The Harmonic Picture of Nuclear Mean Kinetic Energies in Heavy Water

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Abstract. This paper presents a study of the total mean kinetic energy, $\langle E_K \rangle$, and of individual projections along a given molecular axis, $\langle E_K \rangle_\alpha$, for D and O nuclei in D_2O, derived using a harmonic model. Our theoretical approach assumes decoupling amongst translational, rotational and vibrational modes. Resulting values of these dynamical quantities are discussed in terms of the anisotropy of the quantum kinetic energy tensor, its relation to the local potential, and deviations from the hypothesis of harmonicity and mode decoupling. Results are compared with corresponding quantities obtained from Deep Inelastic Neutron Scattering experiments performed on liquid and solid D_2O, where the short-time dynamics and local environment of D and O atoms were probed. The present study confirms an overall picture where even small changes in the short-range environment of D and O nuclei have a strong influence on the quantum behaviour of heavy water.

1. Introduction

The microscopic dynamics of liquid water still continues to challenge and attract great interest from theorists and experimentalists due to the fundamental relevance of this system in the biological and physical sciences [1]. A number of properties and anomalies of this molecule are associated with the presence of hydrogen bonds (HBs), influencing the structure and network in bulk ice and water, as well as its interaction with the surrounding environment. The quantum dynamics of hydrogen participating in HB influences the HB structure network, due to the non-commutativity of nuclear position and momentum operators, through nuclear quantum effects (NQEs) [2, 3]. Deep Inelastic Neutron Scattering (DINS), also known as Neutron Compton Scattering (NCS), is a unique and quantitative tool particularly well suited to probe the quantum behaviour of atomic nuclei. DINS allows one to highlight NQEs associated with HB breaking and distortion, through the measurement of single-particle dynamical quantities, *i.e.*, nuclear momentum distributions, $n(p)$, and mean kinetic energies, $\langle E_K \rangle$ [4–6]. Most recent DINS studies have shown that the merits and strengths of the technique have expanded beyond measurements of $n(p)$ for light elements (hydrogen, deuterium, helium, lithium), as it is now possible to obtain information on heavier nuclides such as carbon, oxygen, fluorine or sodium [4, 7–14].

In recent years, several *ab initio* Path Integral Molecular Dynamics (PIMD) simulations [15–18] and DINS experiments supplemented by PIMD simulations [19–28] have been performed to study the structure and dynamics of liquid water over a wide range of temperatures and pressures to investigate how these are directly influenced by NQEs. Moreover, some phenomenological models [29, 30] assuming harmonicity and decoupling amongst translational, rotational and vibrational modes have been used to calculate values of the total mean kinetic energy $\langle E_K \rangle$, as well as individual contributions $\langle E_K \rangle_\alpha$ along the three principal axes of the quantum kinetic energy tensor of the anisotropic $n(p)$. These models have been applied to describe the single-particle H dynamics in water [31–34] and in H_2S [35] by recourse to inter- and intra-molecular frequencies obtained from optical spectroscopy and Inelastic Neutron Scattering (INS).

In the following, we introduce a harmonic model for a generic triatomic molecule and discuss differences with other models in the literature. This model is used to predict kinetic energies for the particular case of D and O atoms in heavy water. These predictions are discussed and compared against data from a previous DINS experiment [8].

2. Harmonic model

Let us consider a molecule (D_2O) with the $N = 3$ atoms in the $y - z$ plane. For each of its $3N - 6 = 3$ internal modes, one can define a symmetry-adapted coordinate system (S_1, S_2, S_3) as illustrated in Figure 1. To first order, each atom undergoes harmonic motions along the normal coordinates S_i ($i = 1, 2, 3$). Quantum mechanically, these motions necessarily lead to the emergence of a zero point energy proportional to the vibrational frequency ω_i. The potential energy of the system is the result of three pair interactions with restoring forces proportional to the displacement from the mean nuclear positions. The proportionality constant for the two D-O pairs is given by

$$k_{OD} = \frac{m_D \lambda_3 (1 + \mu \cos^2 \alpha)}{(1 + \mu \sin \alpha \cos \alpha)^2}, \tag{1}$$

where $\omega_3 = \sqrt{\lambda_3}$ is the asymmetric stretch frequency, $\mu = 2m_D/m_O$ and m_D and m_O the nuclear masses. Likewise, the proportionality constant for the D-D pair is given by

