Emergence of correlated proton tunneling in water ice

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I.   Open System Dynamics of Proton Motion

The state of pseudo-spins lives in a 2^{12}-dimensional Hilbert space $\mathcal{H}$, that is to say that the density matrix ρ describing this state has $2^{12} \times 2^{12}$ elements. In this respect, it is not straightforward to present the details of its open system dynamics. For the sake of simplicity, and without loss of generality, we will focus on the motion of a single proton between the locations 1 and 2 in the hexamer in what follows (see Fig. 1-a for the details). Hence, instead of working with the twelve-site self-Hamiltonian H_{Hex} given in Eq. (2.1), we will use the following two-site Hamiltonian

$$H_{HB} = \sum_{j=1}^{2} W_j \, \hat{n}_j - J_{12}(a_1^\dagger a_2 + a_1 a_2^\dagger) + V_{12} \, \hat{n}_1 \hat{n}_2 + \lambda \, \mathbb{I}_{12} \tag{1}$$

to describe the closed system dynamics. Note that asymmetric version of this Hamiltonian ($W_1 \neq W_2$) was also used in [1] to investigate the role of proton tunneling in biological catalysis.

After applying the Jordan-Wigner transformation given in Eq. (2.3) on this two-site Hamiltonian, we end up with the two-qubit Hamiltonian

$$H_{HB} = J_x \left(\sigma_x^{(1)} \otimes \sigma_x^{(2)} + \sigma_y^{(1)} \otimes \sigma_y^{(2)} \right) + J_z \, \sigma_z^{(1)} \otimes \sigma_z^{(2)} + B \left(\sigma_z^{(1)} + \sigma_z^{(2)} \right) + \tilde{\lambda}, \tag{2}$$

where $J_x = J_{12}/2$, $J_z = V_{12}/4$, $B = -(2W + V_{12})/4$, and $\tilde{\lambda} = \lambda + (4W + V_{12})/4$. Eigensystem of this Hamiltonian can be written in an increasing order of the eigenvalues as

$$\begin{cases} e_1 = -J_z + 2J_x + \tilde{\lambda}, & |e_1\rangle = (|01\rangle + |10\rangle)/\sqrt{2}, \\ e_2 = -J_z - 2J_x + \tilde{\lambda}, & |e_2\rangle = (|01\rangle - |10\rangle)/\sqrt{2}, \\ e_3 = -2B + J_z + \tilde{\lambda}, & |e_3\rangle = |11\rangle, \\ e_4 = +2B + J_z + \tilde{\lambda}, & |e_4\rangle = |00\rangle. \end{cases} \tag{3}$$

A.   Local proton-phonon coupling

First, we examine the O−H stretch vibrations by considering them as two independent thermal baths existing around the proton locations and having the individual self-Hamiltonians $H_B^{(j)}$ given in Eq. (2.5). Also, we will describe the interaction of the proton with these vibrations using the interaction Hamiltonian given in Eq. (2.6):

$$H_I^{local} = \sum_j \hat{n}_j \sum_k \left(g_{j,k} b_{j,k}^\dagger + g_{j,k}^* b_{j,k} \right) \propto \sum_j \sigma_z^{(j)} \sum_k \left(g_{j,k} b_{j,k}^\dagger + g_{j,k}^* b_{j,k} \right). \tag{4}$$

1.   Bath operators in interaction picture

If we switch into the interaction picture, the bath operators $B_j = \sum_k (g_{j,k} b_{j,k}^\dagger + g_{j,k}^* b_{j,k})$ become

$$\begin{aligned} B_j(t) &= e^X B_j e^{-X} \\ &= B_j + [X, B_j] + [X, [X, B_j]]/2! + [X, [X, [X, B_j]]]/3! + \dots \end{aligned} \tag{5}$$

where $X = i\,H_{\mathcal{B}}^{(j)}\,t/\hbar$. To evaluate the commutators above, first we need to find the commutators $[H_{\mathcal{B}}^{(j)}, b_{j,k'}^\dagger]$ and $[H_{\mathcal{B}}^{(j)}, b_{j,k'}]$. In this respect, the bosonic commutation relations imply that

$$
\begin{aligned}
[H_{\mathcal{B}}^{(j)}, b_{j,k'}^\dagger] &= \sum_k \hbar\omega_{j,k}\,[b_{j,k}^\dagger b_{j,k},\, b_{j,k'}^\dagger] \\
&= \sum_k \hbar\omega_{j,k}\left(b_{j,k}^\dagger[b_{j,k},\, b_{j,k'}^\dagger] + [b_{j,k}^\dagger,\, b_{j,k'}^\dagger]b_{j,k}\right) \\
&= \sum_k \hbar\omega_{j,k}\,b_{j,k}^\dagger\delta_{k,k'} = +\hbar\omega_{j,k'}\,b_{j,k'}^\dagger,
\end{aligned}
\tag{6}
$$

$$
\begin{aligned}
[H_{\mathcal{B}}^{(j)}, b_{j,k'}] &= \sum_k \hbar\omega_{j,k}\,[b_{j,k}^\dagger b_{j,k},\, b_{j,k'}] \\
&= \sum_k \hbar\omega_{j,k}\left(b_{j,k}^\dagger[b_{j,k},\, b_{j,k'}] + [b_{j,k}^\dagger,\, b_{j,k'}]b_{j,k}\right) \\
&= \sum_k \hbar\omega_{j,k}\,(-\delta_{k,k'})\,b_{j,k} = -\hbar\omega_{j,k'}\,b_{j,k'}.
\end{aligned}
\tag{7}
$$

