

## Effects of Subfemtosecond Quantum Correlations in Neutron Scattering on Water

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Several recent experiments have shown that protons, and to some extent also deuterons, show anomalous cross sections when the neutrons have energies in the range 10–100 eV (this results in a Compton scattering process where an essential part of the energy is transferred to one of the scattering particles). Here, an experiment on partially deuterated water, carried out by Chatzidimitriou-Dreismann *et al.*, is analyzed in terms of a theory, which assumes that during the short duration ( $<10^{-15}$  s) of this scattering process, protons are exchange correlated and cannot be considered as independent scattering objects. The quantum decoherence time for protons in liquid water is estimated from a simple model for the interaction of the water protons with hydrogen bonds.

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Several recently published experiments [1–3] using neutron Compton scattering (where an essential part of the neutron energy is transferred to the scattering particle) have shown strong reductions of cross sections for protons as compared to the standard value found in thermal neutron scattering tables. Scattering on deuterons in the same types of compounds shows much smaller anomalies. All data have been obtained by the EVS spectrometer at the Rutherford-Appleton Laboratory, U.K., in which energy selection is done on the outgoing neutrons by transmission through a foil with a sharp nuclear resonance, usually Au-197. It is important to note that neutron Compton scattering is a very fast process, with a duration of  $10^{-16}$  to  $10^{-15}$  s. As has been shown in Ref. [2], it is possible to follow the time dependence of the cross sections over about one decade of observation times, and in metal hydrides it was found that there is a transition towards the normal standard cross-section values when the duration of the scattering event  $\tau_{sc}$  exceeds  $10^{-15}$  s. In other systems [3], the short-fall in cross section remains practically constant over the time range observed.

An explanation, demonstrated theoretically for a model system of two quantum correlated protons or deuterons, has been proposed by Karlsson and Lovesey [4,5]. It is based on the assumption that, during these short times, effects of the indistinguishability of particles must be taken into account, in the same way as is done for the (much slower) thermal neutron scattering by the para ( $J = 0$ ) and ortho ( $J = 1$ ) molecules of  $H_2$ . It is also included in the model that in Compton scattering there is a large momentum transfer, which leads to a final liberation of one of the particles with an energy of several eV.

Here, this solvable model is shown to provide an interpretation of the data on Compton scattering on water, published by Chatzidimitriou-Dreismann *et al.* [1]. These data were taken on a series of water samples with different D content,  $X_D = c_D/(c_H + c_D) = 0.3, \dots, 0.9$  and the results were presented as measured cross-section ratios

$[\sigma_H/\sigma_D]_{obs}$ , compared to what is expected from standard tables,  $[\sigma_H/\sigma_D]_{table} = 10.7$ . Cross sections  $\sigma_H$  and  $\sigma_D$  could not be obtained individually in the work reported in Ref. [1], and these experimental results have been criticized in Ref. [6], as artifacts of the data evaluation process caused by partly overlapping H and D peaks in the time-of-flight spectra. However, later experiments [7] where both H and D intensities could be compared to that of oxygen have fully confirmed the previous results. It was found in [7] that for pure D, the D/O intensity was close to normal and that for a 50%-50% mixture of H and D the H/O cross-section ratio was  $12.5 \pm 1.5$  instead of the expected value 19.4, i.e., the same reduction for H as in Ref. [1].

The theoretical model [4,5] considers a system consisting of two identical particles  $\alpha$  and  $\beta$ , with spin  $I$ , in total isolation from the environment. The spins are coupled to a spinor  $\chi_M^J(\alpha, \beta)$  with  $J = 0, \dots, 2I$ . The spatial wave functions are described in terms of nonoverlapping functions  $\phi_1(\mathbf{R})$  and  $\phi_2(\mathbf{R})$  localized around two nonequivalent sites, labeled 1 and 2. The initial state is

$$|i\rangle = (1/\sqrt{2})\{\phi_1(\mathbf{R}_\alpha)\phi_2(\mathbf{R}_\beta) + \zeta\phi_1(\mathbf{R}_\beta)\phi_2(\mathbf{R}_\alpha)\} \\ \times \chi_M^J(\alpha, \beta), \quad (1)$$