$$k_{DD} = \frac{m_D \lambda_2 \left[k_{OD}(1 + \mu \cos^2 \alpha) - m_D \lambda_2 \right]}{2 \left[k_{OD}(1 + \mu) \cos^2 \alpha - m_D \lambda_2 \right]}, \tag{2}$$

with $\omega_2 = \sqrt{\lambda_2}$ being the bending frequency. Equations (1) and (2) are derived from the secular equation $|B - \lambda A| = 0$, with A and B being the kinetic- and potential-energy matrices expressed in the symmetry coordinates $\{S_1, S_2, S_3\}$, $\lambda_i = \omega_i^2$ are the eigenvalues of the matrix and $|\dots|$ indicates the value of its determinant. The symmetry of the modes allows to express the dynamical 3×3 matrix as a $(2 \times 2)_S \otimes (1 \times 1)_A$ block matrix. Since only two observables, $\omega_2 = \sqrt{\lambda_2}$ and $\omega_3 = \sqrt{\lambda_3}$, are needed in order to fix the free parameters of the model, k_{OD} and k_{DD}, it is possible to evaluate the third eigenvalue of the secular equation, λ_1, and consider the difference with the measured value of ω_1^2 as an estimate of the accuracy of the model. In the case of heavy water, the symmetric stretching frequency evaluated within the present model is 20% higher than the measured one [36]. If one makes use of more than two parameters in an attempt to improve the accuracy of the model, then no prediction can be made on known observables and control on the accuracy of the model is lost.

The asymmetric $(1 \times 1)_A$ block matrix has an eigenvector $s_A = S_3$ that in Cartesian coordinates corresponds to a displacement vector $\xi_A = (y_D, z_D, y_{D'}, z_{D'}, y_O, z_O) = (a, b, a, -b, -\mu a, 0)$, with $a = \sin \alpha$ and $b = \cos \alpha$, with no dependence on the stretching
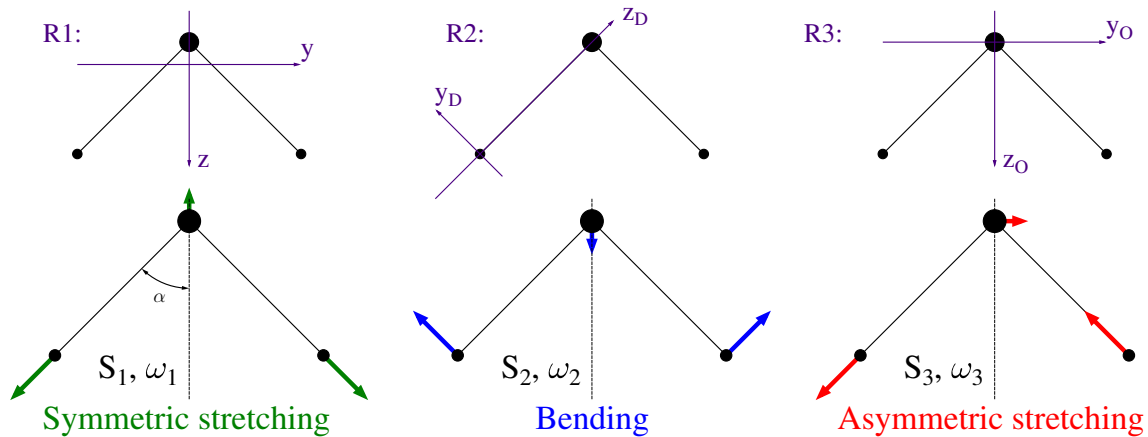
Figure 1. Definition of the symmetry coordinates for an isolated water molecule as used in the derivation of the coefficients f_i. The molecule lies in the $y-z$ plane and each axis may be oriented according to the reference frames R1, R2 and R3 (see text).