Then, it is easy to calculate the commutators in (5) after writing them in terms of (6) and (7):

$$
\begin{aligned}
[X, B_j] &= (i\,t/\hbar)[H_{\mathcal{B}}^{(j)}, B_j] \\
&= \sum_k (i\,t/\hbar)\left(g_{j,k}^*[H_{\mathcal{B}}^{(j)}, b_{j,k}] + g_{j,k}[H_{\mathcal{B}}^{(j)}, b_{j,k}^\dagger]\right) \\
&= \sum_k (i\,\omega_{j,k}\,t)\left(-g_{j,k}^* b_{j,k} + g_{j,k}b_{j,k}^\dagger\right),
\end{aligned}
\tag{8}
$$

$$
\begin{aligned}
[X, [X, B_j]] &= (i\,t/\hbar)[H_{\mathcal{B}}^{(j)}, [X, B_j]] \\
&= \sum_k (i^2\,\omega_{j,k}\,t^2/\hbar)\left(-g_{j,k}^*[H_{\mathcal{B}}^{(j)}, b_{j,k}] + g_{j,k}[H_{\mathcal{B}}^{(j)}, b_{j,k}^\dagger]\right) \\
&= \sum_k (i^2\,\omega_{j,k}^2\,t^2)\left(+g_{j,k}^* b_{j,k} + g_{j,k}b_{j,k}^\dagger\right),
\end{aligned}
\tag{9}
$$

$$
\begin{aligned}
[X, [X, [X, B_j]]] &= (i\,t/\hbar)[H_{\mathcal{B}}^{(j)}, [X, [X, B_j]]] \\
&= \sum_k (i^3\,\omega_{j,k}^2\,t^3/\hbar)\left(+g_{j,k}^*[H_{\mathcal{B}}^{(j)}, b_{j,k}] + g_{j,k}[H_{\mathcal{B}}^{(j)}, b_{j,k}^\dagger]\right) \\
&= \sum_k (i^3\,\omega_{j,k}^3\,t^3)\left(-g_{j,k}^* b_{j,k} + g_{j,k}b_{j,k}^\dagger\right).
\end{aligned}
\tag{10}
$$

By substituting these commutators into (5) and collecting terms involving $b_{j,k}$ and $b_{j,k}^\dagger$ together, we end up with the interaction picture operators given by

$$
B_j(t) = \sum_k \sum_{l=0}^\infty \frac{(-i\,\omega_{j,k}\,t)^l}{l!}g_{j,k}^* b_{j,k} + \sum_k \sum_{l=0}^\infty \frac{(+i\,\omega_{j,k}\,t)^l}{l!}g_{j,k}b_{j,k}^\dagger = \sum_k g_{j,k}^* e^{-i\,\omega_{j,k}\,t}b_{j,k} + g_{j,k}e^{+i\,\omega_{j,k}\,t}b_{j,k}^\dagger.
\tag{11}
$$

2. Thermal bath correlation function and dissipation rates

To calculate the bath correlation function $\langle B_j^\dagger(t)B_{j'}(0)\rangle_{\text{th}}$, we will use the following thermal expectations:

$$
\begin{aligned}
\langle b_{j,k}b_{j,k}\rangle_{\text{th}} &= 0, & \langle b_{j,k}^\dagger b_{j,k}\rangle_{\text{th}} &= N_j(\omega_{j,k}), \\
\langle b_{j,k}b_{j,k}^\dagger\rangle_{\text{th}} &= 1 + N_j(\omega_{j,k}), & \langle b_{j,k}^\dagger b_{j,k}^\dagger\rangle_{\text{th}} &= 0,
\end{aligned}
\tag{12}
$$

where $N_j(\omega_{j,k})$ is the average number of phonons with energy $\hbar\omega_{j,k}$ for the Bose-Einstein statistics and equals to $1/(e^{\beta\hbar\omega_{j,k}} - 1)$. Then, for independent baths, the bath correlation function becomes:

$$\langle B_j^\dagger(t)B_{j'}(0)\rangle_{\text{th}} = \sum_{k,k'} \left\langle \left(g_{j,k}^* e^{-i\,\omega_{j,k}\,t}b_{j,k} + g_{j,k}e^{+i\,\omega_{j,k}\,t}b_{j,k}^\dagger\right)\left(g_{j',k'}b_{j',k'}^\dagger + g_{j',k'}^* b_{j',k'}\right)\right\rangle_{\text{th}}$$

$$= \sum_{k,k'} \left(g_{j,k}g_{j',k'}^* e^{+i\,\omega_{j,k}\,t}\langle b_{j,k}^\dagger, b_{j',k'}\rangle_{\text{th}} + g_{j,k}^* g_{j',k'} e^{-i\,\omega_{j,k}\,t}\langle b_{j,k}, b_{j',k'}^\dagger\rangle_{\text{th}}\right.$$

$$\left. + g_{j,k}g_{j',k'}e^{+i\,\omega_{j,k}\,t}\langle b_{j,k}^\dagger, b_{j',k'}^\dagger\rangle_{\text{th}} + g_{j,k}^* g_{j',k'}^* e^{-i\,\omega_{j,k}\,t}\langle b_{j,k}, b_{j',k'}\rangle_{\text{th}}\right)$$

$$= \sum_k |g_{j,k}|^2 \left(e^{-i\,\omega_{j,k}\,t}\left(1 + N_j(\omega_{j,k})\right) + e^{+i\,\omega_{j,k}\,t}N_j(\omega_{j,k})\right)\delta_{jj'}. \tag{13}$$

