rather expect these regimes to be responsible for different stages of the pairing process. For impurity concentrations $x \lesssim 1\%$ the most probable sequence of diffusion regimes corresponds, with decreasing impurities separations, to (a), (d),$\rightarrow$(c)$\rightarrow$(b), (c). Only the initial stage provides a random walk, while the inevitable presence of the regime (c) with the kinetic repulsion on the intermediate stages is responsible for anomalies in temperature and concentration dependences. The regime (c) is gradually ousted with the lowering temperature.

The presence of the intermediate regime, (c), with the kinetic repulsion leads to a large increase in the pairing time; the elimination of this regime—or a part of it—at low temperatures [when the mechanism (b) becomes more and more important] results even in an effective decrease of the pairing time. Generally, since the tunneling rate for the regime (c) is rapidly decreasing with the decreasing temperature, and the rates for (b) and (d) are basically temperature independent, the presence of (c) results in an increase of the pairing time with the lowering temperature with consequent transition to a temperature-independent plateau. However, there is a relatively wide range of parameters where the (partial) elimination of the regime (c) by (b) at low temperatures results in an effective decrease in the pairing time, but only because the transition from (c) to (b) leads also to the considerable shortening of the pairing trajectories.

Unfortunately, the discussion of transitions between different regimes inevitably results in use of a large number of unknown fitting parameters entering the above expressions for the effective tunneling rates t, especially if one takes into account the doubling of the number of parameters because of some asymmetry of the hcp lattice with respect to two sublattices. Such a large number of fitting parameters allows an easy and accurate fit to the experimental data,[1] but such a fit would to some extent be meaningless. Therefore it seems more sensible to compare with the experiment a more simplified description but with much lower and reasonable numbers of fitting parameters. The two limiting cases below correspond to a rather accurate description at the small radii of pairs with an approximate description at larger radii, and to the case when transition between regimes occurs at the large radii of pairs. The experimental situation should be somewhere in between.

The first approach is based on a simple elimination of (c) between (d) and (b) at low temperatures. It is a mean-field approach neglecting the exact structure of the lattice which enters the equations only through the radii of the pairs corresponding to transitions between different diffusion regimes. Since the tunneling rates in the regimes (b) and (d) are temperature independent [and the

time spent in (b) is less or about the duration of the last jump in (c)], the whole temperature dependence is contained in the intermediate processes (c), Eq. (12):

$$\tau(T) \approx \text{const} + \tau_{(C)}^{(T)} \,,$$

$$\tau_{(c)} \approx t_0^{-2} \hbar\Theta(N_{DC} - N_{CB})^{3\alpha}(\Theta\xi/T)^{3\beta/5}\zeta^{6/5} \qquad (15)$$

$$\simeq \tau_0[1 - (T_1/T)^{\beta\gamma/5}]^{3\alpha}(T_1/T)^{3\beta/5}$$

where the major uncertainty is associated with the effective length of the walk in the regime (C), $N_{DC} - N_{CB}$, indices α, β, γ,

$$\tfrac{1}{3} < \alpha < 1, \quad 7 < \beta < 9, \quad \tfrac{1}{6} < \gamma < \tfrac{1}{5} \qquad (16)$$

(see Sec. II), and with the scaling parameters τ_0 (in s) and T_1 (in K):

$$\tau_0 = (\hbar\Theta/t_0^2)(U/\Theta)^3\zeta^{-3/5}N_{DC}^{3\alpha - 3/\gamma} \simeq 10 \,,$$

$$T_1 = \xi\Theta(U^5/\Theta^5\zeta^3)^{1/\beta}N_{DC}^{-5/\beta\gamma} \simeq 0.1 \,. \qquad (17)$$

The main problem with T_1 and τ_0 is the separation, characterized by N_{DC}, where (d) changes into (c). The fit of $\tau_{(C)}$, Eq. (16), to the experimental data of Ref. 1 is based on the location of the maximum (i.e., on the variation of T_1 and τ_0), and is presented in Fig. 2. The analysis shows that the curve (15) is always very steep irrespective of the value of the indices α, β, and γ; changes of these indices within the limits (16) lead to nearly unnoticeable changes in curve 1 in Fig. 2. The very steep decrease at low temperatures is due to the absence of a cutoff parameter: curve 1 in Fig. 2 describes not the total time τ, but only its temperature-dependent part $\tau_{(C)}$; the total pairing time τ, Eq. (15), contains an additional temperature-independent contribution responsible for a cutoff at low temperatures. The description of this cutoff demands a more accurate study of diffusion at small separations.