where  $\zeta = (-1)^J$ , following the rules for indistinguishable particles. The neutron-nuclear interaction operator is  $V = b_\alpha \exp(i\mathbf{k} \cdot \mathbf{R}_\alpha) + b_\beta \exp(i\mathbf{k} \cdot \mathbf{R}_\beta)$ , where the scattering length operators,  $b$ , are independent of the position variable. It is assumed that the neutron correlation length  $l_{coh}$  is long enough to allow scattering on both nuclear sites, i.e.,  $l_{coh} > d = |\mathbf{R}_1 - \mathbf{R}_2|$ . The scattering matrix elements are taken between  $|i\rangle$  and a final state  $|f\rangle$ , with the proposed form

$$|f\rangle = (1/\sqrt{2})\{\exp(i\mathbf{p}' \cdot \mathbf{R}_\alpha)\Psi(\mathbf{R}_\beta) \\ + \zeta' \exp(i\mathbf{p}' \cdot \mathbf{R}_\beta)\Psi(\mathbf{R}_\alpha)\} \chi_{M'}^{J'}(\alpha, \beta). \quad (2)$$

This expression represents a situation where the wave functions are still entangled, but one of the particles ( $\alpha$

or  $\beta$ , not yet distinguishable) is emitted in the form of a plane wave with momentum  $\mathbf{p}' = \mathbf{k} + \mathbf{p}$ , where  $\mathbf{k}$  is the wave vector transfer and  $\mathbf{p}$  the momentum that the struck particle has initially in its thermal motion. The wave function  $\Psi(\mathbf{R})$  represents the particle that remains in the system after the scattering event. If the nuclear spin is flipped in the process,  $\zeta' = (-1)^J$  is different from  $\zeta$  and  $\chi_M^{\zeta'}(\alpha, \beta)$  is the new spinor state. If  $T_1$  and  $T_2$  are the coefficients in an expansion of  $\Psi$  in terms of  $\phi_1$  and  $\phi_2$ , and all terms consistent with angular momentum coupling are included, the single-particle scattering cross section  $\sigma_{sp}$  is reduced by [5]

$$\begin{aligned} f_{HH} &= \sigma_{\text{eff}} / \sigma_{sp} \\ &= (1/2)(2I + 1)^{-1} \{ |T_1 + \exp(i\mathbf{p} \cdot \mathbf{d})T_2|^2 \\ &\quad + (I + 1) |T_1 - \exp(i\mathbf{p} \cdot \mathbf{d})T_2|^2 \} \end{aligned} \quad (3a)$$

for half-integral particle spins (protons), and

$$\begin{aligned} f_{DD} &= (1/2)(2I + 1)^{-1} \{ (I + 1) |T_1 + \exp(i\mathbf{p} \cdot \mathbf{d})T_2|^2 \\ &\quad + I |T_1 - \exp(i\mathbf{p} \cdot \mathbf{d})T_2|^2 \} \end{aligned} \quad (3b)$$

for integral particle spins (deuterons). Lowest possible values are obtained if  $\mathbf{p} \perp \mathbf{d}$  which gives  $\exp(i\mathbf{p} \cdot \mathbf{d}) = \exp(i\mathbf{p} \cdot |\mathbf{R}_1 - \mathbf{R}_2|) = 1$ . If, furthermore,  $T_1 = T_2 = 1/\sqrt{2}$ , which is valid with no shakeup of the localized states (see Ref. [4]), the result is  $f_{HH} = 1/4$  for proton pairs, and  $f_{DD} = 2/3$  for deuteron pairs. When the entanglement of the spatial and spin degrees of freedom is broken by interaction with the environment the spatial part of Eq. (2) is reduced to a simple product, with the result that  $f_{HH} = f_{DD} = 1$ .

In the water molecule, the H-H (or D-D) distance is 1.4 Å. At the same time such a pair is sufficiently isolated from hydrogen atoms in neighboring molecules for intermolecular H-H correlations to be neglected. This allows the use of the two-particle model for a quantitative comparison with the observed data. The condition  $l_{\text{coh}} \gg d$  for the neutron correlation length is reasonably well fulfilled since the wavelength uncertainty  $\Delta\lambda$  can be calculated from the parameters for the Au-resonance foil to be 0.0034 Å, which gives  $l_{\text{coh}} = \lambda^2/2\Delta\lambda = 2.5$  Å. If the envelope of the neutron wave packet is assumed to have a Gaussian shape of width  $l_{\text{coh}}$ , a value of  $d/l_{\text{coh}} = 0.6$  will correspond to an overlap factor of 0.90; for U foils, which have a sharper resonance, the overlap factor is higher,  $\approx 0.95$  (numbers obtained by considering the decrease of the Gaussian at points  $x = \pm d/2$ ).