Dissipation rates $\gamma_{jj'}$, half of the real part of one-sided Fourier transforms of $\langle B_j^\dagger(t)B_{j'}(0)\rangle_{\text{th}}$, can be calculated by using (13) as

$$\gamma_{jj'}(\omega) = \Gamma_{jj'}(\omega) + \Gamma_{j'j}^*(\omega)$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau\, e^{i\,\omega'\tau}\langle B_j(\tau)B_{j'}(0)\rangle_{\text{th}}$$

$$= \frac{1}{\hbar^2}\delta_{jj'} \sum_k |g_{j,k}|^2\left(\left(1 + N_j(\omega_{j,k})\right)\int_{-\infty}^{\infty} d\tau\, e^{i\,(\omega-\omega_{j,k})\,\tau} + N_j(\omega_{j,k})\int_{-\infty}^{\infty} d\tau\, e^{i\,(\omega+\omega_{j,k})\,\tau}\right)$$

$$= \frac{1}{\hbar^2}\delta_{jj'} \sum_k |g_{j,k}|^2\left(2\pi\delta(\omega - \omega_{j,k})\left(1 + N_j(\omega_{j,k})\right) + 2\pi\delta(\omega + \omega_{j,k})N_j(\omega_{j,k})\right)$$

$$= \frac{2}{\hbar}\,\delta_{jj'} \int_0^{\infty} d\omega'\, J_j(\omega')\left(\left(1 + N_j(\omega')\right)\delta(\omega - \omega') + N_j(\omega')\delta(\omega + \omega')\right)$$

$$= \frac{2}{\hbar}\,\delta_{jj'}\begin{cases} J_j(\omega)\left(1 + N_j(\omega)\right) & \text{for} \quad 0 < \omega < \infty \\ J_j(-\omega)\,N_j(-\omega) & \text{for} \quad -\infty < \omega < 0 \end{cases} \tag{14}$$

$$\equiv \delta_{jj'}\gamma_j(\omega),$$

where the sum over the absolute square of the discrete coupling constants $g_{j,k}$ is replaced by an integral over a continuous function $J_j(\omega)$ that is defined as $\pi/\hbar \sum_k |g_{j,k}|^2\delta(\omega - \omega_{j,k})$ and called the spectral density function. This function encapsulates all the effects of the jth bath on the associated pseudo-spin.

Note that $-N_j(-\omega)$ equals to $1 + N_j(\omega)$. Hence, if $J_j(\omega)$ is an odd function, $\gamma_{jj}(\omega) \equiv \gamma_j(\omega)$ turns out to be $2/\hbar\, J_j(\omega)\left(1 + N_j(\omega)\right)$ for all values of ω. Also note that $\gamma_{jj'}(\omega)$ is reduced to $\gamma_j(\omega)$ above because each pseudo-spin is associated to an independent environment. This is expected for the imaginary part of one-sided Fourier transforms of $\langle B_j^\dagger(t)B_{j'}(0)\rangle_{\text{th}}$ as well, i.e., $S_{jj'}(\omega) = \frac{1}{2i}\left(\Gamma_{jj'}(\omega) - \Gamma_{j'j}^*(\omega)\right) = \delta_{jj'}S_{jj}(\omega) \equiv S_j(\omega)$.

3. Lamb shift Hamiltonian and dissipator

To start analyzing the open system dynamics of pseudo-spins, eigenoperators of the self-Hamiltonian H_{HB} should be calculated using Eq. (2.10) with $A_j = \sigma_z^{(j)}$. Since H_{HB} has 4 non-degenerate energy levels, there are $\binom{4}{2} = 12$ different transitions in the system. Each possible nonzero value of Bohr frequency ω corresponds to one of these transitions. However, an interaction with the environment does not need to give rise to a transition always. Hence, to account for such situations where no transition is enabled, ω can take one more value that is equal to zero.

Only 3 of the 13 values of ω correspond to non-zero eigenoperators, which are

$$A_j(0) = -|e_3\rangle\langle e_3| + |e_4\rangle\langle e_4|,$$
$$A_j(\omega_{12}) = (-1)^j|e_2\rangle\langle e_1|, \tag{15}$$
$$A_j(\omega_{21}) = (-1)^j|e_1\rangle\langle e_2|.$$

Then, the Lamb shift Hamiltonian H_{LS} becomes $H_{LS}^{(1)} + H_{LS}^{(2)}$ such that

$$H_{LS}^{(j)} = S_j^0\left(|e_3\rangle\langle e_3| + |e_4\rangle\langle e_4|\right) + S_j^{1,2}|e_1\rangle\langle e_1| + S_j^{2,1}|e_2\rangle\langle e_2| \tag{16}$$

where $S_j^0 = S_j(0)$ and $S_j^{j'j''} = S_j(\omega_{j'j''})$. Similarly, the dissipator $\mathcal{D}(\rho)$ is decomposed into two dissipators each of which takes the following form

$$
\begin{aligned}
\mathcal{D}^{(j)}[\rho] = & - 2\gamma_j^0 \big(\wp_{3,4}|e_3\rangle\langle e_4| + \wp_{4,3}|e_4\rangle\langle e_3| \big) \\
& - \frac{1}{2} \big(\gamma_j^0 + \gamma_j^{1,2} \big) \big(\wp_{3,1}|e_3\rangle\langle e_1| + \wp_{1,3}|e_1\rangle\langle e_3| + \wp_{4,1}|e_4\rangle\langle e_1| + \wp_{1,4}|e_1\rangle\langle e_4| \big) \\
& - \frac{1}{2} \big(\gamma_j^0 + \gamma_j^{2,1} \big) \big(\wp_{3,2}|e_3\rangle\langle e_2| + \wp_{2,3}|e_2\rangle\langle e_3| + \wp_{4,2}|e_4\rangle\langle e_2| + \wp_{2,4}|e_2\rangle\langle e_4| \big) \\
& - \frac{1}{2} \big(\gamma_j^{1,2} + \gamma_j^{2,1} \big) \big(\wp_{1,2}|e_1\rangle\langle e_2| + \wp_{2,1}|e_2\rangle\langle e_1| \big) - \big(\gamma_j^{1,2}\wp_{1,1} - \gamma_j^{2,1}\wp_{2,2} \big) \big(|e_1\rangle\langle e_1| - |e_2\rangle\langle e_2| \big) \qquad (17)
\end{aligned}
$$