The second model accounts of the change from (c) to (b) at very small distances with the approximate description at larger distances. It provides one with a more accurate description at small separations, while the description at the radii of higher pairs is somewhat analogous to the above one (hence some similarity of the high-temperature results). The total pairing time τ is
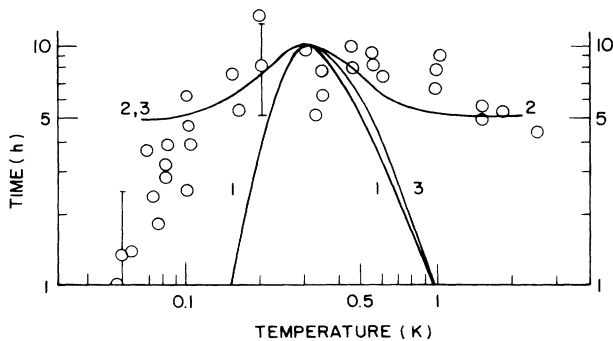
parametrized as

$$\tau = \tau_0 bd \left[\frac{1/bdn}{1+\eta} + \left[\frac{1}{n} + \frac{1}{c+\eta} \right] \left[1 + \frac{1}{d} - \frac{1}{1+\eta} \right] \right] \,,$$
$$(18)$$

where $c \approx 5 \times 10^{-4}$ and $d \approx 4 \times 10^3$ *are not* fitting parameters and are determined only by the ratios of corresponding δE, $n > 1$ characterizes the ratio of jumps in the regimes (c) and (d), and τ_0 (in s) and η are the scaling factors:

$$\tau_0 = (\hbar\Theta/t_0^2)(\zeta\Theta/E_0)^3 \simeq 10^5 \,,$$

$$\eta = (T/T_1)^\beta = \tfrac{1}{2}(T/\xi\Theta)^\beta(\zeta\Theta/E_0)^3(\Theta/E_1)^2 \simeq 10^{-1}(T)^\beta \,,$$

with $E_0 \simeq E_1 \simeq 5$ K. Parameters τ_0 and T_1 (i.e., practically ζ and ξ), and n were used as fitting parameters in comparison with experiment (see Fig. 2). The parameters τ_0, T_1, as in the above case, within the reasonable variation gave the location of the maximum. The behavior to the left from the maximum does not depend on the remaining adjustable parameter, n, and was determined only by nonfitting parameters c, d in Eq. (18). The situation with the parameter $n > 1$ (18) responsible for the
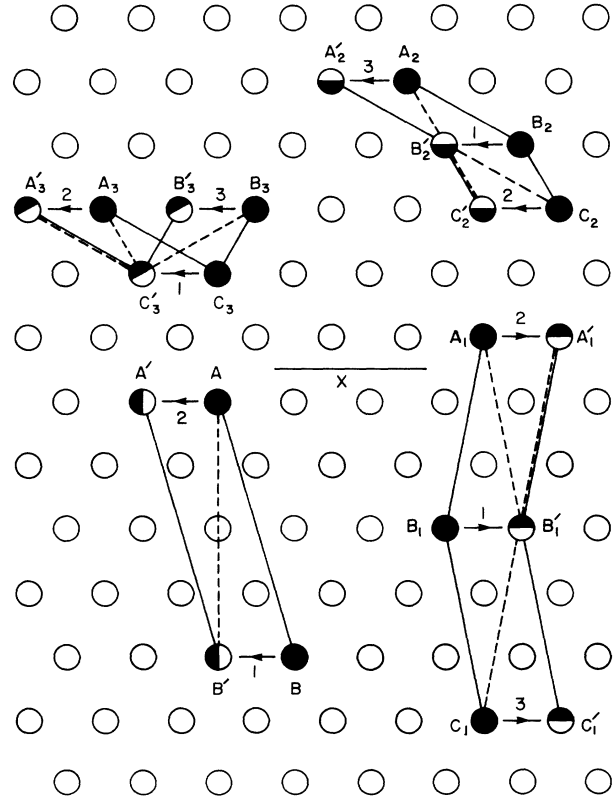

FIG. 3. Examples of crablike moving pairs and triads with effective tunneling rate (20) along the axis x. Pairs AB tunnel to the state $A'B'$ through nonequivalent state AB' (coherent transitions 1 and 2). Triads $A_1B_1C_1$, $A_2B_2C_2$, and $A_3B_3C_3$ tunnel to equivalent states $A'B'C'$ (consequent coherent transitions 1,2,3) through one nonequivalent state.