In the free water molecule there are three fundamental modes, the symmetric stretching (frequency  $\nu_s \approx 1.096 \times 10^{14} \text{ s}^{-1}$ ), the bending ( $\nu_b \approx 0.445 \times 10^{14} \text{ s}^{-1}$ ), and the asymmetric stretching ( $\nu_{as} \approx 1.126 \times 10^{14} \text{ s}^{-1}$ ). The H-O-H angle is  $104^\circ$  and the momentum vectors  $\mathbf{p}$  [cf. Eqs. (3a) and (3b)] of the local vibrations lie at

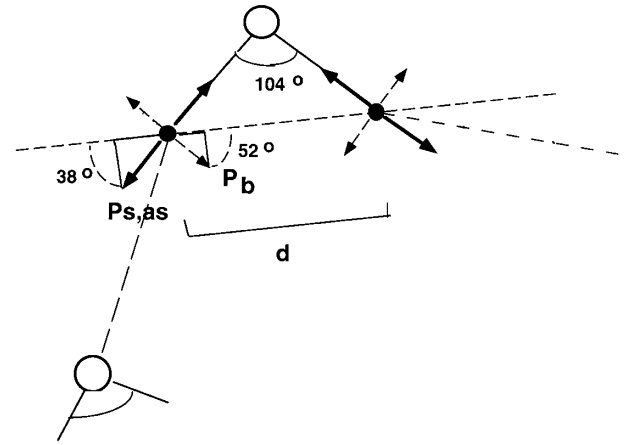


FIG. 1. Illustrating the geometry of symmetric (*s*) and asymmetric (*as*) stretching vibrations and bending vibrations (*b*) in the free water molecule. In liquid water there are slight modifications in geometry and the vibrations are perturbed by interaction with neighboring molecules.

$38^\circ$  for the stretching modes, and  $52^\circ$  for the bending mode (cf. Fig. 1). The (*s*) and (*as*) vibrations have weight factors  $\cos^2 38 = 0.621$  and the (*b*) mode has the factor  $\cos^2 52 = 0.379$  for vibrations parallel to  $\mathbf{d}$ . For  $\mathbf{p} \perp \mathbf{d}$  [ $\cos(\mathbf{p} \cdot \mathbf{d}) = 1$ ], the corresponding factors are 0.379, respectively, 0.621. The (*s*) and (*as*) vibrations are dominant and a proper weighting leads to factors 0.580 and 0.420 for parallel and perpendicular components.

The expressions  $|T_1 \pm \exp(i\mathbf{p} \cdot \mathbf{d})T_2|^2$  in Eqs. (3a) and (3b) can be written, for  $T_1 = T_2 = 1/\sqrt{2}$ , as  $(1/2)|1 \pm \exp(i\mathbf{p} \cdot \mathbf{d})|^2 = 1 \pm \cos(\mathbf{p} \cdot \mathbf{d})$ , which has the trivial value  $(1 \pm 1)$  for the component with  $\mathbf{p} \perp \mathbf{d}$ . For  $\mathbf{p} \parallel \mathbf{d}$ ,  $\cos(\mathbf{p} \cdot \mathbf{d})$  must be averaged over the momentum distribution  $n(\mathbf{p})$  of the local vibrations, but it is found that  $\langle \cos(\mathbf{p} \cdot \mathbf{d}) \rangle = \int n(\mathbf{p}) \cos(\mathbf{p} \cdot \mathbf{d}) d\mathbf{p} \ll 1$  because the cosine function oscillates strongly within the range of  $\mathbf{p}$ . Consequently, the prediction for proton pairs, i.e., pure  $\text{H}_2\text{O}$ , is

$$\begin{aligned} f_{HH} &= 0.58f_{\perp} + 0.42f_{\parallel} \\ &= 0.58(1/4)[(1/2) + (3/2)] + 0.42(1/4)(2) \\ &= 0.395. \end{aligned} \quad (4)$$

The estimated neutron overlap factors will reduce the cross-section anomaly  $(1 - f)$  by 0.90 for Au foils and 0.95 for U-foil analysis and give the effective  $f_{HH} = 0.45$  for Au foils and 0.42 for U foils. For deuteron pairs, the corresponding prediction is  $f_{DD} = 0.65$  and 0.63. Since there are no exchange correlations between H and D, the model predicts  $f_{HD} = 1$ .