frequency. The symmetric $(2 \times 2)_{\mathcal{S}}$ block matrix has eigenvectors $s_{\mathcal{S}} = S_1 + v(\lambda)S_2$, with

$$v(\lambda) = \frac{\left(2k_{OD}\mu(1+\mu\cos^2\alpha) - 4k_{DD} - m_O\lambda\mu^2\right)\sin(2\alpha)}{8k_{DD}\cos^2\alpha + k_{OD}\mu^2\sin^2(2\alpha) - 2m_O\lambda\mu(1+\mu\sin^2\alpha)} \tag{3}$$

and with the limits $v(\lambda) \ll 1$ for $\lambda \to \lambda_1$ and $v(\lambda) \gg 1$ for $\lambda \to \lambda_2$. The corresponding displacement vector $\xi_{\mathcal{S}} = (c, d, -c, d, 0, -\mu d)$ in Cartesian coordinates is defined by $c = \sin(\alpha) + v(\lambda)\cos(\alpha)$ and $d = \cos\alpha - v(\lambda)\sin\alpha$. Each $i-th$ mode contributes to the kinetic energy of atom j with a fraction $f_{j,i} = \epsilon_{j,i}/\sum_j \epsilon_{j,i}$ of the mode energy, with $\epsilon_{j,i} = m_j(\dot{y}_{j,i}^2 + \dot{z}_{j,i}^2)/2$. The conditions imposed on the components of $\xi_{\mathcal{A}}$ and $\xi_{\mathcal{S}}$ reflect conservation of linear momentum in the two directions y and z only when these axes are defined as shown by reference frame R1 in Figure 1. However, the quantities $\epsilon_{j,i}$ depend only on the modulus of the vector (y_j, z_j) and then the energy fractions $f_{j,i}$ are invariant under axial rotation.

Following the previous discussion, one can numerically evaluate the parameters $f_{j,i}$ through Eqs. (1), (2) and (3) and the definition of $\xi_{\mathcal{S}}$ and $\xi_{\mathcal{A}}$. The calculation can be readily implemented in a computer routine and applied to any triatomic molecule. The sequential character of this procedure distinguishes the present model from others based on three independent force constants, the latter leading to a hard-to-solve system of coupled nonlinear equations.

Assuming an average frequency ω_τ corresponding to the translational modes, we can define $\tau_j = m_j/\sum_j m_j$. This parameter dictates the amount of energy that the $j-th$ atom draws from this particular vibration. Similar considerations apply to the rotational modes of frequency ω_ρ, whose contribution to the kinetic energy is defined by the ratio of moments of inertia $\rho_j = \bar{I}_j/\sum_j \bar{I}_j$. The quantity $\bar{I}$ corresponds to the spatial average of moments of inertia. With these definitions, the total mean kinetic energy of one atom (D or O) can be written as

$$\langle \mathcal{E}_K \rangle = 3\tau\langle \mathcal{E} \rangle_\tau + 3\rho\langle \mathcal{E} \rangle_\rho + \sum_{i=1}^{3} f_i\langle \mathcal{E} \rangle_i, \tag{4}$$

that is, as the sum of three translations, three rotations and three vibrations, each one with energy $\langle \mathcal{E} \rangle_s = \frac{\hbar\omega_s}{4}\coth\frac{\hbar\omega_s}{2k_BT}$, where $s = \tau, \rho, 1, 2, 3$. Let us now consider a reference frame

		τ	ω_τ [meV]	ρ	ω_ρ [meV]	f_1	ω_1 [meV]	f_2	ω_2 [meV]	f_3	ω_3 [meV]	2α [degrees]
Ice	D	0.1	17.7	0.456	52.7	0.479	278	0.405	151	0.460	294	108.4
	O	0.8		0.088		0.042		0.190		0.079		
Water	D	0.1	15.1	0.457	46.9	0.499	296	0.410	150	0.458	310	106.0
	O	0.8		0.086		0.001		0.180		0.084		

Table 1. Optical frequencies and $\widehat{DOD}$ angles taken from Refs. [36–40], along with calculated values for τ, ρ, f_i using our model.

x,y,z (with the x axis perpendicular to the molecular plane) centred at the average position of each nucleus, representing the three principal axes of an anisotropic $n(\mathbf{p})$. The following interpretation of the DINS observables is based on the definition of a particular orientation of (y, z) for each atom. In the case of the D (Fig 1, R2), the z axis is taken in the direction of the stretching mode, $i.e.$, the mode that mostly contributes to the kinetic energy, the y axis in the direction of the bending mode and the rotation mode around the x axis. Rotations around y and z will contribute to the kinetic energy in the x direction. By considering an additional translational contribution along each direction, one can define for the D atom

$$\langle \mathcal{E}_K \rangle_x = \tau\langle \mathcal{E} \rangle_\tau + 2\rho\langle \mathcal{E} \rangle_\rho; \quad \langle \mathcal{E}_K \rangle_y = \tau\langle \mathcal{E} \rangle_\tau + \rho\langle \mathcal{E} \rangle_\rho + f_2\langle \mathcal{E} \rangle_2; \quad \langle \mathcal{E}_K \rangle_z = \tau\langle \mathcal{E} \rangle_\tau + f_1\langle \mathcal{E} \rangle_1 + f_3\langle \mathcal{E} \rangle_3. \quad (5)$$