FIG. 2. Comparison with the experimental data (Ref. 1). Curve 1, $\tau_{(C)}$, Eq. (15); curves 2 and 3, τ, Eq. (18), with $n = 2$ and $n \to \infty$.

high-temperature behavior of τ was less favorable: it is difficult to give an independent estimate of this parameter because the transition from and to the regime (d) is not well defined mathematically. Therefore the real curve is somewhere between curves 2 ($n = 2$) and 3 [$n \to \infty$, $\tau(T \to \infty) \to 0.1$ h; here at high temperatures the model—and the result—is close to Eq. (15)].

The overall agreement of the above descriptions with the experimental data seems to be satisfactory. In order to improve agreement at low temperatures one would need to pay more attention to the exact neighbor configurations at small distances, and to combine both above models. A somewhat worse agreement with experiment at high temperatures was due to a nearly complete neglect of regime (d): at higher temperatures the fraction of the pairing time spent in this regime becomes more noticeable.

The observed absence of the concentration dependence at these concentrations and temperatures is not very puzzling. The main sources of the concentration dependence in this range of temperature and concentrations are associated with the time spent in the regime (d) and the number of jumps in the regime (c) [the transition point from (d) to (c) is certainly concentration dependent]. However, according to the above results, most of the time is spent in the regime (c) at small pair radii, and the time in the regime (d) is negligible. What is more, the concentrations were not low enough to notice the concentration dependence: the coordination number for the hcp lattice is very high, and the mean distances between particles were about 4 at $x = 1\%$, and about 5 for $x = 0.2\%$. Therefore the transitions from (d) to (c) in both cases occurred at the distances 2–3, and were not very noticeable to be reflected on the pairing time even if one neglects the fluctuation corrections to the impurity distribution. To see a considerable concentration dependence of the pairing time one should go either to much lower concentrations, or to higher temperatures where the time in the regime (d) is more important.

The significant concentration dependence (and the absence of the temperature dependence) at higher concentrations are caused by the fact that regime (c) is automatically eliminated, and one deals either only with (d), or with a (d)–(b) sequence. However, in this case the simple mean-field model based on Eqs. (13) and (14) is also not very accurate. Here the pairing trajectories consist of less than three jumps, and as a starting point one should use other geometric considerations. One should calculate the probabilities of fluctuations in particle distributions and in configurations of different small clusters, and to evaluate the pairing time for different cluster configurations. This problem is very different from the one approached above, and should be studied without any mean-field (continual) simplifications.

IV. QUANTUM DIFFUSION OF PAIRS AND TRIADS

There is a general understanding that the diffusion of dilute impurities takes place via independent motion of single particles while the contribution of correlated motion of pairs, triads, etc., is small. Below I demonstrate that it is not always so, and that in case of quantum diffusion with vanishingly small tunneling rate, t_0, the contribution of pairs may sometimes be of the same order as for singles and may become important on some stages of clustering.

The conventional argument is that the correlated motion of particles of a pair is proportional to the product of individual hopping rates and is negligible. The hopping rate for a pair as a whole is proportional to t_0^2 (or to higher degrees of t_0; see below). However, for single impurities, the effective hopping rate is also often proportional to t_0^2, $t = t_0^2 / \Omega$ (1), where Ω is some energy parameter determined by the energy mismatch and the hopping mechanism. Therefore, the comparison of effective tunneling rates for pairs and singles should be done more carefully.

The most effective way of a pair motion in hcp crystals is a crablike motion[8] when a pair comes to a translationally equivalent position via intermediate, slightly disoriented, configuration (see Fig. 3). For several initial and intermediate pair configurations, the energy in the intermediate state is, due to symmetry arguments, exactly the same as in initial and final states;[8] in this case the pair tunneling rate, t_p, is proportional to t_0, $t_p \propto t_0$. If the energy in the intermediate state differs by the quantity δE_i from the energy of equivalent initial and final states, then the effective pair tunneling rate is

$$t_p = \sum_i t_0^2 / \delta E_i \ , \tag{19}$$

where we assumed that energy mismatches are not accompanied with changes in forms of the barriers. Since most of the intermediate states have different energy shifts, it is possible to leave in the sum (19) only the term(s) with the smallest δE_i,

$$t_p = t_0^2 / \delta E \ . \tag{20}$$

It is quite evident that the pair moves mostly in the direction nearly perpendicular to its axis.