In partially deuterated water, the probability to form  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , and  $\text{HDO}$  can be expressed in terms of the partial concentrations  $c_H$  and  $c_D$  (where  $c_H + c_D = 1$ ) as  $p_{HH} = c_H^2$ ,  $p_{DD} = c_D^2$ , and  $p_{HD} = 2c_H c_D$ , respectively. These values are calculated for the different deuterium

fractions  $X_D = c_D/(c_H + c_D) = c_D$  used as a mixing parameter in Ref. [1], by which the cross-section ratio can be expressed as

$$\begin{aligned} [\sigma_H/\sigma_D]_{\text{eff}} &= \{[\sigma_H]_{\text{sp}}(f_{\text{HH}} \cdot p_{\text{HH}} + (1/2)p_{\text{HD}})/c_H\} / \{[\sigma_D]_{\text{sp}}(f_{\text{DD}} \cdot p_{\text{DD}} + (1/2)p_{\text{HD}})/c_D\} \\ &= [\sigma_H/\sigma_D]_{\text{sp}} \{f_{\text{HH}} + c_D(1 - f_{\text{HH}})\} / \{1 - c_D(1 - f_{\text{DD}})\}, \end{aligned} \quad (5)$$

where  $[\sigma_H/\sigma_D]_{\text{sp}} = 10.7$ . The factors  $f_{\text{DD}}$  are taken as free parameters since deuterium systems are known [2] to show much smaller anomalies than the corresponding proton systems. In Fig. 2(a) the experimental data taken with the Au-analyzer foil are compared with the model prediction (for parameter values  $f_{\text{HH}} = 0.45$ ;  $f_{\text{DD}} = 0.90, 0.95$ , and  $1.00$ ) and in Fig. 2(b) the U-foil data are compared with predictions for  $f_{\text{HH}} = 0.42$ ;  $f_{\text{DD}} = 0.80, 0.90$ , and  $1.00$ . It is no doubt that the large reduction of the cross-section ratio  $\sigma_H/\sigma_D$  originates essentially from the quantum correlations of the protons in the water molecule. The smaller reduction for deuterium pairs is a consequence of their spin coupling [see Eqs. (3a) and (3b)] and of their higher mass. It was assumed in [4,5] that the exchange correlations are fully developed only for HH

pairs, that they are weaker for DD pairs, and practically absent for heavier nuclei. An overall average of the fits indicates that  $f_{\text{DD}} \neq 1$  and has a value  $\approx 0.90$ . Attempts have also been tried to introduce reduction factors  $f_{\text{HD}} \neq 1$  in Eq. (5) above, multiplying the  $p_{\text{HD}}$  terms, but this leads to disagreement with the experimental facts. Proton-deuteron entanglement (which is conceivable, but must then be caused by other mechanisms than exchange of indistinguishable particles) does not therefore seem to play any essential role.

At this point it is relevant to ask if it is reasonable that quantum correlations can be sustained over the times involved in neutron Compton scattering. Actually, the experimental method itself offers a possibility to perform an analysis in terms of the scattering time  $\tau_{\text{sc}}$ , i.e., the effective duration of the interval over which the system is observed. Reiter and Silver [8], and later Watson [8] have derived the relation  $\tau_{\text{sc}}(\theta) \approx M/[k(\theta)\langle p^2 \rangle^{1/2}]$ , where  $\theta$  is the scattering angle for the neutrons,  $M$  is the mass of the scattering nucleus,  $k(\theta)$  is the momentum transfer, and  $\langle p^2 \rangle^{1/2}$  is proportional to the square root of the mean kinetic energy of the local vibrations. This relation was first exploited in the work of Karlsson *et al.* [2] to analyze scattering on protons in metal hydrides. The largest cross-section anomalies were found in the high-angle data, which correspond to the shortest observation times. For  $\tau_{\text{sc}} > 10^{-15}$  s, standard values of  $\sigma_H/\sigma_M$  ( $M = \text{Nb}$ ) were observed. For scattering on water the data fall in a shorter time range. The anomalies in  $\sigma_H/\sigma_D$  in water persist up to at least  $5 \times 10^{-16}$  s, a time that corresponds to motion over a distance of about  $0.1 \text{ \AA}$  for a recoiling proton.