with $\gamma_j^0 = \gamma_j(0)$, $\gamma_j^{j'j''} = \gamma_j(\omega_{j'j''})$, and $\wp_{j,j'} = \wp_{j,j'}(t) \equiv \langle e_j|\rho(t)|e_{j'}\rangle$ are the elements of the pseudo-spin density matrix in energy eigenbasis $\{|e_j\rangle\}$.

4. Exact solution of the master equation

When we substitute (2), (16) and (17) into Eq. (2.7), we end up with a master equation for the system of our interest. It is straightforward to solve this master equation analytically. Exact solution in the energy eigenbasis is given by

$$
\begin{aligned}
\wp_{1,1}(t) &= \frac{\tilde{\gamma}_{2,1}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \big(\wp_{1,1}(0) + \wp_{2,2}(0) \big) + e^{-(\tilde{\gamma}_{1,2}+\tilde{\gamma}_{2,1})t} \Big(\frac{\tilde{\gamma}_{1,2}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{1,1}(0) - \frac{\tilde{\gamma}_{2,1}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{2,2}(0) \Big), \\
\wp_{1,2}(t) &= e^{-i\left(\tilde{S}_{1,2} - \tilde{S}_{2,1} + \omega_{12} \right)t} e^{-\frac{1}{2}\left(\tilde{\gamma}_{1,2}+\tilde{\gamma}_{2,1} \right)t} \wp_{1,2}(0), \\
\wp_{1,3}(t) &= e^{+i\left(\tilde{S}_0 - \tilde{S}_{1,2} + \omega_{31} \right)t} e^{-\frac{1}{2}\left(\tilde{\gamma}_0 + \tilde{\gamma}_{1,2} \right)t} \wp_{1,3}(0), \\
\wp_{1,4}(t) &= e^{+i\left(\tilde{S}_0 - \tilde{S}_{1,2} + \omega_{41} \right)t} e^{-\frac{1}{2}\left(\tilde{\gamma}_0 + \tilde{\gamma}_{1,2} \right)t} \wp_{1,4}(0), \\
\wp_{2,2}(t) &= \frac{\tilde{\gamma}_{1,2}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \big(\wp_{1,1}(0) + \wp_{2,2}(0) \big) - e^{-(\tilde{\gamma}_{1,2}+\tilde{\gamma}_{2,1})t} \Big(\frac{\tilde{\gamma}_{1,2}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{1,1}(0) - \frac{\tilde{\gamma}_{2,1}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{2,2}(0) \Big), \\
\wp_{2,3}(t) &= e^{+i\left(\tilde{S}_0 - \tilde{S}_{2,1} + \omega_{32} \right)t} e^{-\frac{1}{2}\left(\tilde{\gamma}_0 + \tilde{\gamma}_{2,1} \right)t} \wp_{2,3}(0), \\
\wp_{2,4}(t) &= e^{+i\left(\tilde{S}_0 - \tilde{S}_{2,1} + \omega_{42} \right)t} e^{-\frac{1}{2}\left(\tilde{\gamma}_0 + \tilde{\gamma}_{2,1} \right)t} \wp_{2,3}(0), \\
\wp_{3,3}(t) &= \wp_{3,3}(0), \\
\wp_{3,4}(t) &= e^{-i\omega_{34}t} e^{-2\tilde{\gamma}_0 t} \wp_{3,4}(0), \\
\wp_{4,4}(t) &= \wp_{4,4}(0), \qquad (18)
\end{aligned}
$$

where $\tilde{S}_0 = S_1^0 + S_2^0$, $\tilde{S}_{j'j''} = S_1^{j'j''} + S_2^{j'j''}$, $\tilde{\gamma}_0 = \gamma_1^0 + \gamma_2^0$, and $\tilde{\gamma}_{j'j''} = \gamma_1^{j'j''} + \gamma_2^{j'j''}$.

5. Steady state of the master equation

$\wp_{3,3}$ and $\wp_{4,4}$ are found to be constants of the open system dynamics in (18). Besides this, $\wp_{1,1}$ and $\wp_{2,2}$ seem to go to nonzero constant values as well in the asymptotic limit. On the other hand, all the other elements of density matrix vanish when t goes to infinity. Let's show it more clearly by checking the stationary state that is obtained by taking the left-hand side of master equation given in (2.7) as zero:

$$
\rho^\infty = \wp_{3,3}(0)|e_3\rangle\langle e_3| + \wp_{4,4}(0)|e_4\rangle\langle e_4| + \frac{1 - \wp_{3,3}(0) - \wp_{4,4}(0)}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \big(\tilde{\gamma}_{2,1}|e_1\rangle\langle e_1| + \tilde{\gamma}_{1,2}|e_2\rangle\langle e_2| \big). \qquad (19)
$$

To elaborate on this calculation, we need to find $\tilde{\gamma}_{1,2}/(\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1})$ and $\tilde{\gamma}_{2,1}/(\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1})$. We can evaluate them for two baths at the same temperature, e.g, $N_1(\omega) = N_2(\omega) = N(\omega)$ by using (14) together with the fact that