The rate t_p (20) should be compared with the hopping rate (1) for singles. First of all, there are qualitative differences. While all the mechanisms responsible for (1) are essentially inelastic (energies in initial and final states are different), the result (20) corresponds to an energy conserving motion—the energy is different only in intermediate (virtual) states. What is more, the tunneling rate t_p (20) corresponds to one-dimensional zone motion of pairs with the energy spectrum $\varepsilon(\mathbf{p}) = 2t_p \cos(\mathbf{p} \cdot \mathbf{a}/h)$, while (1) determines incoherent jumps of singles on the adjacent sites.

Of course, at low temperatures when the motion of singles is determined by the two-phonon mechanism (c), i.e., when $T_0 \ll \delta E$, the pair hopping rate t_p (20) is much larger than for singles (9):

$$t_p / t_C = \delta E / T_0 \gg 1 \ . \tag{21}$$

Up to the values of $\delta E = \zeta^{3/4} \Theta$ the pair hopping rate (20) is also larger than for singles in channel (b), Eq. (3),

$$t_p / t_B = \zeta^2 (\Theta / \delta E)^4 \ . \tag{22}$$

Therefore for dilute impurities, the pairing—and clustering—always go through the stage when the pair mobility becomes much faster, Eqs. (21) and (22), than the change of the distance between particles within the pair. What is more, the most probable trajectories of pair formation (see Fig. 1) go through the pair configurations for which $\delta E_i = 0$, and the corresponding pairs propagate with the tunneling rate t_0 (Ref. 8) which is much larger than all the single rates involved. The pairs stop, and the diffusion is again dominated by singles, only after the pair encounters one or more additional particles, and the larger stable cluster of strongly interacting particles is formed (except for peculiar mobile triads[8]).

There are also some triads—see Fig. 3—for which the effective tunneling rates are the same as for pairs (20): the symmetry considerations make it possible that only in one of two intermediate states the energy is different from an initial (and final) one.

The above diffusion mechanism for pairs—and triads—is reasonable only when the pair radius is much smaller than the average separation between particles: otherwise the initial and final translationally equivalent states would be dephased due to the interaction with other particles, and the pair hopping rate would become determined by inelastic processes with $t_p \propto t_0^3$. As a result, the tunneling (2) is important only if average separations are not less than 10 $(x < 10^{-3})$. For these very dilute systems, clustering inevitably goes through the intermediate stage when the formation of the larger clusters takes place mainly by coherent motion of pairs and triads, while on earlier and later stages the clustering is dominated by an independent motion of single impurity particles. Experimentally this should manifest itself, for example, by roughly the same times of decay for pairs and single signals in the NMR spectrum. If the pairs mobilities were much lower than for singles, the decay of NMR signal for pairs would have been much longer than for singles.

V. SUMMARY

It is shown that the important features of the pairing of o-H$_2$ impurities are not reduced to a proper choice of the appropriate mechanism of quantum diffusion, but should include also a detailed analysis of the diffusion (pairing) trajectories. Only the combination of diffusion regimes with their trajectories allowed to explain the anomalous temperature dependencies of the pairing time observed some time ago. The corresponding concentration dependence, i.e., the lack of it, can also be explained.

The most interesting type of trajectories is associated with the two-phonon mechanism of quantum diffusion when because of the kinetic repulsion the trajectories become rather long. All other tunneling mechanisms result in much shorter trajectories. Since the effective tunneling rates for all known mechanisms of quantum diffusion either decrease or, at least, saturate with decreasing temperatures (at temperatures below approximately 0.3 K), the considerable decrease in pairing times at low temperatures may be explained only by a drastic shortening of pairing trajectories which accompanies a transition from the mechanism with kinetic repulsion to some other low-temperature mechanism of quantum diffusion.

Two numerical models with the minimal set of fitting parameters provided a reasonable agreement with experimental data. The improvement of theory should include a more accurate account for a transition between regimes with random and determinate energy mismatches, and to description of some asymmetry of the hcp lattice with respect to two sublattices. However, such an improvement would demand an introduction of several new, presently unknown constants thus increasing the set of fitting parameters.

At smaller concentrations the clustering of o-H$_2$ impurities is influenced on the intermediate stages of the coherent motion of pairs or triads which sometimes is faster than the diffusion of singles.

The results of the above analysis may also be used in the description of pairing and recombination of atomic hydrogen in crystals of molecular hydrogen or in metals.

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