In the case of O, the most relevant contribution to the kinetic energy arises along the direction of the bending and the symmetric stretching modes (see Fig 1). Consequently, we take the z axis along this direction, while the y axis remains orthogonal and along the asymmetric stretching and the rotation around the x axis. For O one can then define

$$\langle \mathcal{E}_K \rangle_x = \tau\langle \mathcal{E} \rangle_\tau + \rho\langle \mathcal{E} \rangle_\rho; \quad \langle \mathcal{E}_K \rangle_y = \tau\langle \mathcal{E} \rangle_\tau + f_3\langle \mathcal{E} \rangle_3; \quad \langle \mathcal{E}_K \rangle_z = \tau\langle \mathcal{E} \rangle_\tau + f_1\langle \mathcal{E} \rangle_1 + f_2\langle \mathcal{E} \rangle_2. \quad (6)$$

These contributions are calculated using frequencies from optical spectroscopy [36–40] as shown in Table 1. The corresponding $\langle \mathcal{E}_K \rangle$ and $\langle \mathcal{E}_K \rangle_\alpha$ are reported in Table 2. The values for the energy fractions τ, ρ, f_i have also been evaluated within the present model. These results are in good agreement with those reported in the literature [32, 33].

3. Results and Conclusion
We compare calculated values for $\langle \mathcal{E}_K \rangle$ and $\langle \mathcal{E}_K \rangle_\alpha$ with the results of DINS measurements on D$_2$O at $T = 274$ K (ice) and $T = 280$ K (liquid) [8], performed using the VESUVIO spectrometer at the ISIS Pulsed Neutron and Muon Source (Rutherford Appleton Laboratory, UK) [41, 42]. DINS measurements are conducted at high momentum and energy transfers ($\hbar q$ and $\hbar\omega$, respectively) thus allowing the scattering process to be described within the framework of the Impulse Approximation (IA) [43, 44]. The latter assumes that neutron scattering is incoherent and occurring within time scales much shorter than the typical relaxation times of collective excitations. Under these conditions, the struck particle recoils freely from the collision, with negligible inter-particle interactions in its final state ($i.e.$, the wave function of the particle in its final state is a plane wave). The incoherent dynamic structure factor $S(\mathbf{q}, \omega)$ is then expressed in terms of the single-particle momentum distribution $n(\mathbf{p})$

$$S_{IA}(\mathbf{q}, \omega) = \int n(\mathbf{p})\delta\left(\omega - \omega_r - \frac{\mathbf{p} \cdot \hat{\mathbf{q}}}{M}\right) d\mathbf{p}, \quad (7)$$

with $\hbar\omega_r = \hbar^2 q^2/2M$ being the recoil energy and M the mass of the struck atom. One can then model the $n(\mathbf{p})$, whose variance is in turn related to the single-particle mean kinetic energy $\langle E_K \rangle$,

	$\langle E_K\rangle_x$ [meV]	$\langle \mathcal{E}_K\rangle_x$ [meV]	$\langle E_K\rangle_y$ [meV]	$\langle \mathcal{E}_K\rangle_y$ [meV]	$\langle E_K\rangle_z$ [meV]	$\langle \mathcal{E}_K\rangle_z$ [meV]	$\langle E_K\rangle$ [meV]	$\langle \mathcal{E}_K\rangle$ [meV]
D								
Liquid	18.8±1.1	15.1	38.6±2.5	22.9	54.2±2.4	73.6	112±2	112
Solid	22.5±1.8	15.9	37.4±2	23.8	48.1±3.4	68.3	108±2	108
O								
Liquid	16.0±2.3	10.4	21.0±0.6	16.1	24.1±2.1	16.4	61.1±3.1	43.4
Solid	16.2±2.3	11.0	20.1±1.6	15.4	24.2±1.4	19.7	60.4±4	46.1