$\omega_{12} = -\omega_{21} < 0$:

$$\frac{\tilde{\gamma}_{1,2}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} = \frac{N(\omega_{21})}{N(\omega_{21}) + (1 + N(\omega_{21}))} = \frac{1}{1 + e^{+\beta(e_2 - e_1)}} = \frac{e^{-\beta e_2}}{e^{-\beta e_2} + e^{-\beta e_1}}, \tag{20}$$

$$\frac{\tilde{\gamma}_{2,1}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} = \frac{(1 + N(\omega_{21}))}{N(\omega_{21}) + (1 + N(\omega_{21}))} = \frac{e^{+\beta(e_2 - e_1)}}{1 + e^{+\beta(e_2 - e_1)}} = \frac{e^{-\beta \epsilon_1}}{e^{-\beta e_2} + e^{-\beta \epsilon_1}}. \tag{21}$$

Then, the steady state solution given in (19) can be cast into the following simple form:

$$\rho^\infty = \wp_{3,3}(0)|e_3\rangle\langle e_3| + \wp_{4,4}(0)|e_4\rangle\langle e_4| + \frac{1 - \wp_{3,3}(0) - \wp_{4,4}(0)}{e^{-\beta e_1} + e^{-\beta e_2}}\left(e^{-\beta e_1}|e_1\rangle\langle e_1| + e^{-\beta e_2}|e_2\rangle\langle e_2|\right). \tag{22}$$

For the initial states satisfying $\wp_{3,3}(0) = e^{-\beta e_3}/\sum_i e^{-\beta e_i}$ and $\wp_{4,4}(0) = e^{-\beta e_4}/\sum_i e^{-\beta e_i}$, this stationary state turns out to be the thermal state. However, it doesn't mean that thermalization is the underlying mechanism for this result. Actually, a partial dephasing appears to be in charge: environment washes out all the coherence in the basis of $\{|e_3\rangle, |e_4\rangle\}$, while it imposes a detailed balance between $|e_1\rangle$ and $|e_2\rangle$. As none of the eigenoperators of H_{HB} that corresponds to a transition from and/or to e_3 or e_4 survives in (15), environment can only exchange information with these two energy levels and this results in a partial dephasing in the associated energy eigenstates. On the other hand, the same environment can exchange heat with the remaining energy levels since there are non-zero eigenoperators for these transitions and so, it equilibrates energy eigenstates $|e_1\rangle$ and $|e_2\rangle$.

In the meantime, note that this two-qubit steady state shares exactly the same form with the twelve-qubit steady state given in Eq. (3.1).

B. Nonlocal proton-phonon coupling

We will extend the open system dynamics to include the oscillations of $O-O$ separation R_{12} in what follows. Assume that $\hat{u}_j$ is the displacement of the jth O atom from its reference position. Then the deviation of R_{12} from its equilibrium value R_{12}^{eq} can be defined as $\Delta R_{12} = \hat{u}_2 - \hat{u}_1$. By considering this, let's expand the hopping constant J_{12} about the point $R_{12} = R_{12}^{\text{eq}}$:

$$J_{12}(R_{12}) \approx J_{12}(R_{12}^{\text{eq}}) + \frac{\partial J_{12}}{\partial R_{12}}\Bigg|_{R_{12} = R_{12}^{\text{eq}}} (\hat{u}_2 - \hat{u}_1) \equiv J_{12}^{(0)}(R_{12}^{\text{eq}}) + J_{12}^{(1)}(R_{12}^{\text{eq}})(\hat{u}_2 - \hat{u}_1). \tag{23}$$

To reduce in complexity and extent, we assume that the first O atom is stationary, i.e., $\hat{u}_1 = 0$. Then, we switch into the second-quantization representation of $\hat{u}_2$ replacing it with $\sum_k \sqrt{\hbar/(2\mu\Omega_k)}(d_{2,k}^\dagger + d_{2,k})$ where Ω_k are the frequencies of the oscillation of R_{12}, and $d_{2,k}^\dagger$ and $d_{2,k}$ are respectively the phonon creation and annihilation operators associated with the vibration of the second O atom. After this replacement, substitution of (23) into (2) causes the transformation $H_{HB} \rightarrow H_{HB} + H_I^{nl}$ where the value of parameter J_x in H_{HB} turns out to be $-J_{12}^{(0)}(R_{12}^{\text{eq}})/2$ and the H_I^{nl} is a nonlocal proton-phonon interaction described by

$$\begin{aligned} H_I^{nl} &= \left(\sigma_x^{(1)} \otimes \sigma_x^{(2)} + \sigma_y^{(1)} \otimes \sigma_y^{(2)}\right)\sum_k h_k\left(d_{2,k}^\dagger + d_{2,k}\right) \\ &\equiv A_3 \otimes B_3, \end{aligned} \tag{24}$$

with h_k equals to $-J_{12}^{(1)}(R_{12}^{\text{eq}})\sqrt{\hbar/(8\mu\Omega_k)}$. This new proton-phonon interaction requires to entail the calculation of one more non-zero eigenoperators of H_{HB}:

$$A_3(0) = 2(|e_1\rangle\langle e_1| - |e_2\rangle\langle e_2|), \tag{25}$$

that give rise to the emergence of the following Lamb-shift Hamiltonian in addition to the ones given in (16):

$$H_{LS}^{(3)} = 4S_3^0\left(|e_1\rangle\langle e_1| + |e_2\rangle\langle e_2|\right), \tag{26}$$

and the following dissipator in addition to the ones given in (17):

$$
\begin{aligned}
\mathcal{D}^{(3)}[\rho] = & - 2\gamma_3^0 \big(\wp_{3,1}|e_3\rangle\langle e_1| + \wp_{1,3}|e_1\rangle\langle e_3| + \wp_{4,1}|e_4\rangle\langle e_1| + \wp_{1,4}|e_1\rangle\langle e_4| \big) \\
& - 2\gamma_3^0 \big(\wp_{3,2}|e_3\rangle\langle e_2| + \wp_{2,3}|e_2\rangle\langle e_3| + \wp_{4,2}|e_4\rangle\langle e_2| + \wp_{2,4}|e_2\rangle\langle e_4| \big) \\
& - 8\gamma_3^0 \big(\wp_{1,2}|e_1\rangle\langle e_2| + \wp_{2,1}|e_2\rangle\langle e_1| \big).
\end{aligned}
\tag{27}
$$