The dynamics of  $\text{H}_2\text{O}$  molecules in water at ambient temperatures has been studied extensively by means of vibrational spectroscopy [9,10]. The vibrations are similar to those in free  $\text{H}_2\text{O}$  molecules, but perturbed by the presence of the H bridges to the nearby molecules. In a simple molecular dimer model, with one of the H atoms free to vibrate as in the gaseous state and the other one involved in a hydrogen bond, the stretching vibrations  $\nu_s$  (or  $\nu_{as}$ ) of the latter will be coupled [9] to the vibration in the H bond itself (characteristic frequency  $\nu_\sigma$ ) to bands with frequency  $\nu_s \pm \nu_\sigma$ . These couplings are changing considerably with time during a full vibrational period and give rise to a band with width about  $0.03 \text{ eV}$  [11].

Decoherence theory states that the entanglement in a system is broken only when the environment vectors, to which it is coupled, form an orthogonal set. This means that, as long as only a few vibrational modes are present, as in the OH stretching and bending vibrations in the free  $\text{H}_2\text{O}$  molecule, the entanglement will not vanish

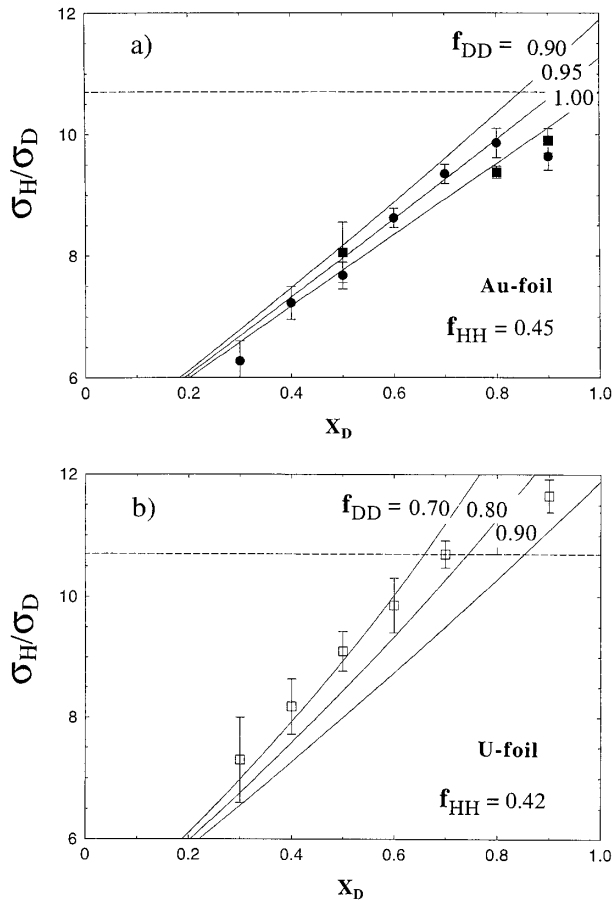


FIG. 2. (a) Experimental data from Ref. [1], using Au-resonance foils, for the ratio of proton/deuteron cross sections at different deuterium concentrations, compared with predictions from the present theory with deuteron reduction factors as indicated. (b) As in (a), but comparing data taken with U-resonance foils.

but will disappear and reappear under the time evolution. For complete decoherence it is necessary that the two protons in the pair couple to modes whose frequencies are changing randomly. Here, the disruption of the proton entanglement will simply be considered by returning to

$$|f'\rangle = (1/\sqrt{2})\{\exp[i\mathbf{p}' \cdot (\mathbf{R}_\alpha - \mathbf{R}_1)]T_2\phi_2(\mathbf{R}_\beta) + \exp[i\mathbf{p}' \cdot (\mathbf{R}_\alpha - \mathbf{R}_2)]T_1\phi_1(\mathbf{R}_\beta) \\ + \zeta'\{\exp[i\mathbf{p}' \cdot (\mathbf{R}_\beta - \mathbf{R}_1)]T_2\phi_2(\mathbf{R}_\alpha) + \exp[i\mathbf{p}' \cdot (\mathbf{R}_\beta - \mathbf{R}_2)]T_1\phi_1(\mathbf{R}_\alpha)\}\}. \quad (7)$$

This is one of two possible final states. The other one,  $|f''\rangle$ , is obtained by interchanging indices  $\alpha$  and  $\beta$ . From (7) it can be distinguished what happens if the two emission sites are perturbed differently by the environment.