Table 2. Comparison between experimental $\langle E_K\rangle$ and $\langle E_K\rangle_\alpha$ from Ref. [8] and our model using the parameters in Table 1.

through a spherical average of a multivariate Gaussian momentum distribution [8, 17, 35, 45, 46]

$$n(\mathbf{p}) = \frac{1}{\sqrt{8\pi^3}\sigma_x\sigma_y\sigma_z} \exp\left(-\frac{p_x^2}{2\sigma_x} - \frac{p_y^2}{2\sigma_y} - \frac{p_z^2}{2\sigma_z}\right) \qquad (8)$$

with x, y and z being the three molecular axes. This choice highlights the anisotropy of the local atomic potential. In particular, σ_α (with $\alpha = x, y, z$) represents the average nuclear momentum along a given axis. These definitions can be then used to define directional contributions to the kinetic energy $\langle E_K\rangle_\alpha = \sigma_\alpha^2/2M$ and a total mean kinetic energy $\langle E_K\rangle = \sum_\alpha \langle E_K\rangle_\alpha$. The resulting values for $\langle E_K\rangle$ and $\langle E_K\rangle_\alpha$ are reported in Table 2.

As far as D is concerned, our results show good agreement between $\langle \mathcal{E}_K\rangle$ and $\langle E_K\rangle$. In a recent study of liquid and solid light water [31], a similar agreement was found between the DINS value for $\langle E_K\rangle$ and $\langle \mathcal{E}_K\rangle$ derived from vibrational INS frequencies. Our model also reproduces quantitatively changes in directional kinetic energies associated with the liquid-to-solid phase transition, as observed by DINS. In this case, the decrease of the $z-$component in this transition is caused by an increase in HB strength in the solid phase – *i.e.*, stronger HBs lead to a red-shifted stretching frequency. Thus, both DINS experiment and our model agree on a small decrease by 5-6 meV of the kinetic energy along the z direction

The situation is markedly different for the component $\langle E_K\rangle_z$ and $\langle \mathcal{E}_K\rangle_z$. In this case, we find that the discrepancy between our model and DINS measurements is of approximately 20 meV (see Table 2). More generally, the observed differences between $\langle \mathcal{E}_K\rangle_\alpha$ and $\langle E_K\rangle_\alpha$ may be traced back to the assumption built into our model of decoupled motions when z is along the direction of the covalent bond (stretching mode). Moreover, intermolecular forces (neglected in our model) can lead to a redefinition of normal-mode coordinates. Interestingly, we note that much closer agreement with DINS may be achieved via a tilt of the z axis so as to maximize the contributions of the symmetric stretching and bending modes to $\langle \mathcal{E}_K\rangle_z$, resulting in a value for this energy of ca. 50 meV. Similar considerations would also apply to the y direction, with an associated kinetic energy of 40 meV. In summary while calculated and DINS values of $\langle \mathcal{E}_K\rangle$ and $\langle E_K\rangle$ yield information on the overall magnitude of NQEs, the directional components $\langle \mathcal{E}_K\rangle_\alpha$ and $\langle E_K\rangle_\alpha$ highlight the role of intermolecular interactions on single-particle momentum distributions.

From Table 2, one observes that for O atom the $\langle \mathcal{E}_K\rangle$ is underestimated of about 15 meV relative to $\langle E_K\rangle$ [8]. This finding may be ascribed to the long-range order of the HB network and to its effect on translational motions. It is entirely plausible that the present model underestimates these effects: for example, in Table 1 one can see that the contribution from translational modes dominates $\langle \mathcal{E}_K\rangle$.

In conclusion, comparison between our model and DINS shows that $\langle E_K\rangle$ for D in D_2O may be determined by combining translational, rotational and vibrational frequencies from optical

spectroscopy and INS, in agreement with previous work on light water [31]. These results suggest that a combined use of optical spectroscopy, INS and DINS measurements can give simultaneous access to the magnitude of underlying NQEs in water, as well as both local and intermediate-range-scale properties.

The implementation of the present model as part of the VESUVIO data analysis suite may be also used as a predictive tool in experimental design. As such, it would pave the way for detailed exploration of directional parameters σ_α using a multivariate Gaussian line shape for $n(p)$. Further, this method could in principle be generalized to more complex materials.

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