Inclusion of these additional terms into the master equation changes the exact solution from (18) to:

$$
\begin{aligned}
\wp_{1,1}(t) &= \frac{\tilde{\gamma}_{2,1}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \big(\wp_{1,1}(0) + \wp_{2,2}(0) \big) + e^{-(\tilde{\gamma}_{1,2}+\tilde{\gamma}_{2,1})t} \Big(\frac{\tilde{\gamma}_{1,2}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{1,1}(0) - \frac{\tilde{\gamma}_{2,1}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{2,2}(0) \Big), \\
\wp_{1,2}(t) &= e^{-i\big(\tilde{S}_{1,2}-\tilde{S}_{2,1}+\omega_{12}\big)t} e^{-\frac{1}{2}\big(\tilde{\gamma}_{1,2}+\tilde{\gamma}_{2,1}+16\gamma_3^0\big)t} \wp_{1,2}(0), \\
\wp_{1,3}(t) &= e^{+i\big(\tilde{S}_0-\tilde{S}_{1,2}-4S_3^0+\omega_{31}\big)t} e^{-\frac{1}{2}\big(\tilde{\gamma}_0+\tilde{\gamma}_{1,2}+4\gamma_3^0\big)t} \wp_{1,3}(0), \\
\wp_{1,4}(t) &= e^{+i\big(\tilde{S}_0-\tilde{S}_{1,2}-4S_3^0+\omega_{41}\big)t} e^{-\frac{1}{2}\big(\tilde{\gamma}_0+\tilde{\gamma}_{1,2}+4\gamma_3^0\big)t} \wp_{1,4}(0), \\
\wp_{2,2}(t) &= \frac{\tilde{\gamma}_{1,2}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \big(\wp_{1,1}(0) + \wp_{2,2}(0) \big) - e^{-(\tilde{\gamma}_{1,2}+\tilde{\gamma}_{2,1})t} \Big(\frac{\tilde{\gamma}_{1,2}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{1,1}(0) - \frac{\tilde{\gamma}_{2,1}}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \wp_{2,2}(0) \Big), \\
\wp_{2,3}(t) &= e^{+i\big(\tilde{S}_0-\tilde{S}_{2,1}-4S_3^0+\omega_{32}\big)t} e^{-\frac{1}{2}\big(\tilde{\gamma}_0+\tilde{\gamma}_{2,1}+4\gamma_3^0\big)t} \wp_{2,3}(0), \\
\wp_{2,4}(t) &= e^{+i\big(\tilde{S}_0-\tilde{S}_{2,1}-4S_3^0+\omega_{42}\big)t} e^{-\frac{1}{2}\big(\tilde{\gamma}_0+\tilde{\gamma}_{2,1}+4\gamma_3^0\big)t} \wp_{2,3}(0), \\
\wp_{3,3}(t) &= \wp_{3,3}(0), \\
\wp_{3,4}(t) &= e^{-i\omega_{34}t} e^{-2\tilde{\gamma}_0 t} \wp_{3,4}(0), \\
\wp_{4,4}(t) &= \wp_{4,4}(0).
\end{aligned}
\tag{28}
$$

On the other hand, since the diagonal elements have no dependence on either γ_3^0 or S_3^0, the stationary state remains the same as

$$
\begin{aligned}
\rho^\infty &= \wp_{3,3}(0)|e_3\rangle\langle e_3| + \wp_{4,4}(0)|e_4\rangle\langle e_4| + \frac{1 - \wp_{3,3}(0) - \wp_{4,4}(0)}{\tilde{\gamma}_{1,2} + \tilde{\gamma}_{2,1}} \big(\tilde{\gamma}_{2,1}|e_1\rangle\langle e_1| + \tilde{\gamma}_{1,2}|e_2\rangle\langle e_2| \big) \\
&= \wp_{3,3}(0)|e_3\rangle\langle e_3| + \wp_{4,4}(0)|e_4\rangle\langle e_4| + \frac{1 - \wp_{3,3}(0) - \wp_{4,4}(0)}{e^{-\beta e_1} + e^{-\beta e_2}} \big(e^{-\beta e_1}|e_1\rangle\langle e_1| + e^{-\beta e_2}|e_2\rangle\langle e_2| \big).
\end{aligned}
\tag{29}
$$

In this respect, $\mathrm{O-O}$ vibrations change the dynamics of the system, but do not affect its steady state.

II.   Model Parameters

A.   Estimation of the parameters

Note that if the twelve-qubit initial state $\rho(t = 0)$ lives only in the 64-dimensional subspace $\mathcal{H}_{ice}$, the steady state of the chosen master equation depends on two free parameters, J_x and $J_z^{(\text{intra})}$. Here, J_x equals to half of the orbital interaction energy J which is responsible for the tunneling of the protons between O atoms, while $J_z^{(\text{intra})}$ is a quarter of the inter-proton interaction energy V_{intra} which is responsible for the ionic defect penalty.

The values of these free parameters are extracted comparing the temperature dependent behaviour of probability P_{BF} with the phase transition temperatures predicted by recent dielectric constant measurements [2, 3] as follows.