If the local function  $\phi_1(\mathbf{R})$  at site 1 is coupled to a vibration with angular frequency  $\omega_s = 2\pi\nu_s$  and  $\phi_2(\mathbf{R})$  at site 2 to a vibration with  $\omega_s + \omega_\sigma = 2\pi(\nu_s + \nu_\sigma)$ , for the two H atoms in a water dimer, the coupled wave function will be of the form (extracting the common phase factor  $\exp[i\omega_s t] \exp[i\mathbf{p}' \cdot \mathbf{R}_1]$ ),

$$(1/\sqrt{2})\{\exp[i\mathbf{p}' \cdot \mathbf{R}_\alpha]T_2\phi_2(\mathbf{R}_\beta) + \zeta' \exp[i\omega_\sigma t] \exp[i\mathbf{p}' \cdot \mathbf{R}_\alpha] \exp[i\mathbf{p}' \cdot \mathbf{d}]T_1\phi_1(\mathbf{R}_\beta)\} \\ = (1/\sqrt{2})\{\exp[i\mathbf{p}' \cdot \mathbf{R}_\alpha]T_2\phi_2(\mathbf{R}_\beta) + \exp[i\phi] \exp[i\omega_\sigma t] \exp[i\mathbf{p}' \cdot \mathbf{d}] \exp[i\mathbf{p}' \cdot \mathbf{R}_\beta]T_1\phi_1(\mathbf{R}_\alpha)\}. \quad (8)$$

In the last line, this has been written with  $\zeta' = (-1)^{J'} = \exp[i\phi]$ , where  $\phi = \pi$  for  $J'$  odd, and  $\phi = 0$  for  $J'$  even. Here, the spatial proton-proton entanglement disappears and reappears with the factor  $\exp[i(\phi + \omega_\sigma t)]$ . However, if  $\omega_\sigma$  changes with time during the observation by the neutron this factor will decay with a characteristic decoherence time. In reality, both H atoms in water are taking part in hydrogen bonds (cf. Fig. 1) and the actual spread in  $\omega_\sigma$  is about  $\sigma \approx 0.5 \times 10^{14}$  rad/s, corresponding to the 30 meV found in Ref. [11]. If the distribution in  $\omega_\sigma$  is represented by a Gaussian function, centered on  $\omega_{\sigma 0}$ , one obtains for the mean value of the phase factor in Eq. (8),

$$\int \exp[-(\omega_\sigma - \omega_{\sigma 0})^2/4\sigma^2] \exp(i\omega_\sigma t) d\omega_\sigma = \exp[-\sigma^2 t^2] \exp(i\omega_{\sigma 0} t), \quad (9)$$

where the decay factor  $\exp[-\sigma^2 t^2]$  measures the decoherence due to the naturally occurring processes in water at room temperature. This leads to a characteristic decoherence time of  $2 \times 10^{-14}$  s (or 20 fs). In violent measuring processes, like the neutron Compton scattering, the environment will be strongly perturbed by the recoiling particle at times longer than femtoseconds. Weakly inelastic neutron scattering may still be able to follow the decoherence in water up to the  $10^{-14}$  s range.

With this, it has been shown that the reductions of neutron cross sections for hydrogen observed under Compton scattering conditions can be well explained by the assumption that protons (and to a lesser extent deuterons) are exchange correlated. H-D quantum correlations seem to be absent. The proton-proton exchange correlations in water are expected to remain over several femtoseconds, but not over the longer times characteristic for thermal neutron scattering. The consequences for hydrogen bonding of these short-lived correlations should be investigated further; correlation effects may be important for the initial stages of bonding and chemical reactions. Such effects are expected to be much smaller if the systems are deuterated.

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the spatial part of the final state in the Karlsson-Lovesey model [4,5], which can be written as a superposition of states with particle  $\alpha$  starting from  $\mathbf{R}_\alpha = \mathbf{R}_1$  (with  $\beta$  staying at site  $\mathbf{R}_\beta = \mathbf{R}_2$ ), and  $\alpha$  starting from  $\mathbf{R}_\alpha = \mathbf{R}_2$ , with  $\beta$  remaining at site  $\mathbf{R}_\beta = \mathbf{R}_1$ .

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