First, we set J_x to zero and search for the appropriate $J_z^{(\text{intra})}$ values that give the expected temperature dependence of P_{BF}, i.e., $P_{BF}(T)$ should be sufficiently close to unity at temperatures lower than the experimentally determined phase transition temperatures and show a decrease during the phase transition. In this way, we try to reproduce the experimental data without any need to assume that proton tunneling takes place during the phase transition. As shown in Table I and Fig. 1, 10 meV is the maximum value consistent with the experimental data when compared to its close neighborhood. We set $J_z^{(\text{intra})}$ to 10 meV in this respect.

Secondly, we gradually decrease J_x and search for its minimum value that preserves the consistency with the experimental data. The value of J_x found in this way is -0.5 meV as shown in Table II.

Note that this two-step procedure does not exclude the likelihood of the presence of any other $(J_z^{(\text{intra})}, J_x)$ pair in the phase space that might lead to exactly the same $P_{BF}(T)$ as shown in Fig. 2 in the manuscript. However, it offers a physically motivated $(J_z^{(\text{intra})}, J_x)$ pair as described above.

B.   Sensitivity of the parameters

The sensitivity of $P_{BF}(T)$ to the changes in the free parameters J_x and $J_z^{(\text{intra})}$ will be investigated in what follows.

Although $P_{BF}(T)$ should be sufficiently close to unity at low temperatures, Fig. 4-a given in the manuscript shows that it cannot reach to this limit at any temperature when $J_z^{(\text{intra})}$ is kept constant at $+10$ meV but J_x is set to a value less than -0.5 meV, e.g. to -5 meV. Furthermore, Fig. 2 given below displays that it is impossible to readjust the value of $J_z^{(\text{intra})}$ to bring the temperature dependence of P_{BF} back to the expected behaviour after decreasing J_x down to -5 meV. In fact, some values of $J_z^{(\text{intra})}$ are found to raise P_{BF} up to unity at low temperatures, but $P_{BF}(T)$ never decreases for these particular $J_z^{(\text{intra})}$ values, even at temperatures quite higher than the experimentally determined phase transition temperatures. Note that $P_{BF}(T)$ should show a decrease during the phase transition. Hence, an increase in the proton tunneling rate, up to a value ten times higher than the fixed value used in the manuscript, cannot be compensated by a further change in the energy of ionic defect penalty.

On the other hand, according to Fig. 4-b given in the manuscript, a change in the value of $J_z^{(\text{intra})}$ from 10 meV to 20 meV (5 meV) sets the temperature at which $P_{BF}(T)$ deviates from unity to a value higher (lower) than the experimentally determined phase transition temperatures. Also, $P_{BF}(T)$ fails to exhibit its proper behaviour after (before) this turning point when compared to Fig. 2 given in the manuscript. Here, Fig. 3 (Fig. 4) demonstrates that no further adjustment in J_x can regenerate the expected temperature dependence of P_{BF} after varying $J_z^{(\text{intra})}$ to 20 meV (5 meV). Hence, a change in the energy of ionic defect penalty, up to a value twice as high (low) as the fixed value used in the manuscript, cannot be neutralized by readjusting the proton tunneling rate.

In this respect, the expected temperature dependence of P_{BF} exhibits a sensitivity to our free parameters, i.e., deviations from the fixed value of one parameter prevent the appearance of a slow decline in $P_{BF}(T)$ from unity around $58.9 - 73.4$ K, and this behaviour cannot reappear when the second parameter is also allowed to deviate from its fixed value at the same time.

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[2] Yen, F. and Chi, Z. H, 2015, Proton ordering dynamics of H$_2$O ice. *Phys. Chem. Chem. Phys.* **17**, 12458–12461.
[3] Yen, F. and Gao, T., 2015, Dielectric Anomaly in Ice near 20 K: Evidence of Macroscopic Quantum Phenomena. *J. Phys. Chem. Lett.* **6**, 2822–2825.

TABLE I. Dependence of $P_{BF}(T)$ and $S(T)$ to $J_z^{(\text{intra})}$ when $J_x = 0$.

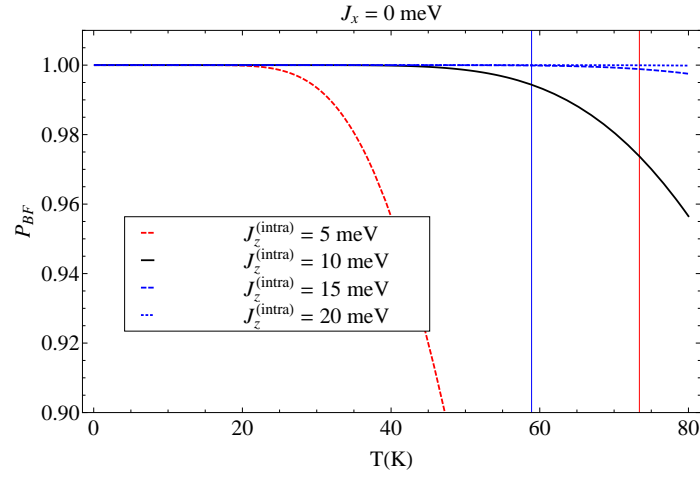| $J_z^{(\text{intra})}$	$S(20\,\text{K})$	$P_{BF}(20\,\text{K})$	$P_{BF}(58.9\,\text{K})$	$P_{BF}(73.4\,\text{K})$
$0.10\,\text{meV}$	5.99	0.04	0.04	0.03
$1.00\,\text{meV}$	4.65	0.38	0.09	0.07
$8.00\,\text{meV}$	1.00	1.00	0.97	0.91
$9.00\,\text{meV}$	1.00	1.00	0.99	0.95
$10.00\,\text{meV}$	1.00	1.00	0.99	0.97
$11.00\,\text{meV}$	1.00	1.00	1.00	0.99
$12.00\,\text{meV}$	1.00	1.00	1.00	0.99
$0.10\,\text{eV}$	1.00	1.00	1.00	1.00
$1.00\,\text{eV}$	1.00	1.00	1.00	1.00

FIG. 1. The behaviour of probability $P_{BF}(T)$ with respect to changes in the energy of ionic defect penalty when the orbital interaction energy vanishes. Vertical solid lines coloured blue and red respectively pinpoint the experimentally determined phase transition temperatures 58.9 K and 73.4 K [2].

TABLE II. Dependence of $P_{BF}(T)$ and $S(T)$ to J_x when $J_z^{(\text{intra})} = +10$ meV.

J_x(meV)	$S(20\,\text{K})$	$P_{BF}(20\,\text{K})$	$P_{BF}(58.9\,\text{K})$	$P_{BF}(73.4\,\text{K})$
-1.00	1.00	0.98	0.98	0.96
-0.90	1.00	0.99	0.98	0.96
-0.80	1.00	0.99	0.98	0.96
-0.70	1.00	0.99	0.99	0.97
-0.60	1.00	0.99	0.99	0.97
-0.50	1.00	1.00	0.99	0.97
-0.40	1.00	1.00	0.99	0.97
-0.30	1.00	1.00	0.99	0.97
-0.20	1.00	1.00	0.99	0.97
-0.10	1.00	1.00	0.99	0.97
-0.00	1.00	1.00	0.99	0.97
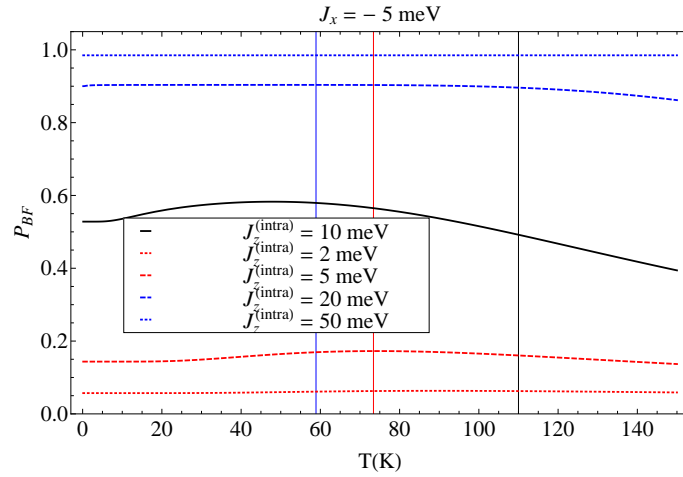
FIG. 2. The behaviour of probability $P_{BF}(T)$ with respect to further changes in the energy of ionic defect penalty after the orbital interaction energy is reduced to a value lower than the fixed value used in the manuscript.
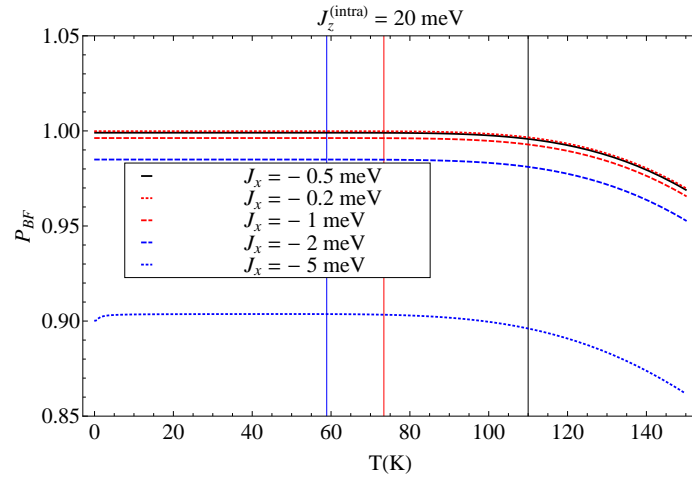
FIG. 3. The behaviour of probability $P_{BF}(T)$ with respect to further changes in the orbital interaction energy after the energy of ionic defect penalty is raised to a value higher than the fixed value used in the manuscript.
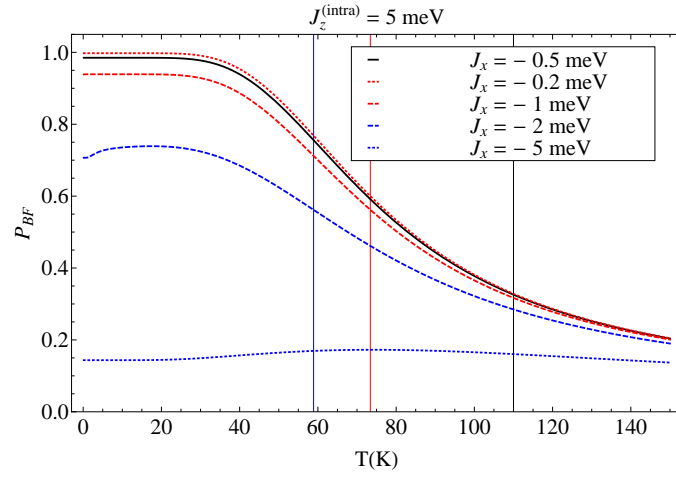

FIG. 4. The behaviour of probability $P_{BF}(T)$ with respect to further changes in the orbital interaction energy after the energy of ionic defect penalty is reduced to a value lower than the fixed value used in the manuscript.